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DISCUSSION OF THERMODYNAMIC DATA OBTAINED BY ADSORPTION GAS CHROMATOGRAPHY OF HYDROCARBONS ON GRAPHITIZED CARBON BLACKS

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SUMMARY

Thermodynamic data, such as the enthalpy, entropy and free energy of sorption, were determined by adsorption gas chromatography on graphitized carbon blacks for C_3–C_6 *n*-alkanes and benzene. The data are compared with those available in the literature obtained by either gas chromatography or static methods. The adsorptive properties of graphitized carbon blacks were also evaluated by considering the changes in the isosteric heat of adsorption when a non-polar stationary phase (squalane) was added to the adsorbent.

INTRODUCTION

In recent years, gas–solid chromatography (GSC) has often replaced the traditional static methods for the study of the nature of the adsorption process. Thus, adsorbent surface area, adsorption isotherms and thermodynamic functions such as the heat, entropy and free energy of adsorption have been determined by this technique[1–6]. Methods based on GSC (i) are less time consuming, (ii) do not require elaborate apparatus, (iii) need only small amounts of adsorbate and (iv) yield reliable results with very low surface coverage. The last point applies when the adsorbent is sufficiently homogeneous, so that the effect of heterogeneous sites can be neglected with respect to that of the rest of the surface. This effect allows one to carry out measurements on the linear part of the adsorption isotherm, where lateral interactions are negligible and the thermodynamic parameters depend exclusively on adsorbate–adsorbent interactions.

Graphitized carbon blacks (GCBs) have been shown to possess a sufficiently homogeneous surface and several of them have been used as standard adsorbents[7–13], *i.e.*, Graphon, Sterling FTG and Sterling MTG. In this work, thermodynamic data were determined by gas chromatography on some commercially available graphitized carbon blacks, such as Carbopack B, C and F. The data obtained are compared with those previously determined on other carbon blacks by either GSC or conventional methods. Changes in the isosteric heats of adsorption when the adsorbent is coated with different amounts of a liquid stationary phase (squalane) are also reported.

GCBs are used extensively nowadays in practical gas chromatography with excellent results; for this reason, we believe that the data presented here may be useful for a better understanding of the mechanism of action of these adsorbents.

EXPERIMENTAL

Carbopack B, C and F (Supelco, Bellefonte, PA, U.S.A.) are graphitized carbon blacks with surface areas of 95, 10 and 6 m^2/g, respectively. The packing materials were sieved to 80–100 mesh and the deposition of the stationary phase was carried out using the following well established procedure. A suitable amount of squalane dissolved in 50 ml of *n*-hexane was added to a weighed amount of carbon black (50 g of Carbopack F, 10 g of Carbopack B and C) with gentle stirring, and the solvent was slowly evaporated at room temperature (25°C) as fast evaporation may result in inhomogeneous coating of the adsorbent. Then fresh solvent was added in order to recover possible traces of squalane remaining on the container walls and again evaporated at room temperature. Finally, the carbon black previously dried at 60°C for 12 h in an oven was sieved again to 80–100 mesh.

A series of glass columns of identical geometric characteristics (1.8 m × 2 mm I.D.) were packed with either the uncoated or coated adsorbent. The columns were filled by gravity and packed by gentle vibration; 2.0, 4.2 and 3.7 g of stationary phase were used to pack the Carbopack B, C and F columns respectively, and the differences within the single sets of columns, based on flow-rate measurements, did not exceed ±3%. The columns containing the uncoated adsorbent were conditioned before use for 24 h at 250°C under a flow of nitrogen, whereas those containing the coated adsorbent were conditioned at 115°C.

A Dani 3900 gas chromatograph (Dani, Monza, Italy) equipped with a flame ionization detector was used, with nitrogen as the carrier gas. A Shimadzu Chromatopack CR-1B electronic integrator was used to obtain retention times. The temperature was maintained within ± 0.1°C and the carrier gas flow-rate was maintained within ±0.3% during the day. The flow-rate measured at room temperature and atmospheric pressure was corrected for temperature and pressure drop. The temperature ranges of adsorption were 318–473, 333–483 and 333–513 K for Carbopack F, C and B, respectively.

Calculations

The thermodynamics of the adsorption process can be conveniently described by the well known equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{1}$$

where ΔH°, ΔG° and ΔS° are the integral changes in standard molar enthalpy, free energy and entropy, respectively. ΔG° and ΔH° can be obtained from gas chromatographic data (*i.e.*, the net retention volume) and ΔS° can easily be obtained from eqn. 1. This is true if the adsorption process takes place in the Henry's law region so that the adsorbate–adsorbate interactions are negligible and the net retention volume does not depend on sample size.

Under these conditions, if we consider n_p mol of a gas at a given pressure p

in equilibrium with n_a mol of gas adsorbed per unit volume, Henry's law and the Clausius–Clapeyron equation yield the following relationships:

$$K_c = \frac{dn_a}{dn_p} \tag{2}$$

and

$$Q_{st} = RT^2\left(\frac{\delta \ln p}{\delta T}\right)_{n_a} = -R\left(\frac{\delta \ln p}{\delta 1/T}\right)_{n_a} \tag{3}$$

where K_c is Henry's constant and the isosteric heat of adsorption, Q_{st}, is a differential entity that at near-zero surface coverage is related to the integral change of enthalpy by the equation

$$\Delta H^\circ = -Q_{diff} = -Q_{st} + RT \tag{4}$$

From eqn. 2 and taking into account the material balance for an elementary layer, Kiselev and Yashin[14] showed that

$$K_c = \frac{V'_R}{m} = \frac{V_R - V_0}{m} = V'_m \tag{5}$$

where V'_R is the net retention volume, m the mass of adsorbent and V'_m the retention volume per unit mass of adsorbent.

$$V_s = V'_m/S \tag{6}$$

where S is the total surface area of the adsorbent contained in the column and V_s the retention volume per unit surface area of the adsorbent or specific retention volume. The following relationships are obtained according to Kiselev and Yashin[14]:

$$K_c = V_s \tag{7}$$

$$K_p = \frac{V_s}{RT} \tag{8}$$

On the other hand, the adsorbed layer can be considered as a two-dimensional gas and if the adsorbate behaves ideally in both the gaseous and the adsorbed states, then the following equations can be written:

$$\pi S = n_a RT \tag{9}$$

$$pV = n_p RT \tag{10}$$

$$K = \frac{\pi}{p} \tag{11}$$

Taking into account eqn. 6, it can be easily seen that π, the two-dimensional pressure, is related to the three-dimensional pressure, p, and to the specific retention volume, V_s, by the relationship

$$\pi = V_s p \qquad (12)$$

Eqn. 3 can now be written in the form

$$Q_{st} = -RT^2\left(\frac{\mathrm{dln}\ K_p}{\mathrm{d}T}\right) = R\left(\frac{\mathrm{dln}\ K_p}{\mathrm{d}(1/T)}\right) = -RT^2\left(\frac{\mathrm{dln}\ (V_s/T)}{\mathrm{d}T}\right) = \frac{R\ \mathrm{dln}\ (V_s/T)}{\mathrm{d}(1/T)}$$

and, as S and m are independent of T:

$$Q_{st} = R\left(\frac{\mathrm{dln}\ (V_R/T)}{\mathrm{d}(1/T)}\right) \qquad (13)$$

Hence, the isosteric heat of adsorption can be obtained by plotting ln V_r/T, ln V_s/T or ln V_m/T *versus* $1/T$, where T is the column temperature. Plots of ln V_r/T *versus* $1/T$ were used in our calculations. Heats of adsorptions calculated in this way are independent of the surface area and the density of the various graphitized carbon blacks.

The integral change in standard free energy, ΔG°, at a fixed temperature, T_1, of 1 mol of adsorbate on adsorption from a standard gaseous state at a pressure p' to a value p in equilibrium with a standard adsorbed state at a pressure π is given by

$$\Delta G^\circ = -RT_1 \ln\left(\frac{p'}{p}\right) \qquad (14)$$

and combining eqns. 12 and 14:

$$\Delta G^\circ = -RT_1 \ln\left(\frac{pV_s}{\pi}\right) \qquad (15)$$

If the standard state values are chosen following De Boer's approach[15] so that $p = 101$ kN/m^2 $= 1.01 \cdot 10^6$ dyne/cm^2 and $\pi = 0.338$ dyne/cm, eqn. 14 becomes

$$\Delta G^\circ = -RT \ln(2.99 \cdot 10^6\ V_s) \qquad (16)$$

where V_s is expressed in cm.

The integral change in standard entropy can be calculated from eqn. 1:

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T_1}$$

From eqns. 3 and 15:

$$\Delta S^{\circ} = \frac{-Q_{\text{st}} + RT_1 + RT_1 \ln(2.99 \cdot 10^6 \, V_s)}{T_1}$$

$$= \frac{-Q_{\text{st}}}{T_1} + [R + R \ln(2.99 \cdot 10^6)] + R \ln V_s$$

$$\Delta S^{\circ} = \frac{-Q_{\text{st}}}{T_1} + 39.62 + R \ln V_s \tag{17}$$

The entropy of adsorption is also independent of the surface area of the adsorbent.

RESULTS AND DISCUSSION

The isosteric heats of adsorption were calculated from the slopes of the straight lines obtained by plotting ln V_R/T *versus* $1/T$. A typical example is shown in Fig. 1 for propane, butane, pentane, hexane, benzene and Carbopack B at zero surface coverage.

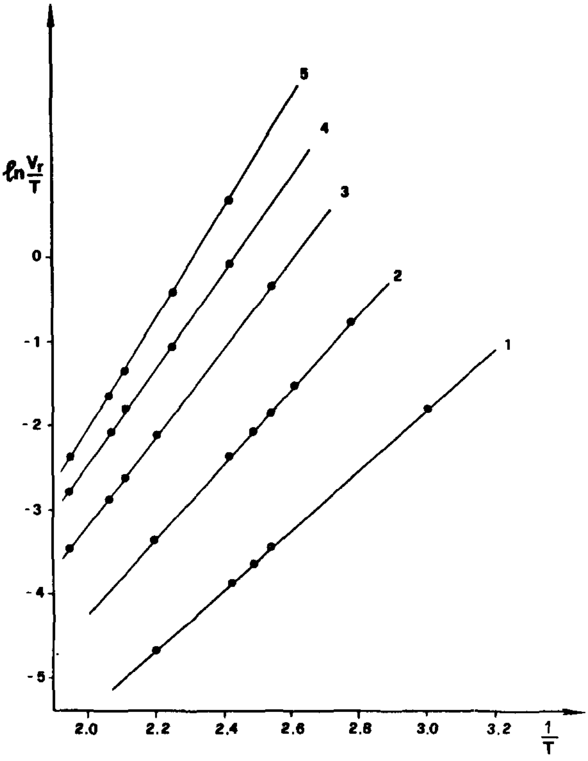

Fig. 1. Variation of ln V_r/T with reciprocal temperature on Carbopack B at zero surface coverage: (1) propane; (2) butane; (3) pentane; (4) benzene; (5) hexane.

The Q_{st} values of the five compounds determined on Carbopack B, C and F are reported in Table I together with the values obtained by other workers for different kinds of carbon blacks.

The isosteric heats of adsorption on Carbopack B are higher than those on Carbopack C and F (*ca.* 2 kcal/mol). This means that the average energy of the adsorptive sites is higher. These sites consist of geometrical irregularities such as cracks, channels or crystal defects where a molecule of adsorbate may interact with more than one graphitic plane[11], rather than intersections of graphitic planes.

This can also explain the fact that on Carbopack C and F there is a regular increase (*ca.* 1.2 kcal/mol) of Q_{st} values with increasing number of carbon atoms, whereas on Carbopack B this does not occur, particularly on passing from *n*-pentane to *n*-hexane. The isosteric heats of adsorption on Carbopack B are lower than those on Graphon by 1.0–2.0 kcal/mol for all the compounds.

Carbopack C and F show similar values so that they can be considered as adsorbents with the same surface properties. VG3 (see Table I), where the heat of adsorption of *n*-hexane is 8.08 kcal (this is the only value available), seems to behave

TABLE I

ISOSTERIC HEATS OF ADSORPTION (kcal/mol) AT ZERO SURFACE COVERAGE

Numbers in parentheses are literature references.

Adsorbent	*Surface area* (m^2/g)	*Adsorbate*				
		C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_6H_6
Carbopack B	95	7.20	8.84	10.34	12.91	11.23
Carbopack C	9	6.10	7.35	8.45	10.23	9.52
				9.80(12)		
Carbopack F	6	5.80	7.00	8.44	9.65	8.97
Hydrogen-treated Carbopack B		7.00	9.81	14.40	18.63	17.84
Hydrogen-treated		6.82	9.78	11.37	14.23	12.85
Carbopack C			6.9(17)	8.4 (17)	9.9(17)	9.3(17)
				9.25(12)		
Graphon[11]	138	8.40	12.20	11.02	15.08	
Hydrogen-treated Graphon[11]		5.90	7.35	8.41	9.87	
Sterling FTG	14	6.10(11)	7.54(11)	8.82(11)	10.50(11)	
		5.87(19)	7.45(19)			
				9.15(5)		
				8.88(7)		9.98(7)
				9.35(12)		
Hydrogen-treated		6.15(11)	7.45(11)	8.55(11)	10.25(11)	
Sterling FTG				9.15(5)		
				8.84(7)		9.83(7)
				9.25(5)		
Sterling MTG	8	6.26(8)	8.10(8)	8.61(8)	9.83(8)	
				8.84(7)		9.87(7)
				8.90(18)	10.10(18)	9.40(17)
				8.90(20)	10.40(20)	
VG3[16]					8.08	

completely different. In fact, although its surface area is high (62 m^2/g) the heat of adsorption is lower than for Carbopack C and F.

If the data obtained on Carbopack C are compared with those available in the literature[12,17] on the same adsorbent, either hydrogen-treated or not, the only possible conclusion is that the Carbopack C available today is different so far as the energy of the adsorption sites is concerned. In fact, the variations are too large to be explained by experimental errors or by the use of different GCB samples and the values measured are almost identical with those obtained on the hydrogen-treated form[17].

In this work, the heats of adsorption increase on passing from Carbopack C to hydrogen-treated Carbopack C and our values are higher than those reported in literature for the treated form. The same trend is observed for Carbopack B. A possible explanation is that the hydrogen treatment removes some residues adsorbed on the carbon black during and after the graphitization procedure, which mask to a certain extent the number of non-specific active sites. This effect might outweigh the positive effect of the elimination of the geometric irregularities, so that the net result is an increase in the Q_{st} values. This means that the Q_{st} values measured at zero coverage depend very much on the history and origin of the carbon black, and different values may be obtained from batch to batch.

Finally, the heats of adsorption of benzene for the three Carbopacks are lower with respect to *n*-hexane, as expected. In fact, it is well established[18] that the geometric configuration and not the electronic structure is the factor that governs the adsorption of these molecules. Therefore, the carbon atoms of *n*-hexane can penetrate into the centre of the graphitic planes where the energy of interaction is higher, whereas the atoms of *n*-benzene can not, so that the heat of adsorption of the latter is lower.

In Table II the entropies of adsorption are reported, together with the values obtained by Di Corcia and Samperi[11] on other kinds of graphitized carbon blacks and by Hoory and Prausnitz[19]. Table II also includes the data obtained on VG3[16].

TABLE II

STANDARD ENTROPIES OF ADSORPTION (cal/mol · K) AT ZERO SURFACE COVERAGE

Numbers in parentheses are the temperatures (K) of retention volume measurements.

Adsorbent	*Adsorbate*				
	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_6H_6
Carbopack B	−8.9(333)	−10.2(333)	−11.2(483)	−12.7(483)	−11.5(483)
Carbopack C	−6.0(333)	−6.3(333)	−6.5(483)	−7.3(483)	−7.0(483)
Carbopack F	−7.6(333)	−8.0(333)	−8.3(388)	−8.8(388)	−7.7(473)
Graphon[11]	−15.1(326)	−21.4(331)	−14.5(483)	−20.6(483)	
Hydrogen-treated Graphon[11]	−9.5(326)	−10.8(326)	−10.8(410)	−10.5(410)	
Sterling FTG[11]	−9.6(330)	−10.6(330)	−9.9(387)	−11.9(387)	
Hydrogen-treated Sterling FTG[11]	−9.7(330)	−10.5(380)	−10.4(387)	−12.2(387)	
Sterling FTG[19]	−9.6	−11.2			
VG3[16]				−9.3(333)	

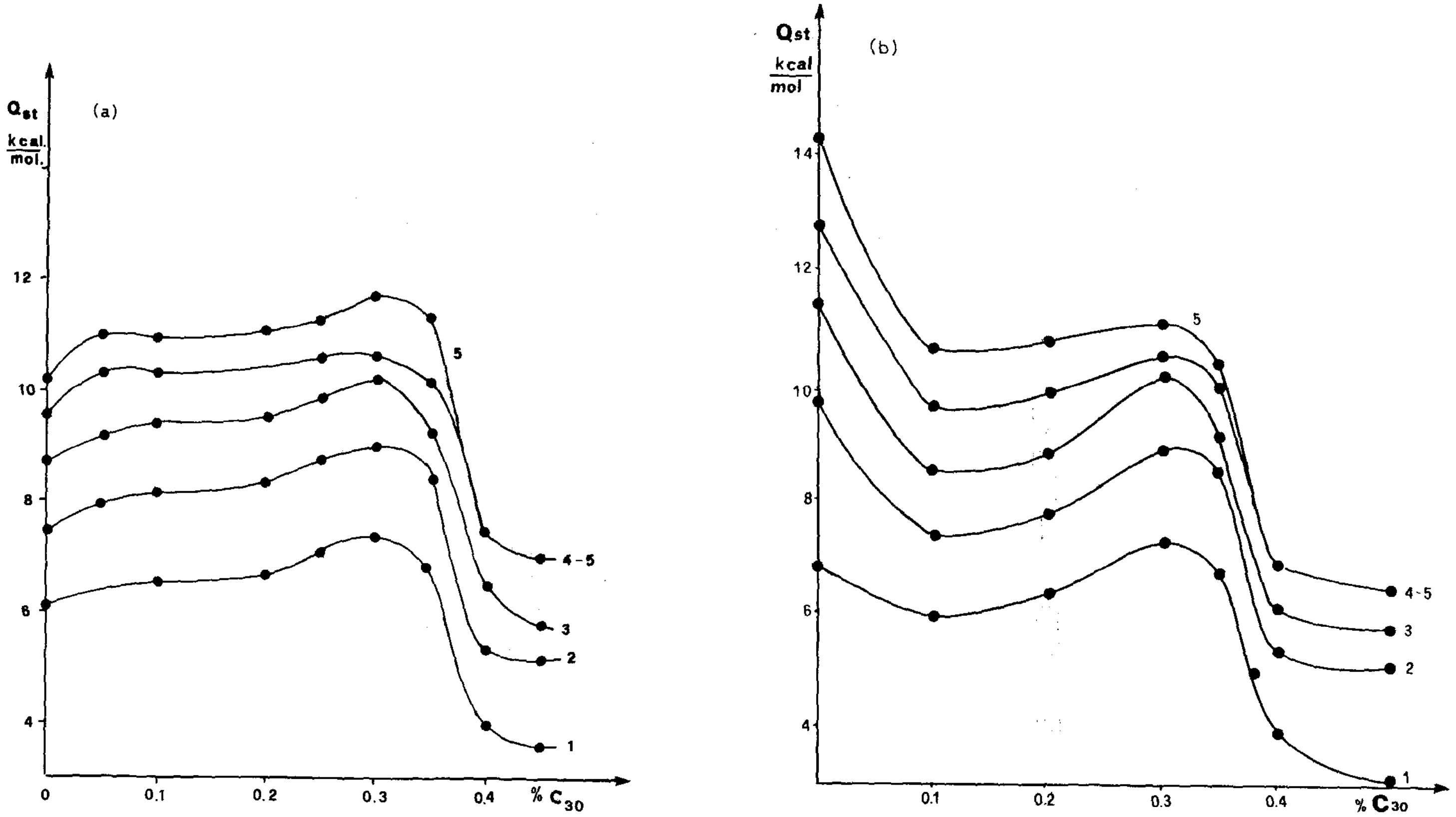

Fig. 2. Isosteric heats of adsorption of hydrocarbons *versus* percentage (w/w) of squalane. (a) Carbopack C; (b) hydrogen-treated Carbopack C. (1) C_3H_8; (2) C_4H_{10}; (3) C_5H_{12}; (4) C_6H_{14}; (5) C_6H_6.

All data were obtained by gas chromatography, with the exception of those of Hoory and Prausnitz, who employed a static method. The temperatures used to measure the retention volumes for entropy calculations are also given.

On adsorption, there is a loss of one degree of translational freedom with a consequent loss of translation entropy and a loss of rotational entropy which is negligible for monoatomic and spherical molecules. There is also a gain in vibrational entropy because of the vibration of the adsorbed molecule perpendicular to the surface. As a consequence, the loss of entropy increases with increasing molecular size on all Carbopacks and decreases from *n*-hexane to benzene. On Graphon and Sterling FTG[11] an interruption was noticed on going from *n*-butane to *n*-pentane, but this did not happen in this work.

Carbopack B shows entropy changes similar to those obtained on hydrogen-treated Graphon and both Sterling FTG and hydrogen-treated Sterling FTG. The differences in the loss of entropy after hydrogen treatment, which are large for Graphon but negligible for Sterling FTG, have been explained by the fact that cavities of molecular dimensions are present in the former and completely absent from the latter.

In fact, the data obtained on Carbopack C and F seem to indicate that geometrical irregularities are present on the Sterling FTG surface which are not removed by hydrogen treatment. When the adsorption takes place in cracks or cavities instead of the flat surface, the number of degrees of freedom of the molecule decreases and the entropy of the adsorbed phase is lower.

In Table III the $\Delta G°$ values as a function of the number of carbon atoms for Carbopack B and C are reported. $\Delta G°$ increases by about 1.1 kcal/mol with increasing molecular size. This means that the molecules are adsorbed in a "lying-down" position and not in a "standing-on-end" position, and the adsorption process becomes more spontaneous as the number of carbon atoms increases. The process of adsorption is more spontaneous on Carbopack B, as expected, as higher $\Delta G°$ values are obtained with respect to Carbopack C.

Further information on the adsorptive properties can be obtained by considering the variation of the isosteric heats of adsorption when a stationary phase is added to the adsorbent. In Fig. 2 the isosteric heats of adsorption *versus* the percentage of stationary phase (squalane) for (a) untreated and (b) hydrogen-treated Carbopack C are reported. The most striking difference is in the Q_{st} values at zero coverage, which are much higher for the treated form. A possible explanation for this has already been given, while discussing the data reported in Table I.

TABLE III

STANDARD FREE ENERGIES OF ADSORPTION (kcal/mol)

Temperature of retention volume measurements, 453 K.

Adsorbent	*Adsorbate*				
	C_3H_8	C_4H_{10}	C_5H_{12}	C_8H_{14}	C_6H_6
Carbopack B	−1.77	−2.87	−4.08	−5.37	−4.89
Carbopack C	−1.41	−2.51	−3.69	−4.91	−4.37

At low coverages the heats of adsorption decrease as a consequence of the deactivation by the stationary phase and ultimately the values are essentially the same as for the untreated carbon black. In both instances an increase up to a maximum is then observed owing to the effect of lateral interactions followed by a decrease in the monolayer region (0.35%), as expected[10]. The Q_{st} values are very similar for both the untreated and treated forms, which leads to the conclusion that the chromatographic properties are not dependent on the batch used when the adsorbent is coated with amounts of stationary phase $\geq 0.1\%$. Fig. 3 shows the curves obtained for hydrogen-treated Carbopack B.

At lower surface coverages the same qualitative behaviour as with Carbopack C is observed. However, as Carbopack B shows a more heterogeneous surface and a higher surface area, higher Q_{st} values are measured at zero surface coverage and larger amounts of stationary phase are needed for the initial deactivation of the active sites.

A peculiar situation arises when the concentration of squalane is 1.5%. In fact, the heats of adsorption of propane and butane increase, whereas those of pentane,

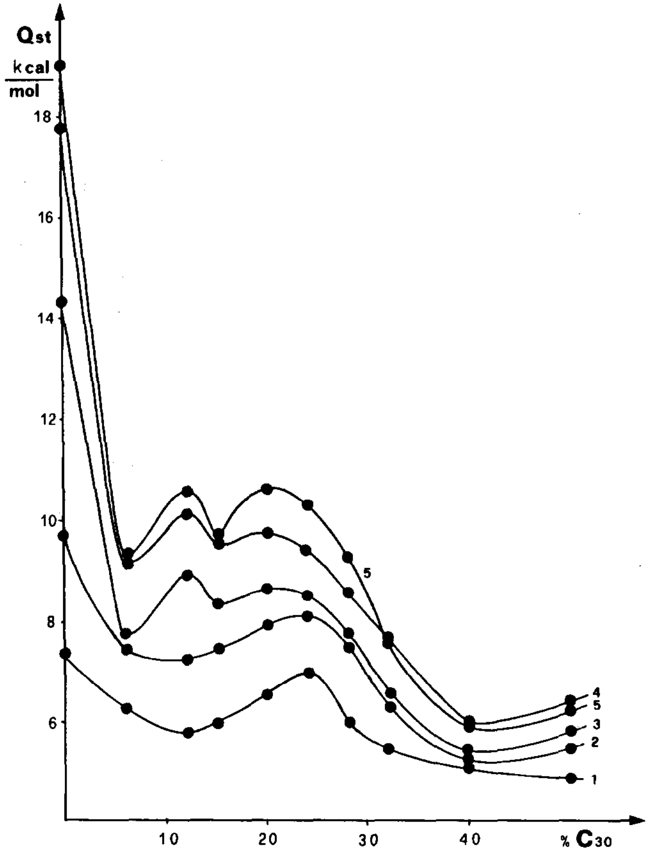

Fig. 3. Isosteric heats of adsorption of hydrocarbons *versus* percentage (w/w) of squalane on hydrogen treated Carbopack B. (1) C_3H_8; (2) C_4H_{10}; (3) C_5H_{12}; (4) C_6H_{14}; (5) C_6H_6.

benzene and hexane decrease. This can be explained in terms of the relative molecular dimensions. The smaller propane and butane molecules can penetrate the "holes" left on the carbon surface by the stationary phase, whereas the larger pentane, benzene and hexane molecules cannot.

When the concentration of squalane is raised to 2.0% the smaller molecules also are not able to penetrate the holes on the carbon surface and the Q_{st} values increase for all the molecules because of the lateral interactions. Hence, depending on molecular dimensions, a maximum can be observed before the actual maximum close to the monolayer.

Another interesting effect is the cross-over of the hexane and benzene curves at the monolayer. This is feasible if one thinks that polarizability is the driving mechanism in GSC, whereas at the monolayer competition occurs with the driving mechanism of gas–liquid chromatography, *i.e.*, the relative vapour pressure.

In Fig. 4, the variation of the isosteric heats of adsorption of *n*-pentane with surface coverage on Carbopack C and B is compared with that on Carbopack F and Sterling FTG [12,13]. A large number of active sites are present on the Carbopack B surface and their energy distribution is largely non-uniform. In fact, the heat of adsorption does not show a sharp maximum and its decrease at the monolayer is smooth. The effect of lateral interactions is barely noticeable on Carbopack B and increases markedly for Carbopack F, Carbopack C and Sterling FTG. Sterling FTG shows a more uniform energy distribution of the active sites than the other carbon blacks, as a sharper maximum and a steeper decrease are observed in the monolayer region. Finally, the treatment with hydrogen increases the number of active sites on

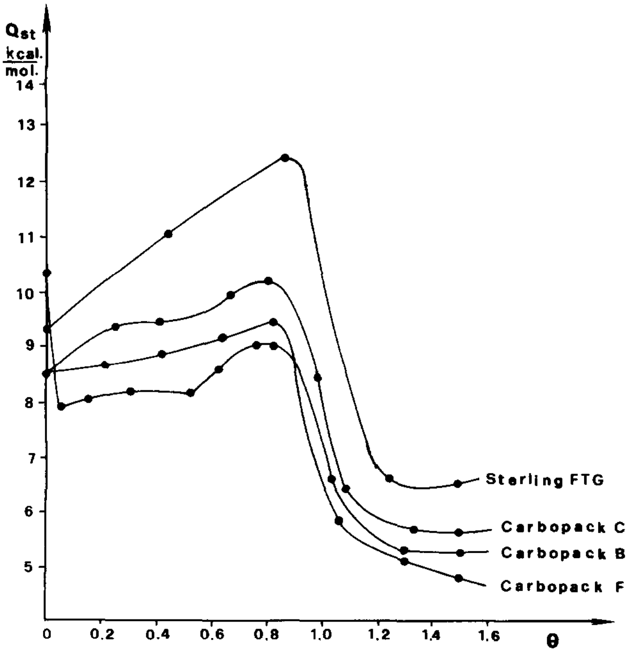

Fig. 4. Isosteric heats of adsorption of pentane on various carbon blacks.

Carbopack C and B but has no effect on Carbopack F and Sterling FTG. However, after the initial decrease in the heats of adsorption, the curves obtained for both hydrogen-treated and untreated Carbopack B and C are virtually identical.

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