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ADSORPTION OF HYDROCARBONS ON GRAPHITES AND GRAPHITIZED CARBON BLACK AT ZERO SURFACE COVERAGE

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SUMMARY

The Henry's law region of the adsorption isotherms for a homologous series of *n*-alkanes on graphites and a graphitized carbon black was studied by gas chromatography. The three thermodynamic functions at zero surface coverage were determined. A linear relationship between the standard free energy, the enthalpy and the entropy and the number of carbon atoms was found. The low heats of adsorption at zero coverage indicated a virtual absence of high-energy sites. Attempts were made to estimate the London contribution to the surface free energy of the adsorbents; it was estimated to be 100 mN m⁻¹ for the graphitized carbon black and 80 mN m⁻¹ for the graphites.

INTRODUCTION

Gas-solid chromatography has been widely used to determine different thermodynamic data since Greene and Pust¹ showed that the heats of adsorption could be measured by using this technique, provided that the adsorption-desorption equilibrium was reached. This technique has also been applied to the determination of adsorption isotherms², surface areas³, thermodynamic parameters⁴ and molecular parameters⁵. The results obtained have often been compared with those obtained by static measurements, generally showing good agreement.

On the other hand, gas-solid chromatography has the advantage over conventional methods of adsorption that it needs only a small amount of adsorbate and it is capable of higher precision in the low-coverage region of the isotherms where the concentration of the sample in the gas phase is very small. In this part of the isotherms the adsorbate-adsorbate lateral interactions are negligible, and the thermodynamic functions depend only on adsorbate-adsorbent interactions. Therefore, such determinations are very interesting for establishing the adsorption process and the surface homogeneity of the adsorbent.

Some carbon blacks graphitized at high temperatures are used as standard adsorbents as their surface homogeneity gives a non-specific adsorbate-adsorbent interaction⁶. However, this surface homogeneity has been questioned⁷ on the basis

of data obtained by gas-solid chromatography because of the existence of some irregularities on the surface of these adsorbents. Therefore, in this work we measured the adsorption behaviour of *n*-alkanes on a graphitized carbon black (V3G), which has been used as a support for metallic catalysts⁸⁻¹¹, and found a relationship between the surface homogeneity of V3G and the dispersion of platinum when the latter was supported on it. From the adsorption of *n*-alkanes (using a gas chromatographic technique), we obtained the thermodynamic functions and the London dispersion component of the surface free energy of the substrate in the Henry's law region. The results obtained with V3G were compared with those obtained with two different graphites, pyrolytic and artificial (Acheson).

EXPERIMENTAL

The materials used as adsorbents were a graphitized carbon black (V3G) obtained by graphitizing⁸ a carbon black (V3) and supplied by Cabot (U.S.A.), an artificial graphite from Degussa (F.R.G.), manufactured by the Acheson method and supplied by JEN (Spain), and a pyrolytic graphite, supplied by Union Carbide (U.S.A.). In Table I are shown their surface areas obtained by the BET method applied to the nitrogen isotherm at 77°K^{9,12,13}, particle sizes and amounts used in the chromatographic runs.

The hydrocarbons *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane, analytical reagent grade, supplied by Merck (F.R.G.), were used as adsorbates and were employed without further purification.

The gas chromatograph was a Carlo Erba Model Fractovap 2350 with a flame-ionization detector. The column dimensions were 20 cm × 3 mm I.D. and ultra-high purity nitrogen was used as the carrier gas. The pressure of the carrier gas was measured at the column inlet, and was considered equal to atmospheric pressure at the column outlet. The carrier gas flow-rate was adjusted in all instances to 5 cm³ min⁻¹. The measured flow-rate was corrected for temperature and pressure drop according to ref. 14. Before the adsorption runs, the column with the adsorbate was conditioned at 453°K for 12 h under a flow of nitrogen. The adsorption temperatures were 333, 343, 353 and 363°K.

Nitrogen saturated at 293°K with the vapour of a particular hydrocarbon was kept in a gas sampling bulb. Amounts of adsorbate of about 10⁻³ μl were withdrawn from the bulb with a syringe, at least three different amounts of samples being injected into the column. Symmetrical elution peaks were obtained, which indicates that the Henry's law region was attained. The dead volumes were corrected according to the relationship given by Peterson and Hirsch¹⁵.

TABLE I
CHARACTERISTICS OF THE ADSORBENTS

Adsorbent	$S_{N_2}(77^\circ K, BET)$ (m ² g ⁻¹)	Particle size (μm)	Weigh of carbon (g)
V3G	62.10	0.235	0.15
Pyrolytic	3.26	150-200	1.16
Acheson	3.18	150-200	1.34

Thermodynamics of adsorption at zero surface coverage

The fundamental parameter measured in gas chromatography is the net retention volume, which is constant and independent of the vapour concentration in the gas phase when the Henry's law region is considered. Under our experimental conditions, the chromatographic peaks were symmetrical and the maxima were independent of the amount of hydrocarbon injected.

It can be assumed that the adsorbate behaves as an ideal gas when the adsorption process takes place in the Henry's law region and the adsorbate concentration, in both the vapour and the adsorbent phases, are very low. Under these conditions, the standard state of an adsorbed species is devoid of adsorbate-adsorbate interactions¹⁶, that is, the molecular interactions on the surface are the same as at an infinity low coverage (the reference state for the adsorbed layer). Then, the equilibrium constant of the adsorption process can be expressed by the equation¹⁶

$$K = \frac{V_R}{SRT} = \frac{V_s}{RT} \tag{1}$$

where K is Henry's constant, V_R the net retention volume and S the total surface area of the adsorbent contained inside the column.

The adsorbed layer (at zero surface coverage) behaves as a two-dimensional gas and by analogy with three-dimensional gases an equation of state for this ideal two-dimensional gas can be written:

$$\pi = \sigma RT \tag{2}$$

where π is the two-dimensional pressure and σ is the surface concentration. In the Henry's law region of the isotherm $\sigma = Kp$, where p is the reference state for the adsorbed layer. Then, from eqns. 1 and 2, the following equation can be obtained:

$$\pi = \sigma RT = KpRT = V_s p \tag{3}$$

This equation provides the connection between the two- and three-dimensional pressures that allows us to calculate numerical values for standard free energy and entropy of adsorption.

The standard free energy of adsorption, ΔG_A^0 , of 1 mole of adsorbate from the standard gaseous state at a pressure $p_{s,g}$ to a standard state on the surface is given by^{16,17}

$$\Delta G_A^0 = -RT \ln (p_{s,g}/p) \tag{4}$$

where p can be written in terms of the two-dimensional standard pressure π by eqn. 3, and from this equation and eqn. 4, the following equation can be deduced:

$$\Delta G_A^0 = -RT \ln (p_{s,g}V_s/\pi) \tag{5}$$

There are several approaches to choosing the standard surface state¹⁶ and we used De Boer's approach¹⁸, from which the standard gaseous state, $p_{s,g}$, is equal to 101 kN m^{-2} (1 atm) and π is equal to 0.338 mN m^{-1} . The latter value, arbitrarily proposed by De Boer, defines the standard surface pressure as that pressure where

the average distance of separation between molecules in the adsorbed phase equals that in the standard gas phase. Under these conditions eqn. 5 takes the form

$$\Delta G_A^0 = -RT \ln (2.99 \cdot 10^8 V_s) \quad (6)$$

in which V_s is expressed in meters.

The Gibbs-Helmholtz equation allows the calculation of ΔH_A^0 for the same standard process to which ΔG_A^0 refers¹⁶, given the temperature dependence of V_s :

$$\ln V_s = -\frac{\Delta H_A^0}{RT} + C \quad (7)$$

assuming that ΔH_A^0 is independent of T . This standard enthalpy of adsorption, ΔH_A^0 , can be related to the differential heat of adsorption, q_d , and from now on we shall use this term. The standard entropy of adsorption can then be calculated from eqn. 8:

$$\Delta S_A^0 = \frac{q_d - \Delta G_A^0}{T} \quad (8)$$

RESULTS

As has been pointed out, the different amounts of hydrocarbons injected gave chromatographic peaks the retention volumes of which were independent of the amount of hydrocarbon, so that the adsorption processes took place in the Henry's law region. The surface coverages obtained with Gale and Beebe's equation¹⁹ were of the order of 10^{-3} . This value corresponds to the final surface coverage reached before the vapour is eluted.

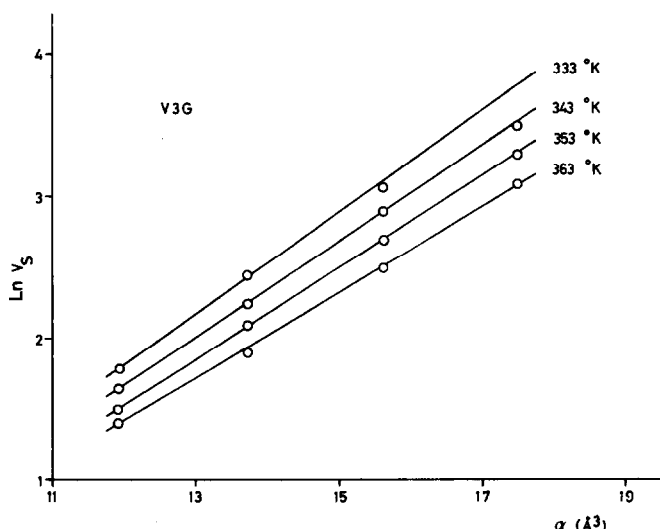


Fig. 1. Variation of the net retention volumes with the polarizability of n -alkanes for V3G.

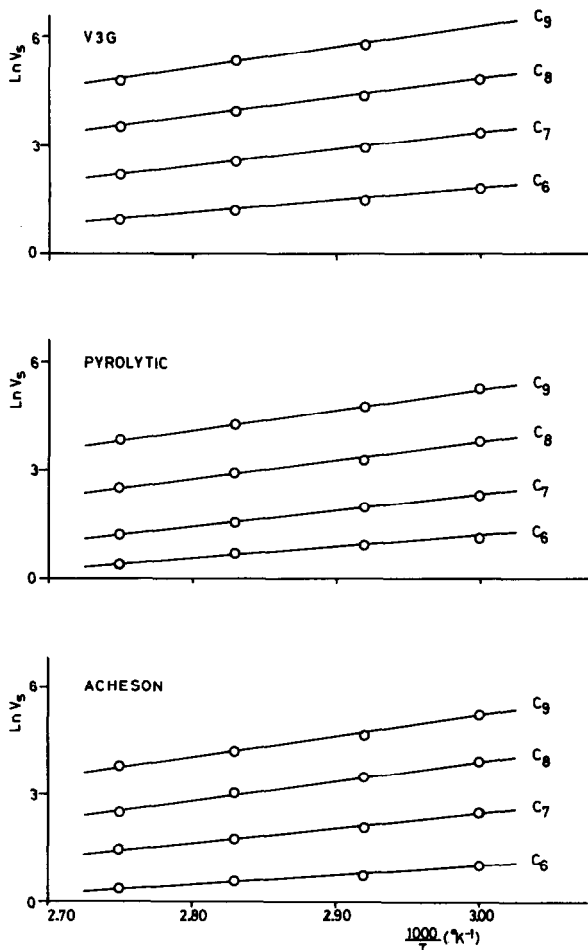


Fig. 2. Variation of the Henry's law coefficients with reciprocal temperature for *n*-alkanes on graphites and graphitized carbon black.

Net retention volumes were obtained from the maxima of the chromatographic peaks and from the dead volume.

There was always a linear relationship between $\ln V_s$ and the polarizability of the hydrocarbons, as can be seen in Fig. 1 for V3G. The adsorption of a given hydrocarbon decreases with increase in temperature. Similar behaviour was shown by the two graphites. The three adsorbents used are non-porous materials, so under the conditions used V_s increases with the polarizability of the molecules (at a given temperature and carrier gas flow-rate). This behaviour is in agreement with the work by Kiselev and Yashin²⁰ on the adsorption of saturated hydrocarbons on graphitized carbon blacks.

The V_s values were obtained from the net retention volumes and the surface areas of the adsorbents (Table I). The plots of $\ln V_s$ against $1/T$ are given in Fig. 2. The q_d values were calculated from the slopes of the straight lines obtained, adjusted

TABLE II
THERMODYNAMIC FUNCTIONS OF ADSORPTION OF *n*-ALKANES ON THE ADSORBENTS AT ZERO SURFACE COVERAGE

Adsorbate	$-q_d$ (kJ mol^{-1})		$-\Delta H_L$ (kJ mol^{-1})		$-\Delta G^0$ (333°K) (kJ mol^{-1})		$-\Delta S^0$ (333°K) ($\text{J mol}^{-1} \text{ }^\circ\text{K}^{-1}$)	
	V3G	Pyrolytic	Acheson	V3G	Pyrolytic	Acheson	V3G	Pyrolytic
<i>n</i> -Hexane	33.8	26.7	26.3	31.7	20.9	18.7	38.7	23.1
<i>n</i> -Heptane	39.2	36.3	35.8	37.1	25.1	22.8	42.3	42.0
<i>n</i> -Octane	44.2	42.5	42.9	42.9	29.2	26.6	45.0	48.6
<i>n</i> -Nonane	48.8	47.5	47.5	47.5	—	30.2	—	51.4

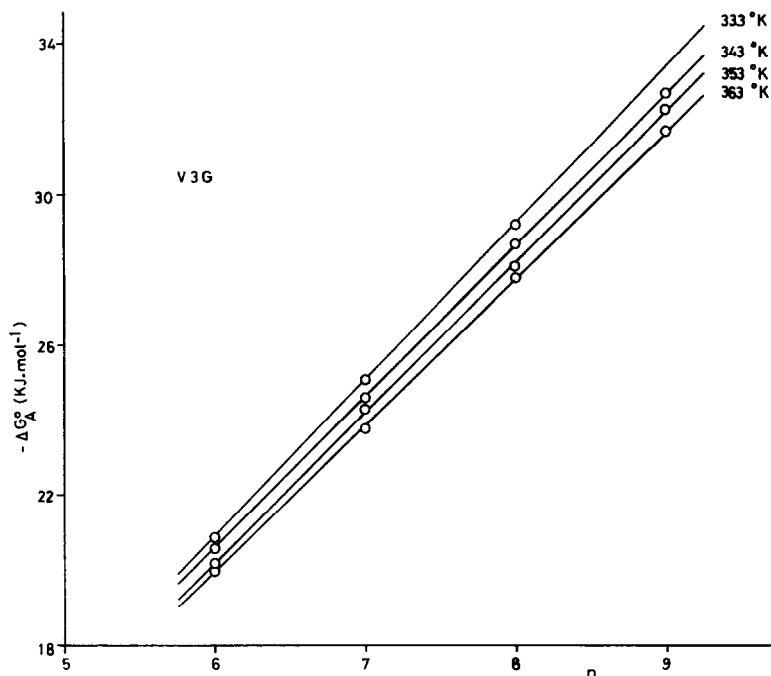


Fig. 3. Variation of standard free energy for the adsorption of n -alkanes on V3G as a function of the number of carbon atoms.

by the least-squares method, and are shown in Table II, together with the heats of liquefaction (ΔH_L) taken from refs. 21 and 22.

The free energy values at zero surface coverage, ΔG_A^0 , were obtained from eqn. 6, and those obtained at 333°K are given in Table II as examples. The variation of ΔG_A^0 with the number of carbon atoms (n) is depicted in Fig. 3 for V3G.

The standard entropy of adsorption at zero surface coverage, ΔS_A^0 , was calculated from the q_a and ΔG_A^0 values, and Table II gives those obtained at 333°K. These three thermodynamic functions are plotted against n in Fig. 4 for the three adsorbents used.

DISCUSSION

The q_a values are very low for the three adsorbents, although they are smaller with the two graphites. This shows that the adsorbents are energetically homogeneous, but this homogeneity is higher with the graphites as they have more basal planes. Further, it can be seen in Fig. 4 that with V3G the graph of q_a against n is a straight line. However, the q_a values for n -hexane with the graphites deviate from this linear relationship shown by the higher hydrocarbons (Fig. 4).

The ΔH_A^0 (or q_a) values calculated with eqn. 7 can be compared with the heats of liquefaction (ΔH_L) for the hydrocarbons. As can be seen in Table II, in general, the q_a are close to the heats of liquefaction. The low heats of adsorption indicate a low concentration on the adsorbent surface of high-energy sites and for this reason the adsorption of the hydrocarbons is non-specific.

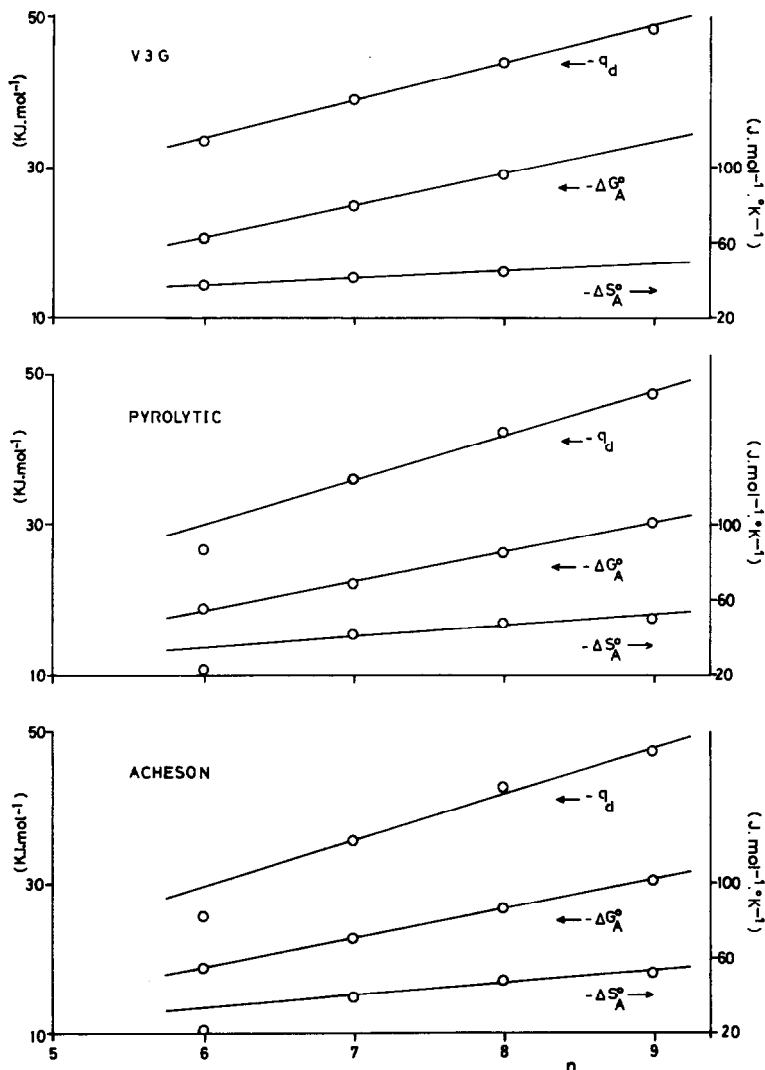


Fig. 4. Thermodynamic functions of adsorption at 333°K on graphites and graphitized carbon black as a function of the number of carbon atoms in the alkanes.

As can be seen from Table II and Fig. 3, there is a linear variation of ΔG_A^0 with n , which means that on increasing the number of carbon atoms of the hydrocarbon the adsorption process becomes more spontaneous. On the other hand, there is a constant increment of about 4 kJ mol^{-1} per CH_2 in ΔG_A^0 (Traube's effect), that is, the adsorbates are adsorbed in a flat position on the surface of the adsorbents²². The relatively weak adsorption of the n -alkanes, illustrated by the small heats of adsorption, indicates that the adsorbate may be mobile. This mobility is, however, better characterized by the entropy of adsorption. The three-dimensional translation entropy of the adsorbate as an ideal gas is given by

$${}_3S_t = R \ln (M^{3/2} T^{5/2}) - 2.30 \quad (9)$$

where M is the molar mass and the entropy is expressed in $\text{JK}^{-1} \text{mol}^{-1}$. Similarly, the entropy of the adsorbate as an ideal, mobile, two-dimensional gas may be calculated from

$${}_2S_t = R \ln (MTA_s) + 273.32 \quad (10)$$

where A_s is the area available for a molecule in the standard adsorbed state and for an ideal gas¹⁸ $A_s = 22.70 T \cdot 10^{-16} \text{cm}^2$.

The ${}_3S_t$ and ${}_2S_t$ values were obtained from eqns. 9 and 10. When 1 mole of gas passes from the gas phase to the adsorbed phase there would be a decrease in translational entropy given by $({}_3S_t - {}_2S_t)$. These values range from $37.1 \text{J K}^{-1} \text{mol}^{-1}$ for n -hexane to $38.8 \text{J K}^{-1} \text{mol}^{-1}$ for n -nonane at 333°K , and are very close to the ΔS_A^0 values obtained experimentally (Table II). Therefore, in the adsorption process all the hydrocarbons undergo the loss of one degree of translational freedom. When n increases the ΔS_A^0 values are higher than the $({}_3S_t - {}_2S_t)$ values. The additional entropy increase found experimentally may result from a rotational or vibrational freedom on the surface.

As was pointed out earlier, the adsorption of the hydrocarbons is non-specific. For this reason, the attractive forces between the adsorbate molecules and the adsorbent surface are essentially dispersive. According to Fowkes²³, the work of adhesion, W_A , between a saturated hydrocarbon and a second phase is given by the geometric mean of the London components of the surface free energies of cohesion of the two pure phases such that

$$W_A = 2 (v_2^L \times v_1^L)^{\frac{1}{2}} \quad (11)$$

as phase 1 is a saturated hydrocarbon, Fowkes postulated that v_1^L is equal to its surface tension, while v_2^L represents the London part of the total surface free energy of phase 2. Dorris and Gray¹⁷ checked that in many adsorbents the work of adhesion for a hydrocarbon is very close to the free energy of adsorption per mole of CH_2 group. They proposed the following equation for the calculation of the London component of the surface free energy of the adsorbent, v_2^L :

$$\frac{-\Delta G_A^{(\text{CH}_2)}}{Na_{\text{CH}_2}} = 2 (v_{\text{CH}_2}^L v_2^L)^{\frac{1}{2}} \quad (12)$$

where $\Delta G_A^{(\text{CH}_2)}$ is the increase in free energy of adsorption per CH_2 group, calculated from Table II, N is Avogadro's number, a_{CH_2} is the cross-sectional area of a methylene group (0.06nm^2) and v_{CH_2} is the surface tension of an infinite polyethylene chain (33.5mN m^{-1})²⁴.

The London component of the surface free energy, v_2^L , was calculated from eqn. 12 and was 100mN m^{-1} for V3G and 80mN m^{-1} for the graphites. These data show that the surface energy is lower for the graphites than for V3G. The v_2^L values obtained in this work are of the same order as those reported recently by Donnet *et al.*²⁵ for different carbons. This result could show the validity of the assumptions made by Dorris and Gray¹⁷. However, the v_2^L obtained for the V3G and the graphites are higher than those reported^{17,22,26} for other adsorbates with low surface energy such as cellophane, cellulose and glass-fibre.

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