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Physical adsorption and the porosity of carbons, with special reference to the structure of micropores[1]

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Summary

The problem of porosity in carbonaceous materials is briefly reviewed. Microporosity is investigated from the point of view of physical adsorption from the gas phase on graphite-like surfaces. Theoretical considerations show that the micropores can be treated as slots between the graphitic planes of the microcrystallites. The minima of the adsorption potentials are derived from the limiting heats of adsorption, measured by GSC.

1 Carbons and porosity

Graphite and microporous carbons are two limiting forms of microcrystalline carbons, which include a variety of graphitizing and non-graphitizing materials[1]. These solids are made up by agregates having the structure shown in fig. 1. As shown by various authors[2-4], the size of the crystallites varies according to the origin and the treatment of the solid. Table 1 gives typical values for various materials.

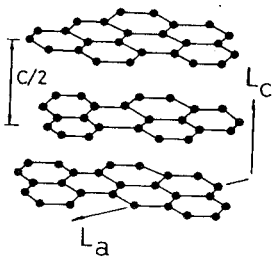

Fig. 1. The structure of the microcrystallites (see also table 1)

Graphite and carbon blacks which have been graphitized at high temperatures (2000 to 3000 °C) have very homogenous surfaces, even at low surface coverage. Owing to this property and to the structural simplicity of the material, graphitized carbon blacks have received a great deal of attention from surface chemists in the past 15 to 20 years[5].

Table 1. Dimensions of typical microcrystallites

Type of carbon	$(L_a$	L_c	$c/2)$/Å
Natural graphite	2100	940	3.510
Treated C-blacks	$\leqslant$200	$\leqslant$200	3.44–3.50
Untreated C-blacks	15–25	11–15	3.48–3.66
Active carbons	20–25	7–11	3.5 –3.7

[1] Extension of a lecture given in German to the Chemical Society in Bern (June 21st, 1974).

Active carbons, on the other hand, are known for their great adsorption capacity (0.4 to 0.8 cm^3/g) which is related to the existence of a developped system of fine pores[6]. The surface areas corresponding to the spreading of the adsorbed gases in one layer are very high (400 to 900 m^2/g of solid), and sometimes unrealistic (beyond 1500 m^2/g). Therefore, great care has to be taken, as to the meaning of the surface areas derived for such carbons.

According to the classification of M. M. Dubinin[6-8], the porosity of carbonaceous materials (and of other solids as well) falls into three regions, depending on the radius r of the pores:

(a) Macroporosity, for $r > 200$ to 300 Å. This region is usually investigated by mercury porosimetry, which gives results up to about 10^4 to 10^5 Å.

(b) Transitional porosity, in the range of 16 to 20 $< r < 200$ Å approximately. The lower limit represents the smallest pores in which capillary condensation can occur, as the pressure of the gas increases. This effect is responsible for the existence of a hysteresis loop in the adsorption-desorption cycle. In the case of cylindrical pores, the radius r of the pores being desorbed at a given pressure p can be calculated from the equation of Kelvin[9]

$$\ln(p/p_0) = -2V_M\,\gamma/rRT, \qquad (1)$$

where V_m is the molar volume of the condensed gas, γ its surface tension, and p_0 the saturation pressure at the temperature T.

In order to obtain the real radii of the pores, allowance has to be made for the thickness of the film adsorbed on the walls of the pores[8-9]. From the hysteresis loop of the isotherm and eq. (1), it is possible to derive the so-called pore size distribution function, which gives the relative contributions of the various pores to the total pore volume of the solid.

In the case of nitrogen adsorption at 78 K, for example, pore sizes of 200 to 300 Å correspond to relative pressures p/p_0 of 0.95 to 0.97. This represents the upper limit for accurate pore size distributions from adsorption measurements.

As shown by various authors[10-11], there is a good agreement between the pore size distributions obtained

from static adsorption measurements, and from high pressure mercury porosimetry, in the region of 30 to 300 Å.

Transitional porosity can also be investigated by desorption measurements in gas-solid chromatography (GSC), and recent developments of the method have shown satisfactory agreement with static determinations[12].

Following the work of De Boer[9, 13], it is also possible to deal with systems of transitional pores other than cylindrical, by considering the shape of the hysteresis loop. This approach is correlated by electron microscopy, and consequently the problem of transitional porosity can be dealt with in a satisfactory way.

(c) Microporosity. This includes all cavities and cracks with radii or widths of less than 15 to 20 Å, and in which capillary condensation no longer occurs. Adsorption is usually reversible and the isotherms cannot give direct informations about the shape and the size of these pores. This type of adsorption is best described by the theory of M. M. Dubinin[6–9, 14] for the filling of micropores. The basic equation is

$$W = W_0 \exp\left[-B\,(T/\beta)^2 (\log p_0/p)^2\right], \qquad (2)$$

where W is the volume of the liquid-like adsorbate filling the pores at pressure p, W_0 is the total micropore volume, and B and β are constants characterizing the solid and the adsorbate.

The variation of W_0 with the size and the shape of the adsorbed molecule and the adsorption kinetics can give valuable informations about the molecular sieve properties of the solid. The experiments of J. R. Dacey[15], J. J. Kipling[16], and more recently of E. Fitzer[17], lead to values of 4 to 8 Å for the micropores of various carbonaceous materials (thermally decomposed polymers and activated carbons).

Small-angle X-ray investigations by M. M. Dubinin[18] showed that typical active carbons could have two systems of micropores, with effective (or inertia) radii R = 6 to 7 Å and 11 to 14 Å. This quantity R is twice the ratio of the surface of the pore to its circumference. It represents either the radius r of cylindrical pores, or the width L of long slot-like pores, and therefore the problem of the actual shape of the micropores cannot be solved explicitly.

Simple geometrical considerations based on the W_0 values lead to a width L = 6 to 8 Å for parallel-walled micropores, a model suggested by W. F. Wolff[19] and recently by E. Fitzer[17]. (The model implies however that there is only one layer of adsorbate on either wall when the pore is filled.) Such a model is plausible, in view of the planar microcrystallites mentioned above. The presence of graphite-like surfaces in microporous carbons and in graphitized carbon blacks is a good starting point for theoretical comparisons between the adsorption properties of the two types of solids.

2 Adsorption and adsorption potentials

The starting point for informations on adsorption is the isotherm, a function which relates N_a, the amount of gas (in mol/g) taken up by the solid at a given temperature T, to the pressure p. From a minimum of two isotherms it is possible to derive, amongst other quantities, the isosteric heat of adsorption Q^{st}. This is a negative quantity[20] (in agreement with calorimetric experiments), given by the equation

$$\ln (p_2/p_1)_{Na} = (Q^{st}/R)\,(1/T_2 - 1/T_1)\,. \qquad (3)$$

It is a function of the surface coverage, and it can have high initial values in the case of heterogenous surfaces. In recent years, gas-solid chromatography has become an increasingly important tool for the determination of adsorption isotherms and of the limiting heats of adsorption (practically at zero coverage). Fig. 2 shows the relation between different experimental and theoretical quantities which appear in this approach. GSC can be used with success in the case of adsorption on graphitized carbon blacks[5] and by microporous carbons[21]. In the latter case, however, one is restricted to simple molecules, because of the long retention times. (The upper limit is a molecule like benzene, where temperatures of 250 to 300 °C are needed to give fairly symmetrical elution curves.) The limiting heats of adsorption Q_0^{st} which are obtained by this method, can be used to investigate the interactions between the isolated molecules and the solid surface (no lateral interactions).

An important theoretical quantity is the adsorption potential $\Phi\,(Z)$, shown in fig. 3. At a given distance Z from the surface, it is the sum of all pair-potentials $\varphi\,(r)$ between the adsorbate and the atoms of the solid. For simple molecules, $\varphi(r)$ can be expressed by the Lennard-Jones (or 6 : 12) pair-potential[5, 6, 8, 22]

$$\varphi(r) = -C/r^6 + B/r^{12}, \qquad (4)$$

where C and B are constants depending on the interacting atoms or molecules.

$\Phi\,(Z)$ can be obtained either by direct summation over the 50 to 100 nearest atoms in the solid, or by integra-

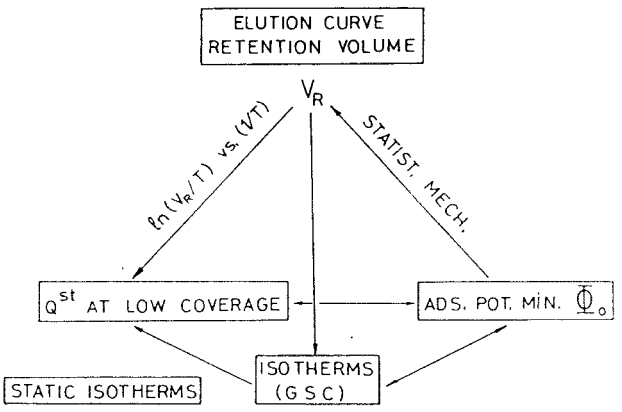

Fig. 2. Gas-solid chromatography and adsorption

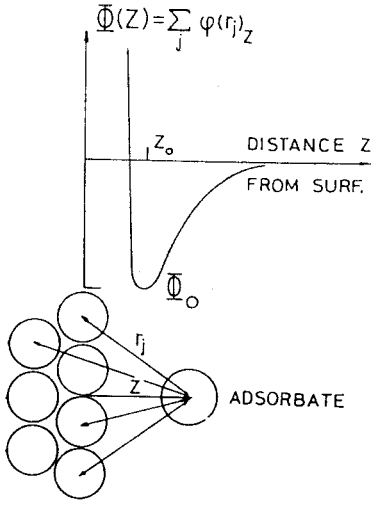

Fig. 3
Adsorption potential $\Phi(Z)$

tion over a continuous or semi-continuous solid[6,22,23,24]. The minimum of the potential, $\Phi_0 = \Phi(Z_0)$, is related to the isosteric heat of adsorption at low coverage as shown in fig. 4 (no lateral interactions). In the case of mobile adsorption the relation is

$$Q_0^{st} = \Phi_0 - (3/2)\,RT \qquad (5)$$

(the small vibration on the surface can be neglected).

Fig. 5 shows the relation between Φ_{0A} (various active carbons) and Φ_{0G} (graphitized carbon blacks) obtained from GSC experiments and by using eq. (5). In the case of simple molecules (such as Ar, Kr, Xe, SF_6 and short *n*-alkanes), there is a linear relation between the minima of the adsorption potentials, and their ratio is near 1.60[24].

Using various theoretical models for the shape of the micropores[25], it is found that parallel-walled pores give better results for the ratio of the adsorption potentials in the pores and on the flat surface. The value of 1.60 leads to a width of 7 to 8 Å for typical active carbons, which is in agreement with the effective radii obtained from X-ray experiments. In the case of cylindrical pores, the radii are too small for a ratio of 1.60 between the adsorption potentials in the pores and on the flat surface. Therefore, the micropores may be considered, in a somewhat idealized picture, as cracks between graphitic layers, or slots resulting from the stacking of the microcrystallites. It is likely that the origin of the material (activation of carbons or thermal decomposition of polymers) has an influence on the extension and the width of the pores[18].

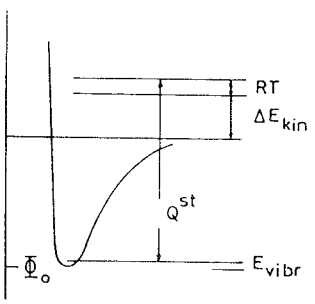

Fig. 4. Adsorption potential and isosteric heat of adsorption (isolated molecule on the surface)

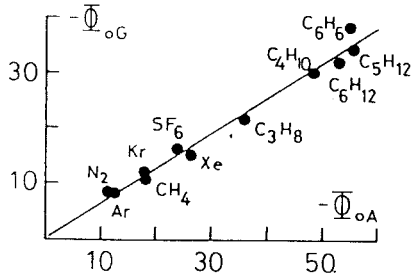

Fig. 5
Adsorption potentials Φ_0 on graphitized carbon blacks and in microporous carbons (values in kJ/mol)

I. A. Dolova reported recently the limiting heats of adsorption obtained from GSC, for simple molecules on a carbon molecular sieve[26]. From the analysis of these results, it is found that the ratio of the adsorption potentials is about 1.90. This corresponds to an average pore width of 6.5 Å for the model of slot-like pores, and agrees with the observation that pores of this type of carbon are smaller than for homogeneous active carbons. This suggests that the method proposed above should be fairly selective for the study of different types of microporous carbons.

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