

The comparison of experimental and calculated pore size distributions of activated carbons

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Abstract

Activated carbons are disorganized materials with variable pore size distributions (PSD). If one assumes that the porosity consists mainly of locally slit-shaped micropores, model isotherms can be obtained by computer simulations and used to assess the PSD on the basis of experimental isotherms. In the present study, CO₂ isotherms have been measured at 273 K on seven well-characterized microporous carbons with average micropore widths between 0.65 and 1.5 nm and analysed with model isotherms obtained with standard Monte Carlo simulations. The resulting PSD are in good agreement with those obtained from a modified Dubinin equation, from liquid probes of molecular dimensions between 0.4 and 1.5 nm, from STM and from modelling based on CH₄ adsorption at 308 K. The present study validates the determination of micropore distributions in active carbons based on CO₂ isotherms, provided that no gate effects are present.

1. Introduction

Unlike zeolites and other well-crystallized materials, activated carbons are disorganized and possess therefore a variety of pore size distributions (PSD). In view of their application in filtration technology, the carbons must be characterized and it is often advisable to obtain accurate information on the different types of porosities. Depending on their pore dimensions, one distinguishes macroporosity (>50 nm), mesoporosity (2–50 nm) and microporosity (<2.0 nm in width), each category playing a specific role in transport and adsorption properties. Microporosity plays an essential role in the retention of the adsorbate and its volume can be as high as 0.6–0.8 cm³ g⁻¹.

Following the pioneering work of Dubinin [1–3], microporosity in activated carbons has been investigated by a variety of direct and indirect techniques such as vapour adsorption [4,5], immersion calorimetry [4–6], small-angle scattering of X-rays (SAXS) [7,8], high resolution transmission electron microscopy (HRTEM) [9], including the

dark-field technique [10] developed by Oberlin et al. [11,12] and scanning tunnelling microscopy (STM) [13–15]. These techniques led to a relatively coherent assessment of microporosity, and different models have been suggested by Stoeckli [5,10], on the basis of Oberlin's work [16], by Kaneko [17], McEnaney [18], Dahn [8], Rodriguez [19], Seaton [20] and recently by Thomson and Gubbins [7].

The predominance of slit-shaped pores, at least in the region of 0.4 to ~1–1.5 nm, is also suggested by the dark-field technique [10–12] and by STM [13–15]. However, less regular shapes are not excluded, in particular for wide micropores. These observations justify, to some extent, the description of microporous carbons as a collection of locally slit-shaped micropores, with variable widths. Such pores can be modelled in a relatively simple fashion and used in advanced computer simulations leading to model isotherms of simple molecules [21–31], relevant to the present study. The analysis of the experimental isotherms leads eventually to a theoretical PSD. As described recently by Thomson and Gubbins [7], the structure of a microporous carbon can also be refined by matching the simulated structure with that obtained from SAXS and from adsorption data (reverse Monte Carlo

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technique). This approach also favours the locally slit-shaped character of typical micropores.

On the basis of modelling, a large number of pore size distributions have been reported and an issue of this Journal has recently been devoted to this approach [21], but it appears that systematic comparison with independent evidence, in order to validate these distributions, is still lacking. For example, in their excellent comparison of various models applied to N_2 , Ar and CO_2 , Ravikovich et al. [31] consider only the quality of the fit of the calculated isotherms with the experimental data, but no indirect evidence is provided for the PSDs. In the present study, we compare therefore the calculated PSDs obtained for a variety of activated carbons, with those of independent techniques. It is an extension of preliminary results presented recently [32].

Although nitrogen [7,21,22,27,29] and CO_2 [23–26,30,31] adsorption have been considered at different temperatures, we preferred CO_2 at 273 K, a temperature at which activated diffusion is virtually absent. For this adsorptive, the entire relative pressure range can also be scanned with standard high pressure equipment ($p_s=3.4$ MPa), as opposed to CH_4 at 308 K, another popular molecule [21,27,28], also used in our preliminary work [32]. In the case of methane, however, the temperature is well above critical (191 K) and the equivalent of the saturation pressure, $p_c(T/T_c)^2$ [3], is relatively high. This means that measurements must be carried out at relatively high pressure in order to scan the isotherm properly.

As shown recently [33,34], CO_2 adsorption at 273 K, using carbon black Vulcan-3G as a reference, is a good alternative to the standard comparison plots based either on N_2 at 77 K (Sing's α -plot) or on C_6H_6 , CH_2Cl_2 and CH_3OH at 298 K proposed by Carrott et al. [35]. It has also been shown by Stoeckli [32] that CO_2 and CH_4 lead to overlapping characteristic curves at temperatures between 253 and 353 K, in agreement with other vapours. Moreover, as pointed out by López-Ramón et al. [36], the adsorption of CO_2 is not affected by the oxygen content of the surface. This means that CO_2 is a suitable candidate for the characterization of activated carbons by comparing the adsorption isotherm with standard isotherms obtained from modelling.

It will be shown that in the absence of gate effects the different techniques lead to a good agreement, even on the basis of activated carbons considered as a collection of slit-shaped micropores.

2. Theoretical background

2.1. Adsorption and immersion techniques

As shown in detail elsewhere [1–5], adsorption of vapours by activated carbons is described by the Dubinin–Astakhov equation

$$N_a = N_{ao} \exp[-(A/E)^n] \quad (1)$$

where N_a represents the amount adsorbed at relative pressure p/p_s , N_{ao} is the limiting amount filling the micropores and $A = RT \ln(p_s/p)$. At high pressures, the ratio p_s/p is replaced by the ratio of the fugacities f_s/f and for temperatures above critical the saturation pressure is replaced by an expression given by Dubinin and Nikolayev [3]. Since Eq. (1) reflects the filling of a volume, it is convenient to replace the limiting amount N_{ao} by the micropore volume $W_o = N_{ao} V_m$, where V_m is the molar volume of the adsorbate at the given temperature. This is a first approximation, since it appears from molecular simulations that the density in the adsorbed state can be different from that of the liquid. For example, in the case of CO_2 , a debate has been going on for several years [34,37,38], since the molar volume in the adsorbed state at 273 K appears to be around $43 \text{ cm}^3 \text{ mol}^{-1}$, in order to correlate the micropore volume W_o with that of other adsorbates. At this temperature, the free liquid has a volume of $48.23 \text{ cm}^3 \text{ mol}^{-1}$.

Exponent $n=2$ corresponds to the familiar Dubinin–Radushkevich equation (DR) and the characteristic energy of the system E depends on the adsorbent and on the adsorptive. One may write that $E = \beta E_o$, where β is a coefficient depending on the adsorptive, benzene being taken as the reference. It has been shown [4], that E_o related to the average width L_o of the slit-shaped micropores by

$$L_o \text{ (nm)} = 10.8/(E_o - 11.4 \text{ kJ mol}^{-1}) \quad (2)$$

and consequently the surface area of the micropores is approximately

$$S_{mi} \text{ (m}^2 \text{ g}^{-1}) = 2000 W_o \text{ (cm}^3 \text{ g}^{-1})/L_o \text{ (nm)}. \quad (3)$$

A reasonable micropore distribution can be obtained from a modified Dubinin equation proposed by Stoeckli [4] and discussed in detail by Carrot [22,39],

$$\theta(A) = N_a/N_{ao} = [a/(a + (A/\beta K_o)^3)]^\nu \quad (4)$$

where a and ν are adjustable parameters and K_o is related to the average micropore width L_o by $K_o = L_o E_o$. Eq. (4) results from the integral transform

$$\theta(A) = \int_0^\infty g(A;L) f(L) dL \quad (5)$$

where

$$g(A;L) = \exp[-(AL/\beta K_o)^3] \quad (6)$$

and $f(L)$ is the distribution of the micropore width L over the volume W_o ,

$$f(L) = 3W_o L^{(3\nu-1)} a^\nu \exp[-aL^3]/\Gamma(\nu). \quad (7)$$

This distribution appears to be in good agreement with the PSD resulting from the enthalpies of the microporous carbon into liquids of molecular dimensions between 0.35 and 1.5 nm, provided that no gate effects are present [4]. Good correlation has also been reported by Carrot et al. [22] in the case of modelling based on N₂ adsorption at 77 K.

Eq. (1) leads, as a thermodynamic consequence, to the following expression for the enthalpy of immersion of the carbon [4–6,9],

$$\Delta_i H \text{ (J g}^{-1}\text{)} = -\beta E_o W_o / V_m (1 + \alpha T) \Gamma (1 + 1/n) + h_i S_e \quad (8)$$

α is the expansion coefficient of the liquid, Γ is the tabulated *Gamma* function and h_i (J m⁻²), a negative quantity, is the specific enthalpy of wetting of the non-microporous surface area S_e of the solid.

As shown elsewhere [4,6], it is possible to calculate the micropore volume W filled by the different liquids, as a function of their critical molecular dimension L_c . This leads to the histogram $\Delta W/\Delta L = f(L)$ corresponding to the distribution of the micropore widths. It has been shown that it is usually in good agreement with the PSD given by Eq. (7) obtained from the adsorption data of small molecules such as CH₂Cl₂ or CS₂ at 293 K and pressures below atmospheric, or from CO₂ at higher pressures and between 253 and 298 K. In the case of immersion calorimetry, CS₂ appears to be a good complement to CO₂, in view of their similar molecular dimensions.

2.2. Adsorption modelling

Computer modelling of adsorption and the determination of pore sizes on the basis of standard isotherms has become increasingly popular in the field of carbons [21]. A number of studies are based on the adsorption of N₂ [7,22,29], CH₄ [27,28] and CO₂ [25,26], owing to their molecular simplicity. In the present study, model isotherms were generated for the adsorption of methane and carbon dioxide, by using a commercially available GCMC program (*CERIUS-2*, from Molecular Simulations Ltd.) with a Silicon Graphics workstation. The main characteristic of this program is the fact that gas–solid and gas–gas interactions are based on the Lennard–Jones 6:12 pair-potential

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (9)$$

and not on the force-field proposed by Steele [40], used by the majority of authors. Eq. (3) is much simpler than the potentials used by some authors [30], who consider a weighted average of the quadrupole–quadrupole interactions. However, since the specific parameters ε_{gs} and σ_{gs} (see Table 1), were obtained from the experimental CO₂ isotherms on carbon blacks Vulcan 3-G at 273 K, the quadrupole interactions are effectively taken into account

Table 1

Best fit parameters for the Lennard–Jones pair potentials (9) used in modelling

| Adsorbate | ε_{gs}/k_B ^a K | σ_{gs} nm | ε_{gg}/k_B K | σ_{gg} nm |
|-------------------------|--|---------------------|-----------------------------|---------------------|
| CH ₄ (308 K) | 64.38 | 0.360 | 148.1 | 0.381 |
| CO ₂ (273 K) | 72.90 | 0.365 | 190.0 | 0.390 |

^a k_B is Boltzmann's constant.

in parameter ε_{gs} . The parameters for the gas–gas interactions, ε_{gg} and σ_{gg} , were those of the literature [25,26].

We considered the active carbon as a collection of slit-shaped pores between stacks of graphitic sheets of 3.9×3.9 nm. The effective pore width $L = H - 0.24$ nm varied from 0.5 to 2 nm, H being the distance between the carbon atoms of opposing walls. The correction of 0.24 nm suggested by Everett and Powl [41] leads to a good agreement, but a number of authors also use the value of 0.34 nm. In our model, the walls of the micropores consisted of four graphitic sheets. This seemed a reasonable approximation for carbons of low and medium activation, in agreement with HRTEM and STM observations. Moreover, as pointed out in the literature [21], major differences in the adsorption energy occur when the thickness varies from one to three sheets.

This approach provided standard CO₂ isotherms at 273 K for micropore widths of 0.5 to 2 nm and pressures up to 3.2 MPa (31.6 atm). The experimental isotherm has to be corrected for adsorption on the external surface area S_e . This is done by subtracting from it the standard isotherm for CO₂ adsorbed on Vulcan 3G at 273 K [34] with a prefactor equal to $S_e/71$ m² g⁻¹ (the surface of Vulcan 3G). S_e , given in Table 2, is the average of the values obtained from the CO₂ (273 K) and C₆H₆ (293 K) comparison plots and from Eq. (4), using the enthalpy of immersion into benzene. This procedure led to a Type I isotherm corresponding to adsorption in the micropore system only.

It is important to point out that the Lennard–Jones potential (9) assumes a spherical symmetry. In the case of CO₂, the molecules being rod-shaped, the simulations will lead to a larger volume than in reality. In agreement with the work of Samios et al. [25,26], it appears that the molar volume of CO₂ in micropores of $L > 0.6$ –0.7 nm would be close to that of the free liquid. However, as mentioned above, the density in the adsorbed state appears to be higher.

3. Experimental

In the present study we considered four activated carbons of different origins (CM, CAF-B, AGB, U-103) one activated fiber (KF-1500) and two microporous carbon blacks (XC-72, XC-72-16). Samples CM and U-103 are

Table 2
Main characteristics of the carbons used in this study

| Carbon | Standard DR analysis | | | | Averages | | | Model isotherm | | | Eqs. (4) and (7) | | |
|----------|--|---|--|---|----------------|--|---|--|----------------|--|------------------------------|---------------|--|
| | C ₆ H ₆ (298 K) | | CO ₂ (273 K) | | <i>L</i> nm | <i>S</i> _{mi} m ² g ⁻¹ | <i>S</i> _c m ² g ⁻¹ | CO ₂ (273 K) | | | <i>a</i> nm ⁻³ | <i>ν</i> - | <i>K</i> ₀ kJ nm mol ⁻¹ |
| | <i>W</i> ₀ cm ³ g ⁻¹ | <i>E</i> ₀ kJ mol ⁻¹ | <i>W</i> ₀ cm ³ g ⁻¹ | <i>E</i> ₀ kJ mol ⁻¹ | | | | <i>W</i> ₀ cm ³ g ⁻¹ | <i>L</i> nm | <i>S</i> _{mi} m ² g ⁻¹ | | | |
| CM | 0.252 | 28.0 | 0.280 | 28.2 | 0.65 | 875 | 5 | 0.29 | 0.84 | 690 | 1.52 | 1.13 | 18.33 |
| CAF-B | 0.266 | 28.3 | 0.274 | 28.1 | 0.65 | 856 | 60 | 0.28 | 0.75 | 749 | 3.11 | 1.69 | 18.26 |
| XC-72 | 0.057 | 22.4 | 0.070 | 22.6 | 0.96 | 145 | 105 | 0.070 | 1.01 | 140 | 0.88 | 1.47 | 21.69 |
| XC-72-16 | 0.13 | 21.3 | 0.15 | 21.3 | 1.08 | 259 | 119 | 0.155 | 1.22 | 294 | 0.34 | 1.1 | 23.06 |
| KF-1500 | 0.580 | 19.1 | 0.620 | 19.4 | 1.38 | 918 | 21 | 0.66 | 1.46 | 904 | 0.40 | 1.30 | 26.77 |
| U-103 | 0.330 | 20.7 | 0.360 | 20.8 | 1.15 | 631 | 39 | 0.40 | 1.28 | 625 | 0.39 | 1.16 | 23.92 |
| AGB | 0.455 | 14.3 | 0.450 | 14.5 | >2 | 300 | 213 | 0.45 | 1.86 | 483 | 0.16 | 1.48 | 34.3 |

industrial carbons based on coal, AGB is based on peat and CAF-B has been obtained from skins of coffee beans. These materials have been activated by steam around 950°C. Their structural characteristics, as well as those of the microporous carbon blacks, were determined by standard adsorption and immersion techniques [4,5]. The adsorption isotherms of N₂ (77 K), C₆H₆ (293 K) and CO₂ (273 K) were analysed in terms of the DR Eq. (1), its modification (4), (7) and by comparison plots, as described in detail elsewhere [4,5,33,34]. As shown in Table 2, the results obtained from the different techniques are self-consistent.

High pressure adsorption measurements of CO₂ (253 to 353 K) were carried out with a device described earlier by Guillot et al. [33,34] and improved, in order to allow measurements up to 6 MPa at the higher temperatures. The techniques were the same as used previously for CH₄ adsorption at 308 K [32].

4. Results and discussion

The experimental adsorption isotherms of CH₄ (308 K) and CO₂ (253, 273, 298 K) on Vulcan 3-G provided the basis for the adjustment of the Lennard–Jones pair potentials used in the computer simulations. The best-fit values are given in Table 1. This provided the basis for the simulations of the standard isotherms used to analyse the experimental isotherms in terms of a weighting scheme proposed by Jagiello [42].

As pointed out earlier [32,33] in the case of carbon CM and KF-1500 the adsorption isotherms of CH₄ at 253, 273 and 323 K and of CO₂ at 253, 273 and 298 K lead to unique characteristic curves when *W* is plotted against *A*/*β*. This pattern indicates that for each carbon the two molecules probe the same micropore system. It follows that the PSD obtained from the individual isotherms, and at different temperatures, should be the same. As mentioned in Section 2, the simulations are based on a

spherical intermolecular potential. This is correct for CH₄, but in the case of CO₂, the simulations overestimate the molar volume of CO₂ (53.2 cm³ mol⁻¹ in pores wider than 0.7 nm). A correction (re-scaling) has therefore been introduced, by considering the effective molar volume of 43.90 cm³ mol⁻¹ given by Ozawa's equation [43] and in good agreement with the estimates of different authors [37,38].

Figs. 1–7 show the agreement between the histograms based on modelling after correcting the experimental isotherm for adsorption on the external surface *S*_c; the curve given by Eq. (7) and, where available, on immersion calorimetry and on STM. The histograms resulting from the model isotherms also lead to average micropore widths *L*, given by a simple weighting procedure, and to the total micropore surface areas *S*_{mi} of the model pores. These values can be compared with those obtained from the classical analysis based on Eqs. (1)–(3). As seen in Figs. 1 and 2, one observes a good overlap between the PSD obtained with CO₂ at 273 K and with CH₄ at 308 K. The latter is also a good test for the technique itself.

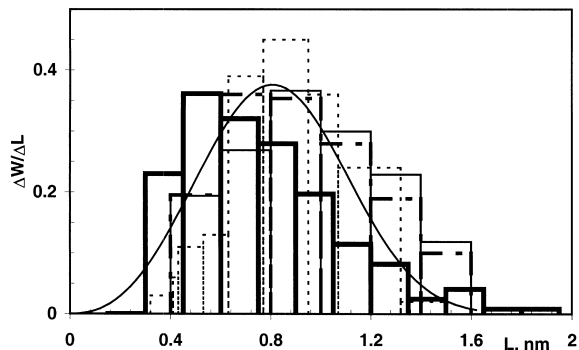


Fig. 1. Pore size distributions of carbon CM obtained by immersion calorimetry (---), STM (—), CH₄ at 308 K (···) and CO₂ at 273 K (— · —). The smooth curve corresponds to Eq. (7).

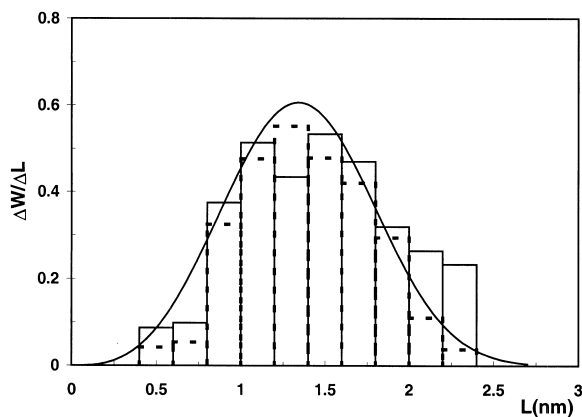


Fig. 2. Pore size distributions of activated fibre KF-1500 obtained from CH_4 at 308 K (---) and CO_2 at 273 K (—). The smooth curve corresponds to Eq. (7).

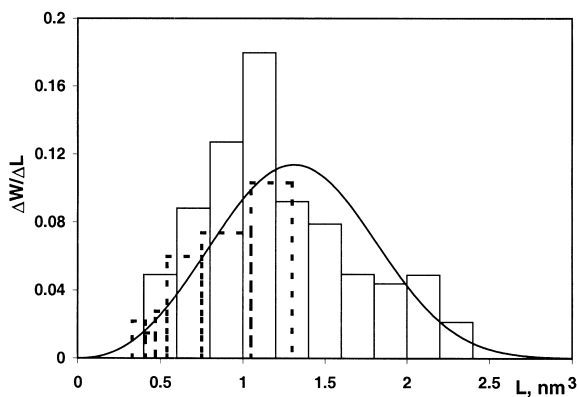


Fig. 5. Pore size distributions of microporous carbons black XC-72-16 obtained by immersion calorimetry (---) and CO_2 isotherm at 273 K (—). The curve corresponds to Eq. (7).

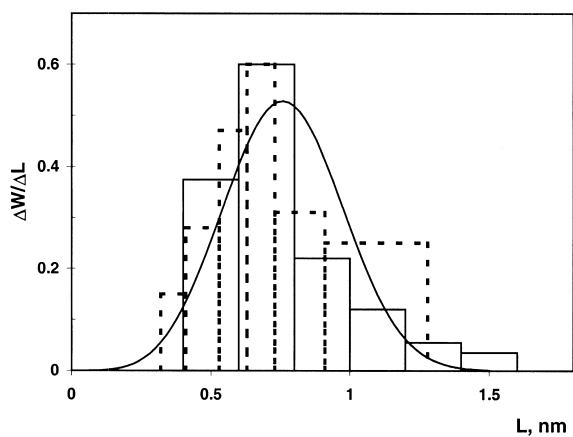


Fig. 3. Pore size distributions of activated fibre CAF-B obtained from immersion calorimetry (---) and CO_2 isotherm at 273 K (—). The curve corresponds to Eq. (7).

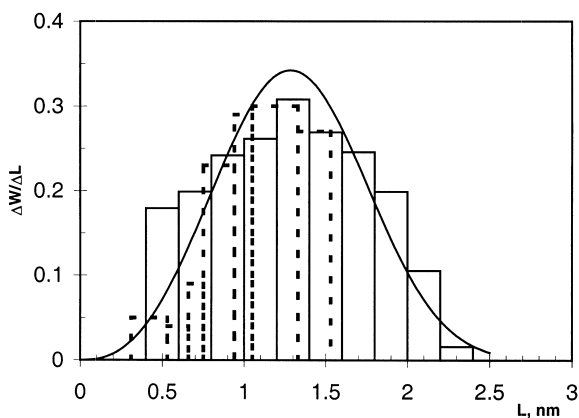


Fig. 6. Pore size distributions of activated carbon U-103 obtained from immersion calorimetry (---) and the CO_2 isotherm at 273 K (—). The curve corresponds to Eq. (7).

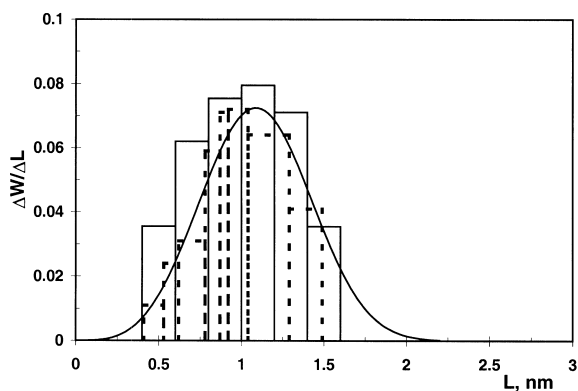


Fig. 4. Pore size distributions of microporous carbons black XC-72 obtained by immersion calorimetry (---) and CO_2 at 273 K (—). The curve corresponds to Eq. (7).

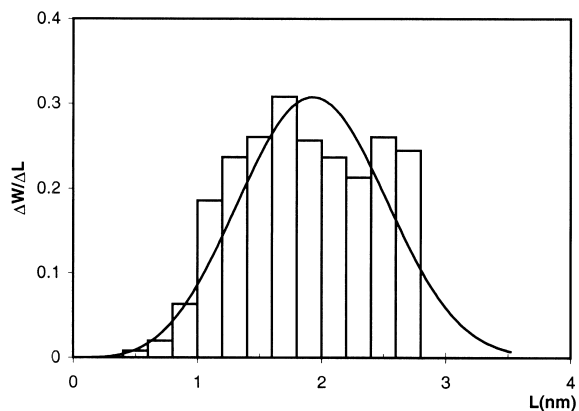


Fig. 7. Pore size distributions of activated carbon AGB from the CO_2 isotherm at 273 K (—). The curve corresponds to Eq. (7).

(7).

5. Conclusions

These results confirm that modelling based on reference isotherms for CO₂ at 273 K and CH₄ at 308 K, obtained with a relatively simple potential, lead to a satisfactory picture for the PSD of active carbons of medium and high activation, when compared with direct experimental evidence. The latter, based on molecular probes and on microscopy, are accurate within 5–10%. This clearly shows the limits of the possibilities at the present time, if refinements are to be introduced in the modelling itself. It is likely, that more advanced experimental techniques, as used by Thomson and Gubbins [7], will lead to a higher accuracy. Finally, the role of gate effects at the entrance of certain micropore systems, should not be underestimated. As a result, the PSD suggested by small molecular probes such as CO₂, will not be the same as the effective PSD, imposed by the constrictions on molecules of different sizes. This problem, of great importance in industrial filtration, will be examined in more detail.

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