Determination of Curves Characterizing the Texture of Microporous Adsorbents

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Abstract. The possibility of determining the curves characterizing the texture of microporous absorbents on the ground of the Dubinin–Stoeckli (DS) equation has been discussed. The DS equation has been shown not to have any universal character. A more general equation of the adsorption isotherm including all cases of isotherms encountered in adsorption studies has been derived.

Key words. microporous adsorbent, adsorption isotherm general equation

1. Introduction

In the theoretical studies of adsorption, more and more attention is being paid to the texture of microporous adsorbents. The most important and difficult problem is the determination of the curve of a physical nature characterizing the distribution of micropore volumes with respect to their radii. Recently, a concept based on the general equation of the adsorption isotherm for systems of heterogeneous microporous structure [1–3]

$$W(y) = \int_0^\infty f(B) \exp(-B \cdot y) \, dB \tag{1}$$

where: $y = (T/\beta)^2 \cdot \log^2(p_s/p)$; W is the volume of the liquid-like adsorbate filling the micropores at relative pressure p/p_s and temperature T; $f(B)$ is the distribution function of micropore volume with respect to B (B is the parameter appearing in the DR [4, 5] equation) and β is a constant characterizing the adsorbate. This equation is found to have the greatest acceptance and interest.

When a Gaussian shape of the function $f(B)$ is assumed, equation (1) leads to the DRS [3] equation. The following modification of the equation dealing with the determination of the curve of micropore volume distribution has been proposed by Dubinin in the form of the so-called Dubinin-Stoeckli equation (DS) [6].

The aims of this paper are: to analyse the DS equation on the basis of our studies of the adsorption of apolar and polar substances on active carbons, to draw attention to the necessity of including the range of micropore dimension variability and, finally, to propose a new form of the modified DS equation including possibly all cases of isotherms encountered in adsorption studies.

2. Theory

In accordance with Dubinin's [6] considerations, the DRS equation has an applicability limited to a fairly narrow range of micropore size dispersion. Taking account of this fact and based on the slit-like model of micropores, Dubinin [6–10] has introduced into

equation (1) the changed form of the Gaussian function $f(B)$

$$f(x) = \frac{dW_0}{dx} = \frac{W_0}{\delta\sqrt{2\pi}} \cdot \exp\left[-\frac{(x_0 - x)^2}{2\delta^2}\right] \tag{2}$$

where: $x = \chi/E_0$ are the slit half-widths approximately proportional to the radii of inertia of the slits R_i (E_0 is the characteristic energy of adsorption from the DA [11] equation (for exponent $n = 2$)); χ is 12.0 kJ nm/mol; x_0 is the micropore half-width at the distribution curve maximum and δ is the dispersion.

With the above assumption, the solution of an analogous equation (1) possessing the characteristic parameter x leads to the known form of the DS equation [6–10].

$$W = \frac{W_0}{2\sqrt{1 + 2m\delta^2 A^2}} \cdot \exp\left(-\frac{mx_0^2 \cdot A^2}{1 + 2m\delta^2 A^2}\right)\left[1 + \operatorname{erf}\left(\frac{x_0}{\delta\sqrt{2}\sqrt{1 + 2m\delta^2 A^2}}\right)\right] \tag{3}$$

where: $m = (1/\beta\chi)^2$ and $A = RT \ln(p_s/p)$ is the differential molar work of adsorption.

Equation (3) does not include those cases where the exponent n from the DA equation has a value higher than 2. As it has been shown in our earlier paper [12], active carbons can have $n > 2$ similar to zeolites for which the exponent n has values within the range of 2 to 6. For such cases we propose the following modification of the DS equation [13]:

$$W = \frac{W_0}{2\sqrt{1 + 2m^{n/2}\delta^n A^n}} \cdot \exp\left(-\frac{m^{n/2}x_0^n A^n}{1 + 2m^{n/2}\delta^n A^n}\right)$$
$$\times \left[1 + \operatorname{erf}\left(\frac{x_0^{n/2}}{\delta^{n/2}\sqrt{2}\sqrt{1 + 2m^{n/2}\delta^n A^n}}\right)\right] \tag{4}$$

where n is a constant integer parameter.

The function of the micropore volume distribution with respect to their radii corresponding to equation (4) has the form:

$$f(x) = \frac{W_0 n x^{(n/2)-1}}{2\delta^{n/2}\sqrt{2\pi}} \cdot \exp\left[-\frac{(x^{n/2} - x_0^{n/2})^2}{2\delta^n}\right] \tag{5}$$

3. Experimental

The measurements were made on active carbons A, B, D and E prepared from chemically pure saccharose. The detailed preparation of carbons and their texture parameters are given in previous papers [14–16]. Adsorption isotherms of spectroscopically pure benzene [17, 18], aliphatic alcohols (MeOH, EtOH) [12, 19], and chemically pure aliphatic amines (MeNH$_2$, Me$_2$NH) [20, 21] were determined using a vacuum apparatus equipped with a MacBain balance. In the case of aliphatic amines the adsorbent was first presaturated with amine. No chemisorption was observed for such pretreated active carbons and the adsorbents were suitable for the measurements of physical adsorption of amines.

Example isotherms of benzene and alcohol adsorption are presented in Figure 1. The data dealing with characteristics of the isotherms are given in Table I.

4. Results and Discussion

The shape of the function $f(B)$ from equation (1) can be significantly influenced by the range of the parameter B's variability. Dubinin [3, 6] has shown, however, that in the case
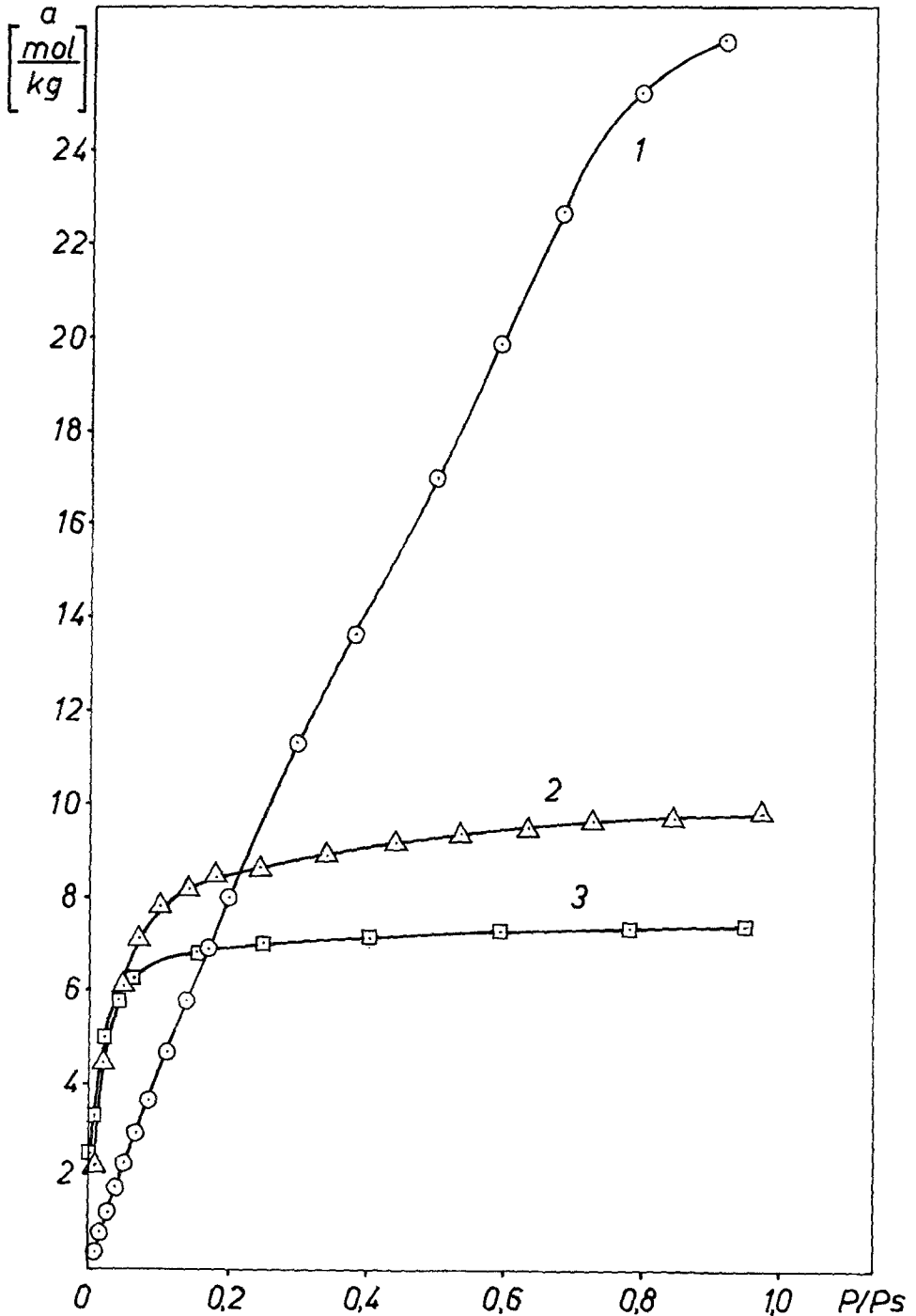
Fig. 1. Isotherms of benzene and alcohol adsorption. 1 – methanol on carbon E; 2 – ethanol on carbon B; 3 – benzene on carbon D.

Table I.   The characteristic of the adsorption measurements
for the studied systems ($T = 298.2$ K).

System	p/p_s		a [mol/kg]	
	from	to	from	to
(A)C_6H_6	0.00020	0.945	1.10	2.37
(B)C_6H_6	0.00060	0.950	2.61	5.96
(D)C_6H_6	0.00060	0.947	2.19	7.40
(E)C_6H_6	0.00023	0.940	0.67	10.99
(A)MeOH	0.00028	0.914	0.22	6.68
(B)MeOH	0.00028	0.914	0.19	15.05
(D)MeOH	0.00028	0.914	0.14	16.77
(E)MeOH	0.00028	0.914	0.14	26.38
(A)EtOH	0.00039	0.970	0.64	4.45
(B)EtOH	0.00039	0.970	0.46	9.83
(D)EtOH	0.00039	0.970	0.29	11.96
(E)EtOH	0.00039	0.970	0.24	18.16
(A)$MeNH_2$	0.00014	0.171	1.85	5.21
(B)$MeNH_2$	0.00037	0.171	1.84	10.75
(D)$MeNH_2$	0.00037	0.171	1.95	12.13
(E)$MeNH_2$	0.00037	0.171	1.51	10.87
(A)Me_2NH	0.00015	0.197	1.48	3.13
(B)Me_2NH	0.00015	0.197	1.95	7.54
(D)Me_2NH	0.00015	0.197	1.76	9.25
(E)Me_2NH	0.00015	0.197	1.24	9.17

of benzene only the micropores of dimensions $0.25 < x < 1.6$ nm have a physical nature.
As the dependence between the parameter x and B is [3, 22]:

$$x = \text{const} \cdot \sqrt{B} \qquad (6)$$

then including the range of variability of x results in the following distribution of the $f(x)$
function described in equation (2)

$$f(x) = \frac{2W_0^N \exp\left[-\dfrac{(x - x_0)^2}{2\delta^2}\right]}{\delta\sqrt{2\pi}\left[\text{erf}\left(\dfrac{x_0 - x_{\min}}{\delta\sqrt{2}}\right) + \text{erf}\left(\dfrac{x_{\max} - x_0}{\delta\sqrt{2}}\right)\right]} \quad ; \quad x_{\min} < x < x_{\max}$$

$$f(x) = 0 \qquad\qquad\qquad\qquad\qquad ; \quad x \leqslant x_{\min} \text{ or } x \geqslant x_{\max} \qquad (7)$$

This expression contains the normalized function $f(x)$ satisfying the necessary condition

$$\frac{1}{W_0^N} \cdot \int_0^\infty f(x)\, \mathrm{d}x = 1 \qquad (8)$$

The form of the isotherm equation corresponding to the function described with equation (7) is

$$W = \frac{W_0^N \exp\left(-\frac{mA^2x_0^2}{z}\right)\left[\operatorname{erf}\left(\frac{x_0}{\delta\sqrt{2}\sqrt{z}} - \frac{x_{min}\sqrt{z}}{\delta\sqrt{2}}\right) + \operatorname{erf}\left(\frac{x_{max}\sqrt{z}}{\delta\sqrt{2}} - \frac{x_0}{\delta\sqrt{2}\sqrt{z}}\right)\right]}{\sqrt{z}\left[\operatorname{erf}\left(\frac{x_0 - x_{min}}{\delta\sqrt{2}}\right) + \operatorname{erf}\left(\frac{x_{max} - x_0}{\delta\sqrt{2}}\right)\right]}$$

(9)

where: $z = 1 + 2m\delta^2 A^2$.

Next, the same range included in equation (5) results in the dependence

$$f(x) = \frac{nW_0^N x^{(n/2) - 1}\exp\left[-\frac{(x^{n/2} - x_0^{n/2})^2}{2\delta^n}\right]}{\delta^{n/2}\sqrt{2\pi}\left[\operatorname{erf}\left(\frac{x_0^{n/2} - x_{min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right) + \operatorname{erf}\left(\frac{x_{max}^{n/2} - x_0^{n/2}}{\delta^{n/2}\sqrt{2}}\right)\right]} \quad ; \quad x_{min} < x < x_{max}$$

$$f(x) = 0 \quad ; \quad x \leqslant x_{min} \text{ or } x \geqslant x_{max}$$

(10)

Table II. The parameters of structural heterogeneity obtained from equations (3), (4), (9) and (11) for carbon A.

Adsorbate	n	Eq.	x (nm)	x_0 (nm)	δ (nm)	W_0^N (dm³/kg)	W_0 (dm³/kg)	DC
C_6H_6	2	3, 4	$0, \infty$	0.52572	0.00000	0.241	0.241	0.99396
	2	9, 11	x_{min}, x_{max}	0.52572	0.00001	0.241	0.241	0.99396
	3	4	$0, \infty$	0.49447	0.20655	0.207	0.207	0.99800
	3	11	x_{min}, x_{max}	0.49222	0.21448	0.208	0.210	0.99802
MeOH	2	3, 4	$0, \infty$	0.53491	0.00000	0.298	0.298	0.99516
	2	9, 11	x_{min}, x_{max}	0.53491	0.00002	0.298	0.298	0.99516
	3	4	$0, \infty$	0.49582	0.21033	0.242	0.242	0.99748
	3	11	x_{min}, x_{max}	0.49301	0.21692	0.242	0.246	0.99746
EtOH	2	3, 4	$0, \infty$	0.51922	0.00000	0.265	0.265	0.99438
	2	9, 11	x_{min}, x_{max}	0.51922	0.00000	0.265	0.265	0.99438
	3	4	$0, \infty$	0.50281	0.23624	0.230	0.231	0.99693
	3	11	x_{min}, x_{max}	0.49428	0.25423	0.231	0.241	0.99701

$$W_0 = \frac{2W_0^N}{\operatorname{erfc}\left(-\frac{x_0^{n/2}}{\delta^{n/2}\sqrt{2}}\right)} \quad ; \quad (0, \infty)$$

$$W_0 = \frac{2W_0^N}{\operatorname{erf}\left(\frac{x_0^{n/2} - x_{min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right) + \operatorname{erf}\left(\frac{x_{max}^{n/2} - x_0^{n/2}}{\delta^{n/2}\sqrt{2}}\right)} \quad ; \quad (x_{min}, x_{max})$$

$$DC = 1 - \frac{\sum_{i=1}^{N}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{N}(y_i - \bar{y}_i)^2}$$

where: y_i is the dependent variable, $\hat{y}_i$ is the value of the dependent variable approximated by the method of the least squares, $\bar{y}$ is the arithmetic mean value of the dependent variable, and N is the number of pairs of experimental data.

and the corresponding adsorption isotherm

$$
W = \frac{W_0^N \exp\left(-\dfrac{m^{n/2} x_0^n A^n}{z}\right)\left[\operatorname{erf}\left(\dfrac{x_0^{n/2}}{\delta^{n/2}\sqrt{2}\sqrt{z}} - \dfrac{x_{\min}^{n/2}\sqrt{z}}{\delta^{n/2}\sqrt{2}}\right) + \operatorname{erf}\left(\dfrac{x_{\max}^{n/2}\sqrt{z}}{\delta^{n/2}\sqrt{2}} - \dfrac{x_0^{n/2}}{\delta^{n/2}\sqrt{2}\sqrt{z}}\right)\right]}{\sqrt{z}\left[\operatorname{erf}\left(\dfrac{x_0^{n/2} - x_{\min}^{n/2}}{\delta^{n/2}\sqrt{2}}\right) + \operatorname{erf}\left(\dfrac{x_{\max}^{n/2} - x_0^{n/2}}{\delta^{n/2}\sqrt{2}}\right)\right]}
$$

(11)

where: $z = 1 + 2m^{n/2}\delta^n A^n$.

The parameters characterizing the microporous structure of all carbon adsorbents studied have been obtained from equations (3), (4), (9) and (11) and are given in Tables II and III.

The representative functions of micropore volume distributions with respect to their radii corresponding to those parameters are shown in Figure 2.

In accordance with Dubinin and Stoeckli [3] and McEnaney [23], the parameter χ is practically independent of the value of the characteristic energy E_0 for micropores of

Table III. The parameters of structural heterogeneity $n = 2$ obtained from equations (3), (4), (9) and (11) for carbons B, D and E.

| System	x (nm)	x_0 (nm)	δ (nm)	W_0^N (dm^3/kg)	W_0 (dm^3/kg)	DC
B-C$_6$H$_6$	$0, \infty$	0.58772	0.01304	0.576	0.576	0.99988
B-C$_6$H$_6$	$x_{\min}, x_{\max}$	0.58772	0.01304	0.576	0.576	0.99988
D-C$_6$H$_6$	$0, \infty$	0.75435	0.15940	0.682	0.682	0.99947
D-C$_6$H$_6$	$x_{\min}, x_{\max}$	0.75488	0.16153	0.683	0.684	0.99947
E-C$_6$H$_6$	$0, \infty$	0.83598	0.23210	0.533	0.534	0.99914
E-C$_6$H$_6$	$x_{\min}, x_{\max}$	0.84480	0.25617	0.542	0.549	0.99926
B-MeOH	$0, \infty$	0.89188	0.21131	0.895	0.895	0.99622
B-MeOH	$x_{\min}, x_{\max}$	0.89308	0.21528	0.897	0.898	0.99616
D-MeOH	$0, \infty$	1.07530	0.28778	1.0406	1.0407	0.99760
D-MeOH	$x_{\min}, x_{\max}$	1.10217	0.30906	1.1025	1.0402	0.99754
E-MeOH	$0, \infty$	1.10862	0.33818	0.645	0.645	0.99833
E-MeOH	$x_{\min}, x_{\max}$	1.21593	0.41357	0.648	0.796	0.99831
B-EtOH	$0, \infty$	0.74916	0.13324	0.690	0.690	0.99453
B-EtOH	$x_{\min}, x_{\max}$	0.74908	0.13332	0.689	0.690	0.99453
D-EtOH	$0, \infty$	0.98931	0.24987	0.908	0.908	0.99664
D-EtOH	$x_{\min}, x_{\max}$	0.99645	0.25935	0.912	0.923	0.99661
E-EtOH	$0, \infty$	1.14986	0.35335	0.736	0.737	0.99695
E-EtOH	$x_{\min}, x_{\max}$	1.29511	0.44668	0.718	0.968	0.99703
B-MeNH$_2$	$0, \infty$	0.46044	0.16640	0.603	0.605	0.99841
B-MeNH$_2$	$x_{\min}, x_{\max}$	-4.7448	1.09288	0.588	241822.8	0.99433
D-MeNH$_2$	$0, \infty$	0.53139	0.21599	0.700	0.705	0.99678
D-MeNH$_2$	$x_{\min}, x_{\max}$	-6.93776	1.47579	0.644	1164273.	0.98846
E-MeNH$_2$	$0, \infty$	0.49582	0.19396	0.470	0.472	0.99301
E-MeNH$_2$	$x_{\min}, x_{\max}$	-4.03734	0.93953	0.379	150714.6	0.98474
B-Me$_2$NH	$0, \infty$	0.45857	0.09363	0.536	0.536	0.99446
B-Me$_2$NH	$x_{\min}, x_{\max}$	0.45430	0.10189	0.564	0.577	0.99448
D-Me$_2$NH	$0, \infty$	0.56974	0.19645	0.689	0.690	0.99642
D-Me$_2$NH	$x_{\min}, x_{\max}$	0.45779	0.32808	0.712	0.967	0.99658
E-Me$_2$NH	$0, \infty$	0.62073	0.21313	0.582	0.583	0.99019
E-Me$_2$NH	$x_{\min}, x_{\max}$	0.55120	0.42881	0.668	0.889	0.99108
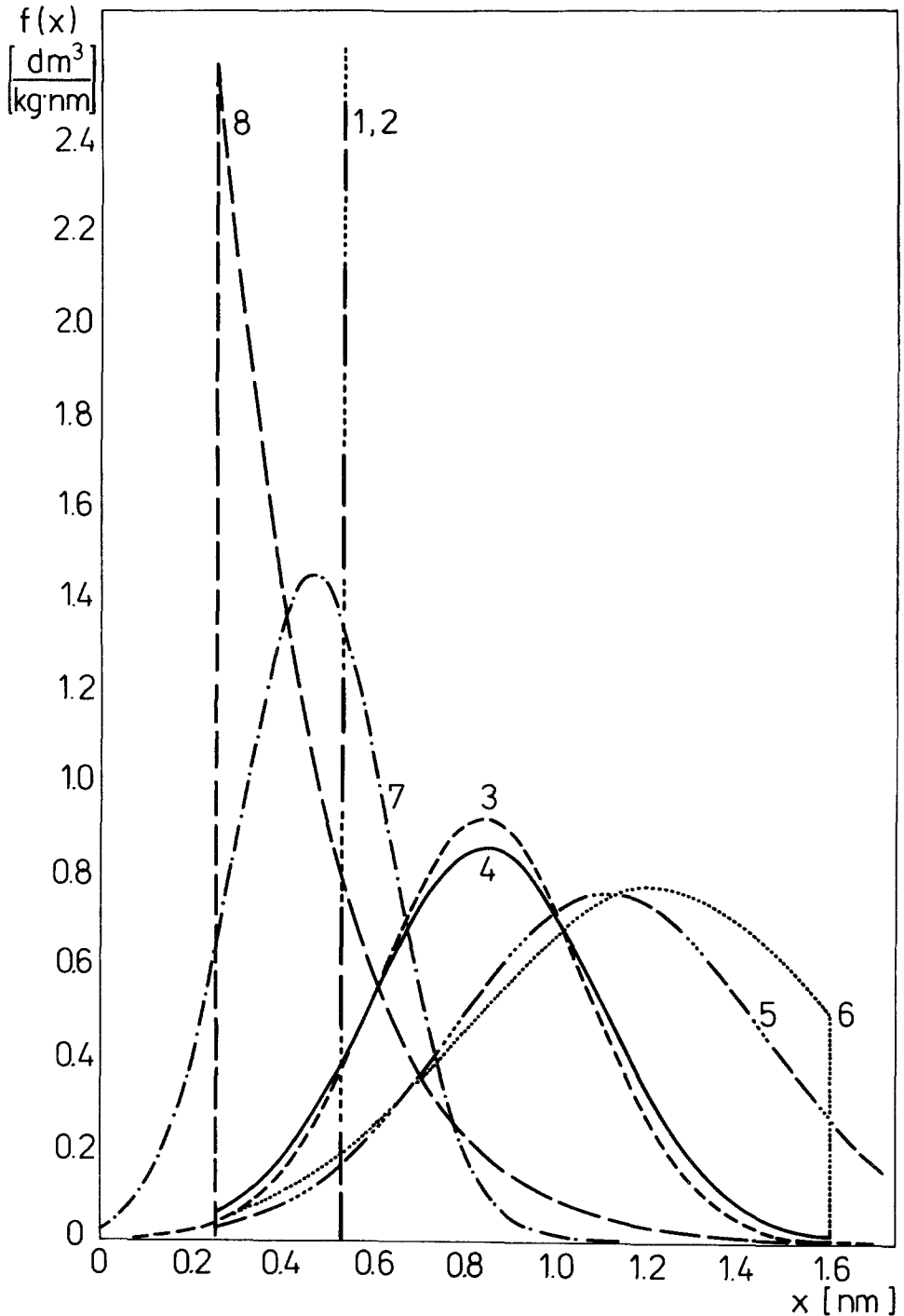
Fig. 2. The curves of micropore volume distribution with respect to their characteristic dimension for the systems studied ($n = 2$). 1 – A-C_6H_6 after eq. (2) or (5); 2 – A-C_6H_6 after eq. (7) or (10); 3 – E-C_6H_6 after eq. (2) or (5); 4 – E-C_6H_6 after eq. (7) or (10); 5 – E-MeOH after eq. (2) or (5); 6 – E-MeOH after eq. (7) or (10); 7 – B-MeNH$_2$ after eq. (2) or (5); 8 – B-MeNH$_2$ after eq. (7) or (10).

dimensions higher than 0.38 nm. Thus the curves in Figure 2 can be distorted only in the case of amines due to the assumption that $\chi = 12$ kJ nm/mol.

The results from Table II show explicitly that the influence of the range of the parameter x's variability on the values of parameters characterizing the texture of micropores depends on the adsorbents studied. In the case of active carbons characterized by great structural heterogeneity and thus by great differentiation of micropore dimensions (sample E), the real range of the parameter x's variability has necessarily to be included. Also the normalization of function $f(x)$ improves the values of parameter W_0 calculated from the isotherm equations. Relatively speaking, the greatest differences, compared to the other results (Table II) are obtained from the measurements of aliphatic amine adsorption. This is most probably due to the necessary pretreatment of carbon samples before the measurements of isotherms of physical adsorption of amines. In such cases the amines are adsorbed firstly at the corners and edges of micropores which thus causes a further narrowing of the pores. This conclusion is also confirmed by the results presented in previous papers [24]. On the other hand, the results from Table II and Figure 1 explicitly prove the limited character of the DS equation for which the function of micropore volume distribution always takes the form of the Dirac function when the parameter n (DA equation) is greater than or equal to 2 (Figure 2). Thus, it can be concluded that the most general equation of adsorption isotherm allowing us to determine the distribution function of micropore volumes for all microporous adsorbents studied is equation (11) and, corresponding to it, the function of micropore volume distribution $f(x)$ (equation (10)).

The functions obtained for the distribution of micropore volumes have a physical nature for micropores of dimensions higher than 0.38 nm.

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References

1. H. F. Stoeckli: *J. Colloid Interface Sci.* **59**, 184 (1977).
2. U. Huber, H. F. Stoeckli and J. Ph. Houriet: *J. Colloid Interface Sci.* **67**, 195 (1978).
3. M. M. Dubinin and H. F. Stoeckli: *J. Colloid Interface Sci.* **75**, 34 (1980).
4. M. M. Dubinin: *Zh. Fiz Khim.* **39**, 1305 (1965).
5. M. M. Dubinin: *Chemistry and Physics of Carbon* (Ed. P. L. Walker Jr.) Vol. 2, pp. 51–120, Marcel Dekker, New York (1966).
6. M. M. Dubinin: *Carbon* **23**, 373 (1985).
7. M. M. Dubinin *et al.*: *Izv. Akad. Nauk SSSR, Ser. Khim.* 255 (1985).
8. M. M. Dubinin and N. S. Polyakov: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1943 (1985).
9. M. M. Dubinin, N. S. Polyakov and E. A. Ustinov: *Izv. Akad. Nauk SSSR, Ser. Khim.* 2680 (1985).
10. M. M. Dubinin and N. S. Polyakov: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1932 (1986).
11. M. M. Dubinin and V. A. Astakhov: *Izv. Akad. Nauk SSSR, Ser. Khim.* 5 (1971).
12. M. Rozwadowski, J. Siedlewski and R. Wojsz: *Carbon* **17**, 411 (1979).
13. R. Wojsz and M. Rozwadowski: *Carbon* (in press).
14. M. Rozwadowski: *Sorption of Aliphatic Alcohols on Active Carbons* (Ed. N. Copernicus University), pp. 1–196, Toruń (1977).
15. M. Rozwadowski: *Chem. Stosow.* **18**, 393 (1974).
16. M. Rozwadowski: *Chem. Stosow.* **18**, 403 (1974).
17. M. Rozwadowski, J. Siedlewski and K. E. Wiśniewski: *Pol. J. Chem.* **55**, 1849 (1981).
18. M. Rozwadowski, K. E. Wiśniewski and R. Wojsz: *Carbon* **22**, 273 (1984).

19. R. Wojsz and M. Rozwadowski: *Z. Phys. Chem.* **132**, 227 (1982).
20. R. Wojsz and M. Rozwadowski: *Pol. J. Chem.* **55**, 2359 (1981).
21. M. Rozwadowski and R. Wojsz: *Pol. J. Chem.* **56**, 159 (1982).
22. M Rozwadowski and R. Wojsz: *Pol. J. Chem.* **58**, 837 (1984).
23. B. McEnaney: *Carbon* **25**, 69 (1987).
24. R. Wojsz and M. Rozwadowski: *Chem. Eng. Sci.* **42**, 2877 (1987).