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## GAS CHROMATOGRAPHIC DETERMINATION OF ADSORPTION ISOTHERMS, SPREADING PRESSURES, LONDON FORCE INTERACTIONS AND EQUATIONS OF STATE FOR *n*-ALKANES ON GRAPHITE AND CARBON BLACKS

M. DOMINGO-GARCÍA and F. J. LÓPEZ-GARZÓN

*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071-Granada (Spain)*

R. LÓPEZ-GARZÓN

*Departamento de Química General, Colegio Universitario, Jaén (Spain)*

and

C. MORENO-CASTILLA\*

*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071-Granada (Spain)*

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### SUMMARY

Adsorption isotherms were obtained for C<sub>6</sub>–C<sub>9</sub> *n*-alkanes on a graphite and two carbon blacks at 363°K by gas chromatography using the peak maximum elution method. The surface areas of the adsorbents were obtained by applying the Brunauer–Emmett–Teller equation, and found to depend on the hydrocarbon used. Increasing differences from that found with nitrogen at 77°K were observed with increasing chain length of the hydrocarbon. This can be attributed to adsorbate–adsorbate lateral interactions. The London component of the surface free energy of the solids,  $v\frac{1}{2}$ , was calculated from the spreading pressure. The values obtained show that the homogeneity of the solids increases in the order V3 < V3G < Acheson graphite. On the other hand, for the same adsorbent,  $v\frac{1}{2}$  depends on the hydrocarbon used. Equations of state were also determined. It was found that for a spreading pressure below 2 mN m<sup>-1</sup> the *n*-alkanes obey the ideal equation, but spreading pressures above 2 mN m<sup>-1</sup> the behaviour of the hydrocarbons increasingly deviates from that of ideality as the spreading pressure and chain length of the *n*-alkane increase. This is attributed to the increase in adsorbate–adsorbate lateral interactions.

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### INTRODUCTION

In a previous study<sup>1</sup> we used gas–solid chromatography (GSC) at zero surface coverage in order to determine the interactions of hydrocarbons with different carbon surfaces. The thermodynamic adsorption functions indicated that the carbon adsorbents were energetically homogeneous.

Gas chromatography (GC) in contrast to static methods is also of considerable interest for studying adsorption at finite surface coverages, because it readily allows measurements of over a wide range of temperature<sup>2</sup>. This method provides a means to determine the adsorption isotherms from which the surface area, porosity and surface energy are determined.

When adsorption takes place at finite surface coverages the isotherms are generally non-linear and hence retention volumes are dependent upon the adsorbate concentration in the gas phase. In addition, a non-linear isotherm results in asymmetrical peaks<sup>3,4</sup>, the shape of which and the retention time being dependent on the volume injected. For different amounts of adsorbate injected, the chromatographic peaks present the front or trailing edge on a common curve<sup>5</sup>.

In this paper, adsorption isotherms at finite surface coverages obtained by means of GSC are reported, for a series of *n*-alkanes on three different carbons. The isotherms were analyzed in terms of the Brunauer–Emmett–Teller (BET) theoretical model. The London component of the surface free energy and the equations of state have also been obtained. The adsorption of hydrocarbons at zero surface coverage has already been studied<sup>1</sup> on some of the carbons used.

## EXPERIMENTAL

Three commercial carbons were used: Acheson (graphite), V3G (graphitized carbon black) and V3 (carbon black). The first two of those were described in detail in previous papers<sup>1,6,7</sup>. V3G was obtained by graphitizing V3 as described elsewhere<sup>8</sup>. The surface area determined by nitrogen adsorption at 77°K (BET) and the particle size of these carbons are given in Table I. It should be emphasized that these three materials are essentially non-porous, which minimizes the problems of intraparticle diffusion.

The adsorbates used were *n*-hexane, *n*-heptane, *n*-octane and *n*-nonane (Merck, reagent grade) and were employed without further purification.

Chromatographic measurements were carried out with a Carlo Erba gas chromatograph, Model Fractovap 2350. Ultra-high-purity nitrogen was used as carrier gas. The flow-rate measured at the outlet of the column was 15 cm<sup>3</sup>/min and it was corrected for the pressure drop across the column and for the difference in temperature<sup>9,10</sup>. Adsorbents were packed in columns made from Pyrex glass (Table I). Before the adsorption experiments, the column with the adsorbate was conditioned at 453°K for 12 h under a flow of nitrogen.

TABLE I  
CHARACTERISTICS OF THE ADSORBENTS AND CHROMATOGRAPHIC COLUMNS

<i>Adsorbent</i>	<i>Column length (cm)</i>	<i>Internal diameter (mm)</i>	<i>Weight of adsorbent (g)</i>	<i>S<sub>N<sub>2</sub></sub>(77°K-BET) (m<sup>2</sup> g<sup>-1</sup>)</i>	<i>Particle size (μm)</i>
V3	20	3.0	0.1442	77	0.235
V3G	20	3.0	0.1632	67	0.235
Acheson	40	4.0	4.4207	3.6	150–200

Isotherms for each alkane were obtained from a series of injections ranging from 0.05 to 5.5  $\mu$ l. Density data for the hydrocarbons were obtained from ref. 11. The adsorption temperature was 363°K in all cases.

CALCULATIONS

Adsorption isotherms were calculated by the peak maximum elution method<sup>12</sup>. This method is based on the measurement of the maximum retention volumes obtained with different amounts of adsorbate. When the adsorption isotherms are non-linear, the retention volumes will be a function of the adsorbate concentration in the gas phase. The recorder displacement at each maximum is proportional to the partial pressure of the adsorbate vapour in the carrier gas if gas-phase ideality is assumed. For example, Fig. 1 shows chromatographic peaks obtained for different amounts of *n*-hexane on Acheson.

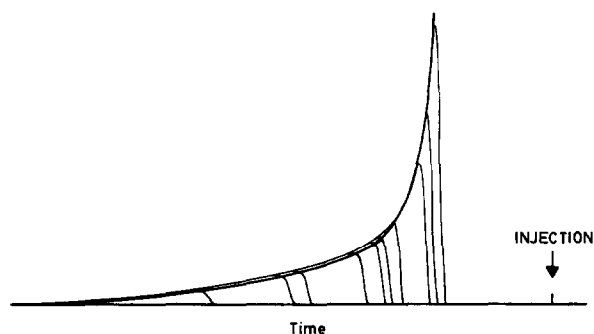


Fig. 1. Chromatographic peaks obtained for different amounts of *n*-hexane with Acheson. Sample sizes range from 0.3 to 2.3  $\mu$ l.

To relate the recorder pen displacement, *h*, to the vapour pressure of each probe<sup>12</sup>, calibration of the detector sensitivity was required. The detector is calibrated by injecting a known amount of sample, *m<sub>cal</sub>* (moles), and the vapour pressure is calculated from the expression

$$p = \left( \frac{m_{cal} X R T}{S_{cal} F} \right) \cdot h \tag{1}$$

where *X* is the chart speed, *F* is the corrected flow-rate, *R* is the ideal gas constant, *T* is the absolute column temperature, *S<sub>cal</sub>* is the area under the calibration peak and *h* is the pen displacement corresponding to adsorbate vapour pressure, *p*. Ideal gas conditions and linear detector response are assumed in this equation. The latter condition was verified.

The amount of sample adsorbed, *q*, corresponding to a particular vapour pressure<sup>12</sup> is then given by

$$q = m_{cal} S_{ads} / W S_{cal} \tag{2}$$

where *W* is the weight of the adsorbent, and *S<sub>ads</sub>* is the chart area bounded by the

axis at time  $t = 0$  and by the GC adsorption envelope of the peak maximum. The dead time was calculated by means of the relationship given by Peterson and Hirsch<sup>13</sup> and it was negligible in all cases. By measuring  $S_{\text{ads}}$  at different values of  $h$ , the isotherm  $q = f(p)$  was calculated.

All graphical integrations were carried out from chromatograms. It should be emphasized that asymmetrical peaks for which trailing edges are on the same curve cannot be used for the calculations. They represent a case of non-ideality which is too complex to deal with<sup>14</sup>.

When using this method to obtain the adsorption isotherms, the sorption effect, that is to say, the change in gas flow-rate caused by the sorption or desorption of the solute molecules in the stationary phase causes the greatest error in the isotherm determination. According to Conder's analysis<sup>15</sup>, for a mole fraction of the solute in the gas phase of  $y \approx 0.03$ , the amount of solute adsorbed would be underestimated by 3%, this error increasing with increasing  $y$ . Therefore, in this paper, for  $y > 0.03$ , we have corrected the data for the sorption effect by taking into account in the flow-rate measured the term  $(1 - jy)$  (ref. 15) where  $j$  is the James-Martin factor.

## RESULTS AND DISCUSSION

### *Adsorption isotherms*

It is seen from Fig. 1 that for all cases the backs of the elution peaks fall on a common curve. Thus, the criteria for using the simple elution technique to determine isotherms are satisfied. The adsorption isotherm of *n*-nonane on V3 could not be calculated since equilibrium conditions were not reached.

GC envelopes were obtained by joining the peak maxima as shown in Fig. 1, and from them, adsorption isotherms were obtained by means of eqns. 1 and 2.

Adsorption isotherms at 363°K expressed as  $q$  (mol g<sup>-1</sup>) versus  $p/p_0$  are shown in Fig. 2. The values of  $p_0$  were obtained from ref. 11. The adsorption isotherms seem to be of Type II in the Brunauer-Deming-Deming-Teller classification<sup>16</sup> and the adsorption of *n*-alkanes on these carbons presents an interesting behaviour. As was shown previously<sup>1</sup>, at very low coverages the adsorption increases with the number of carbon atoms in the hydrocarbon. Now at relatively high coverages at a given value of  $p/p_0$  the adsorption decreases with increasing number of carbon atoms. This behaviour is attributed to the adsorbate-adsorbate lateral interactions which increase with surface coverage. At low surface coverages these interactions are negligible, but at high surface coverages they become more significant. Since the adsorption of *n*-alkanes is expected to occur through dispersion forces<sup>1</sup> with our adsorbents, the amount adsorbed is highly dependent on the molecular size of the adsorbate and hence the observed behaviour is as expected, supposing the same orientation for all adsorbates on the surface of the three adsorbents. A similar behaviour was reported by different authors<sup>17-21</sup> using other adsorbents.

Experimental isotherms were interpreted using the BET equation. For example, in Fig. 3 BET plots for the isotherms obtained on V3G are shown; similar plots were obtained in the other cases. From the range over which the plots were reasonably linear, monolayer capacities,  $q_m$  (mol g<sup>-1</sup>), were estimated using the slope and intercept of the corresponding straight lines as determined by means of the least

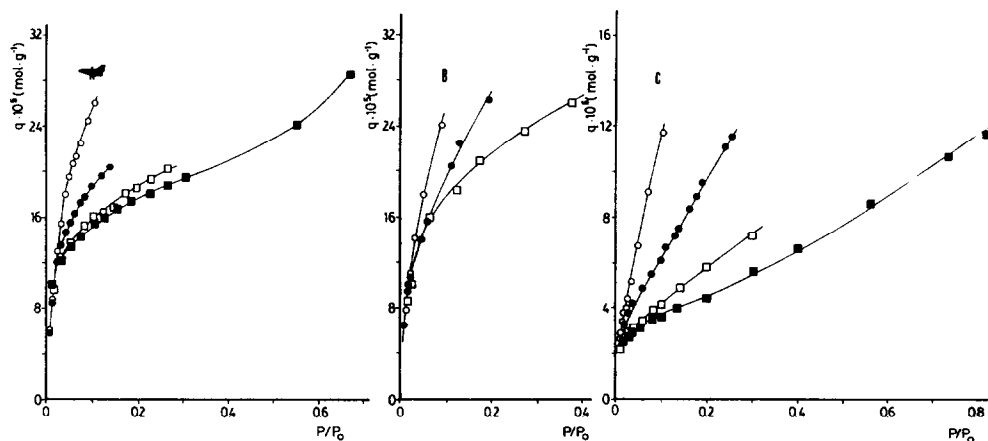


Fig. 2. Adsorption isotherms of *n*-alkanes at 363°K on V3G (A), V3 (B) and Acheson (C). *n*-Alkanes: ○, hexane; ●, heptane; □, octane; ■, nonane.

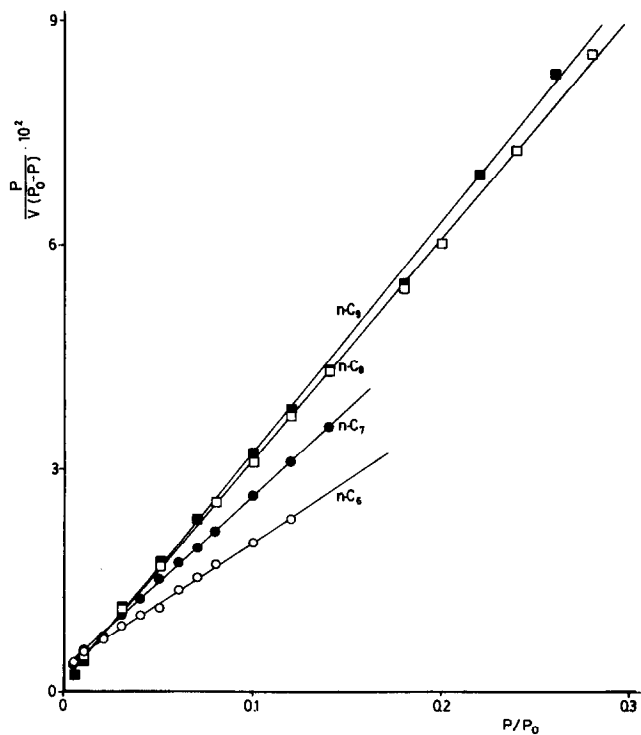


Fig. 3. BET plots for the isotherms of *n*-alkanes on V3G. Symbols as in Fig. 2.

TABLE II  
MONOLAYER CAPACITIES AND SURFACE AREAS

Solute	$q_m \cdot 10^5$ (mol g <sup>-1</sup> )			$A_m$ (nm <sup>2</sup> )	$S$ (m <sup>2</sup> g <sup>-1</sup> )		
	V3	V3G	Acheson		V3	V3G	Acheson
<i>n</i> -Hexane	29.02	27.02	0.94	0.434	75.9	70.6	2.5
<i>n</i> -Heptane	22.72	18.80	0.77	0.462	63.2	52.3	2.1
<i>n</i> -Octane	17.52	15.29	0.55	0.487	51.4	44.8	1.6
<i>n</i> -Nonane	—	14.00	0.41	0.518	—	43.6	1.3

squares method. In Table II the  $q_m$  values obtained with different sorbates on the three carbons are given.

From  $q_m$  data, surface areas can be evaluated by

$$S = Nq_m A_m \quad (3)$$

where  $S$  is the surface area,  $N$  is the Avogadro number and  $A_m$  is the molecular area of the adsorbate. The latter can be estimated using

$$A = 1.091 \left( \frac{M}{\rho N} \right)^{2/3} 10^{14} \quad (4)$$

where  $M$  is the molecular weight and  $\rho$  the liquid density. It is assumed that the arrangement of the molecules on the surface of the adsorbent is the same as on a plane placed within the bulk of the liquid<sup>16</sup>. Values of  $S$  determined by means of eqns. 3 and 4 are shown in Table II, and it is interesting to note some of their features. The surface area obtained from nitrogen adsorption at 77°K (Table I) is in all cases larger than those obtained from adsorption of organic vapours, except for *n*-hexane on V3G. Similar results have been obtained by other authors<sup>17-21</sup> with other adsorbents such as cellulose, coated adsorbents, woodfibres and cellophane. This can be explained in the sense that the  $A_m$  values obtained from eqn. 4 are underestimates<sup>16-22</sup>, probably due to the assumption that the molecular packing on the surface of the solid is the same as in the liquid phase. On the other hand, the surface area of the adsorbents decreases with increasing number of carbon atoms in the hydrocarbon and, therefore, the differences from the surface area obtained with nitrogen at 77°K increase. These results show that the longer the hydrocarbon chain, the less extensive is the packing of the molecules on the surface of the adsorbent, and the more this packing differs from that of the molecules in the liquid phase. The differences in the molecular packing will arise from the adsorbate-adsorbate lateral interactions, which are also responsible for the inversions of the isotherms, as was stated before.

#### Spreading pressure

When a gas is adsorbed on a solid surface the spreading pressure,  $\pi$ , exerted is defined as<sup>14,20,21,23</sup>

$$\pi = v_s - v_{sv} \quad (5)$$

where  $v_s$  is the surface free energy of the solid–vacuum interface and  $v_{sv}$  the surface free energy of the solid at the solid–vapour interface. From eqn. 5  $\pi$  is defined as the lowering of the surface free energy due to vapour adsorption on the solid surface. The determination of  $\pi$  is not usually possible by means of eqn. 5, but the integrated form of Gibbs’ adsorption equation

$$\pi = \frac{RT}{SM} \int_0^{p/p_0} [q/(p/p_0)] d(p/p_0) \tag{6}$$

does enable the calculation of  $\pi$ . Here  $S$  is the surface area of the adsorbent obtained with nitrogen at 77°K. The spreading pressure may be obtained by graphical integration of the area under the curve of  $q/(p/p_0)$  versus  $p/p_0$ .

The spreading pressure over the entire range of  $p/p_0$  is  $\pi^0$ . This is a very important value since it is related to the surface free energy of the solid<sup>24</sup>. A plot of  $q/(p/p_0)$  versus  $p/p_0$  for *n*-nonane on Acheson is shown in Fig. 4. In all cases, the plots of  $q/(p/p_0)$  versus  $p/p_0$  were extrapolated to  $p/p_0 = 1$  in order to obtain  $\pi^0$  values, which are summarized in Table III.

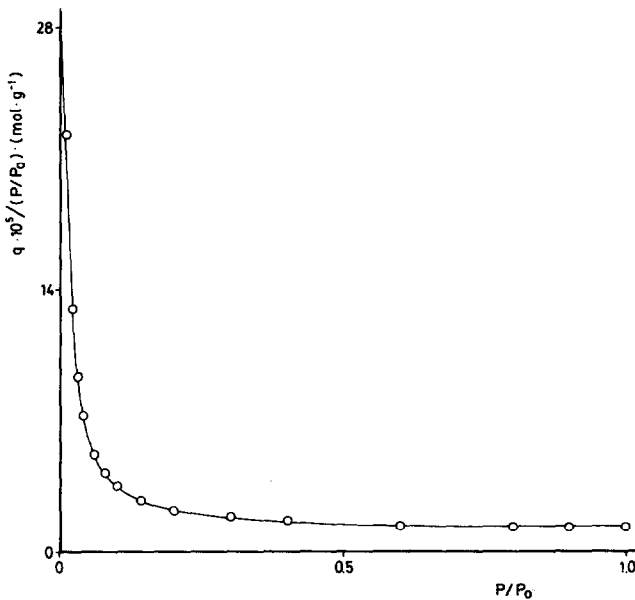


Fig. 4. Plot of  $q/(p/p_0)$  versus  $p/p_0$  for *n*-nonane on Acheson.

The spreading pressure,  $\pi^0$ , is often used to calculate the contribution of the London dispersion forces to the surface free energy of the solid. This is possible from a model developed by Fowkes<sup>24</sup> based on a paper of Girifalco and Good<sup>25</sup>. The interfacial tension,  $v_{12}$ , between a liquid, 1, and a solid, 2, is given by

$$v_{12} = v_1 + v_2 - 2(v_1^{\frac{1}{2}}v_2^{\frac{1}{2}})^{\ddagger} \tag{7}$$

TABLE III  
SPREADING PRESSURE AND LONDON COMPONENT OF THE SURFACE FREE ENERGY

Solute	$\pi^0$ (mN m <sup>-1</sup> )			$v_2^L$ (mN m <sup>-1</sup> )			$v_2^{L**}$ (mN m <sup>-1</sup> )		
	V3	V3G	Acheson	V3	V3G	Acheson	V3	V3G	Acheson
<i>n</i> -Heptane	68.4	61.9	45.1	167.0	145.2	95.9	82.2	75.7	58.9
<i>n</i> -Octane	65.0	51.2	32.4	150.6	110.0	65.0	79.9	66.1	47.3
<i>n</i> -Nonane	—	49.0	20.5	—	102.0	43.3	—	65.3	36.8

\* From eqn. 11.

\*\* From eqn. 12.

where  $v_1$  is the surface tension of the liquid and the superscript L refers to London forces. Combining eqn. 7 with eqn. 8 for the contact angle<sup>20,26</sup> between a liquid and a planar surface

$$v_2 - v_1 - v_{12} = \pi^0 + v_1 (\cos \theta - 1) \quad (8)$$

results in:

$$\cos \theta = -1 - \frac{\pi^0}{v_1} + \frac{(2 v_1^L v_2^L)}{v_1} \quad (9)$$

Since the surfaces of the carbons used in this work are hydrophobic it can be assumed that hydrocarbons will spread on them and hence the contact angle will be zero. Eqn. 9 then becomes:

$$v_2^L = \frac{(2 v_1 + \pi^0)^2}{4 v_1^L} \quad (10)$$

Since the liquid phase is a *n*-alkane, Fowkes postulated that  $v_1^L = v_1$  and hence:

$$v_2^L = \frac{(2 v_1 + \pi^0)^2}{4 v_1} \quad (11)$$

The values of the London component of the surface free energy of the solid,  $v_2^L$ , are summarized in Table III for the three adsorbents and for the *n*-alkanes used. The first observation to make is that  $v_2^L$  varies with the chain length of the hydrocarbon. Similar results have been found for other adsorbents<sup>20,21,26</sup>. This has been explained by Fowkes<sup>27</sup> in terms of the effect of the London force field of the liquid or solid phase on the effective density of the nearest monolayer of hydrocarbon; the *n*-alkanes, having a surface tension smaller than  $v_2^L$ , will experience a stronger force field than in their bulk liquid, giving rise to a stronger interaction than expected from their surface tension. Therefore, this variation shows that the London dispersion component of the surface free energy (as obtained from eqn. 11) is an interfacial parameter rather than a fundamental property of the solid surface<sup>21</sup>. From this point of view no agreement can be expected between the  $v_2^L$  values obtained from Fowkes



theory, applying eqn. 11, and the expression of Dorris and Gray<sup>28</sup>, which was also used by us in a previous paper<sup>1</sup>, applied to zero surface coverage. On the other hand, the  $v_{\frac{1}{2}}$  values obtained from eqn. 11 are larger than those expected for non-specific interactions. Values of  $v_{\frac{1}{2}}$  larger than expected have also been reported by Donnet *et al.*<sup>29</sup>, Zettlemoyer<sup>26</sup> and Luner and Sandell<sup>30</sup>. In order to obtain more reasonable values of  $v_{\frac{1}{2}}$ , Zettlemoyer<sup>26</sup> proposed the use of a new expression, in which the interfacial field is evaluated as an arithmetic mean of the surface energies:

$$v_{\frac{1}{2}} = v_1 + \pi^0 \tag{12}$$

$v_{\frac{1}{2}}$  values obtained from eqn. 12 are also given in Table III. They are lower than those obtained by means of eqn. 11 and therefore they seem more appropriate. Likewise, the  $v_{\frac{1}{2}}$  values decrease with increasing chain length of the hydrocarbon and they are not in good agreement with those reported before<sup>1</sup>. This indicates that it is difficult to determine  $v_{\frac{1}{2}}$  and that the values obtained from either eqn. 11 or 12 cannot be considered as an intrinsic property of the solid. On the other hand, for the same hydrocarbon, the  $v_{\frac{1}{2}}$  value increases in the order Acheson < V3G < V3, the same order in which the surface homogeneity decreases.

*Equation of state*

The molecules of a gas adsorbed on a surface may be treated as a two-dimensional gas, and an equation of state may be deduced. Thus, for an ideal two-dimensional gas, the equation of state is given by

$$\pi A = kT \tag{13}$$

where  $\pi$  is the spreading pressure,  $k$  is the Boltzman constant and  $A$  is the surface area occupied by the molecules at each spreading pressure. Eqn. 13 supposes that the molecules behave as bodies without a volume and without interactions<sup>23</sup>.

Fig. 5 shows plots of  $\pi A/kT$  versus  $\pi$  for *n*-alkanes on V3G. The dotted curve

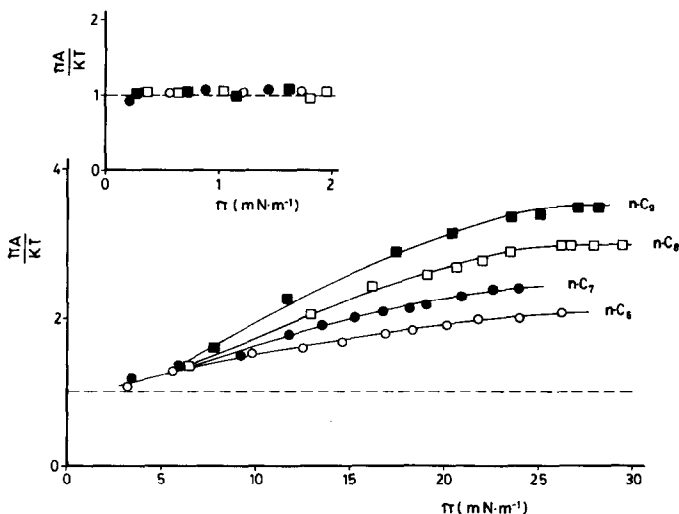


Fig. 5. Eqn. 13 applied to the adsorption of *n*-alkanes on V3G.

represents the ideal equation of state. The spreading pressure,  $\pi$ , was determined from eqn. 6 and the  $A$  values were calculated from

$$A = S/Nq \quad (14)$$

where  $S$  is the surface area determined from nitrogen adsorption at 77°K,  $N$  is the Avogadro number and  $q$  is the amount adsorbed at each relative pressure. It is seen in Fig. 5 that for  $\pi$  values lower than about 2 mN m<sup>-1</sup> the experimental data approach the ideal line, which means that at such  $\pi$  values the adsorbates behave as ideal gases, because the adsorbate-adsorbate lateral interactions will decrease when  $\pi$  decreases. This is in agreement with the data reported for adsorption at zero surface coverage<sup>1</sup>. Above a  $\pi$  value of 2 mN m<sup>-1</sup> the experimental points do not fit the ideal equation of state and  $\pi A/kT$  increases with the spreading pressure,  $\pi$ . On the other hand the deviation from the ideal behaviour increases with the number of carbon atoms of the hydrocarbon. This shift at higher  $\pi$  values is due to the adsorbate-adsorbate lateral interactions.

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