Numerical Analysis of the Horvath–Kawazoe Equation — The Adsorption of Nitrogen, Argon, Benzene, Carbon Tetrachloride and Sulphur Hexafluoride

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ABSTRACT: A previously proposed numerical procedure based on the Horvath–Kawazoe (HK) model for estimating the MPSD (micropore size distribution) from a single nitrogen adsorption isotherm was developed. The results of the calculation of MSPD for two synthetic carbons obtained from numerical studies using the modified procedure are presented and discussed. These allowed the evaluation of the distribution from a single adsorption isotherm of nitrogen, argon, benzene, carbon tetrachloride and sulphur hexafluoride. In addition, the nitrogen and argon adsorption potential distributions were calculated for the same carbons applying the HK and condensation approximation (CA) methods. Agreement between these two independent approaches was observed. Differences between the MSPD obtained from HK and from the Dubinin micropore filling model (using the CONTIN package) were observed and discussed. It was shown that the structural parameter of the Dubinin–Astakov equation had no significant influence on the MSPD curves obtained.

INTRODUCTION

The quantitative evaluation of microstructures is an important aspect of those processes in which carbonaceous materials are used for catalysis or adsorption. It is now generally accepted that microporous carbons are energetically and structurally heterogeneous to a greater or lesser extent (Rudziński and Everett 1992; Do 1998).

The properties of such materials depend strictly on the presence of small pores called micropores [diameter < 2 nm according to the IUPAC classification (Sing *et al.* 1985)] in their internal structure. The existence of such micropores characterised by different shapes and dimensions strongly affects the adsorbent–adsorbate interactions (Rudziński amd Everett 1992; Do 1998). The generally accepted quantitative measure of the structural heterogeneity of microporous solids is the micropore size distribution (MPSD) function. Assuming a homotattic patch approximation, the MPSD can be obtained in many cases by the solution of the global adsorption integral equation from a single adsorption isotherm employing the following equation (Rudziński and Everett 1992; Do 1998; Terzyk *et al.* 1999a,b; Wojsz 1989; Gauden *et al.* 2001):

$$\Theta_{global}(P) = \int_{x_{min}}^{x_{max}} \Theta_{local}(P,x)\chi(x)\,dx \qquad (1)$$

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where $\Theta_{global}(P)$ is the measured adsorption isotherm, $\chi(x)\,dx$ is the fraction of micropores with dimensions between x (the half-width) and x + dx, $\Theta_{global}(P, x)$ is the relative filling of micropores having dimension x, and x_{min}, x_{max} are the lower and upper limits of the micropore system, respectively. For the description of Θ_{global}, the Dubinin–Astakhov (DA) and/or the Dubinin–Radushkevich (DR) equations have often been applied. Then, equation (1) can be rewritten (Wojsz 1989) as:

$$\Theta_{global}(P) = \int_{x_{min}}^{x_{max}} \exp[-\mu A_{pot}^{n} x^{n}]\chi(x)\,dx \qquad (2)$$

where $A_{pot} = -\Delta G = RT \ln(P_s/P)$ is the adsorption potential defined as the change in the Gibbs' free energy taken with a minus sign, R is the universal gas constant, T is the temperature, P and P_s denote the equilibrium pressure and the saturated vapour pressures of the adsorbate, respectively, $\mu = (\kappa\beta)^{-n}$ depends on the adsorbate and the kind of microporous structure involved [β is the coefficient and κ is an empirical constant assumed as being equal to 11.44 kJ/(nm mol) (Bhatia and Shethna 1994)] while n is the equation heterogeneity parameter.

It is well known that the classical numerical Fredholm invert of equation (2) leads to very unstable results (a strongly unphysical oscillation of the MSPD obtained) (von Szombathley *et al.* 1992). For this reason, several numerical algorithms have been proposed for solving equation (2) (Rudziński and Everett 1992). However, most of these equations are not simple to implement and are time-consuming.

In contrast, the method proposed by Horvath and Kawazoe (HK) is simple and usually gives results similar to other methods, for example those obtained from the density functional theory (Terzyk *et al.* 2001b). For this reason, we have recently decided to develop the numerical algorithm applied for evaluating the MPSD from a single nitrogen adsorption isotherm (Kowalczyk *et al.* 2002). The numerical algorithm currently being modified provides the opportunity for evaluating the MPSD from a single isotherm of nitrogen (Horvath and Kawazoe 1983; Horvath 1998; Kowalczyk *et al.* 2002), argon (Rychlicki *et al.* 1993), benzene (Świątkowski *et al.* 1996), carbon tetrachloride (Terzyk and Gauden 2001) and sulphur hexafluoride (Terzyk and Gauden 2001). This new numerical algorithm is applied in the current study for the evaluation of the MSPDs of two strictly synthetic microporous activated carbons. In addition, the adsorption potential distributions have also been calculated for the adsorption of nitrogen and argon. Nitrogen is the most common adsorbate applied for the estimation of MPSD from adsorption data (Webb and Orr 1997) and the HK results have been compared with Dubinin's theory of micropore filling (TOMF) (Dubinin 1975) for this adsorbate.

FORMULATION OF THE PROBLEM

On the basis of thermodynamics and from a numerical point of view, application of the HK method involves the solution of a non-linear equation of the form (Do 1998; Webb and Orr 1997; Gauden 2001; Horvath 1998; Cheng and Yang 1994; Terzyk and Gauden 2001):

$$\Psi(L) = \ln(P/P_s) - \frac{A}{L-d} \times \left[\frac{B}{(L-d/2)^3} - \frac{C}{(L-d/2)^9} - D \right] = 0 \qquad (3)$$

where L is the micropore width (L = 2x), A is a constant given by:

$$A = N_{av} \frac{N_a A_a + N_A A_A}{RT\sigma^4} \tag{4}$$

and N_{av} is Avogadro's number, R and T are the gas constant and temperature, respectively, N_a and N_A are the number of atoms per unit area of adsorbent and the number of molecules per unit area of adsorbate, A_a and A_A are constants given by:

$$A_a = \frac{6mc^2\alpha_a\alpha_A}{\frac{\alpha_a}{\chi_a} + \frac{\alpha_A}{\chi_A}} \tag{5}$$

$$A_A = \frac{3mc^2\alpha_A\chi_A}{2} \tag{6}$$

and m is the mass of the electron, c is the velocity of light, α and χ are the polarisability and magnetic susceptibility of an adsorbent atom (subscript a) and/or an adsorbate molecule (subscript A).

The remaining three constants (B, C and D) in equation (3) are given by:

$$B = \sigma^4/3 \tag{7}$$

$$C = \sigma^{10}/9 \tag{8}$$

$$D = \frac{\sigma^4}{3(d/2)^3} - \frac{\sigma^{10}}{9(d/2)^9} \tag{9}$$

where (Saito and Foley 1991):

$$\sigma = 0.858d/2 \tag{10}$$

$$d = d_a + d_A \tag{11}$$

and d is the sum of the diameter of an adsorbent atom and that of an adsorbate molecule. All necessary constants for the adsorbates studied in the current work are summarised in Tables 1 and 2 (Terzyk and Gauden 2001).

Equation (3) relates the gas-phase pressure with the slit-shaped micropore width (L). Thus, by measuring the adsorption isotherm as a function of the relative pressure:

$$\Theta_{global} = f(P/P_s) \tag{12}$$

the MPSD can be obtained using simple transformations as follows:

$$\Theta_{global} = f(x) \tag{13}$$

TABLE 1. Parameters Applied for MPSD Calculations[a]

Parameter	Carbon adsorbent	Adsorbate				
		Ar	N_2	CCl_4	SF_6	C_6H_6
Diameter d_A (d_a for carbon) (nm)	0.340	0.336	0.300	0.465	0.470	0.459
Liquid density (ρ) (g/cm^3)	–	1.465	0.808	1.565	1.880	0.861
Polarisability (α) (cm^3)	1.02×10^{-24}	1.64×10^{-24}	1.46×10^{-24}	11.20×10^{-24}	6.54×10^{-24}	10.32×10^{-24}
Magnetic susceptibility (χ) (cm^3)	13.50×10^{-29}	3.21×10^{-29}	2.00×10^{-29}	14.15×10^{-29}	7.31×10^{-29}	9.18×10^{-29}
Density (N) (molecule/cm^2)	3.845×10^{15}	7.871×10^{14}	6.707×10^{14}	3.348×10^{14}	3.917×10^{14}	3.531×10^{14}
Temperature (T) (K)	–	77.50	77.50	308.00	222.65	310.15
Molecular mass (Mm) (g/mol)	–	39.95	28.01	153.82	146.05	78.11
Affinity coefficient (β)	–	0.310	0.320	1.060	0.634	1.000

[a]Taken from Terzyk and Gauden (2001).

TABLE 2. Parameters of Equation (3) for Different Adsorbates[a]

Parameter	Adsorbate				
	Ar	N_2	CCl_4	SF_6	C_6H_6
A	77.911	62.380	51.918	34.102	34.986
B	2.385×10^{-3}	1.895×10^{-3}	4.741×10^{-3}	4.860×10^{-3}	4.601×10^{-3}
C	4.6752×10^{-7}	2.7087×10^{-7}	2.6810×10^{-6}	2.8522×10^{-6}	2.4877×10^{-6}
D	0.05294	0.05014	0.06304	0.06343	0.06257

[a]Taken from Terzyk and Gauden (2001).

$$\chi(x) = \frac{d\Theta_{global}}{dx} \tag{14}$$

The adsorption potential distribution can be obtained simply from equation (14):

$$X(A_{pot}) = -\chi(x)\left(\frac{dx}{dA_{pot}}\right) \tag{15}$$

On the other hand, the condensation approximation (CA) defines $X(A_{pot})$ as follows (Cerofolini and Re 1993):

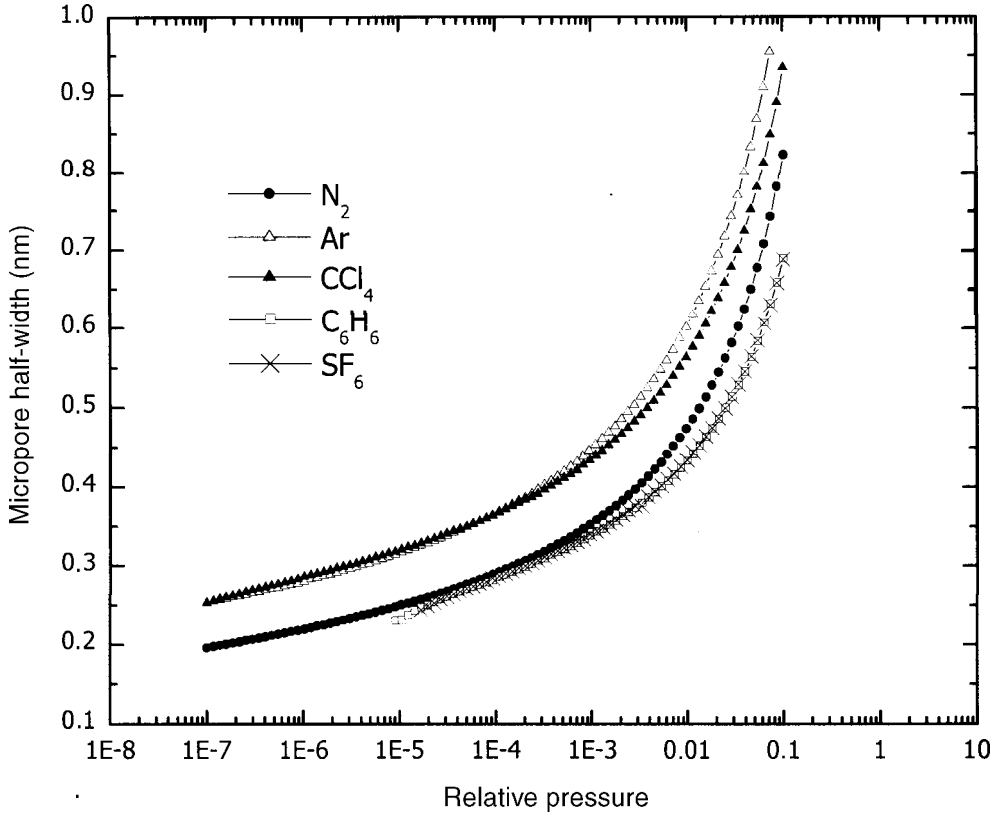

Figure 1. Master curves obtained for all adsorbates considered.

$$X(A_{pot}) = -\frac{d\Theta_{global}}{dA_{pot}} \tag{16}$$

It would appear interesting to compare the $X(A_{pot})$ value obtained from the HK model [equation (15)] with that obtained from the condensation approximation (CA) [equation (16)].

NUMERICAL PROCEDURE

A recently proposed numerical program (Kowalczyk *et al.* 2002) allows for the modification of the estimation of MPSD from a single nitrogen adsorption isotherm (based on the HK model). As previously, the bisection method provided the basis for the modified program since it gives stable results for most non-linear functions and the computations can be undertaken in a very short length of time (allowing the determination of a short range of changes in the micropore width). For each adsorbate introduced, the solution accuracy was assumed equal to 1×10^{-20}, the number of sub-intervals was equal to 1000 and the lower and upper limits of the solution obtained depended strictly on the adsorbate under consideration.

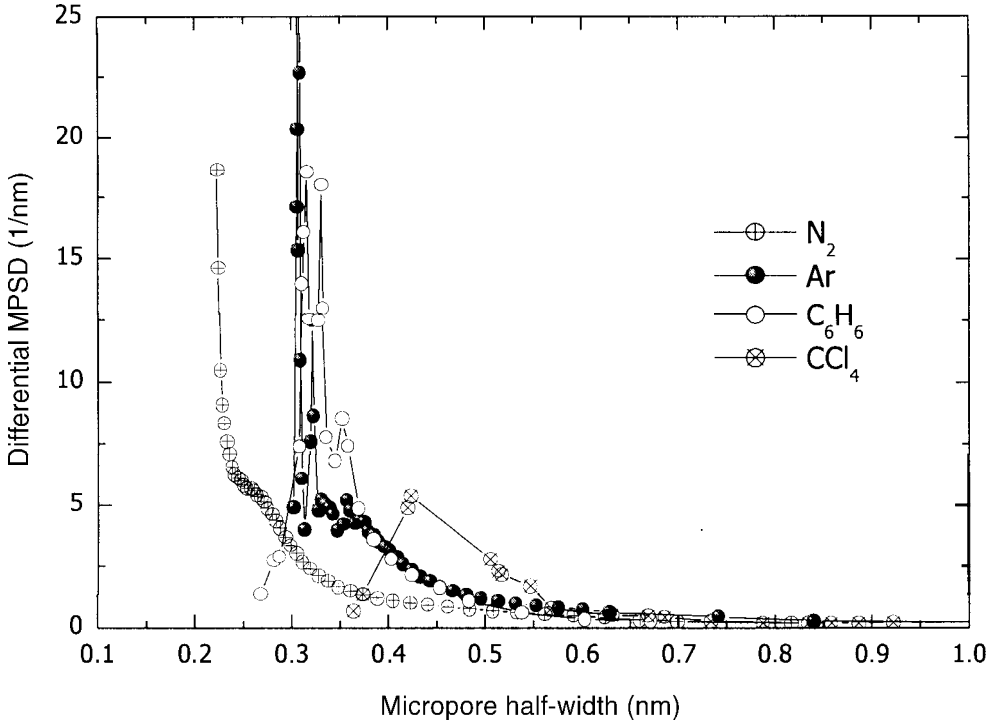

Figure 2. MPSDs obtained for carbon A using different adsorbates.

RESULTS AND CONCLUSIONS

Calculations of the relative pressure versus micropore half-width for the adsorbates studied are presented in Figure 1, the location of the so-called 'master curves' being related to adsorbate type. Thus, curves for argon and carbon tetrachloride were both located in the range corresponding to larger dimensions for the micropores and coincided for $\log(P/P_s) < 1 \times 10^{-3}$. The curves for the remaining adsorbates were situated in a different but simultaneous location. As seen from Figure 1, the curves for argon, benzene and sulphur hexafluoride all coincided over the relative pressure range $0.5 \times 10^{-5} < \log(P/P_s) < 1 \times 10^{-3}$.

The results obtained from adsorption measurements on two synthetic microporous activated carbons (Terzyk and Rychlicki 1999) have been used for the current computations. The MPSDs for these carbons were determined by applying a new numerical program (see Figures 2 and 3). As seen from these figures, the location and shape of the MPSDs for the two carbons were very similar (especially for nitrogen, argon and benzene). On the other hand, both the location and shape of a given MPSD depended strictly upon the adsorbate, with differences between the distributions obtained for the two adsorbates being observed. For example, the MPSD estimated on the basis of the nitrogen adsorption isotherm was exponential in character, suggesting that the main pore fraction was located in the micropore half-width range (0.22–0.40 nm) for both carbons. The shape and location of the distributions obtained from the argon and benzene adsorption isotherms were very similar, with the main pore fraction in these cases being shifted to a larger micropore

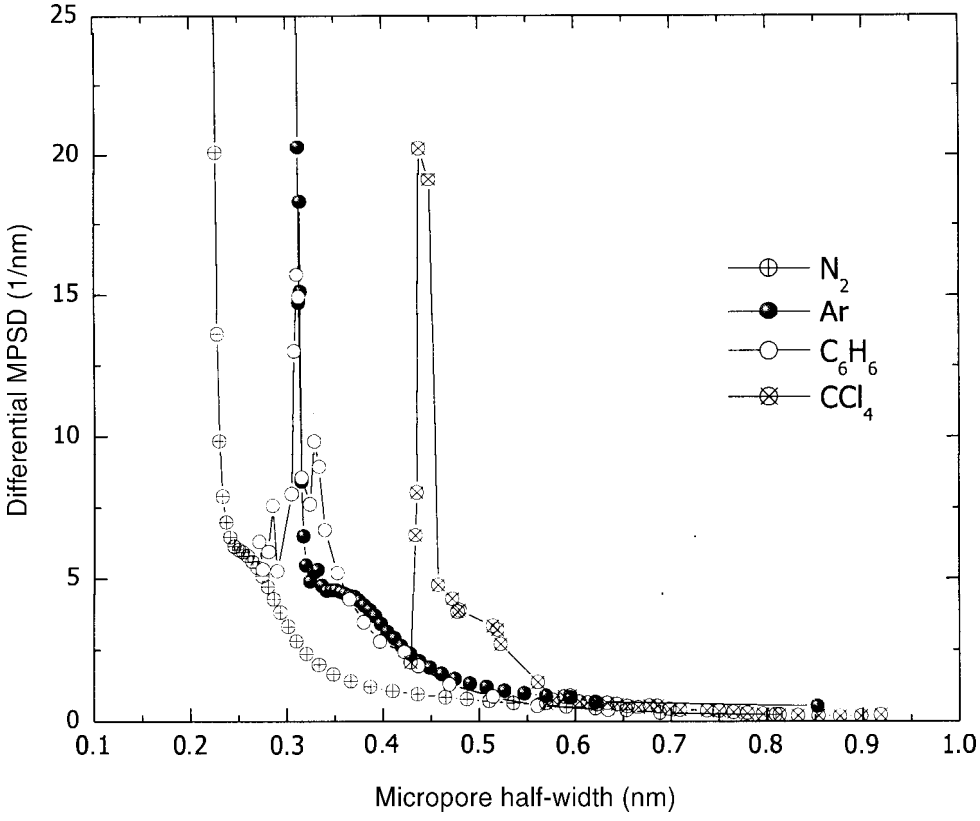

Figure 3. MPSDs obtained for carbon B using different adsorbates.

size (0.32–0.44 nm) for the two adsorbents. Finally, the MPSD from the carbon tetrachloride data clearly showed that the main fraction of micropores in this case was located between 0.45 nm and 0.60 nm.

The adsorption potential distributions obtained for nitrogen and argon as adsorbates are depicted in Figures 4 and 5. Clear agreement is seen between the results of HK and CA calculations, with the adsorption potential distributions being composed of only one main narrow peak which may be connected with the homogeneous structure of the micropores.

Figures 6 and 7 present a comparison between the HK results and those derived from the TOMF approach. Calculations using equation (2) with a variable value of n necessary for the TOMF model were undertaken using CONTIN (Provencher 1982a,b). The figures also contain data as obtained from the new equation proposed recently (Terzyk and Gauden 2001; Terzyk *et al.* 2002).

These figures clearly show that differences occurred between the data derived from the various approaches employed. Thus, the use of CONTIN generated one peak that was Gaussian-like in shape for both carbons considered, with the shape and location of the peak being hardly affected by the value of the structural parameter n employed in the DA equation. In this case, the main pore fraction was located in the range 0.39–0.55 nm for carbon A and in the range 0.39–0.60 nm for carbon B. In contrast, the HK method generated an exponential MPSD shape (as mentioned above) with the main pore fraction apparently lying between 0.22 nm and 0.40 nm. This difference may be

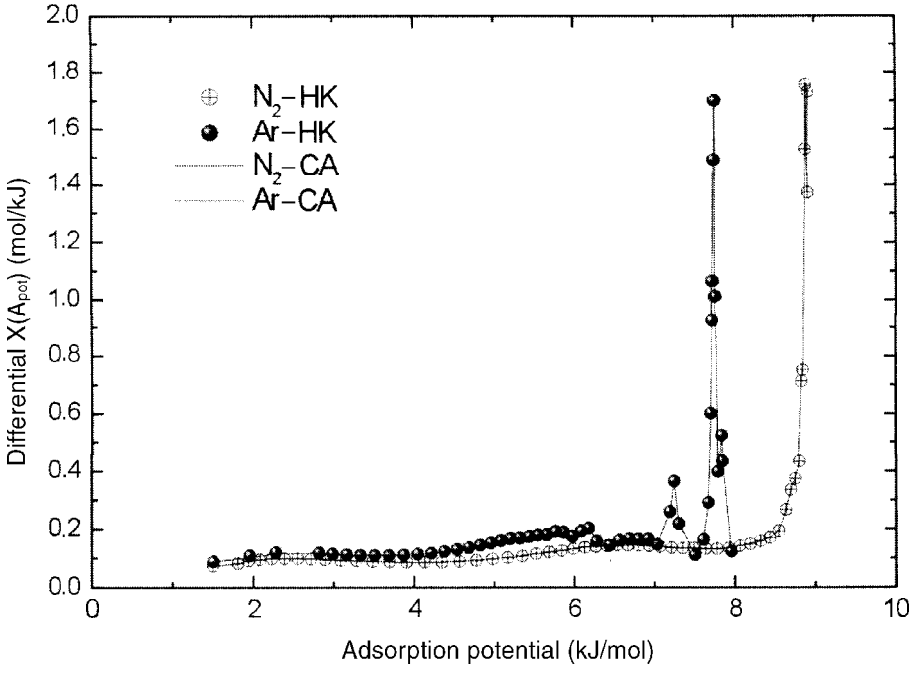

Figure 4. Adsorption potential distributions for carbon A obtained using the HK and CA methods.

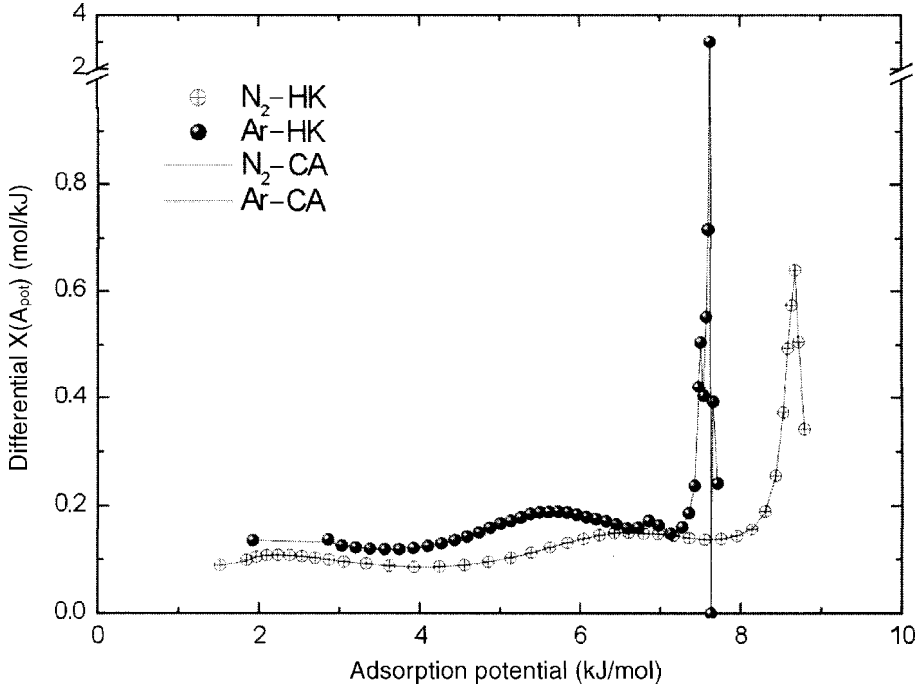

Figure 5. Adsorption potential distributions for carbon B obtained using the HK and CA methods.

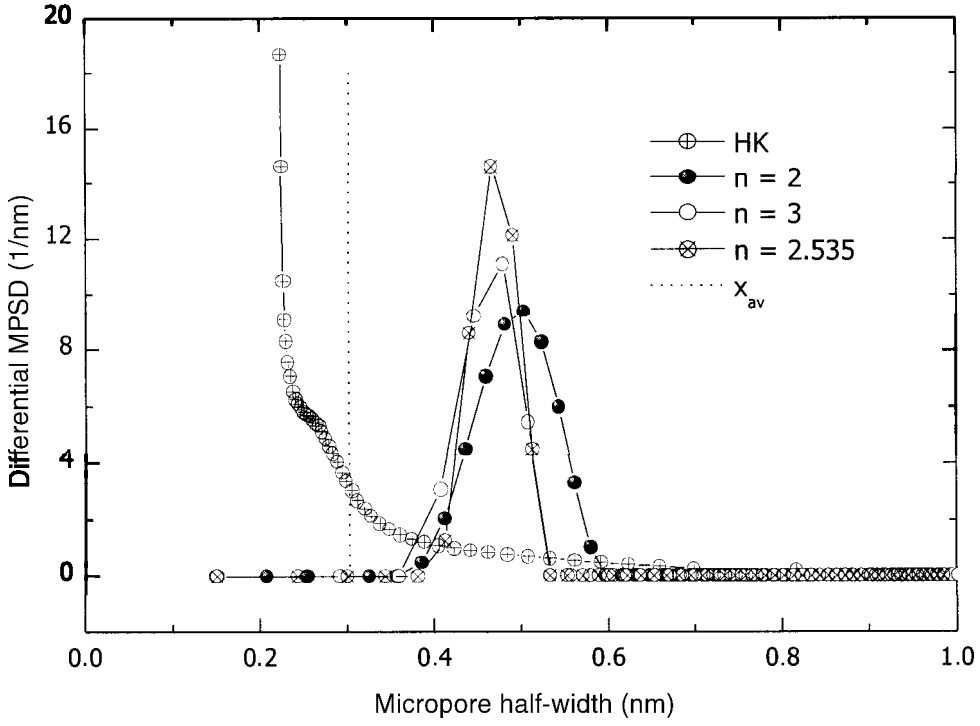

Figure 6. Comparison of the distributions obtained for carbon A applying the HK, TOMF model (with different n values) and the equation proposed recently [x_{av} obtained from equation (7)] by Terzyk and Gauden (2001).

explained by the different physical assumptions employed in the HK and TOMF approaches (Horvath 1998; Chen and Yang 1994; Kruk *et al.* 1998).

The new equation proposed by us recently (Terzyk and Gauden 2001; Terzyk *et al.* 2002) generated values for the average pore diameters which were close to those obtained from the HK model (Figures 6 and 7). The reason for such agreement is that both methods employ the same relationship between the pore diameter and the pore filling pressure [see equation (3)].

However, it should be noted that in contrast to the results described here agreement between the HK and other methods has been observed in several publications (Terzyk *et al.* 2001). This could be the result of the complexity of the micropore structure of activated carbons. In the light of the results described in the present work, it should be emphasised that the HK method is useful and that the proposed numerical algorithm can provide new information about the structure of micropores in activated carbons.

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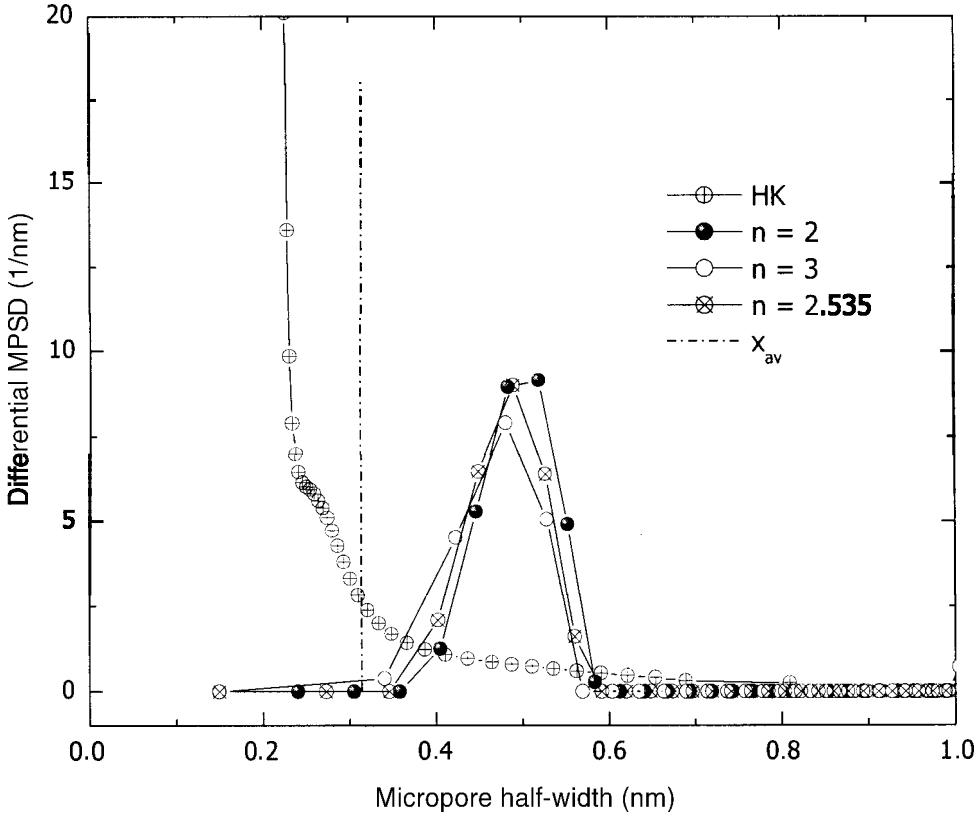

Figure 7. Comparison of the distributions obtained for carbon B applying the HK, TOMF model (with different n values) and the equation proposed recently [x_{av} obtained from equation (7)] by Terzyk and Gauden (2001).

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