

THE PHYSICAL AND CHEMICAL CHARACTERIZATION OF ACTIVE CARBONS, BY ADSORPTION AND IMMERSION TECHNIQUES

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The combination of organic vapour adsorption and immersion calorimetry, both within the framework of Dubinin's theory, leads to information on the micropore system and the external surface area of activated carbons. Immersion into water appears to give the same information on hydrophilic centres, as the isotherm. A minimum of selected experiments can therefore lead to a good characterization of active carbons.

RESUME

La combinaison des techniques d'adsorption de vapeurs organiques et de calorimétrie d'immersion permettent, dans le contexte de la théorie de Dubinin, d'obtenir des informations détaillées sur le système microporeux des charbons actifs, ainsi que sur leur surface externe. L'immersion dans l'eau conduit aux mêmes informations sur les sites hydrophiles que l'isotherme d'adsorption. Un minimum de manipulations permet par conséquent de caractériser de manière satisfaisante les charbons actifs.

1. Introduction

Activated carbons are characterized by their strong sorptive capacity, which can be as high as $0.6 - 0.7 \text{ cm}^3$ of condensed gas, per gramme of solid. At the present time, one may postulate the average structure shown in Figure 1, in agreement with direct observations from TEM (transmission electron microscopy) (1,2). It is a limiting case of the model proposed by Oberlin (3) who investigated typical but not activated carbonaceous materials.

Activation by CO_2 or H_2O , near $800-900^\circ\text{C}$, reduces the number of aromatic sheets in the original stacks, leaving in some cases single, and in general non-planar layers. However, for strongly activated carbons, the usual limit seems to be pairs of layers (4), suggest-



Fig. 1. A schematic representation of the microstructure of active carbons.

ing an effective carbon vacuum interface closer to $1500 \text{ m}^2/\text{g}$ than the theoretical value of $3000 \text{ m}^2/\text{g}$ (the faces of a single carbon layer). For such carbons, the densities in helium measured in our laboratory, are near $2.05 - 2.10 \text{ g/cm}^3$. As shown in the figure, active carbons can be characterized by the following parameters.

A.

The micropore volume W_0 , arising from the spacing between the groups of aromatic sheets (widths up to 1.5 nm) in which adsorption does not lead to capillary condensation. Although the overall structure is not regular, there exists locally some degree of parallelism between the walls, as revealed in TEM by the dark-field technique (5) developed by Oberlin (6). The slit-shaped character of these cavities is also revealed, in some cases, by the faster and larger degree of adsorption of flat molecules (benzene) as opposed to globular ones (CCl_4). An open structure of the type shown in the figure also explains the fact that the limiting heats of adsorption and the adsorption energies of simple molecules in active carbons never exceed twice the value observed for graphitized carbons, the open and flat reference surface (7,8,9).

B.

The true surface area of the micropores S_{mi} , corresponding to their walls. For ideally slit-shaped micropores, of uniform half-width x , this area can be calculated by the simple geometrical relation

$$S_{mi} = W_0/x \quad (1)$$

A relation has also been proposed by Dubinin (10) for a distribution of micropore sizes. For micropores which can accommodate more than two layers of adsorbate ($2x > 0.5 - 0.6 \text{ nm}$), S_{mi} does not correspond to the value obtained from the BET

treatment, nor to the monolayer equivalent of the micropore volume W_0 .

C.

The external or non-microporous surface S_e , which can be as high as 200 m²/g. It corresponds essentially to the walls of the meso- and macropores.

Traditionally, this surface can be estimated (11) from the distribution of the mesopores, the t -plot method of de Boer and the technique developed by Gregg and Langford (12). However, as suggested by the present authors, this surface can also be estimated by a calorimetric technique described below, or by subtracting the micropore contribution from the overall isotherm and fitting the difference to a standard BET treatment. The latter technique is a variation of the so-called t/F method of Dubinin and Kadlec (13) but it does not impose a restriction upon constant c of the BET equation. This constant is already fixed in the case of reference isotherms.

In view of the limited dimensions of the aromatic sheets, edges will also be present in the structures and play a role in adsorption. Their total surface, to be found inside and outside the micropores, will hold the chemical groups usually found in active carbons treated near 600–800 °C. The most frequent edge groups are of the carbonyl type (14,15), but other groups can be introduced by suitable chemical treatments.

In the present paper, we wish to discuss various techniques and suggest procedures for a reliable characterization of the physical and chemical properties of active carbons. These methods are a combination of gas adsorption and immersion calorimetry, with organic compounds and water.

2. Characterization from gas-solid adsorption

2.A. Dubinin's theory

Adsorption of vapours and gases is described by Dubinin's theory for the volume filling of micropores (16), summarized by the Dubinin-Astakhov (D-A) equation

$$W = W_0 \exp \left\{ - (A/\beta E_0)^n \right\} \quad (2)$$

W is the volume of the adsorbate condensed in the micropores at temperature T and relative pressure p/p_0 ; W_0 is the total volume of the micropores, $A = RT \ln(p_0/p)$ and n , β and E_0 are specific parameters of the system under investigation. The so-called affinity coefficient β is a shifting factor which depends on the adsorbate only, and by convention $\beta(\text{C}_6\text{H}_6) = 1$. As shown by Dubinin and Stoeckli (16), the characteristic energy E_0 is related to the inertia radius of the pore R_i , an average dimension involving its width and its depth,

$$R_i E_0 = (14.8 \pm 0.6) \text{ nm kJ/mole} \quad (3)$$

On the other hand, the accessible width $L = 2x$ of slit-shaped micropores is related to E_0 through the approximate equation

$$x = k/E_0 \quad (4)$$

Parameter k is found to vary from 9 to 13 nm kJ/mole, as x increases from 0.25 to 1 nm. The exponent n is linked to the degree of heterogeneity of the micropore system, as suggested by the adsorption of various

molecular probes. In the case of active carbons, the range $2 < n < 3$ corresponds to relatively homogeneous pores and of decreasing size. The range $1 < n < 2$, on the other hand, corresponds to heterogeneous micropore systems (16,17). The case where $n = 2$ corresponds to the well-known equation of Dubinin and Radushkevich (D-R), which can still be used with a good approximation for most industrial carbons. This equation is traditionally written in the form

$$W = W_0 \exp \left\{ - B(T/\beta)^2 \log^2(p_0/p) \right\} \quad (5)$$

or, using a universal coordinate $\gamma = (T/\beta)^2 \log^2(p_0/p)$ (6,16)

$$W = W_0 \exp \left\{ - B\gamma \right\} \quad (6)$$

Parameter B is the so-called structural constant. It also reflects the average micropore size, since E_0 (kJ/mole) = $2.303 \cdot 10^{-3} R/\sqrt{B} = 0.01915/\sqrt{B}$ (16).

Although equations (2)–(5) have an empirical origin, it has been possible to give a formal theoretical basis to the Dubinin-Astakhov equation (18). Model calculation, based on a simple (3:9) adsorption potential in slit-shaped micropores and using graphitized carbons as a reference, gave physical meanings to parameters n and E_0 .

The model implied a distribution of the adsorption energies, and consequently of the micropore sizes, becoming sharper as n increases. On the other hand, a semi-quantitative relation of type (4) was established between the accessible pore width and E_0 .

The calculations based formally on small and well-characterized molecules (Ar, Kr, Xe, CH₄), suggest that in the case of the D-R eqn (5), the corresponding micropore size distributions are relatively narrow, with a cut-off within 0.2 nm of the maximum, approximately.

As observed by Stoeckli *et al.* (6,19), the D-R eqn can hold over a large range of relative pressures and temperature, for the adsorption of small molecules by carbons with molecular-sieve properties (cut-off). However, their micropore system is not monodisperse. This situation is clearly illustrated in Figure 2 and Table I, for carbon CEP-35, prepared from carbonized wood activated in CO₂ at 850 °C, to 35 % burn-off.

The vapours of small molecules such as N₂, N₂O, C₃H₈ and to some extent C₆H₆, follow the D-R equation (6) over a large range of pressure and temperature, leading to $E_0 = 30$ kJ/mole and $W_0 = 0.33$ cm³/g on average.

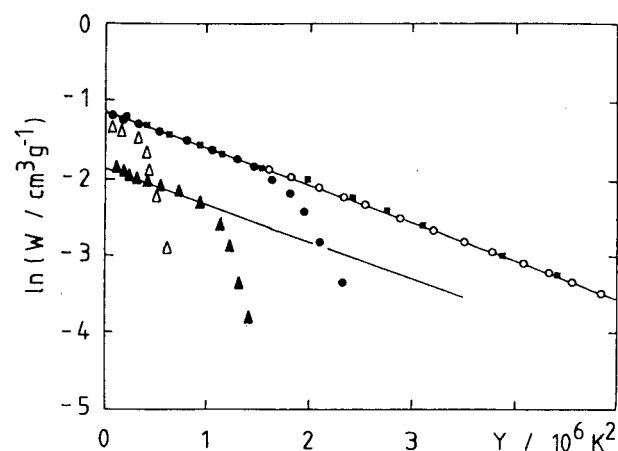


Fig. 2. Adsorption of various vapours by carbon in the logarithmic representation of eqn (6). Adsorbates: N₂ at 77 K (●), N₂O (○), C₆H₆ (Δ), C₃H₈ (■) and CCl₄ (▲) at 293 K.

TABLE I
Experimental micropore volumes of carbon CEP-35, using various molecular probes, and calculated volumes

molecular probe	smallest dimension (nm)	W (cm ³ /g) experimental	calculated
N ₂ ; N ₂ O; n-C ₃ H ₈	0.35	0.330	0.330*
c-C ₆ H ₁₂	0.56	0.194	0.182
CCl ₄	0.63	0.134	0.095
2,5-norbornadiene	0.66	0.118	0.072
α-pinene	0.70	0.105	0.050

* normalization factor

On the other hand, for molecules of larger dimensions (c-C₆H₁₂, CCl₄, 2,5-norbornadiene and α-pinene), the apparent micropore volume decreases rapidly. As illustrated in the figure, molecular sieve effects can also lead to difficulties in adsorption at low relative pressures, in the form of downward deviations in the ln(W) versus y plot. This phenomenon has already been investigated (20).

Table I gives the apparent micropore volumes W₀ obtained from adsorption isotherms and from immersion calorimetry (see section 3.B.), and the values resulting from model calculations. The latter are based on parameters E₀ and W₀ of the D-R equation of the smaller molecules. As before (18), the 3:9 adsorption potential used for the calculation of the pore-size distribution is based formally on CH₄ and Ar, two well-known molecules. In agreement with the model calculations, our experimental results show that a micropore system which is described exactly by the Dubinin-Radushkevich equation for molecules with total accessibility, is not necessarily monodisperse. A certain distribution of micropore sizes, although narrow, can be expected.

In the case of exponent n = 3 in equation (3), on the other hand, the distribution should become very narrow (16,18).

As heterogeneity increases and the accessibility of the structure to larger molecules increases, deviations from the D-R eqns (5) or (6) are observed (5). For typical carbons, after strong activation, this corresponds to 1 < n < 2 in the Dubinin-Astakhov eqn (2) (19). In agreement with the model calculations mentioned above (18), a decrease in n indicates a wider distribution of the adsorption potentials and therefore a wider distribution of the micropore sizes. This is also in agreement with simultaneous observations from small-angle scattering of X-rays (16,21).

From a practical point of view, very heterogeneous carbons can be described by the superposition of either two D-R equations, as suggested by Izotova and Dubinin (22), or by an integral transform (5,16,19) based on eqn (6). In the case of a Gaussian distribution of the micropore volume with parameter B, centered at B₀ and having half-width Δ, the overall isotherm becomes

$$W = W_0^0 \exp\{-B_0 y\} \cdot \exp\{y^2 \Delta^2 / 2\} \cdot 0.5 [1 - \operatorname{erf}(z)] \quad (7)$$

where

$$z = (y - B_0 / \Delta^2) \Delta / \sqrt{2}.$$

Eqn (7) has been discussed in detail by Dubinin and Stoeckli (16,23).

2.B. Water adsorption

The adsorption of water vapours does not follow the general eqn (2), as it proceeds from a different mechanism. According to Dubinin and Serpinski (24,25), the following equation applies

$$p/p_0 = a/c(a_0 + a) (1 - ka) \quad (8)$$

a is the amount adsorbed at relative pressure p/p₀; a₀ characterizes the so-called primary centres through the amount of water adsorbed on them, and c is the ratio between the rates of adsorption and desorption.

Parameter k can be calculated from the condition that at p/p₀ = 1, the limiting amount adsorbed is a = a_s (usually in mmol H₂O/g). As shown by Stoeckli *et al.* (15), in the case of carbons treated above 400-600°C prior to adsorption, and having mainly carbonyl groups on the surface, the enthalpy of immersion into water is

$$\Delta H_f (\text{J/g}) = -25 (\text{J/mmol H}_2\text{O}) \cdot a_0 - 0.6 (\text{J/mmol H}_2\text{O}) (a_s - a_0) \quad (9)$$

The second term reflects the small contribution from the carbon-water interface itself.

Preliminary adsorption and immersion experiments, based on the creation and the titration of carboxylic groups (26), suggest a specific interaction of approximately 55 J/mmol of water fixed to these groups. The recent work of Dubinin (27) also indicates that there exists a direct relation between constant c of the water isotherm and the half-width x of the micropore system.

Moreover, a systematic study of the soviet school (24) suggests that a_{0,6}, the amount of water adsorbed near p/p₀ = 0.6, should correspond the monolayer capacity of the micropores and therefore to S_{mi} calculated by eqn (1). However, as found in our laboratory, these assumptions are only valid for microporous carbons where a₀/a_m < 4-5%.

A more detailed study shows for example, that c also increases with a_0/a_m at given E_0 and W_0 . In the case of water, the combination of data from the DR eqn (organic vapours) and from immersion calorimetry can reduce the tedious task of water adsorption measurements.

3. Characterization from immersion calorimetry

3.A. Theoretical background

It has been shown by the present authors (28,29,30) that an exact relation could be derived from the Dubinin-Astakhov eqn (2), to describe the immersion of microporous carbons into organic liquids. For the usual case where $n = 2$, one obtains

$$\Delta H_i(\text{J/g}) = -\beta E_0(1 + \alpha T) \sqrt{\pi} \cdot W_0 / 2V_m \quad (10)$$

α being the expansion coefficient of the organic liquid and V_m its molar volume at $(T; p)$. This equation has been tested directly with carbons having a very small external surface area S_e , by using a calorimeter designed and built in our laboratory (30).

If S_e cannot be neglected, the experimental enthalpy of immersion will also have a contribution from the wetting of this surface, so that

$$\Delta H_i(\text{exp}) = \Delta H_i(\text{micropores}) + S_e \cdot h_i \quad (11)$$

With a good first approximation, h_i can be taken as the specific enthalpy of immersion of the open reference surface, carbon black for example. Typical values are listed in Table II.

From the combination of eqn (10) and (11), it is possible to recalculate the external surface area S_e , since parameters E_0 and W_0 are known from the adsorption isotherm.

Table 3 compares the values of S_e obtained by this technique and by other independent methods. It appears that for carbons with $S_e > 80$ -100 m^2/g , the agreement is good.

3.B. Molecular-sieve effects

The comparison of adsorption and immersion data has shown that in the case of molecular-sieve effects (carbon CEP-35, for example), eqns (10) and (11) can be used to determine the apparent micropore volume from a series of immersion experiments only. However, for calculations involving the larger molecules, one must use the characteristic energy E_0 corresponding to the smaller molecules such as N_2 , N_2O , C_3H_8 and C_6H_6 . As observed in a number of cases, the adsorption isotherm of relatively large molecules can yield incompatible values of E_0 , when they are partly excluded from the micropore system. The reason, yet unknown, may involve a change in β and/or in the interactions with the micropores, reflected in parameter E_0 (18). The results obtained for carbon CEP-35, from immersion and adsorption experiments are shown in table 1 (section 2.A.).

3.C. Immersion into water

As mentioned above, the enthalpy of immersion into water, combined with specific titrations, can lead to information about the hydrophilic centres. Immersion

TABLE II
Specific enthalpies of immersion for open carbonaceous surfaces (carbon blacks), at room temperature

Liquid	C_6H_6	$n\text{-C}_7\text{H}_{16}$	$n\text{-C}_{16}\text{H}_{34}$	CCl_4
$-h_i(\text{J/m}^2)$	0.114	0.123	0.148	0.115

TABLE III
Comparison of external surface areas

carbon	$S_e(\text{m}^2/\text{g})$ (immersion)	$S_e(\text{m}^2/\text{g})$ (adsorption)
N-125	144 (C_6H_6)	175 (t/F method, C_6H_6 at 293K)
$E_0 = 16.6$ kJ/mole	194 ($n\text{-C}_7\text{H}_{16}$)	145 (Kelvin/mesopores)
$W_0 = 0.64$ cm^3/g	176 ($n\text{-C}_{16}\text{H}_{34}$)	141 (décomposition of N_2 isotherm after $n\text{-C}_9\text{H}_{20}$ preadsorption)
FA	123 (C_6H_6)	111 (t/F method; C_6H_6 at 293K)
$E_0 = 20.0$ kJ/mole	112 ($n\text{-C}_7\text{H}_{16}$)	118 (decomposition of C_6H_6 isotherm)
$W_0 = 0.29$ cm^3/g	106 ($n\text{-C}_{16}\text{H}_{34}$)	105 (t/F method, N_2 at 78K)

experiments carried out after prefilling with hexadecane, indicate that the centres are not confined to the external surface, as to be expected from the structure proposed for active carbons (Fig. 1).

By using immersion calorimetry, it is also possible to follow modifications in the chemistry of the surface, especially when studying series of carbons.

4. Example of a characterization

In order to illustrate the techniques described above, a typical example for the characterization of an industrial active carbon is presented. As shown in Table IV, an extensive characterization was carried out, in order to confirm the results obtained from a minimum set of experiments. The benzene isotherm leads to parameters W_0 and E_0 in the low pressure range, whereas the upper part leads to the external surface area (see Table III). Following Dubinin and Stoeckli (16), the theoretical half-width x and the geometrical surface area of the slit-shaped micropores are obtained. The total surface area $S_t = 991 \text{ m}^2/\text{g}$ is in fair agreement with the value obtained from helium adsorption. On the other hand, the amount of water adsorbed at relative pressure $p/p_0 = 0.6$ does not correspond to the area of the micropore walls. The good agreement reported by Dubinin (24) has not always been observed with our samples. The amount of water fixed to hydrophilic centres, a_0 , obtained through the adsorption isotherm (8), is in good agreement with the value recalculated from the

enthalpy of immersion at 307 K, through eqn (9). These are 0.49 and 0.57 mmol $\text{H}_2\text{O}/\text{g}$ respectively, assuming as a first approximation that only carbonyl groups are present. This seems to be the case, to a large extent, for industrial active carbons prepared near 800-900°C. However, the more complex situation where different groups are present, is under investigation.

The ratio of hydrophilic centres a_0 to the monolayer equivalent of the total surface area a_t is approximately 3%, an important information for the characterization of the sample. Finally, the density in helium, determined from volumetric experiments between 78 and 300 K, is in agreement with the range of 2.05-2.10 g/cm^3 obtained for strongly activated carbons. From the knowledge of the carbon density it could be possible, in principle, to determine by pycnometry the volume of the micropores accessible to large liquid molecules. This approach is complementary to the method based on the enthalpies of immersion.

The techniques described in the present paper and illustrated by carbon N-125 could provide further information in the study of active carbons and their evolution, an important industrial field (31,32,33).

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TABLE IV
Characterization of a typical industrial active carbon (N-125)

W_0 (cm^3/g)	E_0 (kJ/mole)	x (nm)	S_{mi} (m^2/g)	S_e (m^2/g)	S_{He} (m^2/g)	S_t (m^2/g)
0.64	16.61	0.77	834	157 ± 20	715	$991 (\pm 20)$
$S_{\text{H}_2\text{O}}$ (m^2/g)	C	a_0 (mmol $\text{H}_2\text{O}/\text{g}$)	a_t (mmol $\text{H}_2\text{O}/\text{g}$)	a_0/a_t	d_{He} (g/cm^3)	
494	1.66	0.49/0.57	15.7	3.1%	2.09 ± 0.02	

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