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CLUSTER EXPANSION FOR RETENTION VOLUME IN GAS ADSORPTION CHROMATOGRAPHY

ADSORPTION OF HYDROCARBONS ON GRAPHITE

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SUMMARY

A cluster expansion for retention volume in gas adsorption chromatography is developed. Theoretical evaluations are made of the temperature dependence of the integrals W_1, which are directly proportional to Henry's constant, and of the dependence of retention volumes of benzene, hexane and pentane on their density in the free gas phase. The results are compared with experimental gas chromatographic results and with an application of a graphitized lamp-black as an absorbent. Good agreement is found for isosteric heats of adsorption and reciprocal temperature dependence of integrals W_1, but the two evaluations of the dependence of retention volume on adsorbate density are not in agreement. Reasons for these divergences are suggested.

INTRODUCTION

For many years graphitized blacks have found experimental use for theoretical and practical reasons[1–5]. The well-defined topography of the adsorptive centres enables the calculation of many thermodynamic characteristics of the surface adsorption of hydrocarbons and noble gases and the chromatographic separation of many complicated mixtures of hydrocarbons (*e.g.* geometrical isomers, butanes, xylenes)[2].

Molecular statistical adsorption theory has been used for the calculation of the adsorption equilibrium coefficient, the retention volume, and the differential energy and entropy of adsorption for various hydrocarbons of very different molecular

shape, size, and polarizability[1-5]. The aim of this paper is to introduce a cluster expansion for retention volume in gas adsorption chromatography[6,7] which could be used to calculate, from chromatographic measurements, microscopic characteristics of adsorption systems, to predict retention values and to optimize chromatographic separation processes.

CLUSTER EXPANSION FOR RETENTION VOLUME IN GAS ADSORPTION CHROMATOGRAPHY

Consider an assembly of molecules of fixed activity α and volume V, near an inert solid surface (inert in the sense that its own thermodynamic properties are unaffected by the presence of adsorbed gas and merely seem to provide an external potential field). The grand canonical partition function is given by[8]

$$\Xi = \sum_{N>0} \cdot \frac{\alpha^N}{N!} Z_N \tag{1}$$

where Z_N is the configurational integral. Expansion of $\ln \Xi$ into activity power leads to

$$\ln \Xi = \sum_{l=1} B_l \, \alpha^l \tag{2}$$

where B_l's are the generalized cluster integrals, relative to l molecules

$$l! \, B_l = \int_V \cdot \cdot \int dr^l \prod_{i=1}^{l} g_i \sum_{i,j} (\Pi f_{ij})_c \tag{3}$$

In the above $g_i = \exp(-v_i/RT)$, $f_{ij} = \exp(-u_{ij}/RT)-1$, $v_i = v(r_i)$ is the gas–solid potential energy, and $u_{ij} = u(r_i,r_j)$ is the mutual interaction energy of two molecules, localized at r_i and r_j. We neglect the third and higher order effects and assume that $u_{ij} = u(|r_i-r_j|)$. We will also assume that the total interaction energy of l molecules can be represented as a sum of pair-wise energies. The index c in eqn. 3 denotes that to each particular product $(\Pi f_{ij})_c$ there corresponds a connected graph, such that each molecule of the set is represented by a g_i-vertex and each factor f_{ij} by a line joining two vertices. Defining v_i such that

$$g_i = \begin{cases} g_i & \text{for } r_i \in V \\ 0 & \text{for } r_i \notin V \end{cases}$$

integration of eqn. 3 may be extended over all configurational space.

Next, using Bellemans[9,10] procedure of reduction of B_l, we can expand $\ln \Xi$ into density n in the homogeneous ($v_i = 0$) part of system powers.

For this purpose we can define a new type of cluster integral W_l, relative to l molecules[9,10].

$l! \, W_l = \{$the sum of the contributions of all connected graphs of l distinct square vertices, such that the basic part of these graphs consists of white squares, and all terminal subparts of black squares$\}$.

The contribution to W_l from a given graph of l squares has been calculated as follows:

(i) to each white vertex corresponds a factor g_t

(ii) with each terminal subpart of λ black squares is associated a factor

$$\{-1 + \prod_{i=1}^{\lambda} g_i\}$$

(iii) with each link joining two vertices is associated a factor f_{ij}

(iv) integrate over the coordinates in ∞ (in the case of white squares it is is reduced to integration over V).

For example

$$1!\ W_1 = \int_V (g_1 - 1)\, dr_1 = \blacksquare - \square$$

$$2!\ W_2 = \int_V g_1 \left\{ \int_\infty (g_2 - 1) f_{12}\, dr_2 \right\} dr_1 = \blacksquare - \square \tag{4}$$

Thus, using Bellemans' general proof, we have[9,10]

$$l^2\, B_l = (V + W_1) \sum_{[n_k]} \prod_k \frac{(l\beta_k)^{n_k}}{n_k!} + l \sum_{[m,n_k]} m\, W_m \prod_k \frac{(l\beta_k)^{n_k}}{n_k!} \tag{5}$$

$$\Sigma k n_k = l - 1 \qquad \Sigma k n_k = l - m \quad (m > 1)$$

or in the form of Cauchy integrals

$$l^2\, B_l = \frac{V + W_1}{2\pi i} \oint_C \frac{e^{l\varphi(\zeta)}}{\zeta^l}\, d\zeta + \frac{l}{2\pi i} \oint_C \frac{e^{l\varphi(\zeta)}}{\zeta^l} \sum_2^\infty m\, W_m\, \zeta^{m-1}\, d\zeta \tag{6}$$

where $\varphi(\zeta) = \Sigma \beta_k \zeta^k$, β_k are irreducible Mayer integrals and C is a closed contour around the origin leaving outside all singularities of the integrand except the pole in zero.

Substituting eqn. 6 into eqn. 2, and making use of the Lagrange theorem on the existence[11] of a unique root $\zeta_0 = n$, which satisfies the equation $\zeta_0 \exp[-\varphi(\zeta_0)] = \alpha$, we obtain

$$\bar{N} = n\, W_1 + \sum_2^\infty m\, W_m\, n^m \left(1 - \sum_1^\infty k\, \beta_k\, n_k \right)^{-1} \tag{7}$$

where $\bar{N}$ is the average number of adsorbed molecules and n is the bulk density. Consequently, the cluster expansion for retention volume V_N in gas adsorption chromatography, obtained via the Conder–Purnell[12] equation may be written as follows:

$$V_N(n) = W_1 + \left\{ \sum_{k,m} k\, m\, (m - k)\, \beta_k\, W_m\, n^{m+k-1} \right\} \left\{ 1 - \sum_k k\, \beta_k\, n^k \right\}^{-2} \tag{8}$$

The integral W_1 is simply related to Henry's constant

$$W_1 = \frac{K_H}{RT} \tag{9}$$

To describe the adsorption of complex molecules on graphite it is necessary to take into account the dependence of v on the distance between the molecule mass centre and the surface, and on the orientation of the molecule. However, hydrocarbon molecules are composed of few different atoms, so there is evidence in favour of representing v as a sum of the potential functions of intermolecular interactions of atom pairs $v^{(ij)}$, where index i denotes i-th carbon atom of graphite, and index j the j-th atom of adsorbate molecule[1-5]

$$v = \sum_{i,j} v^{(ij)} \tag{10}$$

Generally, the potential energy of interactions $v^{(ij)}$ may be approximated by the Lennard-Jones (W) (12—6) function

$$v^{(ij)} = 4\varepsilon_j \left[\left(\frac{\sigma_j}{\varrho_{ij}} \right)^{12} - \left(\frac{\sigma_j}{\varrho_{ij}} \right)^6 \right] \tag{11}$$

where ϱ_{ij} denotes the distance between the i-th carbon atom of graphite and the j-th atom of adsorbate molecule.

The distance ϱ_{ij} is determined by specifying the origin r_0 and the orientation Θ of a suitable molecular frame with respect to a crystalline reference system. Thus, in the notation of Battezatti et al.[3],

$$\varrho_{ij} = |r_i - r_j| \tag{12}$$

$$r_j = \{\hat{R}(\Theta)|r_0\} r_{0j} \tag{13}$$

where $\{\hat{R}(\Theta)|r_0\}$ is a roto-translation operator[3]. The potential energy interactions of the k-th atom of adsorbate with graphite $v^{(k)}$ may be written[3,8]

$$v^{(k)}(r) = v_0^{(k)}(z) + \sum_1 \omega_{(z)}^{(km)} f_m(s_1, s_2) \tag{14}$$

where

$$v_0^{(k)}(z) = \frac{2\pi \varepsilon_k}{|a_1 \times a_2|} \sum_{n=0} \left\{ \frac{\sigma_k^{12}}{5(z + nd)^{10}} - \frac{\sigma_k^6}{(z + nd)^4} \right\} \tag{15}$$

$$\omega^{(k,m)} = \frac{\pi \varepsilon_k}{|a_1 \times a_2|} \left\{ \frac{\sigma_k^{12} g_m^5}{1920 z^5} K_5(g_m z) - \frac{\sigma_k^6 g_m^2}{2z^2} K_2(g_m z) \right\} \tag{16}$$

where d is the interlayer distance of graphite, K_n is the modified Bessel function of the second kind and order n, $f_m(s_1, s_2)$ are the functions defined by Steele, the vector $s_1 a_1 + s_2 a_2$ is the projection of r on the graphite plane, a_1 and a_2 being the graphite unit lattice vectors, and g_m is the length of the reciprocal lattice vectors, defined by

Steele[8]. As mentioned by Ricca, the principal advantage of this method lies in the functional form of the potential. It is also much more economical in computer time.

Evaluation of integrals W_1 and W_2

The integral W_1 is given by the following equation[2]

$$W_1 = \int_V \{\exp(-v(r_m, \Theta)/RT) - 1\} J \, dr_m \qquad (17)$$

where r_m denotes the coordinates of centre of mass and J is the jacobian. The integration is made over all configurational space available to the adsorbate molecules.

Eqn. 17 is valid for quasirigid molecules and ignores the perturbation from the surface to the internal vibrational degrees of freedom, which is negligible for a non-specific adsorption on homogeneous surface of graphite. On the other hand, perturbations to the internal rotational degrees of freedom are not negligible. In calculations of W_1 we have used the method of Vidal-Madjar et al.[1,2], in which the graphite surface is substituted by a continuum. The potential energy of interactions of a complex molecule with this continuum is treated as an average value averaged over positions of r_m on the graphite lattice. For adsorption of benzene on graphite we have adopted model "C" of Vidal-Madjar et al.[1,2], whereas in the case of adsorption of pentane and hexane we used model "F".

In model C, reserved for the description of planar (or quasi-planar) molecules, the system of coordinates connected with adsorbate molecule OXYZ is chosen so that OX and OY are the two main angles of the molecular plane, OZ corresponds to the largest moment of inertia (perpendicular to the molecular plane), θ is the angle of the molecular plane to the adsorbent surface and ψ defines the orientation of the molecule within that plane. Let us denote by v''_{z_0} the value of $\partial^2 v/\partial z^2$ for $z = z_0$, where z_0 is the equilibrium distance at $\theta = 0$ and $v''_\theta = \partial^2 v/\partial \theta^2$. In this approximation[2]

$$v(z, \theta, \psi) = v_0(z = z_0) + \frac{1}{2} v''_{z_0}(z - z_0)^2 + \frac{1}{2} v''_\theta(\psi) \sin^2\theta \qquad (18)$$

and consequently

$$W_1 = A \sqrt{\frac{2\Pi RT}{v''_{z_0}}} \, 2\Pi RT \exp(-v_0/RT) \int_0^{2\pi} \frac{1}{v''_\theta(\psi)} \, d\psi \qquad (19)$$

where A denotes the surface area.

For the description of adsorption of pentane and hexane we used the model "F". Because of the strong anisotropic field of adsorption these molecules have a preferential orientation with their axis of the lowest moment of inertia roughly parallel to the surface. The angle between OZ and the perpendicular to the adsorbent surface is designated θ.

We assume rotation around OY and oscillation around OZ. The movement around OX can be either a hindered rotation F_a or an oscillation F_b. Thus we have

$$F_a: v(z, \theta, \psi) = v_0 + \frac{1}{2} v''_{z_0}(z - z_0)^2 + \frac{k_\theta}{2}\cos^2\theta + \frac{1}{2} v''_\psi \sin^2\psi \qquad (20)$$

$$F_b: \quad v(z, \theta, \psi) = v_0 + \frac{1}{2} v''_{z_0} (z - z_0)^2 + \frac{1}{2} v''_{\theta, \pi/2} \cos^2 \theta + \frac{1}{2} v''_{\psi} \sin^2 \psi \tag{21}$$

where $(k_\theta, v''_\psi, v''_{\theta, \pi/2})$ are force constants[2]. Consequently[2]

$$F_a: \quad W_1 = \frac{A}{2 \Pi} (2 \Pi RT)^{3/2} (v''_{z_0} v''_\psi k_\theta)^{-1/2} \exp \left(- \frac{v_0}{RT} \right) \tag{22}$$

$$F_b: \quad W_1 = \frac{A}{2 \Pi} (2 \Pi RT)^{3/2} (v''_{z_0} v''_\psi v''_{\theta, \pi/2})^{-1/2} \exp \left(- \frac{v_0}{RT} \right) \tag{23}$$

The problem of numerical evaluation of integrals W_2 is more complicated. For this purpose we assume that the adsorbate molecules interact via simple LJ (12—6) potential

$$u(r) = 4 \, \varepsilon_{gg} \left[\left(\frac{\sigma_{gg}}{r} \right)^{12} - \left(\frac{\sigma_{gg}}{r} \right)^6 \right] \tag{24}$$

with the parameters ε_{gg} and σ_{gg}. These parameters can be treated as averages[4]. The integrals W_2 were evaluated according to eqn. 4.

To investigate the practicality of the above theory, we compared the results of the theoretical calculations of the temperature dependence of integrals W_1 for benzene, hexane and pentane, as well as the dependence of their retention volumes on their densities in the free gas phase, with experimental data. In the theoretical calculations adequate literature data were used.

Experiments were carried out by the chromatographic method using as model adsorbent graphitized lamp-black, which was also examined spectroscopically.

Numerical calculations

The adsorption potential energies were calculated for a whole molecule and for different locations of centre of mass r_m with respect to the graphite plane. The value of v_0 and z_0 were taken as average values, averaged over all considered locations of r_m. These are summed in Table I. Next, the values of W_1 were calculated according to eqns. 19, 22 and 23. They are compared with experimental results in Figs. 1–3. Table II presents the values of isosteric heats of adsorption in the zero coverage limit, calculated according to the equation

$$q^0_{st} = RT + R \frac{\partial \ln W_1}{\partial (1/T)} = RT + u^0_{st} \tag{25}$$

TABLE I

THE VALUES OF v_0 AND z_0 FOR BENZENE, HEXANE AND PENTANE ON GRAPHITE

	Benzene	Hexane	Pentane
z_0 (Å)	3.32	3.78	3.72
v_0 (cal/mole)	−10,260	−11,100	−9740

TABLE II

THEORETICAL AND EXPERIMENTAL VALUES OF q_{st}^0 (cal/mole) AT 360 °K

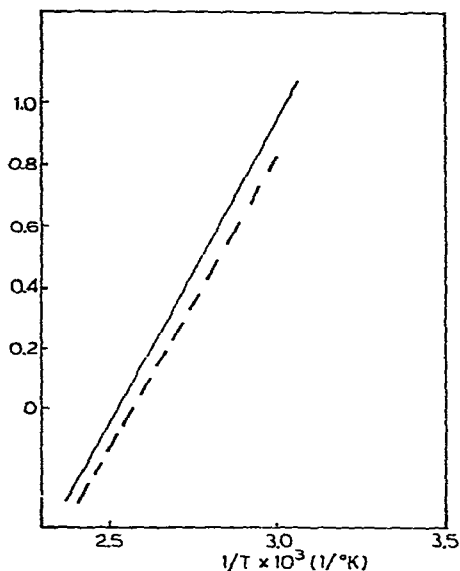| Adsorbate	Theort.	Exptl.
Benzene	10,030	9960
Hexane	10,420	10,240
Pentane	9920	10,030

Fig. 1. Variation of the integrals W_1 as a function of temperature for benzene on graphitized lamp-black. The solid line ($u_{st} = 9.31$) was calculated according to eqn. 19, and the broken line ($u_{st}^0 = 8.934$) was obtained experimentally.
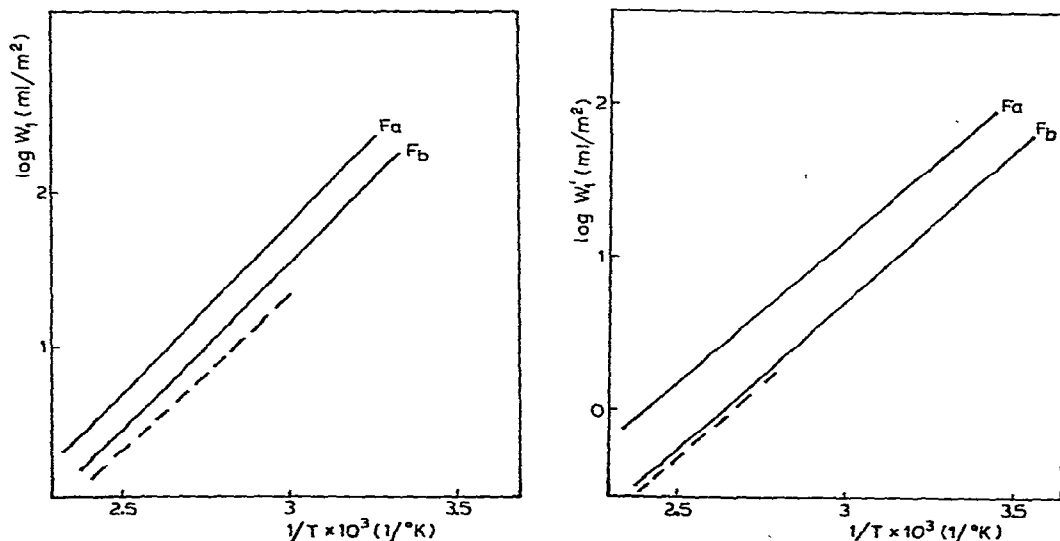

Fig. 2. Variation of the integrals W_1 as a function of temperature for n-hexane on graphitized lamp black. The solid lines denote the results of theoretical calculations ($u_{st}^0 = 10.2$ kcal/mole) and the broken line ($u_c^0 = 9.52$ kcal/mole) was obtained experimentally.

Fig. 3. As for Fig. 2, but for n-pentane. Solid lines: $u_{st}^0 = 9.2$ kcal/mole); broken line: $u_{st}^0 = 9.31$ kcal/mole.

The second part of our calculations are concerned with the evaluation of the initial plot of $V_N = V_N(n)$ for pentane at 387.7 °K and 395.6 °K, calculated according to eqn. 8, truncated at n^2. The effective values of the parameters ε_{gg} and σ_{gg} were taken from the paper by Lal and Spencer[12]. They were $\varepsilon_{gg} = 568$ cal/mole, and $\sigma_{gg} = 4.13$ Å. The results of our calculations are shown in Fig. 4.
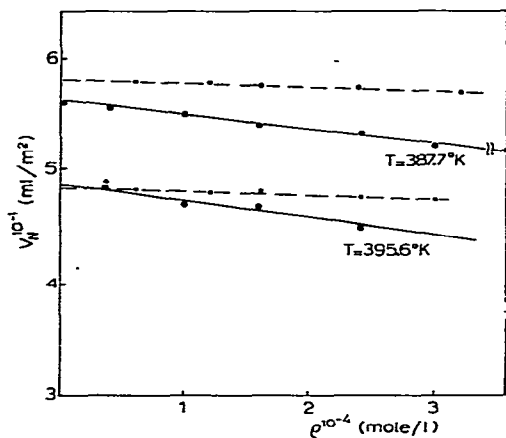

Fig. 4. The initial plot of V_N against n. The points denote the experimental data, whereas the dashed lines were calculated according to eqn. 8, truncated to n^2.

EXPERIMENTAL

Commercial lamp-black, made in the USSR, was graphitized in an Acheson resistance furnace. The specific surface areas of carbon blacks were measured by the method of thermal desorption of nitrogen. Elemental analysis of the adsorbents was carried out using the Hewlett-Packard analyser CHN Model F & M 185. The microcrystalline structure was examined by the Dron-1 diffractometer with a cupric lamp and nickel filter. The degree of graphitization was established measuring the ratio of the intensities of total line 112 and total line 110 in relation to the natural madagascaric graphite. Electron paramagnetic resonance (EPR) measurements were carried out at room temperature using EPR spectrometer type RE-1301, with diphenylpicryl hydrazide as reference. Photomicrographs were obtained with a Tesla B-613 electron microscope with resolving power 4.5 Å. The characterisics of carbon blacks before and after graphitization are summarized in Table III. Photomicrographs of lamp-black before and after graphitization are presented in Fig. 5 and 6.

The chromatographic measurements were carried out on an ICSO Chromatograph with a detector of thermal conductivity. Hydrogen passed over molecular sieves 4A and 5A was used as carrier gas, flow-rate 40 ml/min. The chromatographic column was 1 m long and 4 mm I.D., and contained 6.87 g of adsorbent. The adsorbent particle sizes 0.30–0.49 mm were selected for use. Adsorbate samples (n-pentane, n-hexane and benzene, 0.1 to 1.0 μl) were introduced on the column with the Hamilton syringe. The absolute retention volume and adsorbate density were measured in the

TABLE III

CHARACTERIZATION OF PHYSICOCHEMICAL PROPERTIES OF GRAPHITIZED AND NON-GRAPHITIZED CARBON BLACKS

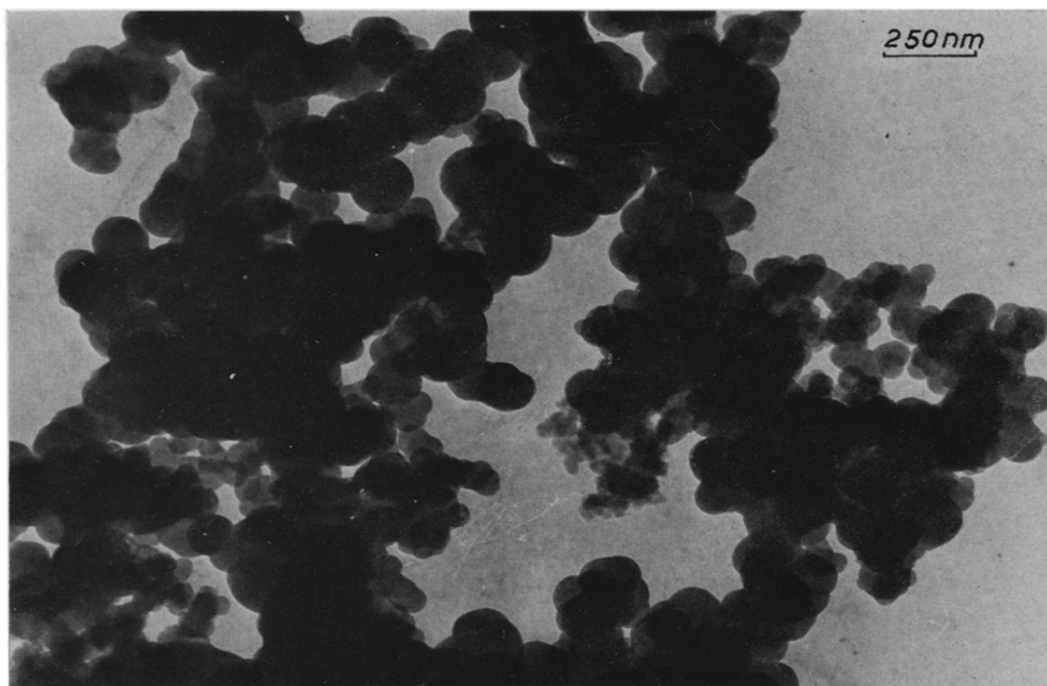| Carbon black	Surface area (m^2/g)	Elementary composition (%)		Size of the crystal (Å)		Concentration of spine ($1/g$)	Degree of graphitization (%)
		C	H	Lc	La		
Lamp-black, non-graphitized	17.0	95.1	0.6	17.3	27.3	$7.4 \cdot 10^{21}$	—
Lamp-black, graphitized	15.2	99.0	0.3	126	197	$1 \cdot 10^{21}$	53

Fig. 5. Electron micrograph of the lamp-black before graphitization.

range 360–420 °K. Conditions were chosen to eliminate dynamic effects as far as possible.

RESULTS AND DISCUSSION

The Henry's constants (integrals W_1) of hydrocarbons adsorbed on graphitized blacks have been evaluated by many authors, using various models. We used the models of adsorption potential proposed by Vidal-Madjar et al.[2], which we felt were applicable because they permitted the authors to obtain excellent agreement between values of retention volume, differential energy of adsorption and entropy of adsorp-
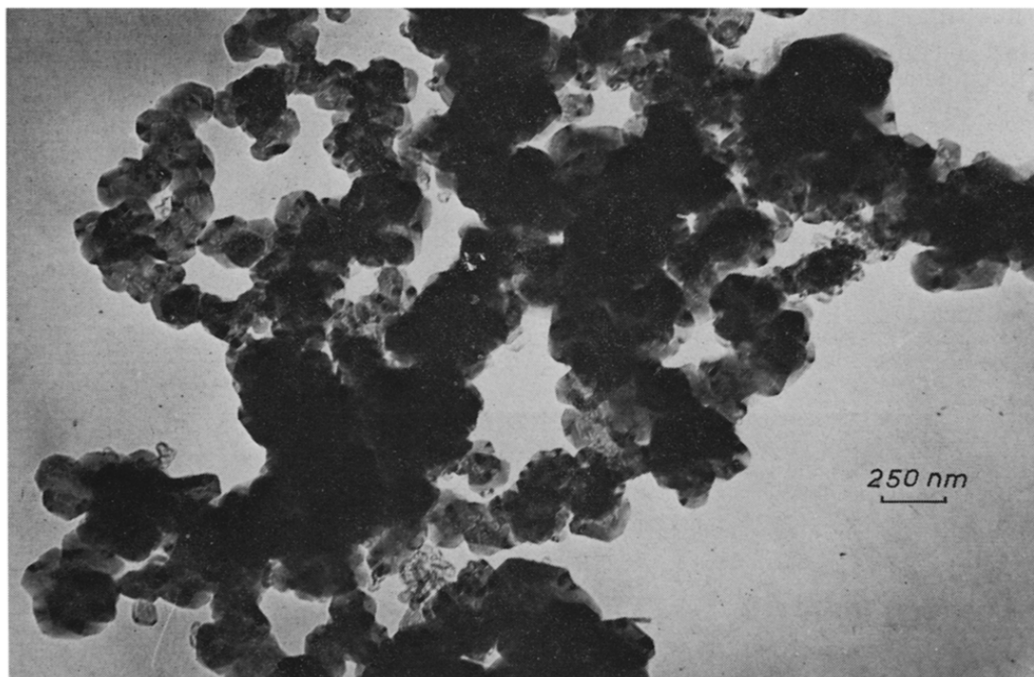
Fig. 6. Electron micrograph of the lamp-black after graphitization.

tion calculated theoretically and obtained experimentally. We also obtained good agreement between the results of theoretical thermodynamic evaluations and experimental data, as can be seen from Figs. 1–3, in which solid lines indicate calculated results and dashed lines experimental results. In theoretical evaluations of integrals W_1 we assumed an adsorbent surface area of 15 m/g, i.e. corresponding to the surface area by tested graphitized lampblack is characterized. Heats of adsorption calculated from eqn. 25 ($T = 360$ °K) were compared with heats measured chromatographically, and were in reasonable agreement (Table II). The main aim of our work was to find a way of evaluating retention volume as a function of adsorbate density in the free gas phase based on the proper model of adsorption and interaction potentials. The results of this type of calculation for pentane adsorbed on tested graphitized black are presented in Fig. 4. In these calculations the surface area was treated as a best-fit parameter. The experimental value for A was 15 m²/g, and the calculated value 11 m²/g. Fig. 4 shows that the agreement between the theoretical dependence $V_N = V_N(n)$ and the experimental data is not good. There are many reasons for this, the two chief being that the experiments were conducted in dynamic conditions, and that the crystalline structure of tested black deviated from the ideal.

The chromatographic process is dynamic by nature, and thus our assumption of perfect equilibrium, which would hold in static conditions, is not entirely valid here. Therefore, although the chromatographic conditions we used secured the minimal influence of diffusion and kinetic effects, the effect of these factors on the retention data could not be eliminated. The imperfect structure of graphitized lamp-black is illustrated by the degree of its graphitization, amounting to 53 °C in

relation to pure madagascaric graphite. Also the blacks adsorb gas molecules on a surface which consists of randomly orientated microcrystallites. These deviations from the perfect structure cause errors in the calculation of W_1.

Another reason for the discrepancies between the results is connected with the assumed model of two molecules of adsorbate in the superficial phase. The energy of interaction between gas and solid state was assumed in accordance with Guiochon's F_b model[1,2]. The assumption of effective values of the LJ (12—6) potential in our calculations has considerable faults, because that approach treats adsorbate molecules as spheres. In addition, we assumed that the energy of interaction does not depend on molecular orientation in relation to the adsorbent surface.

It is obvious that these assumptions are not adequate in the case of adsorbed molecules, as the adsorbent forces molecular orientation of adsorbate (Battezatti et al.[3]). However, these assumptions make it possible to carry out numerical calculations of the adsorption potential. More realistic assumptions would lead to closer agreement between the results.

It would appear that this method of theoretical evaluation of retention volumes can be used to predict retention volumes of chromatographed substances. Graphitized blacks are characterized by a special topography of adsorption centres which makes possible the separation of complex mixtures of organic compounds.

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