

On the description of micropore distributions by various mathematical models

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Jaroniec and Choma [1] recently compared the micropore distributions based on their adsorption isotherm [2,3] and the distribution used by Dubinin [4]. We feel that their interesting paper calls for some comments, which may lead to a possible generalization. Both approaches are based on an integral transform of the type.

$$\theta(A) = \int_a^b f(x) \cdot g(A;x) dx \quad (1)$$

where $A = RT \ln(p_0/p)$, involving a "core" equation $g(A;x)$ and a suitable distribution $f(x)$ of the micropore size x . Dubinin uses a Gaussian, whereas Jaroniec and Choma proposed a Gamma-type distribution, which leads to a simple overall isotherm. It is important to realize that both approaches use the classical Dubinin-Radushkevich (DR) eqn

$$g = \exp[-(A/\beta E_0)^2] \quad (2)$$

as the core and both require a functional relation between the characteristic energy E_0 and a pore dimension, either its width L or its half-value x .

(The latter was used in an earlier correlation based on the gyration radius of the pores [5], but for slit-shaped micropores it can be replaced by their actual width L). If one postulates a relation of the type

$$E_0 = K/L \quad (3)$$

it follows that

$$g(A;L) = \exp[-(A.L/\beta K)^2] \quad (4)$$

By using suitable distribution functions $f(L)$, eqn(1) can be solved within the framework of classical Laplace transforms [6] and overall isotherms $\theta(A)$ of varying complexity are obtained [2-4]. At this stage, two important points must be discussed.

The first is based on the mathematical property [6] that the integral transform of a Dirac δ -function $f(L)$ reduces $\theta(A)$ to the core eqn, i.e. to the original DR eqn in the present case. The analysis of adsorption data which follows the DR eqn would therefore lead to an extremely small distribution $f(L)$. In other words, the overall equations obtained by Dubinin and by Jaroniec and Choma rest on the earlier hypothesis [7] that carbons

following exactly the DR eqn (2) are homogeneous. However, from extended work with molecular probes of various sizes, it appears now that this is only a first approximation [8-10]. As shown in fig. 1, carbon CEP-18 displays some degree of heterogeneity, whereas the DR plot for the adsorption of N_2O and CH_2Cl_2 at 298K is linear over an extended range of relative pressures ($A = 5$ to 25 kJ/mol). This means that isotherms based on the DR core (2) are not suitable for the description of adsorption by carbons of low and medium degrees of activation, nor can they reflect their true micropore distributions. On the other hand, the difference should become less important as the degree of heterogeneity increases and strongly activated carbons should be described in a satisfactory way by such equations.

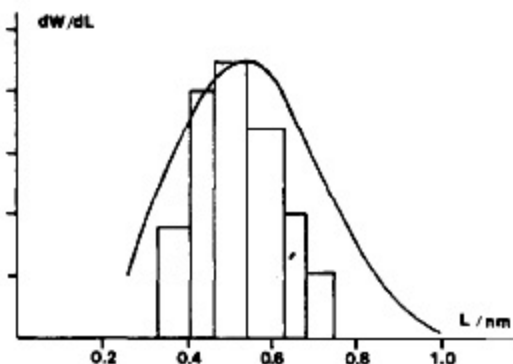


Fig. 1. Experimental and calculated distributions of the micropore widths L for carbon CEP-18, following exactly the DR eqn. The continuous line corresponds to eqn (9), with $\nu = 1.25$ and $a = 6.09 \text{ nm}^{-3}$, obtained by fitting the N_2O adsorption isotherm to eqn (8).

On the basis of earlier observations [5], it was shown by Stoeckli et al. [11] that the DR adsorption isotherm of carbon CEP-18 could be generated from the histogram of fig. 1 by the sum

$$W_i(A) = \sum W_{oi} \exp[-(A/\beta E_{oi})^2] \quad (5)$$

with a relation of type (3) between E_{0i} and L_i . This approach is based on the fact that molecular sieve carbons tend to follow the Dubinin-Astakhov (DA) eqn with values of n close to 3 [5,8]. This suggests the use of

$$g(A;L) = \exp \{-(A/L\beta K)^3\} \quad (6)$$

as the core eqn in (1) rather than eqn (4).

This principle has also been applied successfully by Wojsz and Rozwadowski [12,13] in their generalization of Stoeckli's earlier model [7], based on a Gaussian distribution of the structural constant B . Unfortunately, the corresponding adsorption equation $\theta(A)$ is somewhat difficult to use for data fitting.

A convenient generalization, leading to a relatively simple and acceptable isotherm $\theta(A)$, is based on the use of eqn (6) with a Gamma-type distribution, as in Jaroniec and Choma's treatment [3]. With the important proviso (discussed below) that $E_0 = K/L$, K being a constant, one can use the standard Laplace transform [6]

$$\int_0^{\infty} x^{\nu-1} \exp[-ax] \cdot \exp[-px] dx = \frac{\Gamma(\nu)}{(a+p)^\nu} \quad (7)$$

where $x = L^3$ and $p = (A/\beta K)^3$. This leads to

$$\theta(A) = \left(\frac{a}{a+(A/\beta K)^3} \right)^\nu \quad (8)$$

and to the normalized distribution of the micropore-sizes

$$f(L) = \frac{3L^{(3\nu-1)} a^\nu \exp[-aL^3]}{\Gamma(\nu)} \quad (9)$$

These eqns are similar to those of Jaroniec et al. but have different powers. (It is also preferable to use exponent ν instead of n , in order to avoid confusion with the DA eqn). Their advantage, illustrated by fig. 2, lies in the fact that they also provide reasonable distributions for carbons following closely the DR eqn. It is obvious, however, that for very heterogeneous carbons, the two approaches should yield similar results. From the mathematical analysis of eqn (9) it also appears that the quantity $a^{-1/3}$, expressed in nm, is close to the average pore width L (but not identical with it).

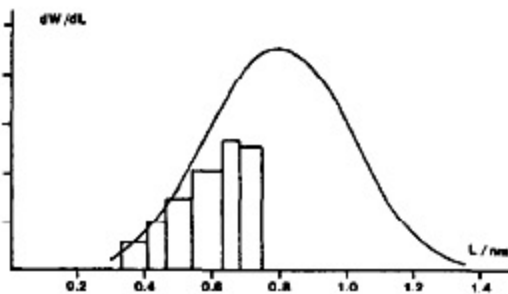


Fig. 2. Molecularsieve data and calculated distribution of the micropore width L for carbon CEP-59. Same procedures as for carbon CEP-18, leading to $\nu = 1.85$ and $a = 2.99 \text{ nm}^{-3}$. N_2O adsorption follows the DA eqn with exponent $n = 1.7$ and CEP-59 is more heterogeneous than carbon CEP-18.

The second important point relates to parameter K in eqn (3). It is generally assumed - but incorrectly - that this quantity is a constant: whereas the gyration radii R_i of the micropores are related to E_0 by a constant equal to $14.8 \pm 0.6 \text{ nm} \cdot \text{kJ/mol}$ [5] this is no longer the case for the actual pore-widths L , where K varies between 16 and 35 when L increases from 0.4 to 2.0 nm [9,14].

The presence of a variable parameter K has direct implications on the integral transforms (1) or (7). Mathematical modelling suggests, however, that the use of a constant value K_0 , corresponding to E_0 of the DR or DA eqn for the given carbon, should lead to a satisfactory agreement. This is shown in fig. 1 ($E_0 = 32 \text{ kJ/mol}$; $K_0 = 16.5 \text{ nm} \cdot \text{kJ/mol}$) and in fig. 2 ($E_0 = 25 \text{ kJ/mol}$; $K_0 = 19.5 \text{ nm} \cdot \text{kJ/mol}$). It may be the result of internal averaging in the integral, $L_0 = K_0/E_0$ being close to the maximum of the distribution $f(L)$.

On the other hand, the use of a unique constant K for the whole range of microporosity close to $24 \text{ nm} \cdot \text{kJ/mol}$, as assumed by different authors, may cast doubts on the validity of the resulting micropore distributions. A direct comparison with experimental data for distributions, as shown in fig. 1-2, is therefore essential to assess the validity of the different models. This stresses again the need for independent data on the micropores of strongly activated carbons.

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