New relationships between the characteristic energy of adsorption and the average effective diameter of carbon slit-like micropores
Part II. Adsorption of nitrogen and benzene in carbon slits and cylinders

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Abstract

The influence of the shape of micropores on the relationship between the parameters of Dubinin–Astakhov (DA) adsorption isotherm equation and the average diameter of pores (x_{av}) is investigated. Nitrogen and benzene are chosen to be adsorbates. For both the molecules the Horvath–Kawazoe (HK) type relationships for adsorption in cylindrical carbon micropores are derived. Line and area average potential models are applied; moreover, for benzene, random and flat arrangement of molecules in cylindrical micropores is assumed. Basing on model calculations, it is shown that the same equations relating the parameters of DA isotherm and (x_{av}) as proposed recently for slit-like micropores are valid also for cylindrical system and the only difference is in the values of constants occurring in both relations. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

It has been widely accepted that there exists a direct relationship between the characteristic energy of adsorption, E_0, the parameter determined from the Polanyi–Dubinin theory of volume filling of micropores and the average slit width x_{av} of carbon micropores [1]. Plenty of such relations [1] (see for example references in [2,3]) have been proposed on the basis of both theoretical and experimental research. For example, some of

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them were developed using the correlation between SAXS and molecular probe data [4,5].

Jagiełło and Schwartz [6] appear to be the first to prove, using a numerical study, that the parameter n of Dubinin–Astakhov (DA) adsorption isotherm equation should be also taken into account in equations of that type; however, they did not derive any relation. The first relationship, which takes into account the parameter n of the DA equation, has been derived recently [2,3] (nitrogen was applied as an adsorbate) and it was proved that the average pore diameter is a function not only of E_0 but also of n. An excellent agreement between pore diameters obtained from the new relations and those predicted by some other equations was observed, especially for E_0

Table 1
The parameters of Eq. (1) calculated earlier [6] for the slit-like micropores and both adsorbates studied

Parameter	Adsorbate	
	N_2	C_6H_6
a_1	0.7775	0.8951
b_1	−9.5761	−15.0715
c_1	2.1227	2.6875
a_2	53.7290	39.7903
b_2	−13.8278	−14.3832
c_2	1.7692	2.1493
The determination coefficient (DC)		
	0.9995	0.9956

Table 2
The parameters of Eq. (2) calculated earlier [6] for the slit-like micropores and both adsorbates studied

Parameter	Adsorbate	
	N_2	C_6H_6
$a_{1(mic)}$	24.1672	18.3776
$b_{1(mic)}$	2.2709	3.2093
$a_{2(mic)}$	0.9960	1.0100
$b_{2(mic)}$	$-1.29 \cdot 10^{-2}$	$-8.92 \cdot 10^{-4}$
$a_{3(mic)}$	−0.8586	−1.0718
$b_{3(mic)}$	1.2266	2.1161
The determination coefficient (DC)		
	0.9979	0.9973

higher than 20 kJ mole^{-1}. Furthermore, more general relations taking into account the type of an adsorbate were also proposed [7]. It was shown that for the group of arbitrary chosen adsorbates, i.e. for nitrogen, argon, carbon tetrachloride, benzene and sulphur hexafluoride two general relations between x_{av}, E_0, and n exist and they can be written as [7]:

$$\frac{x_{av}}{d_A} = \frac{a_1}{1 + b_1 \times \exp[-c_1 \times n]} + \frac{a_2 + b_2 \times n + c_2 \times n^2}{E_0} \tag{1}$$

and

$$\frac{x_{av(mic)}}{d_A} = \left(\frac{a_{1(mic)} \times n}{b_{1(mic)} + n}\right) \times \left(\frac{a_{2(mic)} \times n}{b_{2(mic)} + n}\right)^{E_0} \times E_0^{\left(\frac{a_{3(mic)} \times n}{b_{3(mic)} + n}\right)} \tag{2}$$

where d_A is the diameter of an adsorbate molecule and $a_1, \ldots, c_2, a_{1(mic)}, \ldots, b_{3(mic)}$ are constants depending on the type of molecule adsorbed in the slit-like carbon pores. Eq. (1) was derived assuming that adsorption proceeds (especially at low n and E_0 values) not only in micropores but in small amount in some larger pores as well [2,3,7]. Contrary to that, during the derivation of Eq. (2) it was assumed that only micropores are present in the structure of an adsorbent (therefore, subscript mic is used). Since benzene and nitrogen are investigated in the current study, recently calculated parameters of Eqs. (1) and (2) for those molecules, adsorbed in the slit-like micropores are shown [7] in Tables 1 and 2.

2. The aim of the study and the procedure of calculations

As it was discussed a short time ago [2,3,7], Eqs. (1) and (2) were derived for slit-like micropores. It is well known that the presence of that kind of micropores is the most widely accepted in carbonaceous materials. However, the aim of the current paper is to determine the influence of the geometrical shape of pores on the relationship between the parameters of DA equation and x_{av}.

To describe the applied procedure of calculations, and to derive the equations for adsorption in cylindrical carbon micropores, one can start from the equation of Everett and Powl [8]. They derived the general relationship describing the potential energy of interactions ($\varphi_{10-4}(r_c, r_p)_{cylind}$) of a molecule with a cylindrical pore of the radius r_p:

$$\varphi_{10-4}(r_c, r_p)_{cylind}$$
$$= \frac{5}{2} \pi \varepsilon^* \left[\frac{21}{32} \left(\frac{d_0}{r_p} \right)^{10} \sum_{k=0}^{\infty} \alpha_k \left(\frac{r_c}{r_p} \right)^{2k} \right.$$
$$\left. - \left(\frac{d_0}{r_p} \right)^4 \sum_{k=0}^{\infty} \beta_k \left(\frac{r_c}{r_p} \right)^{2k} \right] \tag{3}$$

where r_c is the distance of the adsorbed molecule from the central axis of the cylinder, and ε^* is the potential energy minimum; $\alpha_k^{1/2}$ and $\beta_k^{1/2}$ are constants equal to:

$$\alpha_k^{1/2} = \frac{\Gamma(-4.5)}{\Gamma(-4.5-k)\Gamma(k+1)} \tag{4}$$

$$\beta_k^{1/2} = \frac{\Gamma(-1.5)}{\Gamma(-1.5-k)\Gamma(k+1)} \tag{5}$$

and d_0 is the average of the sum of the diameter of the adsorbent atom (d_a) and of the adsorbate molecule (d_A):

$$d_0 = \frac{d}{2} = \frac{d_a + d_A}{2} \tag{6}$$

For cylindrical micropores the average potential function can be calculated basing on two relationships:

$$\bar{\varphi}_{10-4}(r_c, r_p)_{cylind(LA)} = \frac{\int_0^{r_p - d_0} \varphi_{10-4}(r_c, r_p)_{cylind} dr_c}{\int_{d_0}^{r_p - d_0} dr_c} \tag{7}$$

$$\bar{\varphi}_{10-4}(r_c, r_p)_{cylind(AA)}$$
$$= \frac{\int_0^{r_p - d_0} \varphi_{10-4}(r_c, r_p)_{cylind} 2\pi r_c dr_c}{\int_{d_0}^{r_p - d_0} 2\pi r_c dr_c} \tag{8}$$

Eq. (7) describes the so-called 'line average' (LA) potential, i.e. molecules in a pore have only one degree of freedom along the diameter of the pore. Contrary to that Eq. (8) describes 'area average' (AA) energy — molecules possess two degrees of freedom and move across the pore.

Following Horvath and Kawazoe (HK) as well as other authors [9–13], it can be assumed that the free energy of adsorption $A_{pot} = R_g T \ln(P_0/P)$ (where R_g is gas constant, T temperature, p and p_0 are equilibrium and saturation pressure, respectively) is equal to the average of the intermolecular potential in the pore. This leads to the relationship between the radius of the pore and the equilibrium pressure of an adsorbate. Thus, basing on HK method, Saito and Folley [14] obtained the following relationships:

$$R_g T \ln \left(\frac{p}{p_0} \right)$$
$$= \frac{3}{4} \pi N_{AV} \frac{N_a A_a + N_A A_A}{d_0^4} \sum_{k=0}^{\infty} \left[\frac{1}{2k+1} \left(1 - \frac{d_0}{r_p} \right)^{2k} \right.$$
$$\left. \times \left(\frac{21}{32} \alpha_k \left(\frac{d_0}{r_p} \right)^{10} - \beta_k \left(\frac{d_0}{r_p} \right)^4 \right) \right] \tag{9}$$

$$R_g T \ln \left(\frac{p}{p_0} \right)$$
$$= \frac{3}{4} \pi N_{AV} \frac{N_a A_a + N_A A_A}{d_0^4} \sum_{k=0}^{\infty} \left[\frac{1}{k+1} \left(1 - \frac{d_0}{r_p} \right)^{2k} \right.$$
$$\left. \times \left(\frac{21}{32} \alpha_k \left(\frac{d_0}{r_p} \right)^{10} - \beta_k \left(\frac{d_0}{r_p} \right)^4 \right) \right] \tag{10}$$

where N_{Av} is Avogadro's number, N_a and N_A are the number of atoms per unit area of adsorbent (a) or adsorbate (A), A_a and A_A are the constants (of Lennard–Jones equation) given by:

$$A_a = \frac{6mc^2 \alpha_a \alpha_A}{(\alpha_a/\chi_a) + (\alpha_A/\chi_A)} \tag{10a}$$

$$A_A = \frac{3mc^2 \alpha_A \chi_A}{2} \tag{10b}$$

where m is the mass of electron, c is the velocity of light, α and χ are the polarizability and magnetic susceptibility of an adsorbent atom and/or

Table 3
Physico–chemical constants applied in calculations for adsorbate–adsorbent system

Parameter	Adsorbent	Adsorbate	
	Carbon	N_2	C_6H_6
Diameter d_A (d_a for carbon) (nm)	0.340 [9]	0.300 [9]	0.459 [16]
			0.370[a] [17]
Liquid density (ρ) (g cm^{-3})	- - - -	0.808 [9]	0.861 [18]
Polarizability (α) (cm^3)	1.02×10^{-24} [9]	1.46×10^{-24} [9]	10.32×10^{-24} [19]
			6.35×10^{-24a} [17]
Magnetic susceptibility (χ) (cm^3)	13.50×10^{-29} [9]	2.00×10^{-29} [9]	9.18×10^{-29} [20]
			15.11×10^{-29a} [17]
Density (N) (molecule cm^{-2})	3.845×10^{15} [9]	6.707×10^{14} [9]	3.531×10^{14}
			2.51×10^{14a} [17]
Temperature (T) (K)	----- -	77.50	310.15
			293.15[a] [17]
Molecular Mass (Mm) (g mole^{-1})	----- -	28.01	78.11
Affinity coefficient (β)	----- -	0.320 [2,3]	1.000 [15]

[a] The data for flat arrangement of molecules.

an adsorbate molecule. Eq. (9) is derived for (LA), whilst Eq. (10) for (AA) potential.

Assuming that adsorption takes place in cylindrical carbon micropores and applying the parameters from Table 3 one can write for nitrogen adsorption and (LA) potential:

$$\ln\left(\frac{p}{p_0}\right) = 78.3811 \left\{ \sum_{k=0}^{\infty} \frac{1}{2k+1}\left(1 - \frac{0.32}{r_p}\right) \times \left[\frac{21}{32}\alpha_k\left(\frac{0.32}{r_p}\right)^{10} - \beta_k\left(\frac{0.32}{r_p}\right)^4\right]\right\} \quad (11)$$

and for (AA) potential:

$$\ln\left(\frac{p}{p_0}\right) = 78.3811 \left\{ \sum_{k=0}^{\infty} \frac{1}{k+1}\left(1 - \frac{0.32}{r_p}\right)^{2k} \times \left[\frac{21}{32}\alpha_k\left(\frac{0.32}{r_p}\right)^{10} - \beta_k\left(\frac{0.32}{r_p}\right)^4\right]\right\} \quad (12)$$

The same procedure can be applied for benzene as an adsorbate. In this case, however, we consider two orientations of the adsorbed molecules, random and flat [17]. For the random orientation and (LA) potential, Eq. (9) can be written as:

$$\ln\left(\frac{p}{p_0}\right) = 44.6747 \left\{ \sum_{k=0}^{\infty} \frac{1}{2k+1}\left(1 - \frac{0.399}{r_p}\right) \times \left[\frac{21}{32}\alpha_k\left(\frac{0.399}{r_p}\right)^{10} - \beta_k\left(\frac{0.399}{r_p}\right)^4\right]\right\} \quad (13)$$

whilst for the same random orientation and (AA) potential:

$$\ln\left(\frac{p}{p_0}\right) = 44.6747 \left\{ \sum_{k=0}^{\infty} \frac{1}{k+1}\left(1 - \frac{0.399}{r_p}\right)^{2k} \times \left[\frac{21}{32}\alpha_k\left(\frac{0.399}{r_p}\right)^{10} - \beta_k\left(\frac{0.399}{r_p}\right)^4\right]\right\} \quad (14)$$

For the flat arrangement of benzene molecules and (LA) potential:

$$\ln\left(\frac{p}{p_0}\right) = 101.2862 \left\{ \sum_{k=0}^{\infty} \frac{1}{2k+1}\left(1 - \frac{0.355}{r_p}\right)^{2k} \times \left[\frac{21}{32}\alpha_k\left(\frac{0.355}{r_p}\right)^{10} - \beta_k\left(\frac{0.355}{r_p}\right)^4\right]\right\} \quad (15)$$

whilst for the same arrangement and (AA) potential:

$$\ln\left(\frac{p}{p_0}\right) = 101.2862 \left\{ \sum_{k=0}^{\infty} \frac{1}{k+1}\left(1 - \frac{0.355}{r_p}\right)^{2k} \times \left[\frac{21}{32}\alpha_k\left(\frac{0.355}{r_p}\right)^{10} - \beta_k\left(\frac{0.355}{r_p}\right)^4\right]\right\} \quad (16)$$

Developed in such a way equations Eqs. (11)–(16) were solved numerically using the method of bisection with the accuracy equal to 10^{-8} for arbitrarily chosen values of the relative pressure.

The limit of each sum was determined by iteration. To do this it was assumed that the difference between sums calculated for two subsequent iterations should be smaller than the assumed error (equal to 10^{-6}). This procedure led to the calculation of the curves $\ln (p/p_0) = f(L)$ (where $L = 2r_p$ for cylinders, and/or x for slits) (Fig. 1). Basing on the results of Eqs. (11)–(16) and writing the DA adsorption isotherm equation in the form [15]:

$$\Theta = \exp\left[-\left(\frac{A}{\beta E_0}\right)^n \right] \qquad (17)$$

where Θ is the degree of micropore filling and β is the affinity coefficient (see Table 3) the adsorption isotherms for both adsorbates were generated assuming different values of E_0 at constant n (from 5 up to 40 kJ mole^{-1} with the step 5 kJ mole^{-1}) and/or different values of n at constant E_0 (from 1.5 up to 3.25 with the step 0.25). Then, each

isotherm was re-plotted in the co-ordinates Θ versus effective micropore diameter $(L - d_a)$. Next, the derivative $\mathrm{d}\Theta/\mathrm{d}(L - d_a)$ was calculated numerically, and, for each isotherm, the average effective pore diameter (x_{av}) was calculated by numerical integration from minimum effective diameter, equal to an adsorbate molecule width, to maximum effective slit width using the Eqs. (2) and (6):

$$x_{av} = \frac{\int_{(L - d_a)_{\min}}^{(L - d_a)_{\max}} (L - d_a) J(L - d_a) \mathrm{d}(L - d_a)}{\int_{(L - d_a)_{\min}}^{(L - d_a)_{\max}} J(L - d_a) \mathrm{d}(L - d_a)} \qquad (18)$$

where:

$$J(L - d_a) = \frac{\mathrm{d}\Theta}{\mathrm{d}(L - d_a)} \qquad (19)$$

For nitrogen, the calculations were applied to two ranges, one from the molecular diameter up to 2 nm (micropore diameter following IUPAC classification), and the second from the molecular diameter up to the pore diameters limited by the adsorption potential (this was necessary for low E_0 and n values). For benzene, the calculations were performed only for the first range.

3. Results and discussion

Fig. 1 shows the results of the calculations obtained for adsorption of nitrogen and benzene in slit-like pores [7] as well as in cylindrical ones (using Eqs. (11)–(16)). It can be noticed that the adsorbates fill the pores with arbitrarily chosen diameter (L) (with increasing relative pressure values) in the following order, benzene in cylinders (AA, flat orientation); benzene in cylinders (LA, flat orientation); nitrogen in cylinders (AA); benzene in cylinders (AA, random orientation); nitrogen in cylinders (LA); benzene in cylinders (LA, random orientation), nitrogen in slits and finally benzene in slits. Thus, generally for both adsorbates a lower relative pressure is necessary to fill a cylindrical carbon pore than a slit-like one with the same effective diameter. Figs. 2–5 show the final results of the influence of n (17) on the function $x_{av} = f(E_0, n)$ for nitrogen and benzene
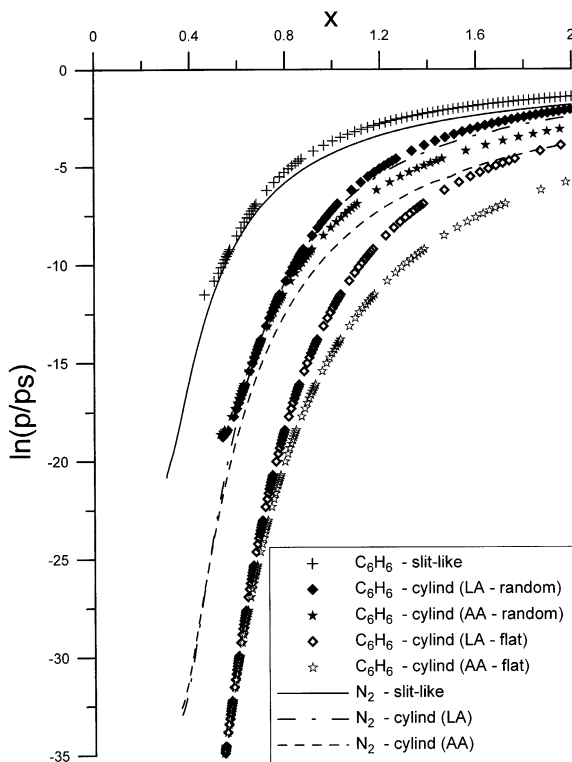

Fig. 1. The general relationships between pore diameter and relative equilibrium pressure for adsorption of nitrogen and benzene in cylindrical and slit-like micropores.
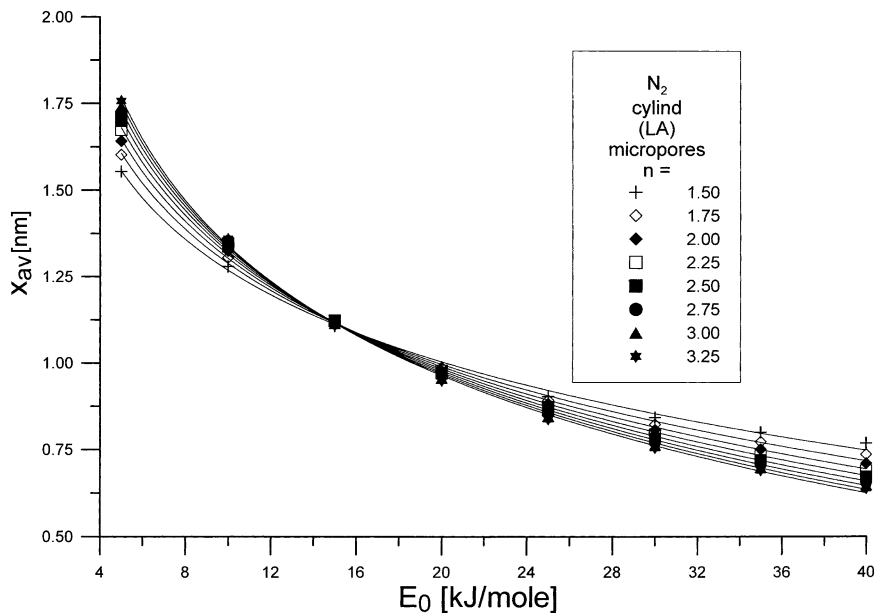
Fig. 2. The influence of n on the function $x_{av} = f(E_0, n)$ for nitrogen adsorbed in cylindrical micropores (LA potential). The points are numerically calculated values and the lines are obtained from Eq. (2) and the data from Table 4 for this adsorbate.

(random orientation of adsorbed molecules) using (LA) and (AA) potentials. In Figs. 6 and 7, the results for benzene, flat orientation using the both potentials are shown, whilst in Figs. 8 and 9 the results of the calculation for the second range and for randomly oriented nitrogen molecules are presented.

As earlier (Fig. 3 in [2,3], Figs. 8–10 in [6]), the intersection points are observed on curves calculated for the micropore range (Figs. 2–6). Only for benzene adsorbed in cylinders (AA flat orientation) the curves do not intersect but coincide at the highest values of energy.

It has been concluded recently, analysing the data calculated for adsorption of different molecules in slit-like micropores [7], that the intersection points occur at larger reduced effective pore diameter (x_{av}/d_A) for molecules with smaller diameters and this is caused by the application of the integration limit. The same upper limit for all adsorbates originates from IUPAC definition; however, the lower limit is different for each adsorbate. Moreover, the results presented in the current study lead to the conclusion that the intersection point occurs at different values of E_0

for LA and AA potentials (Figs. 2–5). The assumption of the occurrence of both micropores and pores with larger diameters than 2 nm in the structure (but in small quantity) leads to the vanishing of these intersection points (Figs. 8 and 9).

As it was presumed, the shapes of $x_{av} = f(E_0, n)$ curves for adsorption in cylindrical micropores are similar to those obtained for slit-like ones [7]. Thus, it can be concluded that the type of mathematical relationships between the parameters of DA equation and x_{av} is independent of the geometrical shape of micropores and Eqs. (1) and (2) describe all the branches of curves from Figs. 2–9. The results of simultaneous minimisation of all the curves $x_{av} = f(E_0, n)$ are shown in Figs. 2–9 (solid lines) and the obtained parameters of Eqs. (1) and (2) are given in Tables 4 and 5 (together with the average, for the whole branch of curves, determination coefficient (DC)). It can be noticed, that a very good correlation occurs between the data calculated numerically and those obtained from Eqs. (1) and (2) using the parameters from Tables 4 and 5.
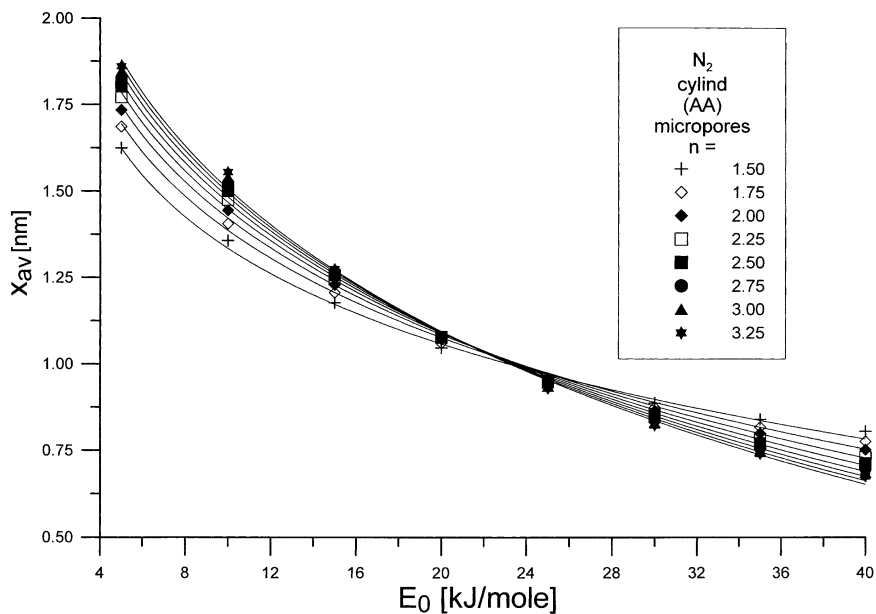
Fig. 3. The influence of n on the function $x_{av} = f(E_0, n)$ for nitrogen adsorbed in cylindrical micropores (AA potential). The points are numerically calculated values and the lines are obtained from Eq. (2) and the data from Table 4 for this adsorbate.
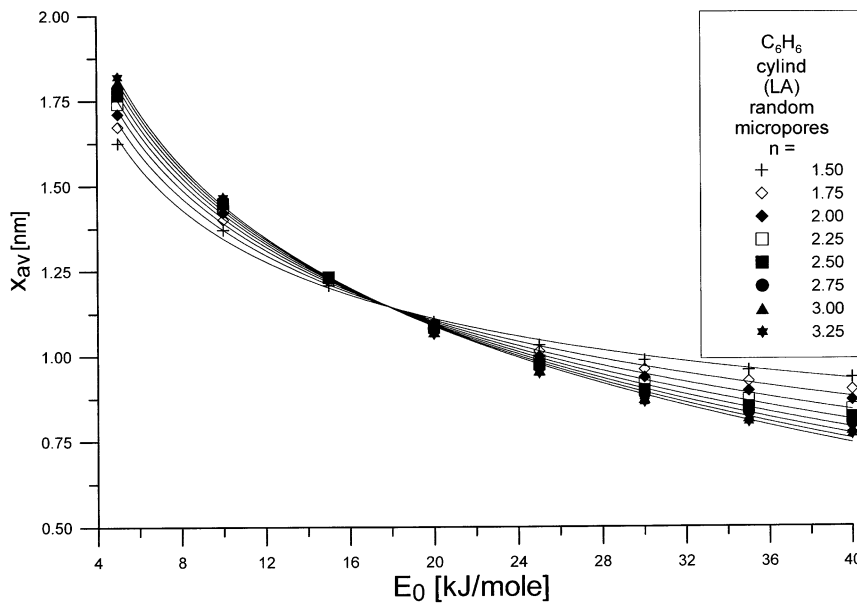

Fig. 4. The influence of n on the function $x_{av} = f(E_0, n)$ for benzene adsorbed in cylindrical micropores (LA potential random orientation). The points are numerically calculated values and the lines are obtained from Eq. (2) and the data from Table 4 for this adsorbate.
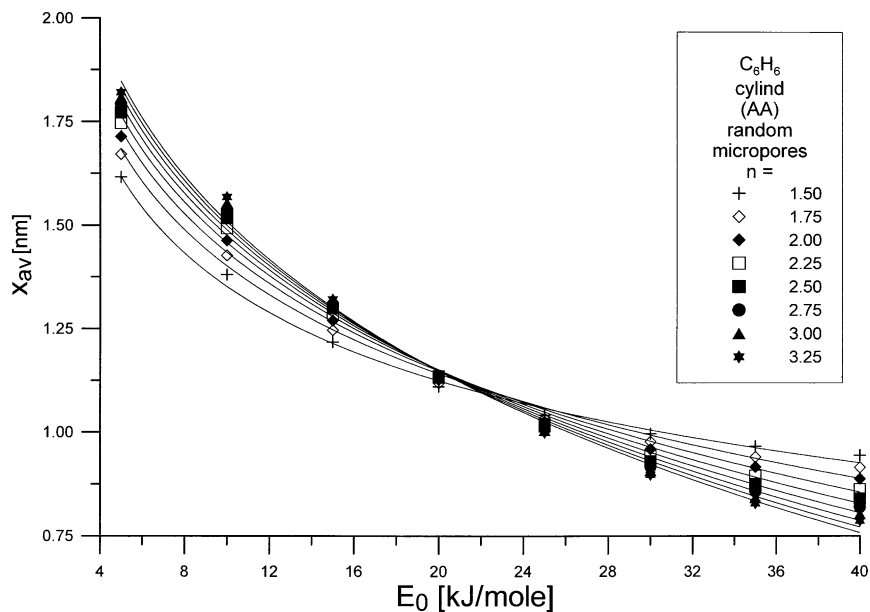
Fig. 5. The influence of n on the function $x_{av} = f(E_0, n)$ for benzene adsorbed in cylindrical micropores (AA potential random orientation). The points are numerically calculated values and the lines are obtained from Eq. (2) and the data from Table 4 for this adsorbate.
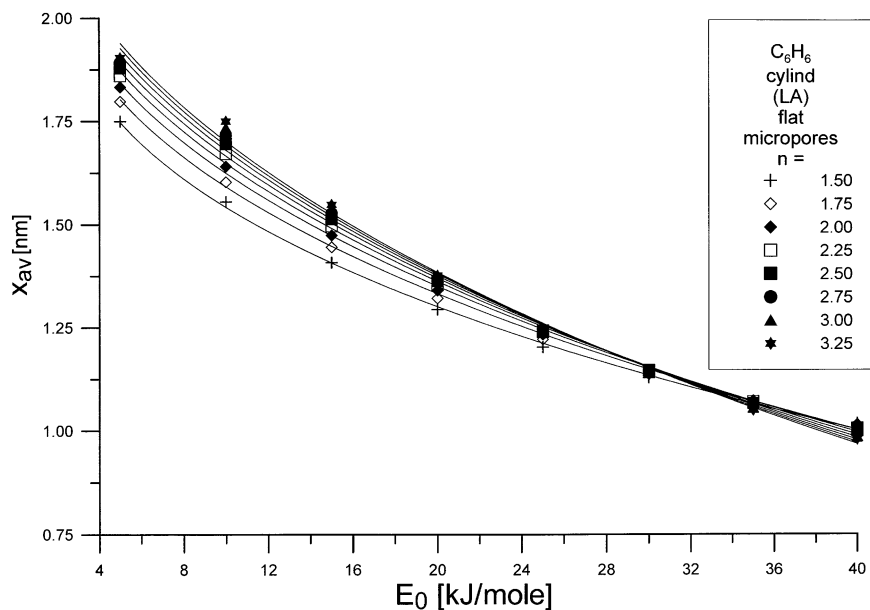

Fig. 6. The influence of n on the function $x_{av} = f(E_0, n)$ for benzene adsorbed in cylindrical micropores (LA potential flat orientation). The points are numerically calculated values and the lines are obtained from Eq. (2) and the data from Table 4 for this adsorbate.
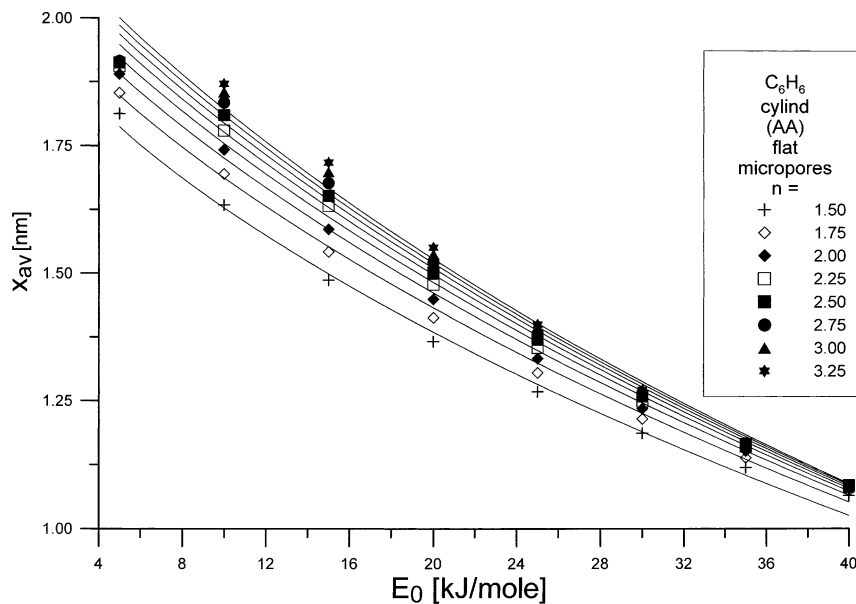
Fig. 7. The influence of n on the function $x_{av} = f(E_0, n)$ for benzene adsorbed in cylindrical micropores (AA potential flat orientation). The points are numerically calculated values and the lines are obtained from Eq. (2) and the data from Table 4 for this adsorbate.
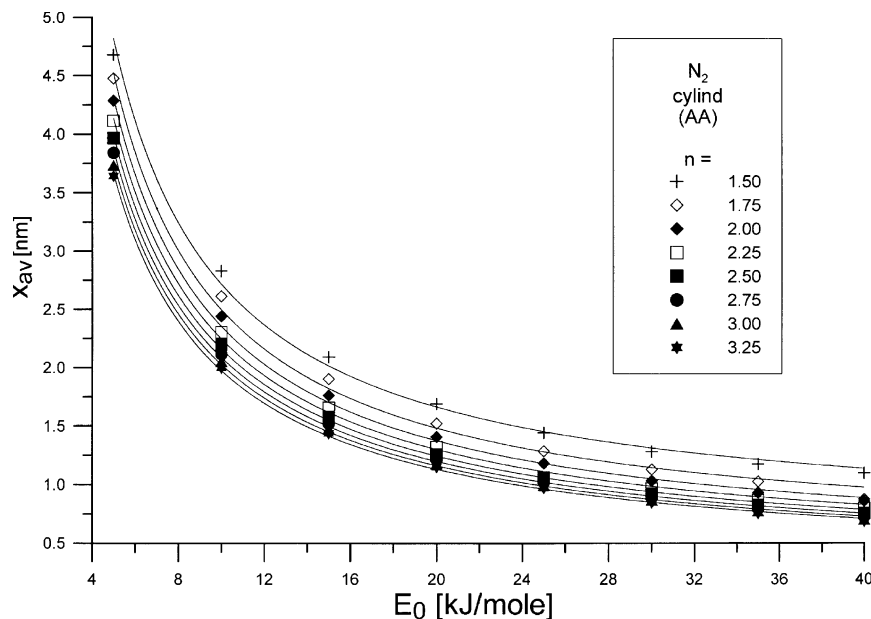

Fig. 8. The influence of n on the function $x_{av} = f(E_0, n)$ for nitrogen adsorbed in cylindrical micropores (AA potential). The points are numerically calculated values and the lines are obtained from Eq. (1) and the data from Table 5 for this adsorbate.

Fig. 9. The influence of n on the function $x_{av} = f(E_0, n)$ for nitrogen adsorbed in cylindrical micropores (LA potential). The points are numerically calculated values and the lines are obtained from Eq. (1) and the data from Table 5 for this adsorbate.
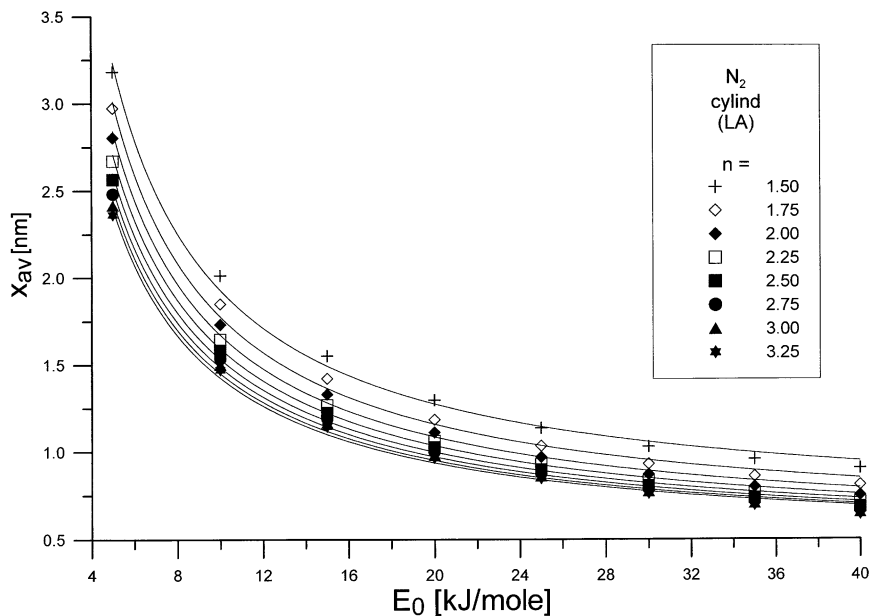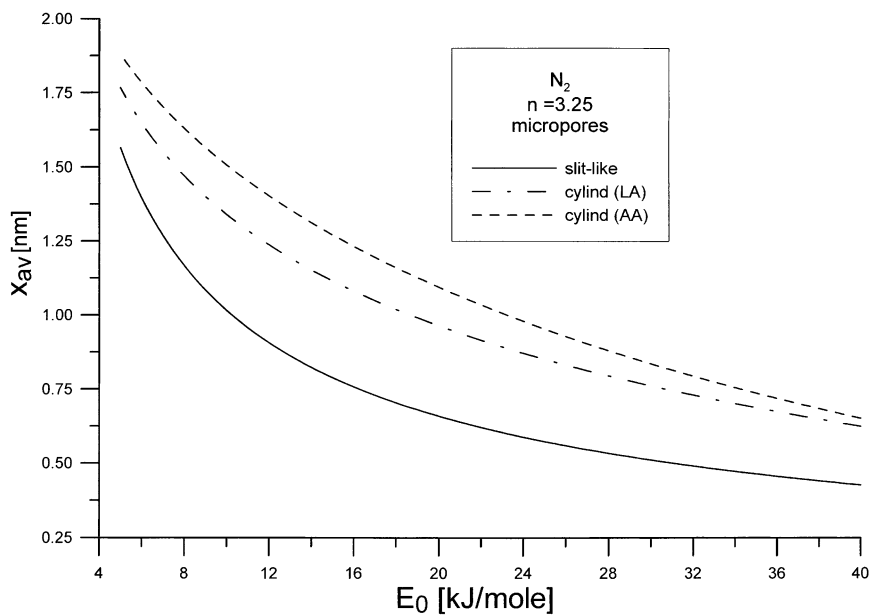

Fig. 10. The influence of the shape of micropores on the function $x_{av} = f(E_0, n)$ (calculated from Eq. (2))for arbitrary chosen value of n and for nitrogen adsorption.

Table 4
The parameters of Eq. (2) for cylinders and both adsorbates studied.

Parameter	Adsorbate					
	N_2		C_6H_6			
			Random orientation		Flat orientation	
	(LA)	(AA)	(LA)	(AA)	(LA)	(AA)
$a_{1(mic)}$	14.2216	10.3138	7.1161	6.4714	6.9084	6.6102
$b_{1(mic)}$	1.1674	0.3940	0.3566	0.3250	0.2434	0.3106
$a_{2(mic)}$	0.9860	0.9700	0.9808	0.9751	0.9799	0.9816
$b_{2(mic)}$	−0.0120	−0.0348	−0.0311	−0.0360	−0.0168	−0.0073
$a_{3(mic)}$	−0.4359	−0.1471	−0.2449	−0.1590	−0.0631	−0.0120
$b_{3(mic)}$	1.1087	−0.5570	−0.2741	−0.5569	−0.6749	−0.9879
The determination coefficient (DC)						
	0.9987	0.9973	0.9964	0.9938	0.9975	0.9943

Comparing the average effective diameters obtained from Eqs. (1) and (2) for pores possessing different geometrical shapes it is seen that for nitrogen (at arbitrarily chosen value of n) the lowest values of x_{av} are observed for adsorption in slits (Fig. 10). The highest diameters occur for cylinders (AA potential), whilst cylinders (LA potential) give the intermediate values. This is a consequence of the results presented in Fig. 1. At the same values of E_0 and n of DA Eq. (17), i.e. for the same two nitrogen adsorption isotherms measured for carbons possessing slit-like and cylindrical micropores the second ones possess larger average effective diameter than the former.

For the adsorption of benzene at the same values of E_0 and n the smaller x_{av} is obtained for an adsorbent possessing slit-like pores and increases in the sentence: cylinders (LA random orientation), cylinders (AA random orientation), cylinders (LA flat orientation) and cylinders (AA flat orientation) (Fig. 11). As in the case of nitrogen, the obtained results are the consequences of the general relations presented in Fig. 1. It should be added that in the case of benzene adsorption as n decreases, the curves generated for adsorption in cylinders (AA random orientation) and for (LA random orientation) almost coincide and in this case the type of $x_{av} = f(E_0, n)$ curve is almost independent of the type of potential applied for the calculation.

4. Conclusions

As it was presumed, the change in the shape of micropores of the activated carbon does not change the type of relationship between the parameters of DA equation and the average diameter of carbon micropores, calculated for benzene and nitrogen. The only differences between the equations derived for adsorption in slits [7] and those for cylindrical pores are in the values of the parameters occurring in Eqs. (1) and (2) (Tables 1, 2, 4 and 5). A good correlation is obtained between the data calculated numerically and those obtained from Eqs. (1) and (2). Using the values of parameters tabulated in Tables 1, 2, 4 and 5,

Table 5
The parameters of Eq. (1) for nitrogen adsorption in cylindrical pores

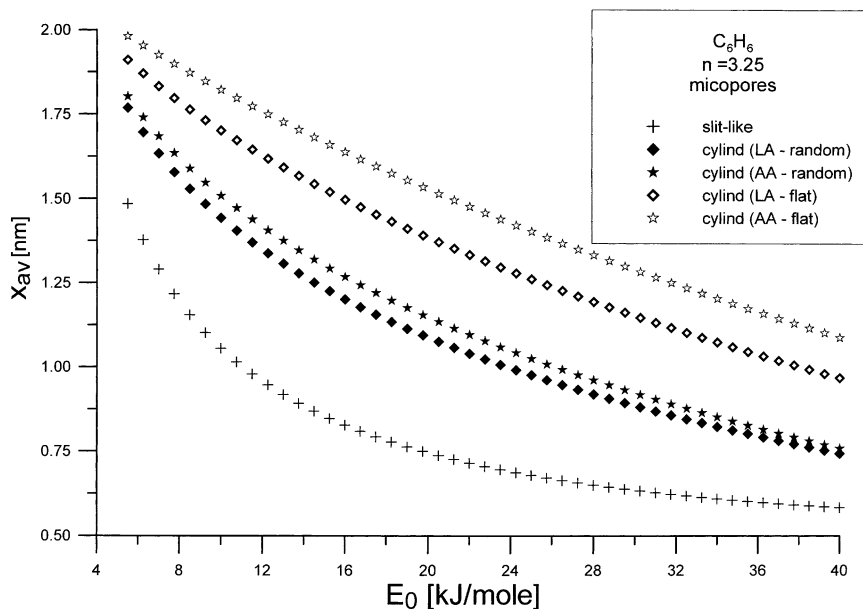| Parameter	N_2	
	(LA)	(AA)
a_1	0.4443	0.2582
b_1	−4.5943	−2.6321
c_1	1.8542	1.0122
a_2	19.1270	26.8441
b_2	−5.0229	−4.5416
c_2	0.6583	0.4535
The determination coefficient (DC)		
	0.9961	0.9989

Fig. 11. The influence of the shape of micropores on the function $x_{av} = f(E_0, n)$ (calculated from Eq. (2)) for arbitrary chosen value of n and for benzene adsorption.

and knowing the parameters of Eq. (17) for benzene and/or nitrogen adsorption isotherm one can calculate the average effective diameter of carbon micropores assuming their slit-like or cylindrical shape.

Appendix. List of symbols

a_1	the parameter of Eq. (1) shown in Tables 1 and 5
$a_{1(mic)}$	the parameter of Eq. (2) shown in Tables 2 and 4
a_2	the parameter of Eq. (1) shown in Tables 1 and 5
$a_{2(mic)}$	the parameter of Eq. (2) shown in Tables 2 and 4
$a_{3(mic)}$	the parameter of Eq. (2) shown in Tables 2 and 4
A_a	constant in Lennard–Jones equation defined by Eq. (10a)
A_A	constant in Lennard–Jones equation defined by Eq. (10b)
A_{pot}	the free energy of adsorption in Dubinin–Astakhov isotherm equation Eq. (17)
b_1	the parameter of Eq. (1) shown in Tables 1 and 5
$b_{1(mic)}$	the parameter of Eq. (2) shown in Tables 2 and 4
b_2	the parameter of Eq. (1) shown in Tables 1 and 5
$b_{2(mic)}$	the parameter of Eq. (2) shown in Tables 2 and 4
$b_{3(mic)}$	the parameter of Eq. (2) shown in Tables 2 and 4
c	the velocity of light
c_1	the parameter of Eq. (1) shown in Tables 1 and 5

c_2	the parameter of Eq. (1) shown in Tables 1 and 5
d	the sum of the diameter of an adsorbent atom and an adsorbate molecule
d_0	the average of the sum of the diameter of an adsorbent atom and of an adsorbate molecule
d_A	the diameter of an adsorbate molecule
d_a	the diameter of an adsorbent atom
E_0	characteristic energy of adsorption calculated from Dubinin–Astakhov isotherm Eq. (17)
$J(L-d_a)$	the pore size distribution defined by Eq. (19)
m	the mass of electron
n	the best fit parameter of Dubinin–Astakhov isotherm equation Eq. (17)
N_A	number of atoms per unit area of adsorbate
N_a	number of atoms per unit area of adsorbent
N_{AV}	Avogadro's number
p	equilibrium pressure of an adsorbate
p_0	saturation pressure of an adsorbate
r_c	the distance of the adsorbed molecule from the centre axis of the cylinder
r_g	gas constant
r_p	radius of the cylindrical pore (Eq. (3))
T	temperature
x_{av}	the average effective pore diameter

Greek letters

α_a	the polarizability of an adsorbent atom
α_A	the polarizability of an adsorbate molecule
χ_a	the magnetic susceptibility of an adosrbent atom
χ_A	the magnetic susceptibility of an adsorbate molecule
Θ	the degree of micropore filling defined by Eq. (17)
β	the affinity coefficient
σ	distance from an atom in the surface layer at zero interaction energy, defined by Eq. (1)g
$\varphi_{10-4}(r_c, r_p)$	the potential energy of interactions ($\varphi_{10-4}(r_c, r_p)$) of a molecule with a cylindrical pore of the radius r_p (Eq. (3))
$\bar{\varphi}_{10-4}(r_c, r_p)$	the average potential energy of interactions ($\varphi_{10-4}(r_c, r_p)$) of a molecule with a cylindrical pore of the radius rp (Eq. (10))
$\beta_k^{1/2}$	constant defined by Eq. (5)
$\alpha_k^{1/2}$	constant defined by Eq. (4)

Subscripts

a	adsorbent
A	assorbate
AA	area average
Cylind	cylindrical
LA	line average
mic	calculated for the range of micropores

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