

THE DUBININ THEORY OF MICROPORE FILLING AND THE ADSORPTION OF SIMPLE MOLECULES BY ACTIVE CARBONS OVER A LARGE RANGE OF TEMPERATURE

H. F. STOECKLI and J. PH. HOURIET

Institut de Chimie de l'Université, CH-2002 Neuchâtel, Switzerland

Abstract—It is shown that the values of the structural constant B and of the micropore volume W_0 can change considerably for certain active carbons, when the adsorption of simple gases is measured over a large range of temperature. The changes are probably related to ultramicroporosity, present in heterogeneous carbons, and to activated diffusion into typical micropores, through constrictions. It is suggested that the quantity B is not necessarily a constant for a given solid, as assumed previously.

1. INTRODUCTION

Physical adsorption of gases by microporous solids can be described by the equation of Dubinin and Radushkevich, in its original form[1]

$$W = W_0 \exp[-B(T/\beta)^2 \log^2 p_0/p], \quad (1)$$

where W is the volume of the liquid-like adsorbate filling the pores at temperature T and a relative pressure p/p_0 , and W_0 represents the volume of the micropores. B and β are two quantities which will be dealt with below. For temperatures higher than critical, adsorption is described by the modified equation of Nikolaev and Dubinin[2]

$$W = W_0 \exp[-B(T/\beta)^2 \log^2 (p_c T^2 / p T_c^2)]. \quad (2)$$

W_0 is now equal to $N_a b$, where N_a is the number of moles of adsorbate, and b its Van der Waals constant.

The theory of micropore filling has been analyzed critically by Marsh and Rand[3] and by Freeman *et al.*[4], amongst others. It is also reviewed periodically by Dubinin himself[5], in the light of new developments. Adsorption by microporous solids such as active carbons and zeolites, can also be described by the approaches of Kiselev[6] and Brunauer (MP method)[7]. The latter is derived from the so-called t -plot method of de Boer[8], and it refers to super-micropores rather than typical micropores (5–8 Å). The differences between the MP method and the theory of Dubinin have been analyzed[9].

Equations (1) and (2) contain two specific parameters, the structural constant B , depending on the solid, and the affinity (or similarity) coefficient β , which is a shifting factor depending on the nature of the adsorbed gas. The analysis of experimental data by a log–log² plot leads to the quantities W_0 and B/β^2 , from the intercept and the slope of the graph. It is important to note that B and β cannot be obtained separately and therefore further assumptions have to be made. From the assumption that B depended only on the solid, Dubinin *et al.* showed that the similarity coefficients β had ratios close or equal to

the ratios of the Sugden increments (parachores) of the adsorbates[1, 5]. Other molecular properties can also be used with some success, instead of the parachores. Benzene was chosen as a reference, and consequently β (C_6H_6) = 1. Since the parachore itself can be expressed in terms of temperature-invariant parameters[10], one may assume that β should be temperature-independent, to a first approximation at least. Coherent results were obtained by the Soviet school, for the adsorption of simple and mostly non-polar substances on various carbons[1, 5]. Although the survey includes relatively large molecules[11], discrepancies are found when the theory is applied to a wider range of molecules, including polar ones. As shown by Reucroft *et al.*[12], the agreement seems to be better, if molar refractions are used instead of parachores. On the other hand, with the total molar polarizabilities, which include the dipole moment, the agreement is poorer. As shown below, it is also found that the quantity B/β^2 is not constant, when the adsorption of a given gas on a given solid is considered over a large range of temperatures.

These different observations raise fundamental questions about the physical meaning of the parameters B and β , in order to understand the basis and the limits of the Dubinin theory. In the present work, we deal with the structural constant B , through the study of the adsorption of simple and non-polar molecules. Polar molecules were not considered, because it is likely that dipole moments are not accounted for in a proper way in the calculation of β from the parachores.

A possible relation between B and the dimensions of micropores has already been suggested by Dubinin twenty years ago[5], since B increases with the degree of activation[13]. The structural constant also seems to be related to the average inertia (or gyration) radius \bar{R}_g of the micropores, by

$$\bar{R}_g \text{ (in Å)} = (62B 10^6)^{1/2} \quad (3)$$

as suggested by Stoekli[14]. This empirical relation is

based on results obtained by Dubinin *et al.* from adsorption measurement[15] and the small-angle scattering of X-rays[16–18]. These carbons had a relatively low volumic porosity, and therefore the scattering could be ascribed to the pores (the diluted phase). The quantity \bar{R}_g , derived from the Guinier plot, was identified with the mean effective pore-radius[17] but this statement was disclaimed later[18], since the gyration radius depends on the size and on the shape of the micropores[19, 20]. It is possible, however, that \bar{R}_g may be close to the average value of the pore-width, depending on the geometry of the micropores. This is the case for the molecular-sieve carbon M-5, described below, where the value of \bar{R}_g calculated from eqn (3) is equal to the pore-width obtained from independent molecular-sieve experiments. For a slot-like micropore, for example, having the shape of a flat disk[20], a diameter of 21 Å and a height of 7 Å correspond to $R_g = 7.6$ Å. The ideal picture of slot-like micropores, resulting from the stacking of crystallites measuring on average $20\text{--}25 \times 7$ Å[16] is also compatible with the widths of 6–8 Å derived for this model from adsorption potentials[21]. This view is also supported by various molecular-sieve experiments, suggesting that flat molecules are better adsorbed than globular ones[22].

A correlation between the quantity B/β^2 of eqns (1)–(2) and pore-sizes is also suggested by the recent work of Cerofolini[23], in the field of the homotactic-patch approach to adsorption. The isotherm of Dubinin, Radushkevich and Kaganer[1, 24]

$$N_s = N_0 \exp[-B'(RT \ln p/p)^2], \quad (4)$$

where

$$B' = B/(R2.30\beta)^2,$$

describes certain cases of adsorption by non-porous surfaces, and it was shown to result from the combination of a local Langmuir isotherm with a distribution of the adsorption energies

$$\chi(\epsilon) = 2B'(\epsilon - \epsilon_0) \exp[-B'(\epsilon - \epsilon_0)^2]. \quad (5)$$

These findings could, theoretically at least, be transposed with their underlying assumptions to the case of adsorption by microporous solids, considered as heterogeneous solids. However, the exact relation between B/β^2 and the average pore-size reflected in eqn (5) is complicated, as it depends on the model chosen for the micropores and on the exact definition of the adsorption energy ϵ .

2. EXPERIMENTAL

Two samples of strongly activated carbons, U-02 (mineral origin) and F-01 (coconut shell), with total micropore volumes between 0.5 and 0.7 cm³/g, and one molecular-sieve carbon (M-5) were investigated as supplied. The adsorption of simple gases was measured in the range of 78–475°K, and for pressure between 10⁻³ and 500 torr. The experiments were carried out in a standard gravimetric apparatus of the McBain type[1], with samples of 0.3–3 g, depending on the temperature. Most isotherms were repeated at least once, and the attainment

of true adsorption equilibria was checked at regular intervals, by following it over longer periods (1–3 days).

The solids were originally outgassed under 10⁻³ torr at least, for 25–40 hr at 300°C and for 1–2 hr near 420°C. Between experiments, the time of outgassing varied according to the different adsorbates used.

Less extensive measurements were also carried out with other samples, similar to U-02 and F-01. The results lead to the same conclusions as described below.

3. RESULTS AND DISCUSSION

Typical results, but corresponding to the less favourable experimental situations, are shown in Fig. 1, in the form of a log-log² plot. The values of B/β^2 and W_0 are obtained from the graph by the method of least squares. In the present case, the error on W_0 is approximately $\pm(0.01\text{--}0.02)$ cm³/g. For each isotherm, the structural constant B is calculated from the quantity B/β^2 by using the experimental values of β given in the literature[1, 5]. Figures 2–4 show that various values of W_0 and B are found, even for a given system, and they generally decrease as the temperature increases. The theoretical inertia radii \bar{R}_g corresponding to the different values of B through eqn (3), can also be read from the figures.

In their earlier experiments leading to eqn (2), Nikolaev and Dubinin[2] found that the adsorption of N₂ and Xe between –95 and 50°C gave practically the same values for W_0 and B , as benzene at 20°C. However, it was pointed out that at very low degrees of filling ($W/W_0 \leq 0.06$), smaller values were found, which were ascribed to ultramicroporosity (pores of less than 5 Å, approximately). The present results must therefore reflect

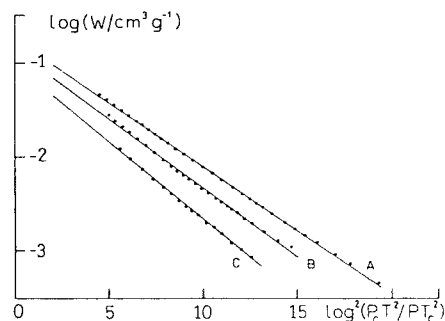


Fig. 1. Dubinin-Radushkevich plot for the adsorption of nitrogen on sample F, at 249, 273 and 318°K (A, B, C).

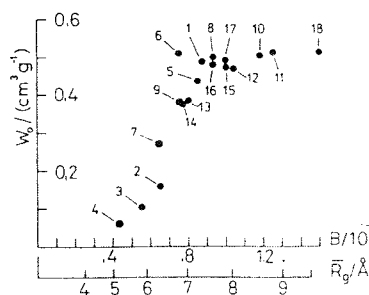


Fig. 2. Adsorption on sample U: N₂ at 78, 233, 273 and 323°K (1–4); Xe at 224, 273 and 323°K (5–7); SF₆ at 273 and 323°K (8–9); benzene at 273, 298, 323, 390 and 475°K (10–14); neopentane at 273 and 323°K (15–16); n-butane and CCl₄ at 273°K (17–18)

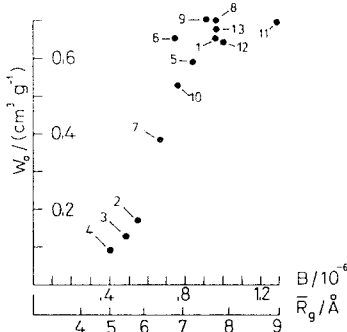


Fig. 3. Adsorption on sample F: N₂ at 78, 249, 273 and 318°K (1-4); Xe at 226, 273 and 323°K (5-7); SF₆ at 255, 273 and 318°K (8-10); benzene at 273 and 323°K (11-12); *n*-butane at 273°K (13).

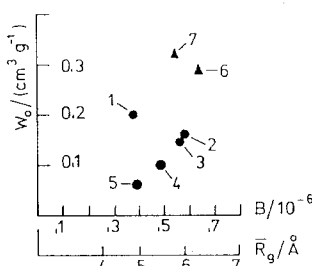


Fig. 4. Adsorption on molecular sieve M-5: N₂ at 78, 226, 242, 273 and 318°K (1-5); Xe at 228 and 273°K (6-7).

structural differences between the types of carbons used, if one postulates that the affinity coefficient β is constant, instead of B . As pointed out above, it is implicitly assumed that the structural constant is invariant for a given solid, and discrepancies are expressed in terms of differences between experimental and theoretical values of β [12]. The hypothesis of a constant affinity coefficient β and a variable structural factor B , is also in agreement with the observed variation of the quantity B/β^2 for a given system.

According to eqn (3), the smaller values of W_0 and B correspond to the filling of small micropores, which do not seem to be present to a great extent in the samples used by Nikolaev and Dubinin [2, 16, 17, 25]. The present situation may also be compared with the one described by Izotova and Dubinin [1, 15], leading to the discovery of two systems of micropores, later confirmed by X-ray scattering [17]. Each system was found to correspond to a set of W_0 and B values, derived from different ranges of relative pressures of the same adsorbate (benzene). The typical micropores (5–8 Å) were filled before the supermicropores (11–15 Å), which corresponded to a gradual departure from the linear section of the log-log² plot at higher pressures. In the present case, for the filling of ultra-micropores at high temperatures, a similar behaviour is not excluded, but the pressures corresponding to the filling of typical micropores could not be reached experimentally.

The curves representing W_0 as function of \bar{R}_g may be interpreted as distributions of the average pore-sizes in the solids, as seen by the test molecules at various temperatures. This also suggests that eqns (1) and (2) are

only locally valid, and therefore a more general expression has to be found for the description of adsorption by microporous solids.

The adsorption of nitrogen and xenon by the molecular-sieve M-5, at different temperatures, also reveals activated penetration into a second system of micropores (Fig. 4). Nitrogen adsorption at 78°K leads to a micropore volume of 0.20 cm³/g and to $\bar{R}_g = 5$ Å, from eqn (3). This value is equal to the average pore-width found by independent molecular-sieve experiments. The adsorption of Xe at 228 and 273°K leads to $W_0 = 0.29$ –0.32 cm³/g, and an average pore-size (\bar{R}_g) of 6 Å. Since xenon leads to slightly smaller values than nitrogen in the case of samples U and F, we may conclude that there exists a second pore system in M-5, which can only be reached at higher temperatures, by an activated process. It has a volume of about 0.12 cm³/g and pores which are greater than 6 Å on average, since the xenon values include both systems. The existence of slit-shaped micropores in the region of 6.5–7 Å, in M-5, is also suggested by GSC measurements and adsorption potential calculations of Perret and Stoekli [21]. Although little is known about this sample, it is possible that it was manufactured as described by Walker *et al.* [26], by coating an activated carbon with a thermosetting polymer. After carbonization, the polymer leaves a system of relatively homogeneous pores on the outside, which plays the role of a gate. In the present case, the second system can only be reached through constrictions which require a certain activation energy [26].

4. CONCLUSIONS

The foregoing discussion shows that the theory of Dubinin for the filling of micropores can lead to information about the microporosity of very heterogeneous carbons, if one postulates that the structural factor B is not constant for a given solid. The results should be compatible with methods such as molecular-sieve experiments [22, 26] and the scattering of X-rays at small angles [1, 16–19, 27], from which more results would be welcome.

The present investigation also reveals that great care has to be taken in the prediction of adsorption isotherms by the Dubinin-Radushkevich equation, when certain types of carbons are used. This is clearly illustrated in the present work by the range of B/β^2 values found for the adsorption of benzene, the usual reference adsorbate, between 0 and 200°C. In the case of heterogeneous carbons, reliable prediction should be expected only from molecules having similar sizes and shapes, and adsorbed at similar temperatures.

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