

RECENT DEVELOPMENTS IN THE DUBININ EQUATION

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Abstract—A combination of techniques—mainly immersion calorimetry and adsorption from the vapor phase—provides independent data for the assessment of micropore sizes and their distribution in relation to parameters E_0 and n of the Dubinin–Astakhov (D–A) equation. It is shown that carbons described by the Dubinin–Radushkevich (D–R) equation ($n = 2$) present some heterogeneity, which can be expressed in terms of contributions from true molecular-sieve carbons with $n = 3$.

Key Words—Micropores sizes and distributions, immersion calorimetry, Dubinin–Astakhov, active carbon.

1. INTRODUCTION

Dubinin's theory for the filling of micropores is expressed, in its modern formulation, by the general equation of Dubinin and Astakhov,

$$W = W_0 \exp [-(A/\beta E_0)^n] \quad (1)$$

where W represents 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 accessible to the given adsorbate, $A = RT \ln(p_0/p)$ and n , β , and E_0 are specific parameters of the system under investigation. The so-called affinity coefficient β is a shifting factor that depends only on the adsorptive and by convention $\beta(\text{C}_6\text{H}_6) = 1$. On the other hand, the characteristic energy E_0 and exponent n depend only on the micropore system. It has been shown experimentally that in the case of active carbons, n varies practically from 3 to 1.5, as the micropore system becomes more heterogeneous[1,2]. It has also been confirmed recently[3], on the basis of adsorption and immersion[4] techniques, that $n = 3$ for true molecular-sieve carbons having homogeneous micropore systems near 0.5 and 0.7 nm, respectively. However, it must be emphasized that the determination of the exact value of n becomes increasingly difficult in the domain $n > 2.5$, the accuracy of the fit to eqn (1) depending on the accuracy of the experimental data and on the domain of relative pressures. For this reason, the choice of $n = 2$, corresponding to the original equation of Dubinin and Radushkevich is often justified when representing the adsorption of vapors by average active carbons and over a limited range of pressures.

From a theoretical point of view, it can be shown[5] that exponent n is related to the width of the distribution curve of the adsorption energy, derived from the D–A eqn (1). It appears that the curve becomes sharper as n increases from 1.5 to 3, which implies an increase in the homogeneity of the micropore system, in agreement with simple model calculations[6] based on slit-shaped micropores.

The characteristic energy E_0 of eqn (1) appears to be an inverse function of the average pore size, as suggested by the adsorption of molecules of different sizes from the vapor and the liquid phase. On the basis of preliminary data, Dubinin and Stoeckli[1] suggested the relation

$$E_0 = k/x \quad (2)$$

between the characteristic energy and the average half-width x of the slit-shaped pores, where

$$k = 13.03 - 1.53 \cdot 10^{-5} \cdot E_0^{3.5} \quad (3)$$

Equation (1) had been suggested[1,7] by the empirical relation

$$E_0 \cdot R_g = 14.8 \pm 0.6 \text{ kJ} \cdot \text{nm/mole} \quad (4)$$

based on independent data for the characteristic energy E_0 [8] and for the gyration radius R_g of the micropores obtained from the small-angle scattering of x-rays (SAXS)[9].

Since R_g depends on the principal dimensions of the slit-shaped pore, it is not necessarily equal to its half-width x . As Dubinin[7] suggested, eqns (2) and (4) become equivalent if $R_g \cong 0.8x$, on average.

Equation (3), and the hypothesis according to which the value $n = 2$ corresponds to a homogeneous system of micropores, have been used by different authors to describe heterogeneous micropore systems[1,7,10–12]. However, in view of recent observations based on adsorption and immersion techniques[3] and on electron microscopy[13], a more refined picture has emerged. We shall, therefore, examine critically the current assumptions and the limitations implied by the relatively limited experimental evidence available at the present time.

2. CORRELATION BETWEEN CHARACTERISTIC ENERGY AND PORE WIDTH

This important correlation, expressed by eqns (3) and (4), has already been discussed by different au-

thors[1,14,15]. Dubinin also showed that the amount of water adsorbed near $p/p_0 = 0.6$ was often in good agreement, when expressed in term of an equivalent monolayer, with the geometrical surface area S_{mi} of slit-shaped micropores given by

$$S_{mi}(\text{m}^2/\text{g}) = \frac{W_0(\text{cm}^3/\text{g})}{x(\text{nm})} \cdot 10^3 = \frac{E_0 W_0}{k} \cdot 10^3 \quad (5)$$

However, since the shape of the water isotherm depends on the number of hydrophilic centers on the carbon[16,17], Dubinin's correlation only holds when the centers cover 5 to 10% of the surface. Furthermore, the assumption that the amount of water adsorbed at $p/p_0 = 0.6$ corresponds exactly to the monolayer capacity of the micropore walls, was derived from experiments with Spheron 950, a nonporous carbon black (as shown in ref. [17], this assumption does not hold for another carbon black, Vulcan 3, where the hydrophilic centers represent approximately 5% of the surface area).

The need for independent experimental evidence is therefore obvious, in order to establish a clear correlation between the characteristic energy E_0 and the average pore width L (or the half-width $x = L/2$). Whereas E_0 and W_0 are readily available from adsorption experiments, L can be obtained either from molecular-sieve experiments, from high-resolution transmission electron microscopy, or from W_0 and independent assessment of S_{mi} , through eqn (5).

In principle, S_{mi} can be determined directly from SAXS[18,19], from the adsorption of helium at different temperatures, and from the selective adsorption of organic molecules from aqueous and other solutions (methylene blue, for example, to be described in detail later). The water adsorption isotherm is a possible source of information, with the limitation mentioned above.

Table 1 provides data for E_0 and L for seven microporous carbons. The pore width L was obtained by at least one independent method, and sometimes by two or more, which provided a check for self-consistency. As a general example, let us consider carbon CS, with a relatively homogeneous micropore system of average pore width L close to 0.65 to 0.70 nm, as suggested by molecular-sieve experiments. The adsorption of benzene vapors at 293 K leads to $E_0 = 24.7$ kJ/mole and $W_0 = 0.35$ cm³/g, and consequently the geometrical area of the micropore walls should be near 1100 m²/g. The adsorption

of helium in the region of Henry's law leads to 1020 m²/g and a value of 1030 m²/g is obtained from water adsorption at $p/p_0 = 0.6$ (a good agreement-in this case).

For carbons where L is larger than 0.7 to 0.8 nm, the pore widths can no longer be assessed from molecular-sieve experiments and it is recalculated from S_{mi} , obtained ideally from different types of experiments (helium, SAXS, and the preferential adsorption of flat organic molecules from aqueous solutions, as in the case of carbon U-02).

Our experimental data for L and E_0 was fitted to an empirical relation, eqn (6),

$$L(\text{nm}) = 25/E_0 + 328/E_0^2 - 0.02 \cdot E_0 - 1.20 \quad (6)$$

As illustrated by Table 1, this equation provides a better fit for the new data presented in Table 1 than the earlier relation based on eqns (2) and (3).

It is interesting to note that both best fits predict somewhat larger values for L near 0.7 to 0.9 nm, than obtained experimentally. However, it should be kept in mind that the experimental error on L is of the order of 5 to 10% and that the model of slit-shaped micropores implied by eqn (5) is oversimplified. As the present time, a linear interpolation based on the experimental data of Table 1 is sufficient to assess the average pore width L corresponding to a given value of the characteristic energy E_0 .

3. THE ASSESSMENT OF HETEROGENEITY

It has been assumed previously that the D-R equation corresponded to homogeneous micropore systems, as observed in the case of water adsorption by Na and Ca bentonites, examined by adsorption and X-ray techniques[20] (each discrete stage of adsorption, characterized by a fixed value of the d_{001} spacing, is described by a D-R isotherm).

However, recent molecular-sieve experiments[3, 21] have shown that there exists some degree of heterogeneity in the case of active carbons described by the D-R equation, as illustrated by the histogram of Fig. 1. As mentioned earlier, careful adsorption and calorimetric experiments shows that truly homogeneous systems correspond to exponent $n = 3$ in eqn (1). The adsorption of benzene by MSC-5 and MSC-7 leads to characteristic energies E_0 of 27.6 and 24.0 kJ/mole ($n = 3$) and consequently constant $K = E_0/L$ varies from 14 to 17 nm · kJ/mole.

Table 1. Data for the correlation between the average pore width L and the characteristic energy E_0 of different active carbons

Carbon	D	M-5	C-35	M-51	CS	C-400	N-125
E_0 (kJ/mole)	37	35.6	30.0	27.1	24.7	21.8	20.0
L (nm) exp	0.45	0.50	0.60	0.64	0.70	1.10	1.3
L (nm) eqn (6)	0.46	0.47	0.60	0.71	0.84	1.07	1.27
L (nm) = $2x$ eqns (2)(3)	0.45	0.50	0.72	0.84	0.96	1.13	1.25

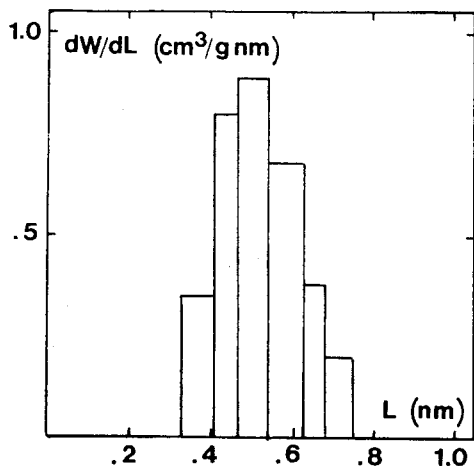


Fig. 1. The micropore distribution of carbon CEP-18 (CO₂ activation to 18% burnoff).

In agreement with the earlier hypothesis[1,8,10], according to which adsorption by a heterogeneous micropore system can be treated as a sum of contributions from homogeneous elements, the D-R equation becomes

$$W_i(p/p_0) = \sum W_{0i} \exp[-(A/\beta E_{0i})^3] \quad (7)$$

Alternatively, we could use an integral with simple distribution functions for dW/dE or dW/dL (As suggested by preliminary calculation[3], Gaussian functions are good first choices to generalize the Dubinin-Radushkevich or the Dubinin-Stoeckli eqns, with $n = 3$).

As illustrated by Fig. 2, the direct summation over the volume elements W_{0i} of Fig. 2 and an average value $K = 14.5$ kJ/mole leads to an overall adsorption isotherm for N₂O which agrees, within experimental error, with the isotherm measured at 293 K. Similar agreements were found for other carbons[3] with average micropore sizes $L < 0.7$ to 0.8 nm, and for which the D-R equation is followed over a relatively large range of the variable $y = (T/\beta)^2 \log^2(p_0/p)$.

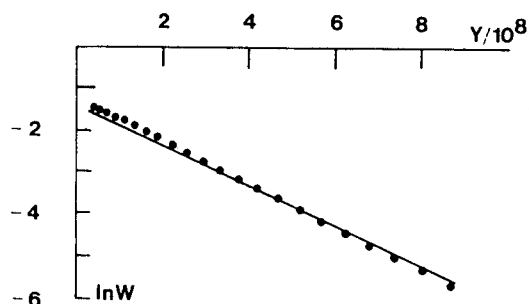


Fig. 2. The logarithmic representations (D-R plots) of the experimental adsorption isotherm of N₂O on carbon CEP-18 at 293 K (—) and of the calculated isotherm (●) obtained from eqn (7) and the histogram of Fig. 1. Variable $y = (T/\beta)^2 \log^2(P_0/P)$ and $\beta = 0.46$.

As expected, the fit is not improved by using various curves (Maxwellian, Gaussian) instead of histograms, owing to the experimental error on the isotherms[10].

4. DISCUSSION

The new experimental evidence presented above provides a better understanding of the physical meaning of parameters n and E_0 of the Dubinin-Astakhov eqn (1), in particular for a practical assessment of microporosity based on the classical D-R equation.

The observation that a truly homogeneous system corresponds to values of n close to 3, in agreement with theoretical predictions, strengthens the background of Dubinin's theory, but at the same time some earlier assumptions must be partly revised. As a direct consequence, it must be accepted that the analysis of heterogeneity in terms of integral transforms based on the D-R equation ($n = 2$) will not lead to the exact spread of the micropore dimensions. This applies in particular to systems regarded as relatively homogeneous and for which E_0 is usually larger than 22 to 23 kJ/mole.

An obvious generalization is one based on eqn (7), with simple and practical (e.g., Gaussian) distribution functions and $n = 3$. This approach also requires new and accurate data for the corresponding quantity $K = E_0 L$ (without this information, the distribution functions have little meaning).

At the present stage, it must be emphasized that experimental evidence is still limited and our assessment of heterogeneity still relies on relatively simple profiles, provided by molecular-sieve experiments[3,21] and by electron microscopy[13]. It is, therefore, too early to distinguish between the merits of distributions resulting from sophisticated theoretical modeling.

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