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Water adsorption by activated carbons in relation to their microporous structure

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Abstract

The present paper examines the adsorption of water by microporous carbons in the absence of specific interactions. The modelling of water adsorption for 293 and 310 K, using variable pore size distributions (PSD), shows that the type V isotherms follow the Dubinin–Astakhov (DA) equation and fulfill the requirement for temperature invariance. Furthermore, the parameters of the DA equation can be related in a simple way to structural properties of the model carbons. For a number of well-characterized carbons, the type V isotherms generated by combining model isotherms with the corresponding PSDs are in good agreement with the limiting isotherms at 293 and 310 K derived on the basis of a recent development of Dubinin's theory. This approach will provide the basis for further studies including specific interactions.

Keywords: A. Activated carbon; C. Adsorption; Modelling; D. Microporosity

1. Introduction

The adsorption of water by activated carbons plays an important role in filtration processes, in particular at relative pressures above 0.5–0.6. Basically, activated carbons are used for their high sorptive capacity and their strong affinity for organic compounds [1]. Water has a low affinity for carbon and in the case of untreated materials, the isotherm practically corresponds to type V, following the usual classification [2]. However, when the number of hydrophilic centres increases (mainly oxygen-containing surface groups and basic centres), the isotherm gradually changes to a type IV and the inflexion point is shifted towards lower relative pressures. This means that competition with other vapours increases, and a better description has to be found for the adsorption of water in micropores. In particular, it is important to understand the influence of the micropore structure and of the surface chemistry on the adsorption of water.

It has been shown recently by Stoeckli [3] how the specific and the non-specific interactions can be identified in the overall water adsorption isotherm considered as a sum of types I and V Dubinin–Astakhov (DA) isotherms [4,5]. This approach reveals the role played by the non-specific filling of the micropores, which corresponds to the type V contribution.

Adsorption in slit-shaped micropores can be calculated by computer simulations (in particular the so-called Monte Carlo techniques [6–8]), and therefore the present study was carried out in order to compare the two approaches to water adsorption. The good agreement found between the limiting type V isotherms and modelling based on the pore size distribution (PSD) confirms the role of the carbon's structure alone on water adsorption. This will enable us later to consider the influence, on the overall isotherm, of the hydrophilic centres and of their location in the microporous structure.

The present approach presents similarities with the work of Gubbins et al. [9] on water adsorption by activated

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carbons. However, we consider the problem from a different side, in particular the correlation with Dubinin's theory [1,10–13] extended to water adsorption [4,5,13].

2. Theoretical

2.1. Water adsorption isotherms and Dubinin's theory

As shown recently by Stoeckli [3], water adsorption by activated carbons can be described by Dubinin's theory. This is due to the fact that water adsorption isotherms fulfill the requirement for temperature invariance, as revealed by the existence of a single characteristic curve [14–16]. The latter is a plot of the relative amount adsorbed at various pressures and temperatures versus the thermodynamic potential $A = RT \ln(p_o/p)$. The basic relation is the Dubinin–Astakhov (DA) equation:

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

where N_a is the amount adsorbed at relative pressure p/p_o and temperature T; N_{ao} is the limiting amount filling the micropore volume $W_o = N_{ao}V_m$, assuming that V_m is close to the molar volume in the liquid state, and E is the so-called characteristic energy of the system. The latter can be written as $E = \beta E_o$, where β is the affinity coefficient of the adsorptive. Benzene is the reference and $\beta(C_6H_6) = 1$; these coefficients have recently been compiled by Wood [17].

It has been shown [3–5] that the overall water adsorption isotherm, which fulfills the principle of temperature invariance, can be considered as a sum of type I and type V DA isotherms:

$$N_a = N_{ao}(I) \exp\left[-\left(A/E_{H_2O}(I)\right)^{n_1}\right] + N_{ao}(V) \exp\left[-\left(A/E_{H_2O}(V)\right)^{n_2}\right] \tag{2}$$

where $N_{ao}(I)$ and $N_{ao}(V)$ are the limiting amounts adsorbed, with the corresponding characteristic energies $E_{H_2O}(I)$ and $E_{H_2O}(V)$. As shown earlier [5], in the case of carbons oxidized with $(NH_4)_2S_2O_8$, the microporous structure is not modified for oxygen contents between 1 and 7 mmol g^{-1}. Exponent n_2 remains practically constant, which suggests that this parameter is essentially related to the pore size distribution of the carbon, as confirmed by modelling (see below).

The validity of the approach based on Eq. (2) was furthermore confirmed by the agreement between the experimental enthalpy of immersion $\Delta_i H$ of the carbons into water, and the value predicted as a thermodynamic consequence of Dubinin's theory [1,12]. It can be shown, that for a vapour following Eq. (1) and fulfilling the principle of temperature invariance, the enthalpy of immersion is given by:

$$\Delta_i H\ (J\ g^{-1})_{mi} = -N_{ao}E(1 + \alpha T)\,\Gamma(1 + 1/n) \tag{3}$$

where α is the expansion coefficient of the liquid filling the micropores and Γ is the tabulated 'Gamma' function (for $1.5 < n < 5$, it varies between 0.88 and 0.92). The experimental enthalpy of immersion contains a supplementary term for the wetting of the external (non microporous) surface area S_e of the solid, which must be taken into consideration. Eq. (3) has been verified for a variety of carbons and adsorbates [12], which may be regarded as a test for self-consistency for the approach based on Dubinin's theory.

Depending on their origin and their treatment, activated carbons contain a variable number of sites which may interact specifically with water. As shown elsewhere [5,19,20], they correspond to oxygen [O] found in surface groups and varying between 0.5 and approximately 7–8 mmol g^{-1}, as well as basic groups characterized by the amount of HCl (mEq g^{-1}) required to titrate them. The latter groups contain little or no oxygen at all, but their interaction energy with water is close to the average water–oxygen interaction [19].

In the recent study by Stoeckli [3], it was confirmed that the type I contribution reflects the specific interactions between water and the [O + HCl] sites, in a 1:1 ratio. Moreover, the specific energy $E_{H_2O}(I) = \beta_{H_2O}(I)\,E_o$, where the affinity coefficient has the average value $\beta_{H_2O}(I) = 0.29 \pm 0.02$. In the type V contribution $E_{H_2O}(V) = \beta_{H_2O}(V)\,E_o$, but $\beta_{H_2O}(V)$ appears to vary with the number of [O + HCl] sites, by analogy with the case of short alcohols adsorbed by activated carbons [21]. A detailed study based on 15 carbons shows that:

$$\beta_{H_2O}(V) = \beta_{H_2O}{}^{\circ}(V) + 5.75\ (kJ\ mol^{-1})[O + HCl]/E_o N_{ao(H_2O)}(1 + \alpha T)\,\Gamma(1 + 1/n_2) \tag{4}$$

The quantity $\beta_{H_2O}{}^{\circ}(V) = 0.059 \pm 0.08$ is the limiting affinity coefficient for the adsorption of water in the absence of specific interactions. (Note the new value of $\beta_{H_2O}{}^{\circ}(V)$ and of the energy parameter, 5.75 kJ mol^{-1}, as suggested by an overall fit with more data than in Ref. [3]). The experimental values of $\beta_{H_2O}(V)$, depending on the surface chemistry, vary between 0.065 and 0.150. Limiting values for β_{H_2O} have also been listed in Wood's recent compilation [17].

Eq. (4) shows that in the presence of hydrophilic surface groups the type V isotherm reflects simultaneously the micropore filling and the chemistry of the surface, but in the limiting case where $[O + HCl] = 0$, the characteristic energy for water is:

$$E_{H_2O}(V) = 0.059 \cdot E_o \tag{5}$$

Consequently, for microporous carbons without specific water adsorption sites, the overall isotherm is of type V and should take the simple form:

$$N_a = N_{ao} \exp\left[-(A/0.059 \cdot E_o)^{n_2}\right] \tag{6}$$

with the corresponding expression for $\Delta_i H(H_2O)_{mi}$ given by Eq. (3).

Coherent adsorption and calorimetric results have been obtained with microporous carbons containing naturally small amounts of oxygen or treated in hydrogen near 600 °C. We may therefore expect that the water adsorption isotherm obtained from simulations based on non-specific interactions and the PSD only, should agree with the isotherm given by Eq. (6).

2.2. PSD in activated carbons

As described previously [22], the PSD of a microporous carbon can be obtained from the analysis of the CO_2 adsorption isotherm at 273 K, using model isotherms. The latter are obtained from Monte-Carlo simulations, assuming slit-shaped micropores. Simultaneously, and provided that no 'gate' effects are present, the PSD can also be derived from the enthalpies of immersion of the carbon into liquids with molecular dimensions between 0.4 and 1.5 nm. For the carbons considered in the present study, the different PSDs obtained from various techniques are shown in Figs. 4–6.

2.3. Modelling of water adsorption isotherms in pure carbons

Adsorption isotherms in single slit-shaped carbon pores were calculated by grand canonical Monte Carlo (GCMC) simulation, as described in the relevant publications [6–8]. In this method, the volume, temperature and chemical potential are kept constant, while the total number of molecules is allowed to fluctuate. For each set of conditions, the system is equilibrated by virtue of molecule displacement, creation and destruction trials. Acceptance or rejection of these trials depends on the potential energy difference between the old and new configurations. After an equilibration period of at least 10^7 Monte Carlo steps, the adsorbed density is sampled during 2×10^6 MC steps divided into 20 blocks. The pressure is calculated from the chemical potential using the Peng–Robinson equation of state. Adsorption isotherms can thus be obtained in a form (adsorbed density versus pressure in the bulk phase) that is comparable to experiments.

Water is represented by the SPC/E potential, with parameters taken from Berendsen et al. [23]. This model includes a Lennard–Jones site in the position of the oxygen atom and three-point charges (negative for oxygen and two positive charges for the hydrogens). Special techniques are used to account for the long-ranged electrostatic interactions between point charges. The method of Heyes and van Swol [24] was used for this purpose. The simulation cell is rectangular, bounded in the *z* direction by the pore walls and replicated in the *x* and *y* directions by using periodic boundary conditions. The length of the simulation cell in the directions parallel to the wall was 3 nm, which is sufficient to avoid any finite-size effects [25]. The walls are graphite sheets, composed of Lennard–Jones centres that are spread out uniformly over the whole area of the walls. The potential between a Lennard–Jones adsorbate centre and this smooth graphite wall is given by the 10–4–3 potential of Steele [26]. Cross-species Lennard–Jones parameters were calculated from the Lorentz–Berthelot combining rules. Further details concerning the efficient implementation of the GCMC algorithm for water adsorption studies can be found in a previous publication [27].

3. Experimental

For the present study three well characterized carbons were used, CARBO-S, CMS and DCG-5 [3,4,12,22]. A fourth carbon, MSC-V [14,28], was also used for comparison purposes, as it is similar to CARBO-S. The choice was dictated by the fact that these carbons have average pore sizes between 0.6 and 1.1 nm and PSDs which have been characterized unambiguously. The latter were obtained from CO_2 adsorption at 273 K, analysed with the help of model isotherms [22], and/or from immersion calorimetry at 293 K using liquids of different molecular dimensions. These distributions are shown in Figs 4–6. The corresponding structural and chemical parameters are given in Table 1 and their determination is described in detail elsewhere [1,4,5,12,14], including the water adsorption isotherms at 293 and 310 K.

Table 1
Main characteristics of the activated carbons

Carbon	W_o ($cm^3\ g^{-1}$)	L_o (nm)	E_o ($kJ\ mol^{-1}$)	$E_{H_2O}(V)$ ($kJ\ mol^{-1}$)	$E_{H_2O}(V)/E_o$ –	n_2 –	[O+HCl] ($mmol\ g^{-1}$)
CARBO-S	0.43	0.8	24.7	1.48	0.060	6	<0.5
MSC-V	0.4	0.68	27.1	1.91	0.070	5.8	<0.5
CMS	0.25	0.75	26.1	2.04	0.078	5	1.64
DCG-5	0.54	1.1	21.2	1.69	0.080	2.5	2.7

4. Results and discussion

4.1. Modelling

Modelling was carried out for water adsorption at 293 and 310 K in slit-shaped micropores of widths between 0.4 and 2.0 nm. The pore widths (*L*) estimated from adsorption methods refer to the 'accessible space', which can be defined in several ways. In this paper, *H* is the pore width defined in the simulations, and refers to the space between the centres of carbon atoms of opposing walls. The correction of 0.24 nm suggested by Everett and Powl [29] ($L = H - 0.24$ nm), and used in this paper, leads to a good agreement, but a number of authors also use the value of 0.34.

The simulated value of p_o at 293 K was found to be 4000 Pa. This value corresponds to the condensation in a pore of 10 nm and it is considered to correspond to the bulk saturation pressure. We note that this value is not equal to the experimental value of 2500 Pa.

The model isotherms were calculated on the basis of the simulated single pore isotherms and the PSD. This is achieved by multiplying the pore volume obtained from the PSD for a given pore width (V_i) by the molar density adsorbed in the corresponding pore (ρ_i), and then performing a summation over all pore widths. This can be represented by the following equation:

$$N_a\ (\mathrm{mmol\ g^{-1}}) = \sum_i \rho_i\ (\mathrm{mmol\ cm^{-3}}) \times V_i\ (\mathrm{cm^3\ g^{-1}}) \qquad (7)$$

Fig. 1 shows the density of water in single pores for $T = 293$ K, as a function of the relative pressure p/p_o. Adsorption corresponds to a sharp condensation, which depends on the pore width, and a similar pattern is observed for $T = 310$ K.

In a first round of investigations, the step-wise model isotherms were combined with formal PSDs corresponding to histograms limited by a Gaussian normalized to 1 cm^3 g^{-1}:

$$\mathrm{d}W/\mathrm{d}L = (1/\sigma\sqrt{2\pi}) \exp\left[-(L - L_o)^2/2\sigma^2\right] \qquad (8)$$

We used blocks of 0.1 nm centred around $L_o = 0.6$, 0.8, 1.0, 1.4, and variable half-widths σ. As a general example, Fig. 2 shows the isotherms for 293 K obtained (a) for $L_o = 0.60$ nm and a narrow distribution ($\sigma = 0.2$ nm), (b) for $L_o = 1.0$ nm and $\sigma = 0.2$ nm, (c) for $L_o = 1.0$ nm and a relatively broad distribution ($\sigma = 0.6$ nm). As suggested by Fig. 2, the complete study (Table 2) confirms that the position of the inflexion point, reflected by $E_{H_2O}(V)$, depends on the average micropore width L_o. On the other hand, the steepness of the isotherm, reflected by exponent n_2, decreases as σ increases. In other words, n_2 is an inverse function of the heterogeneity of the PSD.

The smoothed type V isotherms can be fitted to the DA Eq. (1). From the data shown in Table 2, it appears that $E_{H_2O}(V)$ is essentially an inverse function of the average micropore width L_o, as observed for the classical organic and inorganic adsorbates [1,12], but it also depends, to some extent on the heterogeneity of the material. On the other hand, exponent n_2 depends only on σ, at least to a good first approximation. It follows, that the slope of the type V isotherm reflects the heterogeneity of the micropore distribution, but a quantitative correlation cannot be established yet.

An interesting feature is the fact that exponent n_2 is practically independent of the chemistry of the surface, as suggested by experimental evidence from adsorption by a series of carbons with similar micropore structures but variable oxygen contents [3,5,21]. Furthermore, by using model isotherms for 310 K, it appears that the smoothed type V adsorption isotherms obtained for a given PSD fulfill the requirement for temperature invariance. For example, this is illustrated in Fig. 3 by the DA plots of the isotherms generated from PSDs with $L_o = 1.0$ nm and $\sigma = 0.2$ and 0.6 nm. This important observation means that water adsorption isotherms modelled with PSDs for slit-shaped micropores made of pure carbon, can be described by Dubinin's theory.

This behaviour is in agreement with the observation that real water adsorption isotherms, of type IV and V follow Dubinin's theory within a certain range of temperature and relative pressures [3–5,14,15]. This, in turn, provides a safe background for further studies of water adsorption in microporous carbons and taking also into account specific interactions.

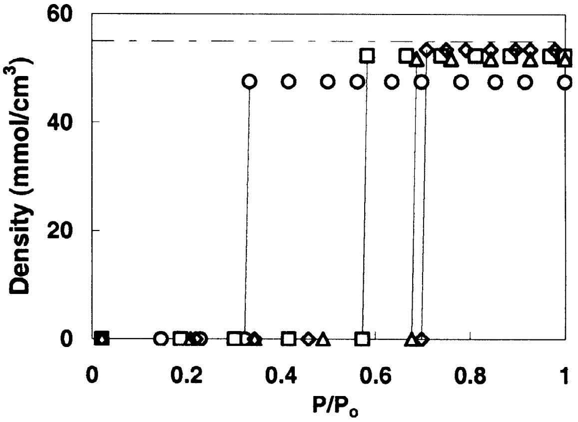

Fig. 1. Density of water adsorbed at 293 K in model pores of accessible widths $L = 0.7$ (○), 1.0 (□), 1.3 (◊), 1.5 nm (△). (- - -) H_2O bulk density, as a function of the relative pressure p/p_o.

4.2. Comparison of simulated and experimental type V isotherms

The techniques outlined above were used in connection with experimental water adsorption isotherms on carbons

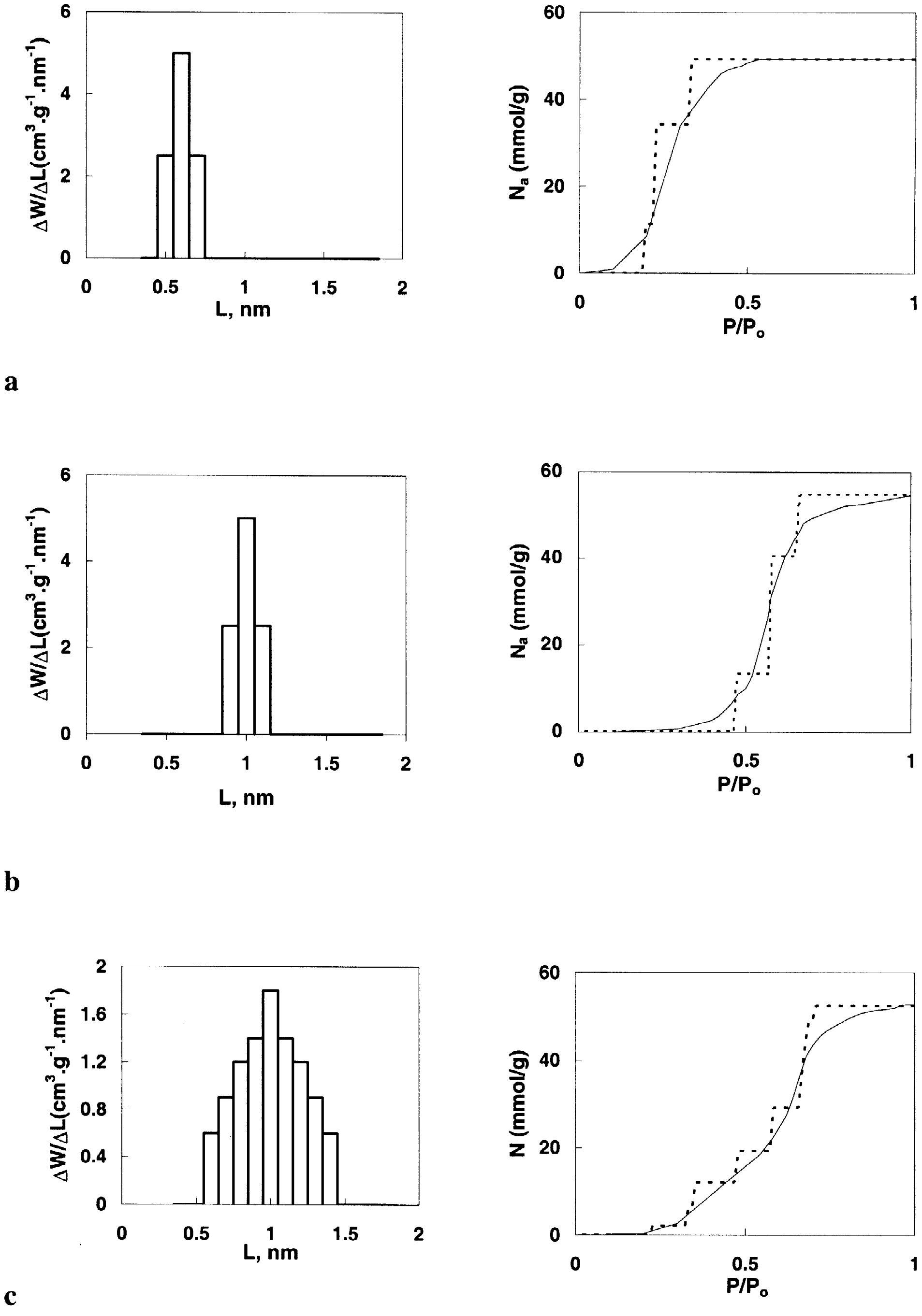

Fig. 2. Model PSD (left) and resulting water isotherms for $T = 293$ K (right), stepwise and smoothed with Eq. (1). (a) $L_o = 0.6$ nm, $\sigma = 0.2$ nm; (b) $L_o = 1.0$, $\sigma = 0.2$ nm; (c) $L_o = 1.0$, $\sigma = 0.6$ nm.

CARBO-S (293 K), CMS (293 K) and DCG-5 (293 K and 310 K). These carbons have well-defined PSDs, determined from CO_2 adsorption at 273 K and/or from enthalpies of immersion into liquids of different molecular dimensions. These carbons were part of an extensive study on water adsorption [3–5,14,18,19], leading to Eqs. (2)–(4). As seen in Figs. 4 and 5, for carbons CMS and DCG-5 one observes a good agreement between the type V isotherms derived from modelling and the PSDs, and the isotherms calculated with the help of Eq. (6). This is

Table 2
Values of $E_{H_2O}(V)$ and n_2 obtained from simulations with various PSDs (see Fig. 2)

L_o (nm)	0.5	0.5	0.6	0.6	0.8	0.8	0.8	1.0	1.0	1.0	1.0	1.4	1.4	1.4	1.4	1.6	1.6
σ (nm)	0	0.2	0	0.2	0	0.2	0.4	0	0.2	0.4	0.6	0	0.2	0.4	0.6	0	0.2
$E_{H_2O}(V)$ (kJ mol^{-1})	3.49	4.05	3.23	3.50	2.13	2.51	2.64	0.88	1.43	1.59	1.64	0.4	0.88	0.98	0.90	0.4	0.88
n_2	–	6.9	–	6.2	–	6.1	3.5	–	6.1	3.4	2.14	–	6.7	3.6	2.9	–	6.4

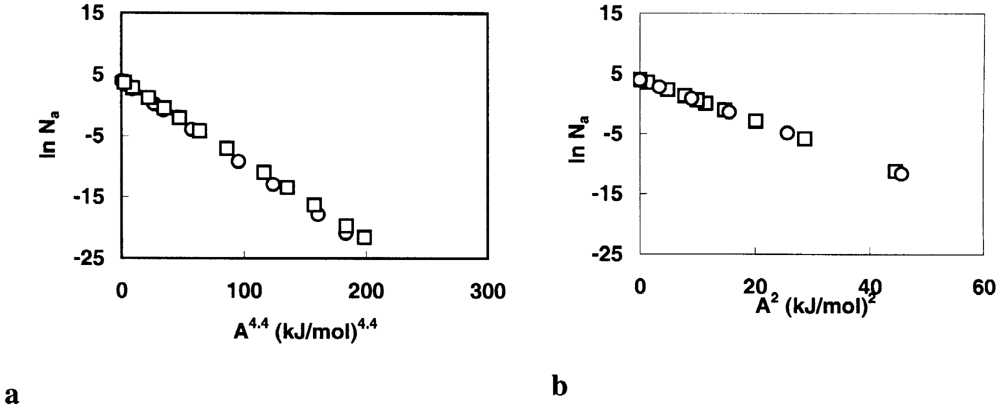

Fig. 3. Logarithmic DA plots for simulated type V isotherms at 293 (□) and 310 K (○). Average pores width $L_o=1.0$ nm, $\sigma=0.2$ nm (a) and 0.6 nm (b). Micropore volume $W_o=1$ cm^3 g^{-1}.

confirmed by the good agreement between the experimental values of parameters $E_{H_2O}(V)=0.059 \cdot E_o$ and n_2, and the values obtained from modelling based on the PSDs (see Table 3).

In the case of carbon CARBO-S (Fig. 6), however, the adsorption isotherm based on model isotherms combined with the PSD, is not in good agreement with the experimental isotherm obtained at 293 K. Due to the low oxygen content of this carbon, the isotherm is of type V and its parameters lead to an enthalpy of immersion which is in good agreement with the experimental value. The simulated isotherm is displaced towards lower relative pressures, with an inflexion point at $p/p_o=0.2$, against 0.5 for the experimental isotherm. In order to confirm this behaviour, experiments were also carried out with a classical and well characterized molecular sieve carbon, MSC-V [28], which has a strong contribution of micropores between 0.4 and 0.6 nm. The same behaviour was observed, which suggests that the model isotherms corresponding to pores below 0.5–0.6 nm lead to a condensation pressure which is too low. As shown in Table 3, this also corresponds to the relatively high affinity coefficient

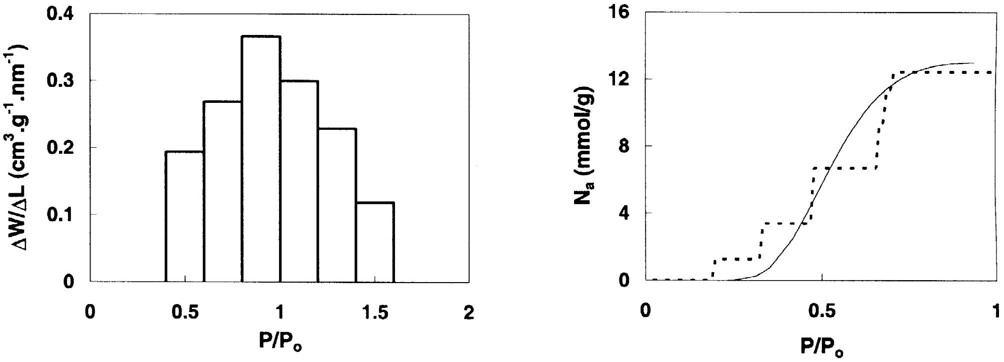

Fig. 4. PSD of carbon CMS (left). Simulated water adsorption isotherm for $T=293$ K (- - -) and the corresponding type V isotherm recalculated from the experimental isotherm (right).

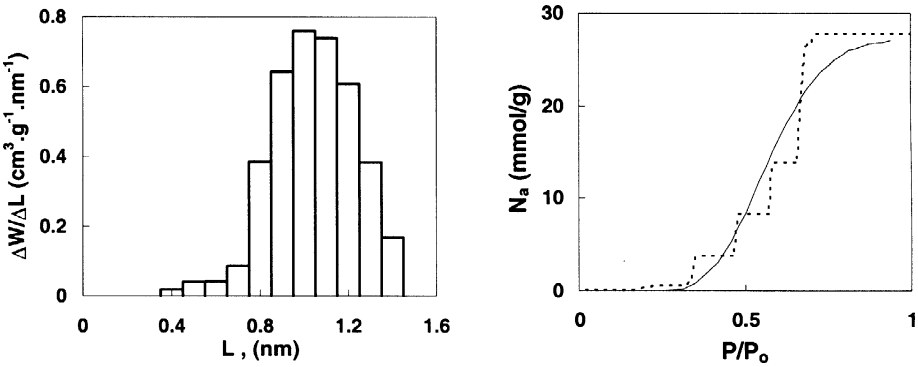

Fig. 5. PSD of carbon DCG-5 (left). Simulated water adsorption isotherm for $T = 293$ K (- - -) and the corresponding type V isotherm recalculated from the experimental isotherm (right).

Table 3
Comparison of parameters $E_{H_2O}(V)$, $\beta_{H_2O}(V) = E_{H_2O}(V)/E_o$ and n_2 of the type V water adsorption isotherms at 293 and 310 K, obtained from modelling and from Eqs. (4) and (2)

Carbon	$E_{H_2O}(V)_{model}$ (kJ mol^{-1})	$\beta_{H_2O}(V)_{model}$ (kJ mol^{-1})	$n_{2\ model}$ –	$E_{H_2O}(V)_{exp}$	$\beta_{H_2O}(V)_{exp}$	$n_{2\ exp}$
CARBO-S (293 K)	3.9	0.157	5	1.45	0.060	6
MSC5 (293 K)	3.25	0.119	5	1.6	0.070	5.8
CMS (293 K)	1.89	0.072	3	1.54	0.078	5.6
DCG-5 (293 K)	1.60	0.075	2.8	1.25	0.080	2.5

$\beta_{H_2O}(V) = E_{H_2O}(V)/E_o$, suggested by the model isotherms (respectively, 0.157 and 0.119, against 0.70 to 0.80 for the other carbons).

It follows, that at the present stage the model can only describe successfully water adsorption in pores above 0.5 nm, but this shortcoming will be examined in detail. It should also be pointed out that modelling of adsorption in very small micropores has not been reported so far, as the majority of authors deal with carbons having wider PSDs. The latter also correspond to standard activated carbons, in particular those of industrial origin, such as DCG-5.

In conclusion, the present study shows that the simulation of water adsorption in slit-shaped micropores containing no hydrophilic groups, leads to a coherent pattern, provided that the majority of the pores are above 0.5 nm. The present approach, which reflects the micropore filling due to non-specific interactions only, is in agreement with Dubinin's theory. It may therefore be used as a reliable initial stage for the modelling of adsorption under more realistic and also more complicated conditions, when hydrophilic centres are present in the micropores. This requires the knowledge of both the PSD and the dis-

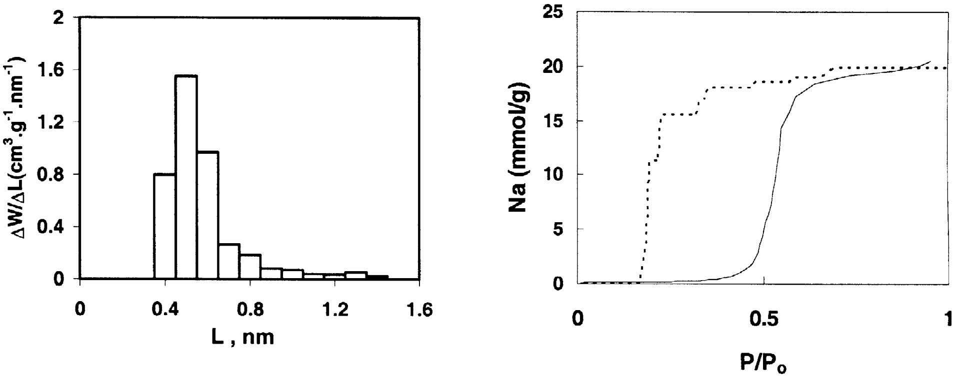

Fig. 6. PSD of carbon CARBO-S (left). Simulated water adsorption isotherm for $T = 293$ K (- - -) and the experimental isotherm of type V (low oxygen content) (right).

tribution of the specific centres within the structure. Further results will be reported later.

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