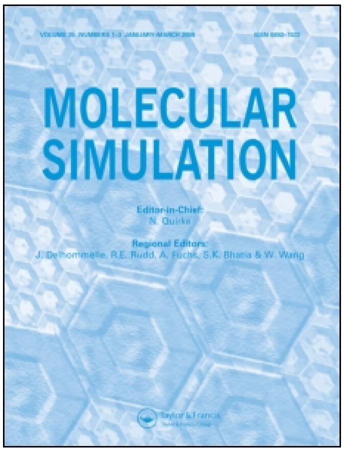

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Simulation Study of Sorption of CO_2 and N_2 with Application to the Characterization of Carbon Adsorbents

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SIMULATION STUDY OF SORPTION OF CO_2 AND N_2 WITH APPLICATION TO THE CHARACTERIZATION OF CARBON ADSORBENTS

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The Monte Carlo method was used in its grand ensemble variant (GCMC) in combination with CO_2 and N_2 experimental isotherm data at low (77 and 195.5 K) and ambient temperatures (298 and 308 K), in order to characterize microporous carbons and obtain the corresponding pore size distribution (PSD). In particular, the CO_2 and N_2 densities and the isosteric heats of adsorption inside single, slit shaped, graphitic pores of given width were found on the basis of GCMC for pre-defined temperatures and different relative pressures. In a further step, we determined the optimal PSD for which the best match is obtained between computed and measured isotherms. Comparisons were made between the PSDs found for the same carbon sample at low and ambient temperatures for different gases, and conclusions concerning the applicability of the method and the reliability of the resulting micropore size distributions were drawn.

Keywords: Pore size distribution; CO_2 adsorption; N_2 adsorption; Monte Carlo simulations; Microporous carbon characterization

INTRODUCTION

Pore structure characterization is an important pre-requisite for the selection and efficient utilization of porous adsorbents and catalysts in a number of industrial applications including separation processes, removal of various pollutants and gas storage. In the case of mesoporous and macroporous materials, there exist several more or less established characterization methods that provide

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information on pore size distribution (PSD), pore network connectivity and other structural parameters of the material [1,2]. On the contrary, the reliable assessment of microporosity (pores of sizes less than 2 nm) in terms of relating sorption properties to the underlying microstructure is much less advanced. The commonly used Dubinin–Radushkevich, Dubinin–Astakhov and Dubinin–Stoeckli methods employ phenomenological models of adsorption based on the thermodynamic approach of Dubinin. The limitations of these and other conventional methods used in practice (like the MP and the Horvath–Kawazoe methods) for micropore size characterization have been repeatedly discussed in the literature (see for example [4,5] and related references therein, see also [6] for a recent assessment of different techniques for the estimation of PSD in carbons). The criticisms raised are related mainly to the fact that the mechanism of molecular adsorption in micropores is still under active debate.

Improved approaches to the micropore structure characterization problem have been recently developed based on molecular level theories and statistical mechanics based simulations. In particular, density functional theory (DFT) in a sufficiently elaborate form has been used to provide an accurate description of simple fluids in geometrically simple confined spaces and develop practical methods for the evaluation of the pore structure over a wide range of pore sizes [7–12]. To capture more accurately, the behavior of the adsorbates in micropores, it is often necessary to model them as non-spherical molecules with electrostatic interactions. Given the limited capabilities of DFT in this context, molecular simulation based on the Grand Canonical Monte Carlo technique has been established lately as an efficient alternative approach for the generation of adsorption isotherms in carbons and the subsequent determination of PSDs [13–21]. Some authors have combined these studies with structural investigations for the densification process in carbon nanopores using spherical molecules, ethane and carbon dioxide and accounting for effects of pore shape and size, temperature, quadrupole interactions and molecule length [19,22–24].

Use of GCMC method for obtaining the PSD of microporous carbonaceous materials evolves the following three major steps [13,20,21]:

1. Determination (and validation whenever possible) of a molecular model for the adsorbate–adsorbate and adsorbate–adsorbent interactions.
2. Generation of a database of sorption isotherms with respect to a specific adsorbate for a set of pore widths, pressures and temperatures.
3. Inversion of the adsorption integral equation:

$$N(p) = \int_{H_{\min}}^{H_{\max}} f(H)n(H)\mathrm{d}H \tag{1}$$

where $N(p)$ is the experimentally measured amount of adsorbate, $n(H,p)$ is the average density of adsorbate at pressure p in a pore of width H, and $f(H)$ is the PSD sought.

The solution of Eq. (1) is an ill-posed problem. Depending on the form of the kernel $n(H,p)$ and the isotherm $N(p)$, there can be from zero to an infinity of solutions for $f(w)$ (detailed discussions on the methods for the solution of Eq. (1) and the application of suitable constraints to force physically sound or appealing solutions including constraints on the smoothness of $f(H)$ and the range of H, (see [14,18,20,21] and references therein). Nonetheless, our work aims at finding useful solutions to Eq. (1) in the sense that the gas adsorption properties of microporous carbons can be reliably predicted. For instance, our efforts concentrate on predicting gas adsorption isotherms for various adsorbents and temperatures from a PSD obtained with a particular gas at a given temperature.

Neimark and co-workers have also used N_2 and Ar at 77 K and CO_2 at 273 K as adsorbates and generated $n(H,p)$, based on DFT methods (for N_2 and Ar) and GCMC for CO_2 up to the pressure of 1 bar employing the Harris and Yung model [25] for adsorbate–adsorbate interactions. They found reasonable agreement between PSDs determined with the different gases on various porous carbon samples. In addition, they reported satisfactory comparisons between PSDs of microporous carbons determined from the DFT and GCMC databases for CO_2.

Sweatman and Quirke [21], have employed molecular simulation techniques including the Gibbs method Monte Carlo to determine the molecular models for N_2, CH_4 and CO_2, as well as GCMC simulations to generate adsorption isotherms in carbon slit-pores at 298 K for pressures up to 20 bar. These data have then been used for the calculation of PSDs for typical activated carbons. They found that the high pressure measurements of CO_2 reveal micropore structure not seen with the other gases or with measurements up to 1 bar. Their results also indicate that the CO_2 based PSDs are the most robust in the sense that they can predict the adsorption of methane and nitrogen at the same ambient temperature with reasonable accuracy.

The work presented in this paper builds upon previous work by Samios *et al.* [13,19] who used GCMC in combination with CO_2 experimental isotherm data at 195.5 K and ambient temperatures to characterize microporous carbons and obtain the corresponding PSDs. Specifically, the databases $n(H,p)$ have been built by determining the mean CO_2 density inside single slit-shaped graphitic pores of given width (from 0.5 to 2.0 nm) along with utilization of N_2 at 77 K. High pressure data for CO_2 are used as well and the isosteric heat of adsorption is employed to further validate the obtained PSDs.

MODELING OF THE MOLECULAR INTERACTIONS

Adsorbates

Carbon dioxide is modeled as a three charged center molecule, according to Murthy and co-workers [26] with the parameters $\varepsilon_{OO}/k_B = 75.2\,K$, $\sigma_{OO} = 0.3026\,nm$, $\varepsilon_{CC}/k_B = 26.3\,K$, $\sigma_{CC} = 0.2824\,nm$. The O–O and C–O distances of the model are 0.2324 nm and 0.1162 nm respectively. The intermolecular potential $u_{ij.}$ is assumed to be a sum of the interatomic potentials between atoms α and β of molecules i and j, respectively (taken of Lennard–Jones 12-6 form), plus the electrostatic interactions due to CO_2 quadrupole moment with the point partial charges $q_O = -0.332e$ and $q_C = +0.664e$, i.e.

$$u_{ij}(r) = \sum_{\alpha\beta}\left\{4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right] + \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r_{\alpha\beta}}\right\} \qquad (2)$$

where ε_0 is the permittivity of vacuum.

Nitrogen was modeled as a two LJ center molecule (the two centers separated by 0.1094 nm) with $\varepsilon_{NN}/k_B = 37.8\,K$, $\sigma_{NN} = 0.3318\,nm$ carrying charges $q_1 = +0.373e$ and $q_2 = -0.373e$, at distances 0.0847 and 0.1044 nm from the molecule center, respectively [27].

Adsorbent

Pore walls are treated as stacked layers of carbon atoms separated by a distance $\Delta = 0.335\,nm$, and having a number density $\rho_w = 114\,atoms/nm^3$ per layer. The adsorbate–wall interaction at distance r_z was calculated by the 10-4-3 potential of Steele [28]:

$$u_w(r_z) = 2\pi\rho_w\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{\alpha\beta}}{r_z}\right)^{10} - \left(\frac{\sigma_{\alpha\beta}}{r_z}\right)^{4} - \frac{\sigma_{\alpha\beta}^4}{3\Delta(0.61\Delta + r_z)^3}\right] \qquad (3)$$

The potential parameters of the solid surface are $\varepsilon_{SS}/k_B = 28.0\,K$ and $\sigma_{SS} = 0.340\,nm$. It must be noticed that Eq. (3) does not take into account the energetic inhomogeneity of the surface along the x and y directions at a distance r_z from the wall. Nevertheless, this lack of surface corrugation is not expected to affect the results significantly especially at ambient temperatures [4].

All the cross interaction potential parameters between different sites ($\alpha \neq \beta$) were calculated according to the Lorentz–Berthelot rules:

$$\sigma_{\alpha\beta} = \frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}}{2}$$

$$\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta})^{1/2}$$

The potential energy U_w due to the walls inside the slit pore model for each atom of the adsorbate molecules is given by the expression:

$$U_w = u_w(r_z) + u_w(H - r_z) \tag{4}$$

where H is the distance between the carbon centers across the slit pore model. For the determination of PSDs, the corrected width H' should be used since this is the one involved in the experimentally obtained isotherms, namely:

$$H' = H - 2z_0 + \sigma_g \tag{5}$$

where σ_g is the root of the adsorbate–adsorbent Lennard–Jones function, and z_0, the root of its first derivative. If the above relation is applied in the present N_2 or CO_2–graphite system, it is found that about 0.24 nm should be subtracted from H to define H' [29].

SIMULATION EXPERIMENTS

Adsorption Isotherms

The Grand Canonical Ensemble Monte Carlo method was employed to probe the statistically important regions of the configuration space in the (μ,V,T) ensemble according to the prescription given elsewhere [30]. For the linear molecules, three types of move are attempted with equal probability: (a) a compound move enabling random displacement and reorientation, with the maximum allowed displacement being adjusted so that the acceptance ratio of the move is about 20% in order to sample phase space more efficiently; (b) a compound move consisting of random insertion of the center of mass of a molecule in a random orientation, by generating a unit vector distributed uniformly on the surface of a sphere centered at the origin of the Cartesian system of coordinates of the simulation box (Marsaglia's algorithm [30]); and (c) a random deletion of a fluid molecule.

Periodic boundary conditions have been applied in the directions other than the width of the slit. For a given simulation, the size of the box (i.e. the two dimensions other than H) was varied in order to ensure that sufficient particles (ca. about 500) remained in the simulation box at each pressure. Statistics were not collected over the first 3×10^6 configurations to assure adequate convergence of the simulation. The uncertainty on the computed equilibrium properties such as ensemble averages of the number of adsorbate molecules in the box and the total potential energy is estimated to be less than 4%.

Isosteric Heat of Adsorption

As noted above, during the simulation runs, the mean potential energy $\langle U \rangle$ of the sorbed molecules is also calculated as an ensemble average. This quantity represents an integral energy of sorption due to adsorbate–adsorbent and adsorbate–adsorbate interaction. A related differential property derived from $\langle U \rangle$ is the isosteric heat of adsorption q_{st}, which is defined as the difference between the molar enthalpy of the adsorbate molecule in the gas phase and its partial molar enthalpy in the adsorbed phase, i.e.

$$\langle q_{\mathrm{st}} \rangle = H^{\mathrm{G}} - \bar{H}^{\mathrm{S}}$$

At low occupancies, in the Henry's law region, the following equation can be derived

$$\lim_{\mathrm{d} \to 0} \langle U \rangle = -\lim_{\mathrm{d} \to 0} q_{\mathrm{st}} + k_{\mathrm{B}} T \tag{6}$$

Equation (6) provides a convenient way of calculating isosteric heat at zero coverage per molecule $q_{\mathrm{st}}^{0} \equiv \lim_{\mathrm{d} \to 0} q_{\mathrm{st}}$ by evaluating numerically the multidimensional integrals

$$\langle U \rangle = \frac{\int \mathrm{d}\mathbf{r}\mathrm{d}\boldsymbol{\psi} U(\mathbf{r}, \boldsymbol{\psi}) \exp(-\beta U(\mathbf{r}, \boldsymbol{\psi}))}{\int \mathrm{d}\mathbf{r}\mathrm{d}\boldsymbol{\psi} \exp(-\beta U(\mathbf{r}, \boldsymbol{\psi}))} \tag{7}$$

For the evaluation of Eq. (7), we used the method of Monte Carlo integration over the configurational space, by calculating the potential energy experienced by one adsorbate molecule for a statistically sufficient number of vectors of position $\mathbf{r}$ and Eulerian angles $\boldsymbol{\psi}$, randomly generated from a uniform probability distribution function.

We have also calculated the isosteric heat of adsorption at zero coverage in a different way by evaluating the integrals of Eq. (7) using the method of Metropolis Monte Carlo, namely by using importance sampling to explore the configurational space. Both techniques gave results in very satisfactory agreement.

GCMC SIMULATION RESULTS

The validation of the adsorbate–adsorbent potential functions used in this study has been made by comparing measured and calculated isosteric heats of adsorption at zero coverage as well as experimental and simulated isotherms on non-porous surfaces [13]. For the comparisons between computed and measured isotherms, the simulation results need to be corrected using H' from Eq. (5). We have used the GCMC method in a previous publication to simulate CO_2 sorption isotherms at 195.5 K in single graphitic pores of various sizes in the micropore range [13]. The selection of the adsorbed gas and the temperature was based on practical considerations regarding the relative ease of obtaining experimental isotherms at dry ice conditions with a molecule that is known for its ability to enter into the narrow microporosity and the realistic equilibration times required. Presently, we attempt to further test and validate the method by extending it to ambient conditions (298 and 308 K, i.e. slightly below and above the CO_2 critical temperature, respectively; pressure up to 35 bar) and comparing the resulting PSD with that obtained by employing other gases (N_2 at 77 K). Comparisons between the PSDs found at low and ambient temperatures are made while the PSDs determined at low temperature from different gases are used to predict isotherms at high temperatures and vice versa.

With reference to [20], the present work employs GCMC for both N_2 at 77 K and CO_2 since their molecules are modeled as quadrupole dumbells with a rigid interatomic bond, under subcritical and supercritical conditions; in addition, our measured isotherms are extended to pressures up to 35 bar.

In Ref. [21], GCMC simulations were used to generate adsorption isotherms for N_2 and CO_2 in carbon slit-pores at 298 K and up to 20 bar. In their concluding remarks, the authors stressed the need for extending CO_2 isotherms to higher pressures, (partly satisfied here), and suggested a comparison of the PSDs obtained from high temperature CO_2 data to those obtained by using low temperature N_2 data as it is attempted in the present work.

The detailed CO_2 and N_2 density profiles across the graphitic slit pore have been computed for widths ranging from 0.5 to 2.0 nm, in steps of 0.05 nm. From this information, the average density in the micropores can be calculated and used to construct the corresponding isotherms as shown in Figs. 1–4. It must be noticed that the x-axis represents the relative pressure for the subcritical cases and the ratio p/p_c with p_c being the critical pressure for the supercritical CO_2 at 308 K. In Figs 1–4 can be seen that at low chemical potential (or equivalent pressure), the adsorbate density is highest in the smaller pores while at high chemical potential, the larger pores exhibit higher adsorptive capability. This reversal of preference can be explained with reference to the adsorbate–

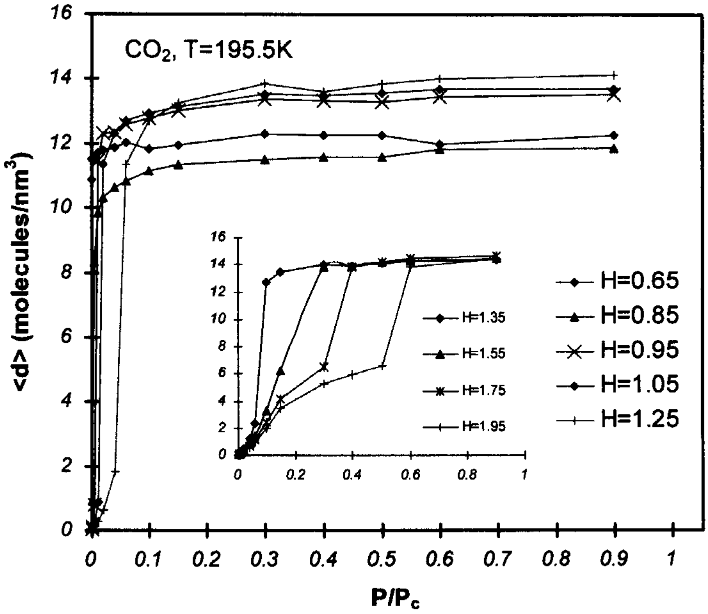

FIGURE 1 Computed CO_2 isotherms for different pore widths at 195.5 K.

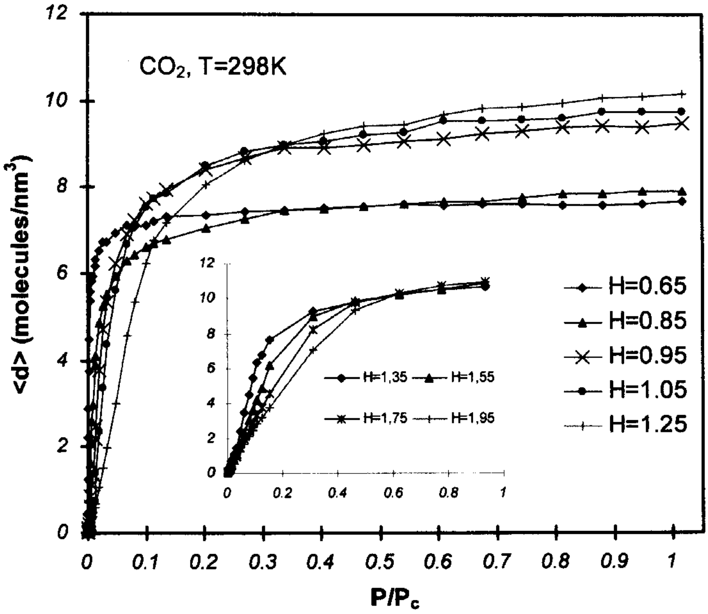

FIGURE 2 Computed CO_2 isotherms for different pore widths at 298 K.

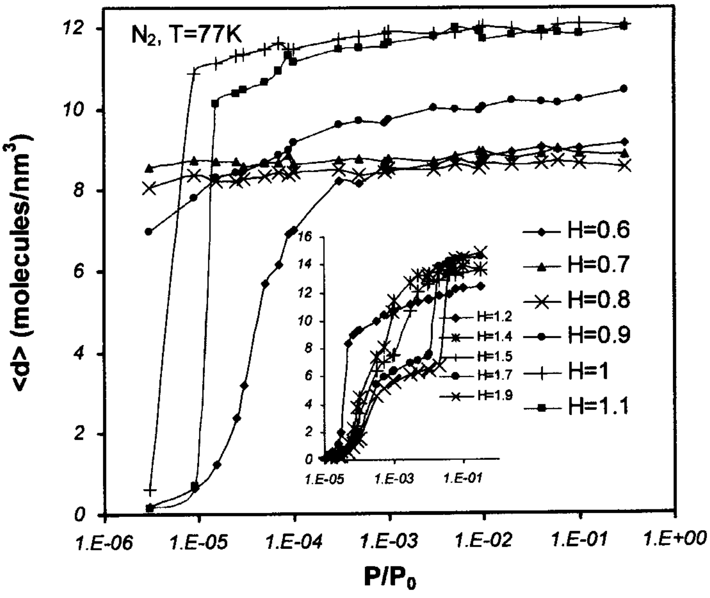

FIGURE 3 Computed CO_2 isotherms for different pore widths at 308 K.

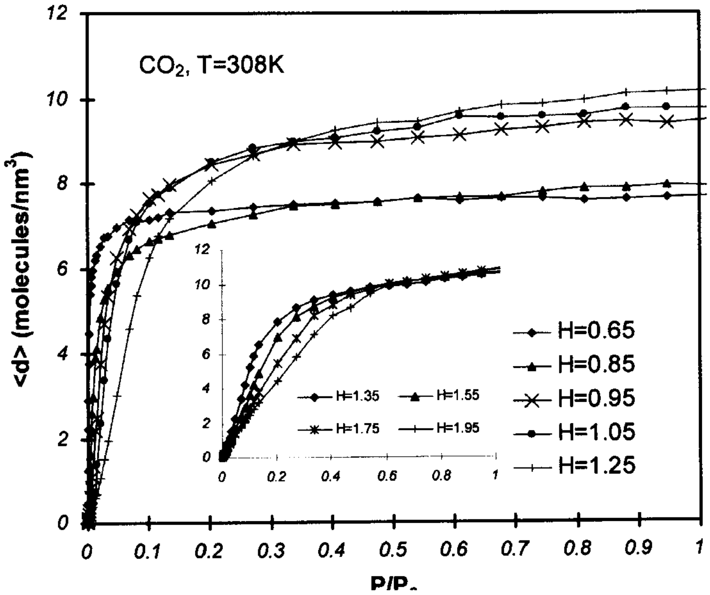

FIGURE 4 Computed N_2 isotherms for different pore widths at 77 K.

adsorbate (aa) and adsorbate–pore (ap) interaction energies. At low loadings, the adsorbate molecules tend to occupy the energetically most favorable positions in the pore and the aa interaction is much smaller than the ap interaction. The attractive potentials due to each wall overlap most in the smallest pore, resulting in deep energy wells. In the wider pores at high loadings, molecules can occupy the central region, as well as the wall regions of the pore. This increased packing efficiency leads to higher densities in the pore [19].

As indicated in Figs. 2 and 3, the general behavior found for CO_2 at 298 K (just lower than the critical temperature) is quite similar to the slightly supercritical case (308 K), both qualitatively and quantitatively. At all three temperatures, a moderate jump in final CO_2 density occurs at a pore size of about 0.9 nm. However, the sudden increase in density occurring at dry ice conditions (see Fig. 1) for every pore width at relative pressure values ranging from 0.001 to 0.5 (depending on the pore size) is not present in the high temperature simulations [19].

Turning to the 77 K nitrogen isotherms (Fig. 4), it is seen that the corresponding sudden density increase takes place at lower relative pressures (smaller than 0.05). An interesting remark can be made concerning the isotherms for pore widths between 0.65 and 0.95 nm. They appear to be almost straight horizontal lines down to the lowest experimental relative pressure value (3×10^{-6}) implying that the method when based on 77 K nitrogen data is not sensitive enough in this particular range of pore widths. This is an important issue to bear in mind when interpreting the outcome of the method in terms of PSD and is in contrast to the case of CO_2 where the non-linear shape of the different isotherms implies adequate sensitivity of the method for all the pore sizes currently considered.

PORE SIZE CHARACTERIZATION

The CO_2 isotherms at 195.5, 298 and 308 K and the N_2 isotherm at 77 K of the commercially available activated carbon Norit RB4 known to possess pores in the high micropore range have been measured experimentally. For the ambient temperature measurements, a high pressure balance (Sartorius GmbH) has been used. The balance is equipped with an in-house high pressure gas handling system. For the low temperatures, measurements were performed with the micropore upgraded Quantachrome Autosorb-1 nitrogen porosimeter. In all cases, samples were outgassed at 573 K under high vacuum (below 10^{-6} mbar) for at least 12 h. Depending on the case, proper outgassing of the samples was checked by monitoring the weight or pressure change with time.

The micropore range (from 0.5 to 2.0 nm) was subdivided in equidistant intervals (classes of pores) with 0.05 nm spacing between them. The fraction of the total pore volume associated with each interval, was calculated on the basis of an assumed PSD and keeping the total pore volume equal to the measured one. Thus, the amount of gas adsorbed in every class at a certain pressure was evaluated by the simulation, and consequently, a computed isotherm was being constructed, which after being compared to its experimental counterpart was resulting in the optimum micropore size distribution provided by the best fit. The procedure for the determination of the optimum PSD involves the numerical solution of a minimization problem under certain constraints. In practice, the problem consists of minimizing the function:

$$Q_i - \sum_{j=1}^{k} d_{ij} V_j \tag{8}$$

for different pressure values p_i; Q_i is the experimentally sorbed amount measured at pressure p_i; d_{ij} is the calculated fluid density in a pore of width H_j at the same pressure, and V_j represents the volume of the pores with size H_j (as j changes from 1 to k, the whole micropore range from 0.5 to 2.0 nm is spanned with a step of 0.05 nm). The resulting elements of the vector **V** are subject to two constraints. They should be non-negative and their sum should be equal to the measured total pore volume. A routine solving linearly constrained linear least-squares problems based on a two-phase (primal) quadratic programming method (E04NCF of NAG library) has been implemented.

The resulting PSDs from the CO_2 isotherms at 195.5, 298, 308 K and the N_2 isotherm at 77 K are included in the form of histograms in Fig. 5. The pore volumes found are quite similar for all temperatures and both gases. The PSDs obtained from the CO_2 data exhibit (as expected) a calculated structure with the main part of the pore volume concentrated in the vicinity of 1.5–1.7 nm (in terms of H; it should be reminded that use of Eq. (5) is required to convert to the experimentally determined H).

The N_2 based PSD is characterized by a rather broad band of prevalent pore sizes between 0.95 and 1.9 nm. Other workers have reported differences of this kind between PSDs obtained from different gases as well [20,21]. The exact form of those differences may vary depending among others on the "smoothing" constraints used in each case during the procedure of inverting the adsorption integral Eq. (1).

On the basis of these PSD estimations, in Figs. 6 and 7, it is attempted to predict the ambient temperature CO_2 isotherm and the low temperature N_2 isotherm, respectively.

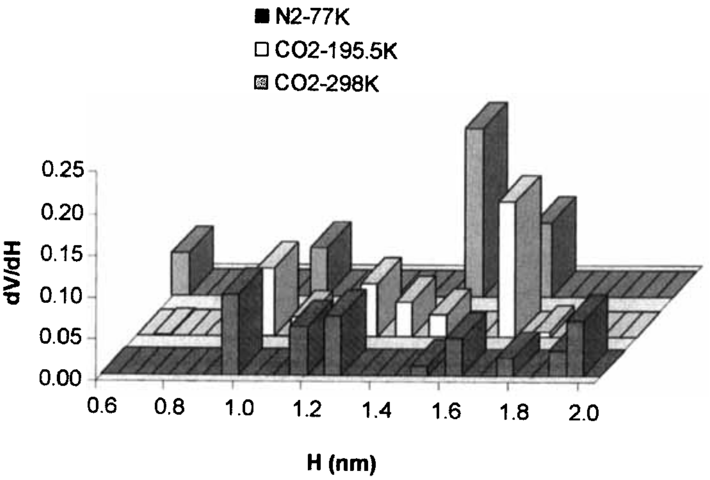

FIGURE 5 Optimal PSDs for Norit RB4 carbon sample.

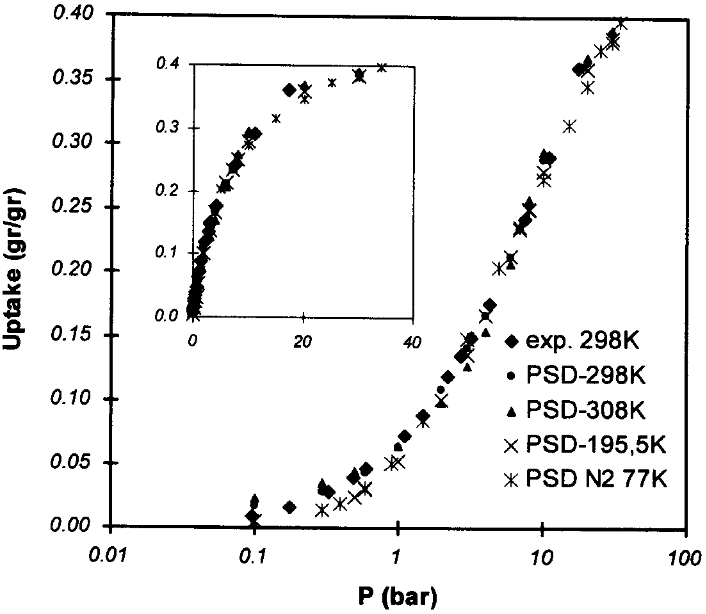

FIGURE 6 Experimental and computed CO_2 isotherms at 298 K from PSDs of Fig. 5.

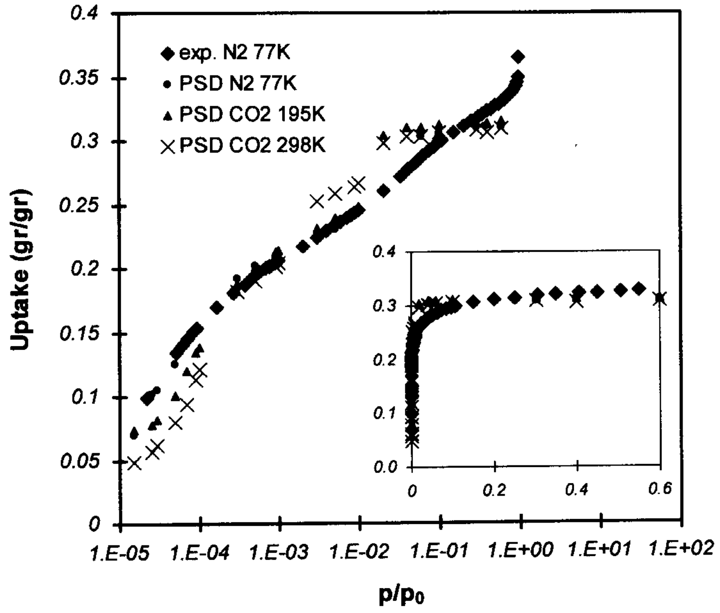

FIGURE 7 Experimental and computed N_2 isotherms at 77 K from PSDs of Fig. 5.

It is shown that the 298 K isotherm is predicted satisfactorily using the PSDs that resulted from the data of CO_2 at 195.5 and 308 K and the data of N_2 at 77 K (Fig. 6). Very similar results are obtained when attempting to predict the 308 K CO_2 isotherm as well. In Fig. 7, it appears that the prediction of the low temperature N_2 isotherm based on the PSDs obtained from the CO_2 data at low and ambient temperatures is not as good as in the previous cases but still quite reasonable.

Given the above mentioned remark on the sensitivity of the method in a certain range of pore sizes when the data of N_2 at 77 K are used and following the conclusions of [21] on the robustness of the CO_2 based PSDs, we also tend to suggest that the CO_2 based PSDs, both at low and ambient temperatures are more reliable in that they assess more accurately the microporous structure of the carbon sample. However, more data especially at high pressures, (higher than the 35 bar reached in this study) and comparisons are needed to strengthen further such conclusions and this kind of work is currently underway.

One more observation adding to the credibility of the CO_2 based PSDs is related to the prediction of the isosteric heat of adsorption at zero coverage. All three CO_2 based PSDs, when used along with the calculated isosteric heats for each pore width, (see section 2) provided a value of 4 kcal/mol for the sample (differences of less than 5% around this value are found, as one employs the three different PSDs). This is favorably compared to the experimentally determined 3.84 kcal/mol for this carbon sample. Interestingly enough, the N_2 based PSD predicts in a satisfactory way, the same isosteric heat (the value obtained using this PSD is 3.57 kcal/mol).

CONCLUDING REMARKS

The CO_2 and N_2 density inside single, slit shaped, graphitic pores of given width is calculated based on Grand Canonical Monte Carlo simulations for low and ambient temperatures and different relative pressures. The aim is to determine microporous carbon PSDs combining simulations and measured isotherms. In the case of CO_2, it is found that the system behavior at ambient temperature exhibits basically the same structural features concerning the CO_2 molecules packing in the individual pores as at 195.5 K. The behavior found at 298 K (just lower than the critical temperature) is quite similar to the slightly supercritical case of 308 K both qualitatively and quantitatively. For N_2, it is noted that attention should be paid to the fact that for pore widths between 0.65 and 0.95 nm the isotherms appear to be almost straight horizontal lines down to the lowest experimental relative pressure value used in our present measurements. This implies that the determination of micropore size distributions when based on the data of N_2 at 77 K may not be sensitive enough in that particular range of pore widths.

The optimal CO_2 based PSDs found at the low and ambient temperatures for the Norit RB4 sample are quite similar and the use of each of them to predict isotherms at different temperatures provides very reasonable agreement with the measured data. The N_2 based PSD shows a more broad structure but it can still predict reasonably well, the CO_2 isotherm at ambient temperature.

It is interesting to summarize here, the main uncertainties and limitations of the methodology for PSD determination in microporous materials outlined above. As the realistic character of simulations and the accuracy of the results depend largely upon the potential energy model used, it is important to ensure validation of the relevant parameters. To employ and exploit our previous work [13], we used in this paper the model parameters for CO_2 from Ref. [26]. A step forward in that respect is the use of the model of Harris and Yung [25] that has been found to reproduce satisfactorily the vapor–liquid coexistence curve [20,21].

The attempted comparison between simulated and measured isotherms requires a relation between the pore width H used in the simulations and the experimentally meaningful width H'. The results of the method are sensitive to that issue and the approximate value of $H - H' = 0.24$ nm used presently needs refinement especially for non-spherical molecules like CO_2. Surface corrugation has been ignored and although it may not bear a significant effect at higher temperatures, the more complete version for the potential representation of Steele [28] must be used.

The treatment of adsorbate–adsorbate long range forces needs refinement by means of the Ewald summation technique [30], instead of the currently adopted Coulomb-type approach. In addition, other than slit pore geometries (e.g. cylinders) should be invoked to obtain an idea of the sensitivity of the method on the pore model geometry used.

Work on all these issues is in progress by our group and will be reported soon.

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