

# Effects of pore shape models on the micropore structure analysis

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The paper evaluates the effects of the applied model of the geometrical shape of pores in the interpretation of the adsorption isotherm for the structural analysis of microporous substances. Presented are the adsorption potentials, equations for structural characteristics, and their relative deviations when the applied model of the pore shape is changed.

Оценено влияние используемой модели геометрической формы пор при интерпретации адсорбционной изотермы для структурного анализа микропористых веществ. Приведены адсорбционные потенциалы, уравнения структурных характеристик и их относительных расхождений при изменении используемой модели формы поры.

The evaluation of experimental adsorption isotherms is connected with the accepted theory of pore filling and with the model of the shape of pores. In case that under conditions of determining the adsorption isotherm successive filling of pores according to their size takes place, existence of the relation of the relative pressure of vapours of adsorbate and the value of the parameter characterizing the dimension of pore (which can be used as a distribution variable) is presupposed.

The total volume and surface of pores, volume and surface distribution functions, and the extreme values of distribution variables are the basic structural characteristics of porous materials. The dependence between the adsorption volume ( $W$ ) and the relative pressure ( $p/p_s$ ) enables to carry out a pore structure analysis, *i.e.* determination of the structural characteristics from adsorption isotherms ( $W = f(p/p_s)$ ). If the conditions enabling to express the differential molar work of adsorption ( $A$ ), both as a function of the relative pressure ( $A = f(p/p_s)$ ) and as a function of the size and geometrical shape of pores ( $A = f(q, k)$ ) are fulfilled, adsorption volume distribution may be expressed. The results of such structure analysis depend on the model of the geometrical shapes of pores.

The micropore structure analysis is based on the experimentally found adsorption volume dependence on the relative pressure [1]

$$W = f_1(p/p_s) \quad (1)$$

On the basis of the relation between the relative pressure and the distribution variable ( $q$ ), characterizing the size of pores of given geometrical shapes

$$p/p_s = f_2(q) \quad (2)$$

and by using the relations between the surface and volume of a certain pore model

$$S_i = f_3(W_i) \quad (3)$$

the individual characteristics of the micropore structure analysis may be expressed as follows

$$W_0 \dots \text{experimental value} \quad (4)$$

$$W = g_1(q) \quad (5)$$

$$W' = g'_1(q) \quad (6)$$

$$S' = g'_2(q) \quad (7)$$

$$S = g_2(q) = \int_{q_n}^{q_a} g'_2(q) dq \quad (8)$$

$$S_0 = \int_{q_n}^{q_x} g'_2(q) dq \quad (9)$$

$$q_{w_m} = (q)_{W=0} \quad (10)$$

$$q_{s_m} = (q)_{S=0} \quad (11)$$

where  $q_{w_m}$  and  $q_{s_m}$  are the values  $q$  for  $W'' = 0$  and  $S'' = 0$ .

The function  $g_1$  is formed by combining relations (1) and (2), the function  $g_2$  is derived from the function  $g'_1$  using relation (3). The functions  $g'$  are the derivatives of the functions  $g$ .

If we may expect the micropore volume filling the potential theory of adsorption shows to be advantageous. In this case, the adsorption isotherm is expressed by the *Dubinin—Radushkevich* [2] equation

$$W = W_0 \exp - \left( \frac{A}{E} \right)^n \quad (12)$$

where  $W_0$  is the limiting adsorption volume and  $E, n$  are the empiric constants.

*Kiselev* [3] pointed out that between the differential molar work of adsorption ( $A$ ) and the adsorbed molecule potential energy (adsorption potential) the following relation exists

$$-\Phi = A + RT \ln (p_w/p_s) \quad (13)$$

where

$$A = RT \ln (p_s/p) \quad (14)$$

$p_u$  — the equilibrium pressure in the region of heterogeneity,  
 $p_s$  — the pressure of saturated vapours of adsorbate,  
 $p$  — the equilibrium pressure of adsorbate vapours.

If the  $p$ ,  $V$ ,  $T$  relations of adsorbate in a small volume of a micropore are the same as those in the bulk volume, eqns (15) and (16) are valid

$$p_u/p_s = 1 \quad (15)$$

$$-\Phi = A \quad (16)$$

On the basis of the relation between  $\Phi$  and  $A$ , the relative pressure, corresponding to the value of the distribution variable  $p/p_s = f(q)$  or the adsorption volume corresponding to the value of the variable  $q$  may be expressed by

$$W = f(q) \quad (17)$$

We assume at the same time that the adsorbent energetic heterogeneity is caused exclusively by the distribution of micropores according to their size, whilst the walls of pores are energetically homogeneous.

The expression for the adsorbed molecule potential energy

$$\Phi = \sum_i \Phi_i \quad (18)$$

is replaced [4] with the integral

$$\Phi = \int \int_V \int \eta N \, dV \quad (19)$$

where  $N$  — the number of adsorbent atoms in the volume unit [4],

$\eta$  — the potential of intermolecular forces,

$\Phi_i$  — the contribution of potential energy of adsorbate single molecule.

*De Boer* and *Custers* [4] used for potential  $\eta$  the expression

$$\eta_A = -C_A R^{-6} \quad (20)$$

which does not cover the contribution of the repulsive forces.  $C_A$  is the constant from the *Kirkwood—Müller* formula [5, 6] and  $R$  is the distance of two interacting force centres.

The model idea of the pore geometrical shapes is reflected in the value of potential energy of the adsorbed molecule  $\Phi$  and thus also in the relation between the adsorption volume ( $W$ ) and the parameter  $q$  (17). Furthermore, the shapes of the pores are reflected in the relation between the surface and volume of the pore (3). Owing to this, presented structural characteristics (5—11) depend on the accepted model of the pore geometrical shapes.

An important factor for individual model ideas of the shapes of pores is the number of parameters characterizing the body to be the model. A more general approach, *i.e.* taking multiparameter pore shapes into consideration or considering more shapes of pores simultaneously, exceeds the information which may be obtained from the adsorption isotherm itself. Due to this only single- or multiparameter models should be taken into account from which further parameters are eliminated by additional presumptions.

Further part of the paper presents the adsorption potentials ( $\Phi$ ) and relations between the surface and volume of pores for the individual geometrical shapes. In conclusion the effect of pore shapes on the values of individual characteristics is evaluated.

### Adsorption potentials

The value of the adsorption potential (potential energy of adsorbed molecule), characteristic of a pore of a certain size, is similarly as in the *De Boer* and *Custers* study [4], given by the potential of a molecule on the bottom of a pore, in the distance from the bottom equal to the pore parameter. *De Boer* and *Custers* [4] calculated the adsorption potential  $\Phi$  according to eqns (19) and (20) for pores of spherical shapes (T-43), as well as for those of cylindrical ones of circular cross section with a half-sphere bottom (T-32, T-31).

Considerations of the effects of the model shapes of pores on the micropore structure analysis cover the shapes presented in Fig. 1. The individual models are

		1	2	3	4	5
cross section	condition for $v$					
1	$v \gg q$					
2	$v > q$					
3	$v = q$					

$\overline{z \ q}$

Fig. 1. Survey of the pore shape models.

Individual shapes are denoted by a pair of numbers, the first index indicates the shape of the cross section of a pore or its bottom, the second one the relative height of the pore.

indexed with two numbers ; the first one indicating the shape of the section or of the bottom and the second one denoting the pore relative height. Cross section of the pore (T-21), representing a more general shape of pores, is presented in Fig. 2.

The adsorption potential  $\Phi$  is obtained by the integration

$$\Phi_A = N \iiint_V -C_A R^{-6} dV \tag{21}$$



Fig. 2. Model of the shape T-22.

$a, b$  — semiaxes ;  $v$  — height of a pore ;  $\rho$  = polar radius ;  $\bar{\psi}$  — angle.

A more general shape of a cylindrical pore of elliptic cross section and with a flat bottom covers the types T-22, T-21, T-23, T-12, T-11, and T-13. The value of the adsorption potential for these types is defined by the expressions

$$\Phi = \iiint_V N\eta dV = \Phi_{p1} + \Phi_{p2} + \Phi_{p3} \tag{22}$$

$$\Phi_{p1} = \int_0^{2\pi} \int_0^\infty \int_0^v N\eta\rho d\varphi d\rho dz \tag{23}$$

$$\Phi_{p2} = \int_0^{2\pi} \int_0^\infty \int_0^q N\eta\rho d\varphi d\rho dz \tag{24}$$

$$\Phi_{p3} = \int_0^{2\pi} \int_0^\infty \int_q^\infty N\eta\rho d\varphi d\rho dz \tag{25}$$

where

$$Q = q \sqrt{\frac{1}{X^2} \cos^2 t + \sin^2 t}$$

$X$  — the ratio of semiaxis of the elliptical cross section ( $b/a$ ),

$t$  — the parameter of equation of ellipse,  $\varphi, \varrho, z$  — the cylindrical coordinates.

For pores with spherical bottoms (T-32, T-31, and T-33), the terms  $\Phi_{p2}$  and  $\Phi_{p3}$  in the expression for  $\Phi$  (22) are replaced with  $\Phi_s/2$ . Quantity  $\Phi_s$  is the adsorption potential of the spherical pore (T-43)

$$\Phi_s = \int_q^\infty \int_0^{2\pi} \int_0^\pi N \eta R^2 \sin \vartheta \, dR \, d\varphi \, d\vartheta \quad (26)$$

where  $R, \varphi, \vartheta$  are the spherical coordinates. For slit-like pores (T-51)

$$\Phi = 2 \Phi_{p3} \quad (27)$$

Integration of expression (21) for individual models leads to equations defining the adsorption potential in the form

$$\Phi_A = -k_A/q^3 \quad (28)$$

or

$$\Phi_A = -NC_A \pi (f_A/q^3) \quad (29)$$

Between the coefficients  $k_A$  and  $f_A$ , presented in Tables 1 and 3 for the models of the pore shapes under consideration, the following relation is applied

$$k_A = NC_A \pi f_A \quad (30)$$

In Table 1 we used for the general types with the not defined value of the parameters  $X$  or  $v$  the symbols  $J_A, I_A, I_{AJ}$ , and  $\vartheta$ . The interpretation of these symbols is as follows

$$J_A = (2/NC_A) \Phi_{p1} \quad (31)$$

$$I_A = (2/NC_A) \Phi_{p2} \quad (32)$$

$$I_{AJ} = (J_A)_{v \gg q} \quad (33)$$

$$\vartheta = \pi - 2\tilde{\psi} + \sin \tilde{\psi} \quad (34)$$

The values of the integrals  $I_A, I_{AJ}$  are shown in Table 2.

Table 1 presents for the presupposed models of the pore shapes the distribution variables and expressions for  $f_A$ . The values  $f_A$  and  $k_A$  for the system C—C<sub>6</sub>H<sub>6</sub> are shown in Table 3; the constants  $N = 1.123 \times 10^2 \text{ nm}^{-3}$  and  $C_A = 1.411 \times 10^{-2} \text{ kJ mol}^{-1} \text{ nm}^6$  were used [7].

Table 1

Expressions for the coefficients  $f_A$  of different shapes of pores. Adsorption potential in the centre of pore is expressed by the equation  $\Phi_A = -NC_A\pi f_A/q^3$

$$\Phi_A = -NC_A\pi\left(f_A \frac{1}{q^3}\right)$$

T	q	$f_A$
22	b	$\frac{1}{2\pi} I_A + \frac{1}{2\pi} I_A + \frac{1}{6}$
12	r	$\frac{1}{8} \vartheta + u_A + \frac{1}{6}$
32	$r_s$	$\frac{1}{8} \vartheta + \frac{2}{3}$
21	b	$\frac{1}{4} I_{A'} + \frac{1}{2\pi} I_A + \frac{1}{6}$
11	r	$\frac{1}{8} \pi + u_A + \frac{1}{6}$
31	$r_s$	$\frac{1}{8} \pi + \frac{2}{3}$
51	$\frac{L}{2}$	$\frac{1}{3}$
23	b	$\frac{1}{\pi} I_A + \frac{1}{6}$
13	r	$2u_A + \frac{1}{6}$
33	$r_s$	$u_A + \frac{2}{3}$
43	$r_s$	$\frac{4}{3}$
$u_A = 0.32135$		$\vartheta = \vartheta(\bar{\psi})$

Table 3 also compares values of adsorption potential and coefficients  $f_A$  for different types of pores. The pore model T-11 (cylindrical pore of circular cross section with a flat bottom) has been chosen as the basis for the comparison. Comparison is carried out on the basis of the relative quantities ( $\Delta\Phi_A$ ) for which we can use

$$(\Delta\Phi_A) = \frac{\Phi_A - \Phi_A^+}{\Phi_A^+} = \frac{f_A}{f_A^+} - 1 \tag{35}$$

Table 2

Values of the integrals  $I_A, I_{A'}$  for different values of ratio  $X = b/a$ 

$X$	$I_{A'}$	$I_A$
1	1.571	2.011
0.75	1.099	0.639
0.50	0.828	0.475

Table 3

Values of the coefficients  $f_A$  and  $k_A$  and comparison of the potentials  $\Phi_A$  for different shapes of pores for the system carbon—benzene

T	$X$	$f_A$	$k_A$ kJ nm <sup>3</sup> mol <sup>-1</sup>	$\frac{f_A}{f_A^+}$	$\frac{\Phi_A - \Phi_A^+}{\Phi_A^+}$
11	1	0.881	4.403	1	0
21	0.75	0.544	2.719	0.617	-0.383
	0.50	0.450	2.249	0.511	-0.489
51		0.333	1.666	0.378	-0.622
31		1.059	5.294	1.203	+0.203
13		0.809	4.045	0.919	-0.081
33		0.988	4.938	1.122	+0.122
43		1.333	6.664	1.514	+0.514

The above tables display an obvious influence of the pore shapes on the value of the adsorption potential.

### Relation between the volumes and surfaces of pore

On the basis of the geometrical idea of the pore shapes the relation between the surface and volumes of pores may be defined. Further of models presented in Fig. 1 and being under consideration are two extreme cases of the pores, i.e. the pores the height of which is considerably superior to the value of the parameter  $q$  ( $v \gg q$ ) and those the height of which is equal to the value of the parameter  $q$  ( $v = q$ ). In the first case in the ratio  $S_i/W_i$  instead of the overall surface only the surface of the jacket is taken into consideration. In the second case ( $v = q$ ) to which the spherical pore model also pertains, the overall surface should be considered.

For pores of elliptic cross section the areas of these sections are given by the formula  $P = \pi ab$  and the perimeter  $o = aE_e$  where  $a$  and  $b$  are the semiaxes of ellipses and  $E_e$  is the tabulated complete elliptic integral of the second kind [8]

$$E_e = 4 \int_0^{\pi/2} \sqrt{1 - \varepsilon_e^2 \sin^2 \varphi} \, d\varphi \quad (36)$$

For the presupposed models of the pore shapes given in Table 1 ( $v \gg q$  or  $v = q$ ) the relation between the pore surface and volume (3) may be expressed by

$$\frac{S_i}{W_i} = \frac{B}{q} \quad (37)$$

For pores of elliptic cross sections the relation  $B = E_e/\pi$  is valid. Table 4 presents the values of the shape factor  $B$  for individual models.

Table 4

Shape factor  $B$  of different shapes of pores.  $E_e$  denotes the elliptical integral value

T	X	q	B	$E_e$
11	1	b	2	2
21	0.9	b	1.9	5.9732
21	0.8	b	1.805	5.6723
21	0.75	b	1.759	5.5258
21	0.7	b	1.712	5.3824
21	0.6	b	1.622	5.1054
21	0.5	b	1.538	4.8442
21	0.4	b	1.465	4.6026
21	0.3	b	1.396	4.3859
21	0.25	b	1.365	4.2892
31	1	r	2	
51	—	$\frac{L}{2}$	1	
13	1	r	2.5	
33	1	r	2.4	
43	—	$r_s$	3	

### Structural characteristics

The experimental isotherm, knowledge of the adsorption potential and its relation to the differential molar work, and relation between the surfaces and volumes of pores enable us to express the individual structural characteristics. When considering relations (12), (14), (16), (19), and (20) in order to express basic eqns (1), (2), and (3), the individual structural characteristics are defined by the expressions

$$W_0 \dots \text{experimental value} \quad (38)$$

$$\frac{1}{W_0} W = \exp [ - (k_s/E)^n q^{-3n} ] \quad (39)$$

$$\frac{1}{W_0} \frac{dW}{dq} = KqE_k \quad (40)$$

$$\frac{1}{W_0} \frac{dS}{dq} = BKE_k \quad (41)$$

$$\frac{1}{W_0} S = BK \int_{q_n}^{q_a} E_k dq \quad (42)$$

$$\frac{1}{W_0} S_0 = BK \int_{q_n}^{q_x} E_k dq \quad (43)$$

$$q_{wm} = K/(3n + 1)^{\frac{1}{3n}} \quad (44)$$

$$q_{sm} = K/(3n + 2)^{\frac{1}{3n}} \quad (45)$$

The expression for the characteristic of  $S$  (43) in the integration in the range  $q_n = 0$ ,  $q_x = \infty$  acquires the form according to [7]

$$\frac{1}{W} S_M = B \left( \frac{E}{k_A} \right)^{\frac{1}{3}} \Gamma \left( 1 + \frac{1}{3n} \right) \quad (46)$$

The interpretation of expressions  $K$  and  $E_k$  is

$$K = 3n(k_A/E)^n \quad (47)$$

$$E_k = \exp [ - (k_A/E)^n q^{-3n} ] q^{-3n-2} \quad (48)$$

In order to compare the influence of the presupposed model of pore shapes on the individual structural characteristics, we used for expressing the relative values of these characteristics ( $H$ ) the designation

$$H_r = H/H^+ \quad (49)$$

$$\Delta H = H_r - 1 \quad (50)$$

where  $H^+$  is the value of the characteristic for the basic model (T-11).

On the basis of theoretical assumptions on the adsorption forces and on the course of adsorption, the influence of the pore shapes on the individual characteristics is shown in this study. The change of the model results in the change of the values  $k_A$  and  $B$  and due to this the majority of the structural characteristics are changed as well. In order to compare the changes of the characteristics, a model (T-11) was used as a basis. The relative characteristics may be expressed by the following equations

$$W_{or} = 1 \quad (51)$$

$$W_r = \exp \left\{ -\frac{1}{E^n} q^{-3n} [(k_A)^n - (k_A^+)^n] \right\} \quad (52)$$

$$W'_r = W_r k_{A_r}^n \quad (53)$$

$$S'_r = W_r k_{A_r}^n B_r \quad (54)$$

$$S_r = k_{A_r}^n B_r \frac{\int_{q_n}^{q_q} E_k dq}{\int_{q_n}^{q_q} E_k^+ dq} \quad (55)$$

$$S_{or} = k_{A_r}^n B_r \frac{\int_{q_n}^{q_x} E_k dq}{\int_{q_n}^{q_x} E_k^+ dq} \quad (56)$$

$$(q_{wm})_r = k_{A_r}^{\frac{1}{3}} \quad (57)$$

$$(q_{sm})_r = k_{A_r}^{\frac{1}{3}} \quad (58)$$

$$S_{Mr} = k_{A_r}^{-\frac{1}{3}} B_r \quad (59)$$

$$S_{M-o} = \frac{S_M}{S_0} = \frac{\frac{1}{3n} \left( \frac{E}{k_A} \right)^{n+\frac{1}{3}} \Gamma \left( 1 + \frac{1}{3n} \right)}{\int_{q_n}^{q_x} E_k dq} \quad (60)$$

## Discussion

The interpretation of adsorption isotherms is dependent, besides the accepted theory of adsorption, on the model idea of the geometrical shapes of pores. The pore shape is applied in the determination of the adsorption potential  $\Phi_A$  and also in the relation between the pore surface and its volume, which is expressed for the pore shapes under consideration by the value of the coefficient  $B$ . The value of the adsorption potential, which is for the given adsorbent—adsorbate system a function of the coefficient ( $q$ ), is characterized by the value of the coefficient  $k_A$  or  $f_A$ . On a comparable basis Table 1 indicates the expression of the adsorption potential for the individual models of pore shapes. The values  $k_A$  given in Table 3 show, in comparison with those presented by *De Boer* and *Custers* [4] for the types (T-31 and T-43), variability in dependence on the pore shape. Here the cylindrical pore flattening is very obvious. The comparison of the values of the potential for

different models, presented in Table 3, is independent of the pore size. The adsorption potential for increasing flattening decreases and attains the highest relative value for the spherical pore (T-43) and the lowest one for the slit-like pores and a very flattened cylindrical pore with a flat bottom. The shape factor  $B$  displaying the value  $B = 2$  (T-11) for the cylindrical pores of circular section, shows the values  $B = 3$  and  $B = 1$  for the spherical pores (T-43) and for the slit-like ones (T-51), respectively. The values of the factor  $B$  for other models range between the values 1 and 3. With the cylindrical pore of elliptic section the value  $B$  decreases with increasing flattening. The course of the structural characteristics in dependence on the value of the parameter  $q$  for selected types of the model (T-11; T-21,  $X = 0.5$ ; T-31; T-43) reveals strong effects of the presupposed model of pore shapes upon the individual characteristics. The comparison for  $q \in \langle 0.4; 1.6 \rangle$  and  $E = 20 \text{ kJ mol}^{-1}$  is presented in Table 5, indicating the overall effects of the presupposed model of pores on the course of the characteristics. Whilst in the expressions for the distribution of the volume ( $W, W'$ ) only the coefficient  $k_A$  is obvious, in the expressions for the surface distribution besides the coefficient  $k_A$  the coefficient  $B$  is also apparent. The course of the distribution curves of the volume  $W' = W'(q)$  and of the surface  $S' = S'(q)$  as well is considerably influenced by the model of the pores applied.

For the cumulative curves  $W = W(q)$  and  $S = S(q)$  the deviations  $W$  and  $S$  for the lower values of the parameter  $q$  are more important. In case of the values of the parameter  $q$  close to the value of 1.6 nm quantity  $\bar{W}$  draws near the value  $\bar{W} = 1$  for all the models. The values  $\bar{S}$  for  $q = 1.6$  are different for the four models presented in Table 5. Table 6 presents the relative values of the specific surface  $S_{M-r}$ , the characteristic parameter  $q_{m-r}$ , and also the relative values of the factors obvious as partial multiple coefficients in the relative characteristics. This comparison is demonstrated for nine models of the pore shape and enables us to observe partial effects of individual coefficients on the structural characteristics. Table 7 presents the values of the relative characteristics in three points of the interval observed. The total value of the specific surface as an important structural characteristic is evaluated in Table 8. The specific surface is for all the four selected models evaluated as the characteristic  $\bar{S}_0$  obtained by integration in the interval  $q \in \langle 0.4; 1.6 \rangle$  nm and as the characteristic  $\bar{S}_M$  obtained by integration  $q \in \langle 0; \infty \rangle$ . As Table 8 indicates, both the characteristics are in good agreement. The values of the relative deviations ( $\Delta S_{M-0}$ ) attain the values 0.2%; 9%; -5.8% and -2.4% for the types T-11, T-21, T-31, and T-43, respectively. The relative deviation of the value of the specific surface ( $\Delta \bar{S}_M$ ) when changing the pore model applied attains the highest value for the spherical model (T-43) +31%, for the cylindrical pore with spherical bottom (T-31) -6%, and for the cylindrical pore of elliptic section T-21 ( $X = 0.5$ ) -3.8%. The values  $S_{M-r}$  for further models of the pore shape are given in Table 6. The characteristic parameters  $q_{wm}$  and  $q_{sm}$ , indicating

Table 5

Course of the structural characteristics  $\bar{W}' = W'/W_0$ ,  $\bar{W} = W/W_0$ ,  $\bar{S}' = S'/W_0$ ,  $\bar{S} = S/W_0$  for the adsorption isotherm ( $E = 20 \text{ kJ mol}^{-1}$ ,  $n = 2$ )  
 $\bar{W}'$  [ $\text{nm}^{-1}$ ],  $\bar{W}$ ,  $\bar{S}'$  [ $\text{nm}^{-2}$ ],  $\bar{S}$  [ $\text{nm}^{-1}$ ]

T	X	$\bar{H}_A$	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.3	1.6
11	1	$\bar{W}'$	0.001	1.676	3.676	2.338	1.152	0.555	0.277	0.046	0.011
		$\bar{W}$	$7 \times 10^{-6}$	0.045	0.354	0.663	0.831	0.913	0.953	0.990	0.997
		$\bar{S}'$	0.006	6.705	12.254	6.680	2.880	1.233	0.554	0.070	0.013
		$\bar{S}$	0	0.219	1.296	2.249	2.727	2.933	2.960	3.054	3.066
21	0.5	$\bar{W}'$	2.113	4.323	2.067	0.827	0.345	0.155	0.075	0.012	0.003
		$\bar{W}$	0.046	0.445	0.763	0.898	0.953	0.976	0.987	0.997	0.999
		$\bar{S}'$	8.125	13.299	5.298	1.818	0.663	0.265	0.115	0.014	0.003
		$\bar{S}$	0	1.284	2.173	2.503	2.626	2.672	2.691	2.711	2.713
31		$\bar{W}'$	$1 \times 10^{-5}$	0.607	3.345	2.815	1.535	0.771	0.392	0.066	0.016
		$\bar{W}$	$4 \times 10^{-5}$	0.011	0.223	0.551	0.765	0.876	0.932	0.986	0.995
		$\bar{S}'$	$5 \times 10^{-5}$	2.428	11.149	8.041	3.836	1.712	0.784	0.102	0.019
		$\bar{S}$	0	0.066	0.805	1.806	2.340	2.677	2.802	2.934	3.067
43		$\bar{W}'$	$7 \times 10^{-9}$	0.070	2.203	3.148	2.079	1.130	0.596	0.104	0.025
		$\bar{W}$	$2 \times 10^{-12}$	0.001	0.093	0.389	0.655	0.811	0.895	0.977	0.993
		$\bar{S}'$	$5 \times 10^{-9}$	0.420	11.018	13.491	7.799	3.766	1.788	0.240	0.046
		$\bar{S}$	0	0.001	0.513	1.845	2.909	3.488	3.766	4.070	4.112

Table 6

Values of the relative characteristics  $S_{M-r}$ ,  $q_{m-r}$  and factors  $k_r$ ,  $B_r$ .  
 $S_{M-r}$  denotes the relative value of specific surface  $S_M$ ,  $q_{m-r}$  denotes the relative value of parameter  $q_m$   
 for adsorption isotherm ( $E = 20 \text{ kJ mol}^{-1}$ ,  $n = 2$ )

T	X	$k_r^2$	$B_r$	$B_r k_r^2$	$k_r^{-1/3}$	$S_{M-r}$	$q_{m-r}$
11	1	1	1	1	1	1	1
21	0.75	0.381	0.880	0.335	1.175	1.034	0.851
21	0.50	0.261	0.769	0.201	1.251	0.962	0.799
31		1.447	1	1.447	0.940	0.940	1.064
51		0.143	0.5	0.071	1.383	0.692	0.723
13		0.845	1.25	1.056	1.029	1.286	0.972
33		1.259	1.2	1.511	0.962	1.155	1.039
43		2.292	1.5	3.438	0.871	1.306	1.148

Table 7

Values of the relative characteristics  $W_r$ ,  $W'_r$ ,  $S'_r$ ,  $S_r$  for the adsorption isotherm  
 ( $E = 20 \text{ kJ mol}^{-1}$ ,  $n = 2$ )

T	X	$q$ [nm]	$W_r$	$W'_r$	$S'_r$	$S_r$
11	1	$q$	1	1	1	1
21	0.5	0.5	9.889	2.579	1.983	5.863
		1.0	1.036	0.271	0.208	0.909
		1.6	1.002	0.273	0.231	0.885
31		0.5	0.244	0.353	0.511	0.302
		1.0	0.978	1.415	2.048	0.947
		1.6	0.988	1.444	2.090	1.0003
43		0.5	0.018	0.041	0.142	0.071
		1.0	0.939	2.152	7.401	1.272
		1.6	0.996	2.283	7.850	1.341

the position of maximum on the distribution curves of both the volume and the surface area range between the values 0.47 and 0.68 nm ( $q_{wm}$ ) and 0.46 and 0.66 nm ( $q_{sm}$ ) for the four selected models. The difference between the values  $q_{wm}$  and  $q_{sm}$  for all the models is negligible.

The foregoing comparison reveals that the results of the structure analysis of microporous substances are dependent on the image of the model shape of pores. The course of the distribution curves of the volume and surface area of pores, derived from the adsorption isotherm is thus substantially influenced. The different

Table 8

Comparison of the specific surfaces  $\bar{S}_0$  and  $\bar{S}_M$  and characteristic parameters  $q_{wm}$ ,  $q_{sm}$  for different shapes of pores for the adsorption isotherm ( $E = 20 \text{ kJ mol}^{-1}$ ,  $n = 2$ )

T	X		$\bar{S}_0$ nm <sup>-1</sup>	$\bar{S}_M$ nm <sup>-1</sup>	$S_{M-o}$	$q_{wm}$ nm	$q_{sm}$ nm
11.	1	$\bar{H}$	3.066	3.073	0.002	0.589	0.576
		$\Delta H$	0	0	—	0	0
21	0.5	$\bar{H}$	2.713	2.956	0.090	0.470	0.460
		$\Delta H$	-0.115	-0.038	—	-0.201	-0.201
31		$\bar{H}$	3.068	2.890	-0.058	0.626	0.612
		$\Delta H$	0.001	-0.060	—	0.064	0.064
43		$\bar{H}$	4.112	4.015	0.024	0.676	0.661
		$\Delta H$	0.341	0.306	—	0.148	0.148

$$S_0 = \bar{S}_0 W_0 \times 10^3; S_{M-o} = (\bar{S}_M - \bar{S}_0) / \bar{S}_0.$$

$$S_0 [\text{m}^2 \text{g}^{-1}], \bar{S}_0 [\text{nm}^{-1}], W_0 [\text{cm}^3 \text{g}^{-1}].$$

results of evaluating the structure of material may probably be explained in some cases on the basis of the shape dependence. The values of the specific surface  $S_M$  show to be in good agreement with the values  $S_0$ .

The choice of the model idea of the shape of pores in evaluating the adsorption isotherm for the structure analysis should be based on the ascertained pore shape by using an independent method.

The use of expression (20) for expressing the potential of the adsorption forces, not covering the influence of the repulsive forces, as well as the determination of the value of this potential at the bottom of the pore centre [4, 9—12] only approximates the characterization of the space distribution of the potential of the adsorption forces. We also used this simplified approach in investigating the influence of the model of pore shapes on the results of the structural analysis of micropores. We suppose that for microporous substances with micropore radii of 0.4 to 1.6 nm, with which the influence of the repulsive forces is obvious but not prevailing, this approximation may offer an opinion on the influence of the pore shapes upon the characterization of these substances.

Our next work will be aimed at calculating the influence of the applied model of the pore shapes upon the structural characterization of microporous substances, including the influence of the repulsive forces and the space distribution of the potential of the adsorption forces.

## Symbols

$a$	shorter semiaxis of the elliptical cross section	[nm]
$A$	differential molar work of adsorption — thermodynamic potential	[J mol <sup>-1</sup> ]
$b$	longer semiaxis of the elliptical cross section	[nm]
$B$	shape factor	
$C_A$	constant of eqn (20)	[kJ nm <sup>6</sup> mol <sup>-1</sup> ]
$E_c$	value of elliptical integral	
$E$	coefficient of eqn (12)	[kJ mol <sup>-1</sup> ]
$E_k$	expression determined by eqn (48)	[nm <sup>-3n-2</sup> ]
$f_A$	coefficient of eqn (29)	
$H$	comprehensive indication of structural quantities	
$I_A, I_{A_j}$	value of integral from eqns (32), (33)	
$J_A$	value of integral from eqn (31)	
$k_A$	coefficient of eqn (28)	[kJ nm <sup>3</sup> mol <sup>-1</sup> ]
$K$	coefficient determined by eqn (47)	[nm <sup>3n</sup> ]
$L$	distance between walls of a slit-like pore	[nm]
$n$	coefficient of eqn (12)	
$N$	number of adsorbent atoms in the volume unit	[nm <sup>-3</sup> ]
$p$	equilibrium pressure of adsorbate vapours	[Pa]
$p_s$	pressure of saturated vapours	[Pa]
$p_u$	equilibrium pressure in the region of heterogeneity	[Pa]
$q$	parameter characterizing the dimension of a pore — argument of distribution function	[nm]
$q_n$	lower limit	[nm]
$q_u$	upper limit determined by value $q$	[nm]
$q_x$	upper limit	[nm]
$Q$	variable value of limit	[nm]
$q_{sm}$	value of $q$ determined by eqn (11)	[nm]
$q_{wm}$	value of $q$ determined by eqn (10)	[nm]
$q_{m-r}$	relative value of $q_{sm}$ and $q_{wm}$	
$r$	radius of a cylinder	[nm]
$r_0$	equilibrium distance of the adsorbed molecule from the surface of solids	[nm]
$r_s$	radius of a sphere	[nm]
$R$	gas constant	[J K <sup>-1</sup> mol <sup>-1</sup> ]
$R$	distance of two interacting force centres	[nm]
$S$	specific surface from eqn (42)	[nm <sup>2</sup> g <sup>-1</sup> ]
$S_0$	limiting specific surface from eqn (43)	[nm <sup>2</sup> g <sup>-1</sup> ]
$S_M$	limiting specific surface from eqn (46)	[nm <sup>2</sup> g <sup>-1</sup> ]
$t$	parameter of ellipse	
$T$	temperature	[K]
$T$	type of pore shape	

$v$	height of a pore	[nm]
$V$	volume of adsorbent	[nm <sup>3</sup> ]
$W$	adsorption volume	[nm <sup>3</sup> g <sup>-1</sup> ]
$W_0$	limiting adsorption volume	[nm <sup>3</sup> g <sup>-1</sup> ]
$X$	parameter $X = b/a$	
$\Gamma$	gamma function	
$\epsilon_e$	numerical excentricity	
$\eta$	potential of intermolecular forces	[J mol <sup>-1</sup> ]
$\vartheta$	spherical coordinate	[°]
$\varrho$	cylindrical coordinate	[nm]
$\varphi$	spherical or cylindrical coordinate	[°]
$\Phi$	potential energy of adsorbate molecule	[J mol <sup>-1</sup> ]
$\tilde{\psi}$	angle (see Fig. 2)	[°]
$\Phi_p$	component of adsorption potential	[J mol <sup>-1</sup> ]
$\Phi_s$	adsorption potential of a spherical pore	[J mol <sup>-1</sup> ]
$\Phi_A$	adsorption potential according to eqn (20)	[J mol <sup>-1</sup> ]

### Indices

m	maximum value
r	relative value ( $H_r = H/H^+$ )

### Exponents

'	derivative of the first order
"	derivative of the second order
-	variable related to value $W_0(\tilde{H} = H/W_0)$
+	variable for basic type of pore shape (T-11)

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