Pore size distributions of active carbons assessed by different techniques

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Unlike zeolites or other crystalline solids, active carbons are disorganized and have, therefore, variable pore size distributions (PSD). These distributions, in particular in the micropore region, can be assessed by a variety of experimental techniques based on X-rays (SAXS), transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and molecular sieve experiments based on the adsorption of molecular probes with different sizes. For example, immersion calorimetry [1,2] provides information on pore widths between 0.35 and approximately 1.5 nm. In the absence of gate effects, reliable PSD can be obtained by this technique, as shown in Fig. 1, for a typical active carbon, CM.

A relatively good agreement can be found between this technique, TEM [3] and STM [4]. In the case of carbon CM (Fig. 1) the frequency of the micropore widths observed by STM on the surface of the solid, ΔN/ΔL, is slightly different from the volumic distribution ΔW/ΔL, since the STM analysis does not take into account the actual depth of the micropores. However, the two distributions are related and STM, like TEM, confirms that the micropores of active carbons are locally slit-shaped. This, in turn, provides the basic model for computer simulations.

In the case of microporous carbons, it has also been possible to derive PSD from adsorption data within the framework of Dubinin’s theory for the volume filling of micropores [5,6]. A possible relation is the so-called Dubinin–Stoeckli (DS) equation [1,7,8], which applies to strongly activated carbons, with relatively wide distributions. As reported by Daley at al. [9], good agreement is found between the PSD derived from the DS equation and the experimental distribution observed by STM on strongly activated carbons.

Recently [1], a modified Dubinin isotherm has also been suggested to obtain PSD in the micropore range,

\[ \theta(A) = [a/(a + (A/\beta K_0)^3)], \]

where \( \theta = N_v/N_{v_0} \) is the reduced isotherm and

\[ A = RT \ln(p_i/p); \text{ and } \nu \text{ are adjustable parameters.} \]

\( K_0 \) is related to the average micropore width \( L \) by \( K_0 = LE_0 \), where \( E_0 \) is the so-called characteristic energy \( E_0 \) of the Dubinin equation [1,5,6]. It can be shown that Eq. (1) results from the integral transform

\[ \theta(A) = \int_0^{\infty} g(A; L)f(L)\,dL \]

(2)

where

\[ g(A; L) = \exp[-(AL/\beta K_0)^3] \]

(3)

and \( f(L) \) is the distribution of the micropore width \( L \) over the volume \( W_0 \).

\[ f(L) = 3W_0L^{3\nu-1}a^\nu \exp[-aL^3]/\Gamma(\nu) \]

(4)

This function, like the distribution based on the DS equation [1,7–9], has a single maximum and it is not suited for the description of bimodal micropore distributions, provided that they exist. In the case of carbon CM the pore size distribution Eq. (4) shown in Fig. 1(b), has been obtained from the adsorption isotherms of CH\textsubscript{4} (253, 273, 308 K) and of CO\textsubscript{2} (253, 273, 298 K) fitted to Eq. (1). This distribution is in good agreement with the histogram of Fig. 1(a), derived from liquids with molecular sizes between 0.4 and 1.5 nm. As confirmed independently by STM, the experimental distribution has no secondary maximum around 1.5 nm.

Computer modeling of adsorption and the determination of pore size distributions based on standard isotherms has become increasingly popular and it has been discussed recently [10]. At the present time, modeling is frequently based on the adsorption of N\textsubscript{2} [11–13], CO\textsubscript{2} [14,15] and CH\textsubscript{4} [16–19], but a systematic comparison with pore size distributions obtained by independent techniques is still lacking. For example, to our knowledge, no direct comparison has been provided so far between computer simulations and experiments based on the use of liquids with different molecular sizes. We wish, therefore, to present results obtained along these lines, as part of a wider study aiming at the validation of pore size distributions obtained on the basis of standard isotherms.
well-characterized solid [1,2] with an average micropore width $L$ around 0.75 nm. The second carbon, activated fibre KF-1500 [20], has an average micropore width of 1.6 nm and no reliable pore size distribution can be obtained with liquid probes. However, the adsorption isotherms of a variety of gases and vapors, in particular CO$_2$ and CH$_4$ at pressures up to 20 bars [20–22] lead to a coherent pore size distribution with the help of Eqs. (1) and (4).

The adsorption data for carbon dioxide and methane at different temperatures can also be analyzed in terms of the so-called characteristic curve [5–7]. It is a representation of the adsorbed volume $W$, or the relative amount adsorbed $\theta = N_a / N_{tot}$, versus $A/\beta = (RT/\beta) \ln(p_a/p)$, where high pressures are usually replaced by the corresponding fugacities $f$. Following Dubinin [5], at temperatures $T > T_c$ the saturation pressure is replaced by $p_c(T/T_c)^\gamma$. An expression, used in the present approach, has also been proposed by Ozawa et al. [23] to calculate molar volumes.

As shown in Fig. 2, single curves are obtained for carbons CM and KF-1500 with the classical values $\beta$(CO$_2$)=0.35 and $\beta$(CH$_4$)=0.35. The latter also corresponds to the value reported for measurements below $T_c$ [24]. The results for N$_2$ at 77 K also fit these curves, but it should be pointed out that for this vapor, the adsorption data for $A > 7000$ J mol$^{-1}$ should not be considered. This domain corresponds to very low relative pressures, where activated diffusion frequently occurs or adsorption may take place under adiabatic conditions.

Since CO$_2$, CH$_4$ and N$_2$ have similar molecular dimensions and overlapping characteristic curves, one may assume that these molecules ‘see’ the same micropore systems. Consequently, the analysis of the corresponding isotherms should finally lead to the same PSD, whatever the underlying mathematical model. It appears, however, that the PSD based on the DFT approach for nitrogen at 77 K, does not provide reliable results for effective pore widths $L < 1$ nm. On the other hand, according to Carrott et al. [13], Monte Carlo simulation for N$_2$ (77 K) lead to a good agreement with the isotherm analysis based on Eqs. (1) and (4).

In the present study, model isotherms were generated for the adsorption of CH$_4$ in slit-shaped micropores, using a commercially available program (CERIUS-2, Molecular Simulations Ltd. with a Silicon Graphics working station). The program is based on direct summations over the

![Fig. 1. Pore-size distributions for active carbon CM obtained by different techniques. (a) From liquids of different molecular sizes (histogram $\Delta W/\Delta L$) and STM (dotted histogram $\Delta N/\Delta L$). (b) From the CH$_4$ adsorption isotherm at 308 K (histogram) and from Eq. (4) (continuous line), using the adsorption data for CO$_2$ (253, 273, 298 K) and CH$_4$ (253, 273, 308 K).](image)

Table 1
Main characteristics of active carbon CM [1,2] and KF-1500 [20]. Parameters $a$ and $\nu$ are obtained from the adsorption of CO$_2$ and CH$_4$ at different temperatures, fitted to Eq. (1)

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$W_a$</th>
<th>$S_a$</th>
<th>$E_a$</th>
<th>$L$</th>
<th>$K_a$</th>
<th>$a$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>0.252</td>
<td>28</td>
<td>26.2</td>
<td>0.75</td>
<td>19.65</td>
<td>1.52</td>
<td>1.13</td>
</tr>
<tr>
<td>KF-1500</td>
<td>0.56</td>
<td>25</td>
<td>18.2</td>
<td>1.6</td>
<td>29.12</td>
<td>0.4</td>
<td>1.3</td>
</tr>
</tbody>
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carbon atoms, instead of the standard 10:4 potential suggested by Steele [25] and used by most authors. The initial force-field parameters had to be slightly modified by a validation process based on the experimental adsorption isotherm of methane on VULCAN-3, also at 308 K. Using a unit cell of 3.9×3.9 nm and walls consisting of four graphitic layers, model isotherms were calculated for pore widths \( H \) in the range \( H = 0.74 \) to 2.84 nm. \( H \) represents the distance between the planes containing the carbon atoms on opposite walls and it was corrected to an effective pore width \( L = H - 0.24 \) nm, as used by Gusev et al. [18]. This value, suggested originally by Everett and Powl [26] and confirmed by TEM [3], is smaller than the value of 0.34 nm used by many authors. Our model isotherms for CH\(_4\) at 308 K are in good agreement with those reported by Gusev et al. [17]. It also appears that our method gives satisfactory results for the simulation of the adsorption isotherm of CH\(_4\) at 273 K, taking into account the external surface area.

The decomposition of the experimental isotherms for CM and KF-1500 into contributions from the model isotherms was carried out as suggested by Jagiello [27], which leads to the histograms shown in Figs. 1(b) and 3. In the case of carbon CM, one finds a good agreement with the histograms obtained from liquid probes and from STM and with the distribution Eq. (4) based on the adsorption of CH\(_4\) and CO\(_2\) at different temperatures. For carbon fibre KF-1500, one obtains a good agreement between the distributions based on modeling and on Eq. (4).

The agreement described here is confirmed by prelimin-

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Fig. 2. Characteristic curves for the adsorption of CO\(_2\) (253, 273, 298 K) and CH\(_4\) (253, 273, 308 K) on carbon CM, lower curve, and for CO\(_2\) (253, 273, 298, 323 K) and CH\(_4\) (273, 298, 323 K) on carbon fibre KF-1500, upper curve. The best fits correspond to \( \beta(\text{CO}_2) \) and \( \beta(\text{CH}_4)=0.35 \).

Fig. 3. Pore size distribution of active carbon fibre KF-1500, obtained from the CH\(_4\) isotherm at 308 K (histogram) and calculated by Eq. (4) (curve), using the adsorption data for CO\(_2\) (253, 273, 298, 323 K) and CH\(_4\) (273, 298, 323 K).