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Distribution Functions of Structural Heterogeneity of Microporous Adsorbents

Roman Wojsz and **Michał Rozwadowski**

Institute of Chemistry, Nicholas Copernicus University Toruń, PL-87-100 Toruń, Poland

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The distribution functions of structural heterogeneity of microporous adsorbents have given. Influences of adsorbents and adsorbates types on this heterogeneity have been studied.

(Keywords: Active carbons; Adsorption; Distribution function of heterogeneity; Microporous adsorbents)

Verteilungsfunktionen für die Struktur-Heterogenität von mikroporösen Adsorbentien

Es werden Verteilungsfunktionen für die strukturelle Heterogenität von mikroporösen Adsorbentien angegeben. Die Einflüsse der Adsorbens- und Adsorbatarten auf diese Heterogenität wurden untersucht.

Introduction

The theory of volume filling of micropores, proposed long ago by *Dubinin* [1], is described by two fundamental isotherm equations: the *Dubinin-Astakhov* (*DA*) [2] relationship and its special form—the *Dubinin-Radushkevich* (*DR*) equation. In 1965, *Izotova* and *Dubinin* [3] postulated that the *DR* equation can be applied only to solids of homogeneous micropore structure and they considered the case of an adsorbent of bimodal pore structure. Recently *Stoeckli* [4, 5] extended this approach using an integral equation describing the process of adsorption on solids with a continuous distribution of the micropores volume:

$$W(y) = \int_0^\infty \mathrm{f}(B)\exp(-B\cdot y)\,\mathrm{d}B \qquad (1)$$

where W is the volume of a liquid-like adsorbate filling the micropores at temperature T and pressure p, B is the structural constant characterizing the solid, $f(B)$ is the distribution function of the micropores volume with respect to B, $y = (T/\beta)^2 \cdot \log^2(p_s/p)$, β is the constant characterizing the adsorbate (affinity coefficient), and p_s is the saturation pressure.

Expression (1) is an integral transform of the *Laplace* type, with the *DR* equation as the core equation. The function $f(B)$ can be described by various equations with known *Laplace* transform in order to obtain an analytical expression for the isotherm $W(y)$. *Stoeckli* [4] used for $f(B)$ the *Gauss*ian distribution as the first approximation and then he obtained the following adsorption isotherm (*DRS*):

$$W(y) = \frac{W_0}{2} \cdot \exp(-B_0 \cdot y) \exp\left(\frac{y^2 \Delta^2}{2}\right) [1 - \mathrm{erf}(x)] \qquad (2)$$

where W_0 is the total volume of the micropores, B_0 and Δ represent the maximum and the half-width of the distribution function $f(B)$, $x = (y - B_0/\Delta^2) \cdot \Delta/\sqrt{2}$, and $\mathrm{erf}(x)$ is the error function.

Rozwadowski and *Wojsz* [6, 7] have examined Eq. (2) for many experimental adsorption isotherms of C_6H_6, *Me*OH, *Et*OH, *Me*NH_2, *Me*$_2$NH and *Et*NH_2 on carbons A, B, D and E at different temperatures. These data have been analyzed and, in spite of *Stoeckli*'s opinion [8], the applicability of the equation is limited to cases where $n \leqslant 2$ in the *DA* equation. Thus, a more general form of Eq. (1) is:

$$W(A) = \int_0^\infty f(k) \exp(-kA^n) \, \mathrm{d}k \qquad (1\,\mathrm{a})$$

where A is the differential molar work of adsorption, k is the structural constant characterizing the solid, and n is an integer constant; in the case when $n = 2$, then $k = B/(R \ln 10)^2$ and $A^2 = y(R \ln 10)^2$.

As zeolites and some active carbons have the parameter n greater than 2, the authors have derived [6] a more general isotherm equation which can be applied to all microporous solids.

$$W(A) = W_0 \exp\left[\frac{\Delta^2}{2}\left(\frac{A}{\beta}\right)^{2n}\right] \exp\left[-k_m\left(\frac{A}{\beta}\right)^n\right] \cdot \frac{\mathrm{erfc}\left[\frac{\Delta}{\sqrt{2}}\left(\frac{A}{\beta}\right)^n - \frac{k_m}{\Delta\sqrt{2}}\right]}{\mathrm{erfc}\left(-\frac{k_m}{\Delta\sqrt{2}}\right)} \qquad (3)$$

where W_0 is the total normalized micropore volume, k_m represents the maximum of the distribution function of micropore volume with respect to k.

Eq. (3) allows to determine the texture parameters W_0, k_m and Δ for all microporous adsorbents without any limitations, where Δ is the parameter characterizing the structural heterogeneity of microporous solids.

The aim of this paper is to determine the influences of microporous adsorbent texture and adsorbate type on the shape of the f(k) function characterizing the distribution of micropores volume with respect to k. We want to show that, besides of the *Gauss*ian distribution for the f(B) function (Eq. 2), other f(k) distributions—real from a physical point of view—are also possible to accept.

Theory

Stoeckli [4] introduced the distribution function of the microporous volume with respect to the parameter B. This distribution function f(B) characterizes the heterogeneous micropore structure of the solid (structural heterogeneity). The *Gauss*ian shape of f(B) function assumed by *Stoeckli* is only one from many possible cases for the solution of integral Eq. (1) determining the global adsorption isotherm $W(y)$. The *Rayleigh* and exponential distributions are also real from a physical point of view. Moreover, *Stoeckli* has not included the normalization of the function f(B), and according to our opinion [7], this may lead sometimes to values of W_0 which are out of physical sens. Thus, in relation to Eq. (3), the authors [6] have assumed the normalized *Gauss*ian distribution function f(k):

$$\begin{aligned} \mathrm{f}(k) &= \frac{2\,W_0}{\Delta\sqrt{2\pi}\cdot\mathrm{erfc}\left(-\dfrac{k_m}{\Delta\sqrt{2}}\right)}\cdot\exp\left[-\frac{(k-k_m)^2}{2\,\Delta^2}\right] && k \geqslant 0 \\ \mathrm{f}(k) &= 0 && k < 0 \end{aligned} \tag{4}$$

In the next considerations only the normalized distributions have been used.

Assuming the *Rayleigh* distribution [9] (the *Gauss*ian distribution with a widening at the right or left hand side) of f(k) one should consider two cases:

a) the distribution with a widening at the right-hand side

$$\begin{aligned} \mathrm{f}(k) &= \frac{W_0}{\Delta^2}(k-k_0)\exp\left[-\frac{(k-k_0)}{2\,\Delta^2}\right] && k_0 \geqslant 0 \text{ and } k \geqslant k_0 \\ \mathrm{f}(k) &= 0 && k < k_0 \end{aligned} \tag{5}$$

where k_0 is the parameter of the *Rayleigh* distribution and $k_0 = k_m - \Delta$.

Eq. (5) substituted into Eq. (1 a) gives

$$W = W_0 \exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right]\left\{1 - \sqrt{\frac{\pi}{2}}\cdot\Delta\cdot\left(\frac{A}{\beta}\right)^n\cdot\exp\left[\frac{\Delta^2}{2}\left(\frac{A}{\beta}\right)^{2n}\right]\cdot\right.$$
$$\left.\cdot\,\mathrm{erfc}\left[\frac{\Delta}{\sqrt{2}}\left(\frac{A}{\beta}\right)^n\right]\right\} \tag{6}$$

b) the distribution with a widening at the left-hand side

$$\begin{aligned} \mathrm{f}(k) &= \frac{W_0(k_0 - k)}{\Delta^2\left[1 - \exp\left(-\frac{k_0^2}{2\Delta^2}\right)\right]}\cdot\exp\left[-\frac{(k_0-k)^2}{2\Delta^2}\right] && 0 \leqslant k \leqslant k_0 \\ \mathrm{f}(k) &= 0 && k > k_0 \quad \text{or } k < 0 \end{aligned} \tag{7}$$

where $k_0 = k_m + \Delta$.

The substitution of (7) into Eq. (1 a) gives

$$W = \frac{W_0}{1 - \exp\left(-\frac{k_0^2}{2\Delta^2}\right)}\left\{\exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right] + \left(\frac{A}{\beta}\right)^n\sqrt{\frac{\pi}{2}}\cdot\Delta\cdot\right.$$
$$\cdot\exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right]\cdot$$
$$\cdot\exp\left[\frac{\Delta^2}{2}\left(\frac{A}{\beta}\right)^{2n}\right]\left[\mathrm{erfc}\left[\frac{\Delta}{\sqrt{2}}\left(\frac{A}{\beta}\right)^n - \frac{k_0}{\Delta\sqrt{2}}\right] - \mathrm{erfc}\left[\frac{\Delta}{\sqrt{2}}\left(\frac{A}{\beta}\right)^n\right]\right] -$$
$$\left. - \exp\left(-\frac{k_0^2}{2\Delta^2}\right)\right\} \tag{8}$$

Assuming an exponential distribution of the f(k) function one should consider also two cases:

a) the distribution for the decreasing exponential function f(k)

$$\begin{aligned} \mathrm{f}(k) &= \frac{W_0}{\Delta}\cdot\exp\left(-\frac{k - k_m}{\Delta}\right) && k_m \geqslant 0 \quad \text{and} \quad k \geqslant k_m \\ \mathrm{f}(k) &= 0 && k < k_m \end{aligned} \tag{9}$$

The substitution of Eq. (9) into Eq. (1 a) leads to

$$W = \frac{W_0}{1 + \Delta\left(\frac{A}{\beta}\right)^n}\cdot\exp\left[-k_m\left(\frac{A}{\beta}\right)^n\right] \tag{10}$$

b) the distribution for the increasing exponential function f(k)

$$\mathrm{f}(k)=\frac{W_0}{\Delta\left[1-\exp\left(-\frac{k_m}{\Delta}\right)\right]}\cdot\exp\left(-\frac{k_m-k}{\Delta}\right)\qquad 0\leqslant k\leqslant k_m \qquad (11)$$

$$\mathrm{f}(k)=0 \qquad\qquad k>k_m \quad \text{or} \quad k<0$$

Eq. (1 a) with the function (11) gives:

$$W=\frac{W_0\left\{\exp\left[-k_m\left(\frac{A}{\beta}\right)^n\right]-\exp\left(-\frac{k_m}{\Delta}\right)\right\}}{\left[1-\Delta\left(\frac{A}{\beta}\right)^n\right]\left[1-\exp\left(-\frac{k_m}{\Delta}\right)\right]} \qquad A^n\neq 1/\Delta \qquad (12)$$

$$W=\frac{W_0\,k_0\exp\left(-\frac{k_m}{\Delta}\right)}{\left[1-\exp\left(-\frac{k_m}{\Delta}\right)\right]} \qquad A^n=1/\Delta$$

Experimental

The investigations have been made on active carbons prepared from chemically pure saccharose. The preparation method and texture of the carbons have been described previously [10–12]. The carbons have been activated with oxygen at 723 K (sample A), with carbon dioxide at 1 123 K (sample B) and also with $ZnCl_2$ in the process of so-called chemical activation (sample D and E). The adsorption isotherms for spectrally pure alcohols (methanol, ethanol) and for chemically pure aliphatic amines ($Me\mathrm{NH}_2$, $Me_2\mathrm{NH}$ and $Et\mathrm{NH}_2$) have been measured within the temperature ranges 298.2–322.0 K and 298.2–335.7 K, respectively, using a *McBain* balance. The benzene adsorption isotherms have been measured at 298.2 K. In order to eliminate the irreversible adsorption in the case of amines, the adsorption process was investigated on carbons presaturated with the amines studied (the relative pressure of conditioning was about 0.2 and the temperature 298.2 K). After the equilibrium state reaching, the samples were desorbed under the pressure of 1 mPa at 335.7 K up to constant mass. Active carbons conditioned this way were next used to study amines adsorption. Examples of isotherms for the studied samples are shown in Figs. 1 and 2.

Results and Discussion

In accordance with considerations by many authors [13–15], there is a proportional dependence between the micropores radius (r_m) and the value of the B parameter in the DR equation

$$r_m=const_1\cdot B^{1/2} \qquad (13)$$

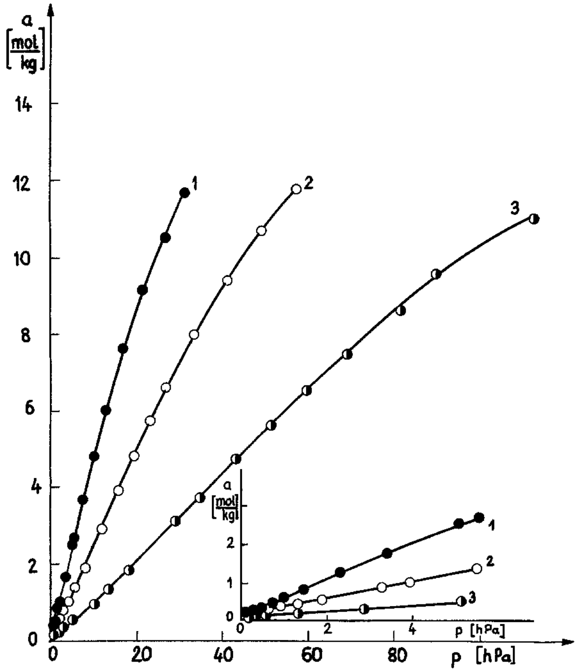

Fig. 1. Isotherms of *Me*OH adsorption on carbon D in the dependence on temperature: *1* 298.2 K; *2* 308.0 K; *3* 322.7 K

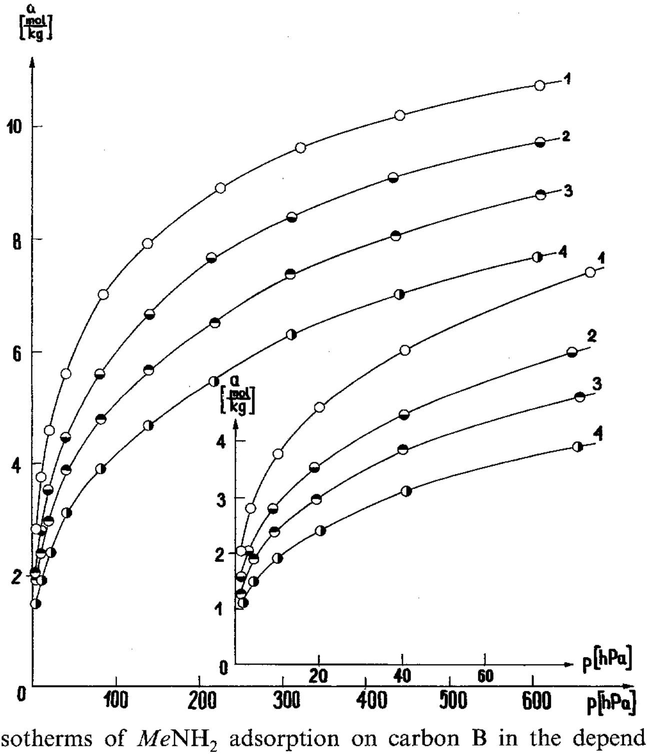

Fig. 2. Isotherms of $MeNH_2$ adsorption on carbon B in the dependence on temperature: *1* 298.2 K; *2* 310.7 K; *3* 323.2 K; *4* 335.7 K

The same dependence occurs also between the r_m value and k in the other equations cited:

$$r_m = const_2 \cdot k^{1/2} \tag{14}$$

The value of the structural parameter k is changing within a definite range depending on values of r_m radii occurring in a given adsorbent. Thus, the value of the Δ parameter occurring in Eqs. (3)–(12) is a measure for changes of the micropores radii. Values of k_m, Δ and W_0 of above equations obtained with the method of the least-squares for all cases studied are listed in Table 1 a–1 c.

Table 1 a. *Parameters of the distribution functions of structural heterogeneity for adsorption systems studied*

$$*\left(\begin{aligned}&[k]=[k_m]=[\Delta]=\left[\frac{\text{mol}^n}{\text{kJ}^n}\right],\ [\mathrm{f}(k_m)]=\left[\frac{\text{kJ}^n\,\text{dm}^3}{\text{mol}^n\,\text{kg}}\right],\ [W_0]=\left[\frac{\text{dm}^3}{\text{kg}}\right];\\ &k\in\langle k_{\text{from}}, k_{\text{to}}\rangle \Rightarrow \mathrm{f}(k)\geqslant 0.01\cdot \mathrm{f}(k_m)\end{aligned}\right)$$

Adsorbent	Adsorbate	*DA*		Eq. (3)					
		n	k $\times 10^6$	Range of k $\times 10^6$ from	to	k_m $\times 10^6$	$\mathrm{f}(k_m)$	Δ $\times 10^6$	W_0
A	*Me*OH	3	57.9	0	186	71.8	2 630	37.7	0.2413
B		2	3 427	0	11 360	5 290	169.2	2 005	0.8467
D		2	3 799	0	16 200	7 149	123.0	2 990	0.9141
E		2	3 352	0	18 600	7 357	61.38	3 696	0.5524
A	*Et*OH	3	58.2	0	223	72.2	1 992	49.6	0.2297
B		2	3 258	190	7 680	3 953	223.4	1 266	0.6865
D		2	3 927	0	14 400	6 474	133.4	2 594	0.8621
E		2	3 699	0	21 010	8 229	65.17	4 198	0.6686
A	*Me*NH_2	2	481.9	0	1 042	521.6	577.0	173.2	0.2504
B		2	861.1	0	4 668	1 334	242.7	1 098	0.5931
D		2	896.3	0	7 284	1 431	185.1	1 937	0.6920
E		2	788.3	0	5 879	1 489	149.9	1 481	0.4587
A	Me_2NH	2	672.2	272	1 092	683.9	675.0	132.4	0.2240
B		2	1 318	0	3 156	1 496	410.1	548.3	0.5619
D		2	1 517	0	6 970	2 123	187.1	1 602	0.6817
E		2	1 559	0	7 935	2 501	137.9	1 786	0.5675
A	*Et*NH_2	2	742.9	0	2 972	662.5	139.0	139.0	0.2137
B		2	1 357	0	3 668	1 587	314.1	686.0	0.5345
D		2	1 539	0	7 851	2 041	164.7	1 913	0.6767
E		2	1 482	0	9 803	2 219	118.2	2 502	0.6021
A	C_6H_6	3	54.5	0	179	71.5	2 389	35.3	0.2069
B		2	2 393	2 080	2 720	2 399	2 240	103.0	0.5761
D		2	2 916	0	8 100	3 937	196.0	1 370	0.6714
E		2	2 823	0	11 200	4 690	97.21	2 148	0.5158

Table 1 b. *Parameters of the distribution functions of structural*

Adsorbent	Adsorbate	Eq. (6)					
		Range of k $\times 10^6$ from	to	k_m $\times 10^6$	$f(k_m)$	Δ $\times 10^6$	W_0
A	*Me*OH	1.52	213	60.7	2 480	59.2	0.2421
B		613.7	16 080	4 942	128.3	4 327	0.9160
D		233.8	25 200	7 228	94.23	6 994	1.0866
E		0	26 700	7 207	51.37	7 568	0.6402
A	*Et*OH	0	243	61.9	1 994	70.5	0.2300
B		1 218	9 320	3 487	184.9	2 269	0.6917
D		460.6	20 340	6 026	100.7	5 563	0.9241
E		0	28 720	7 722	54.24	8 163	0.7290
A	$Me\mathrm{NH}_2$	161.2	1 206	453.4	520.7	292.2	0.2508
B		0	5 187	1 163	239.9	1 561	0.5978
D		0	7 850	1 294	187.2	2 548	0.6967
E		0	6 440	1 228	149.9	2 033	0.4646
A	$Me_2\mathrm{NH}$	416.1	1 184	630.6	633.5	214.5	0.2240
B		351.7	3 682	1 288	365.2	936.2	0.5636
D		0	7 715	1 838	185.5	2 283	0.6850
E		0	8 987	2 171	134.1	2 636	0.5740
A	$Et\mathrm{NH}_2$	0	3 083	610.6	144.3	960.4	0.2138
B		219.8	4 214	1 344	289.0	1 124	0.5357
D		0	8 472	1 798	166.4	2 595	0.6791
E		0	10 690	1 983	118.9	3 377	0.6080
A	C_6H_6	2.95	208	60.3	2 193	57.3	0.2073
B		2 215	2 730	2 360	2 404	145.3	0.5758
D		762.0	10 600	3 509	151.7	2 747	0.6871
E		87.24	14 700	4 180	79.07	4 092	0.5335

As it can be seen from the data presented in the Table 1 a–1 c, the values of Δ and k_m from Eqs. (3), (6), (8), (10), and (12) increase for carbons studied in sequence A, B, D, E. Parameter k_m, similarly like B or k in the *DR* equation can be employed as an indication for the adsorption potential. The lower the values of k_m, the greater is the adsorption potential of the micropore system. At the same time, in the case of carbon of strongly increased adsorption potential (sample A), the heterogeneity parameter Δ usually has a low value. It results from Eq. (14) that the distribution of the micropores sizes becomes broader with an increase of Δ. This means (Table 1 a–1 c) that carbon E has the best developed system *heterogeneity for adsorption systems studied* (as in Table 1 a)*

Eq. (8)					
Range of k $\times 10^6$ from	to	k_m $\times 10^6$	$f(k_m)$	Δ $\times 10^6$	W_0
0	141	83.2	2649	58.1	0.2407
0	8367	5730	191.2	2636	0.8259
0	11530	7665	138.8	3864	0.8736
0	12800	7970	67.69	4870	0.5266
0	167	85.1	1935	82.3	0.2293
30	5990	4318	248.3	1672	0.6835
0	10470	7052	151.0	3422	0.8440
0	14650	9039	72.12	5608	0.6450
0	831.9	580.7	606.8	251.1	0.2502
0	3350	1574	241.1	1775	0.5868
0	5053	1658	180.9	3396	0.6780
0	4048	1618	148.5	2430	0.4464
232	923.7	731.8	707.5	192.0	0.2240
0	2469	1676	432.4	793.1	0.5610
0	5105	2502	184.8	2603	0.6773
0	5664	2915	140.1	2748	0.5586
0	2273	657.2	127.5	1616	0.2135
0	2840	1811	321.8	1028.8	0.5338
0	5722	2394	158.7	3328	0.6723
0	6884	2581	115.3	4304	0.5905
0	135	82.4	2464	52.8	0.2066
2010	2610	2443	2071	168.6	0.5760
0	6140	4301	221.0	1834	0.6658
0	8140	5214	107.7	2926	0.5085

of micropores of different sizes. On the other hand, carbon A with the most increased adsorption potential has a relatively homogeneous system of micropores. One can then accept that the Δ parameter from Eqs. (3)–(12) characterizes the structural heterogeneity of microporous adsorbents.

Examples for the functions of the adsorption energy distribution obtained from Eqs. (3), (6), (8), (10), (12), and (DR) are shown in Figs. 3–4.

It should be stated that, in spite of assumed differences in the shape of the $f(k)$ functions, the distribution curves obtained from those equations contain a broad common range of k values.

Table 1 c. *Parameters of the distribution functions of structural*

Adsorbent	Adsorbate	Eq. (10)					
		Range of k $\times 10^6$		k_m $\times 10^6$	f(k_m)	Δ $\times 10^6$	W_0
		from	to				
A	*Me*OH	25.9	281.4	25.9	4413	55.5	0.2449
B		1731	41250	1731	140.8	8582	1.2083
D		1552	334300	1552	73.80	70760	5.2220
E		1024	5652500	1024	37.66	1227200	46.215
A	*Et*OH	20.7	328	20.7	3486	66.6	0.2322
B		2116	12220	2116	319.7	2192	0.7010
D		1796	53230	1796	106.8	11170	1.1923
E		1132	178330	1132	44.47	38480	1.7113
A	*Me*NH$_2$	296.3	1422	296.3	1030.4	244.4	0.2518
B		220.8	9233	220.8	332.1	1957	0.6500
D		145.0	14930	145.0	247.8	3211	0.7956
E		138.8	14960	138.8	183.6	3217	0.5905
A	*Me*$_2$NH	527.5	1263	527.5	1403.4	159.7	0.2241
B		763.7	4559	763.7	688.9	824.0	0.5676
D		451.0	12270	451.0	279.0	2571	0.7173
E		438.8	18190	438.8	171.9	3862	0.6638
A	*Et*NH$_2$	217.2	3637	217.2	289.8	740.6	0.2146
B		724.5	5167	724.5	557.7	965.2	0.5383
D		393.2	13040	393.2	257.4	2752	0.7084
E		280.1	20490	280.1	159.7	4399	0.7022
A	C_6H_6	24.7	284	24.7	3709	56.4	0.2090
B		2290	2800	2290	5260	109	0.5759
D		1623	17600	1623	209.8	3478	0.7298
E		1117	31900	1117	89.42	6954	0.6218

If assumed that the *Dirac*'s function resulting from the *DR* equation describes the position of maximum of distribution function f(k) most exactly, then Eq. (5) gives the most correct distribution of adsorption energy. On the other hand, Eq. (11) gives the position of the maximum most departing from that assumed in the *DR* equation. It can be also stated that the distribution function f(k) resulting from Eq. (9), contains always the broadest range of k values. If the range of changes of the k values is accepted as a criterion of the applicability of these functions then Eq. (9) should be excluded since it gives results most departing from the other functions of adsorption energy distribution. Besides of that, it *heterogeneity for adsorption systems studied* (as in Table 1 a)*

Eq. (12)					
Range of k $\times 10^6$ from	to	k_m $\times 10^6$	$f(k_m)$	Δ $\times 10^6$	W_0
0	113	113	4 666	61.2	0.2402
0	6 348	6 348	503.1	1 623	0.8003
0	8 404	8 404	354.7	69 570	0.8222
0	9 128	9 128	154.0	3 428	0.4910
0	132.8	132.8	2 769	128.1	0.2289
90	4 812	4 812	670.2	1 023	0.6793
0	7 867	7 867	394.3	2 134	0.8203
0	10 525	10 525	165.4	4 008	0.6148
0	683.8	683.8	1 391.1	184.2	0.2499
0	2 549	2 549	345.0	2 847	0.5809
0	3 824	3 824	196.9	16 208	0.6707
0	2 977	2 977	191.2	5 279	0.4351
250	800.3	800.3	1 880.5	119.2	0.2239
0	2 003	2 003	967.4	600.2	0.5600
0	3 951	3 951	267.7	4 019	0.6734
0	4 282	4 282	223.8	3 465	0.5501
0	1 392	1 392	264.7	1 119	0.2108
0	2 290	2 290	636.3	911.6	0.5330
0	4 439	4 439	194.5	8 297	0.6687
0	5 183	5 183	136.4	12 792	0.5813
0	107.1	107.1	4 729	49.2	0.2063
2 020	2 503	2 503	5 580	103	0.5759
0	4 798	4 798	595.4	1 122	0.6585
0	6 117	6 117	254.7	2 069	0.4995

results from data presented in Table 1 a–1 c as well as partially in Figs. 3–4 that the shape and values of the function of adsorption energy distribution depend also on the type of molecules adsorbed. Considering an increase of k_m values, the examined adsorbates can be most often placed in the order: $Me\mathrm{NH_2} < Me_2\mathrm{NH} \approx Et\mathrm{NH_2} < \mathrm{C_6H_6} < Me\mathrm{OH} \approx Et\mathrm{OH}$. The parameter Δ on the other hand is increasing in the following order: $\mathrm{C_6H_6}$, $Me\mathrm{NH_2}$, $Me_2\mathrm{NH}$, $Et\mathrm{NH_2} < Me\mathrm{OH}$, $Et\mathrm{OH}$. It should be expected that the values of k_m and Δ are influenced not only by the dimensions of adsorbed molecules and adsorbent texture but also by adsorbate-adsorbate and adsorbate-adsorbent interactions.

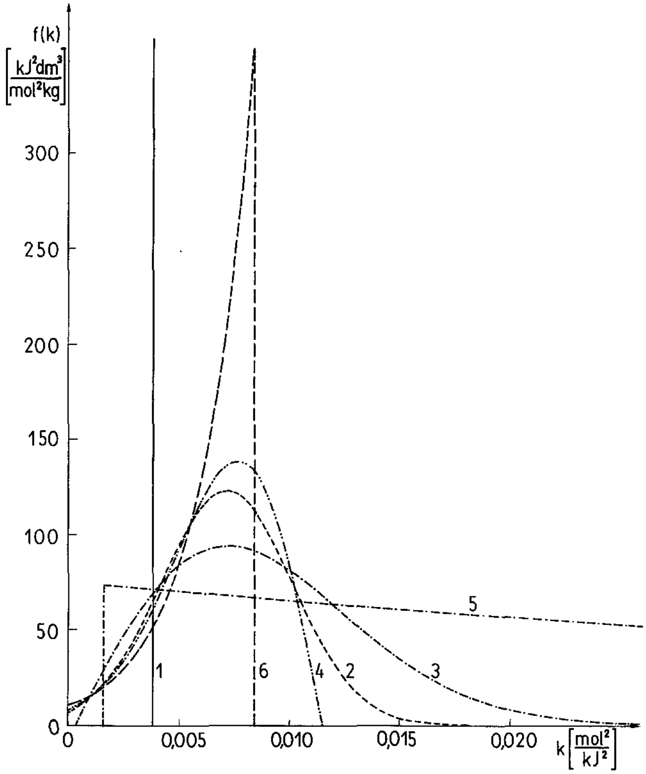

Fig. 3. Functions of the structural parameter distribution for *Me*OH adsorption on carbon D: *1* the distribution resulting from the *DR* equation; *2* the distribution resulting from Eq. (3) described with Eq. (4); *3* the distribution resulting from Eq. (6) described with Eq. (5); *4* the distribution resulting from Eq. (8) described with Eq. (7); *5* the distribution resulting from Eq. (10) described with Eq. (9); *6* the distribution resulting from Eq. (12) described with Eq. (11)

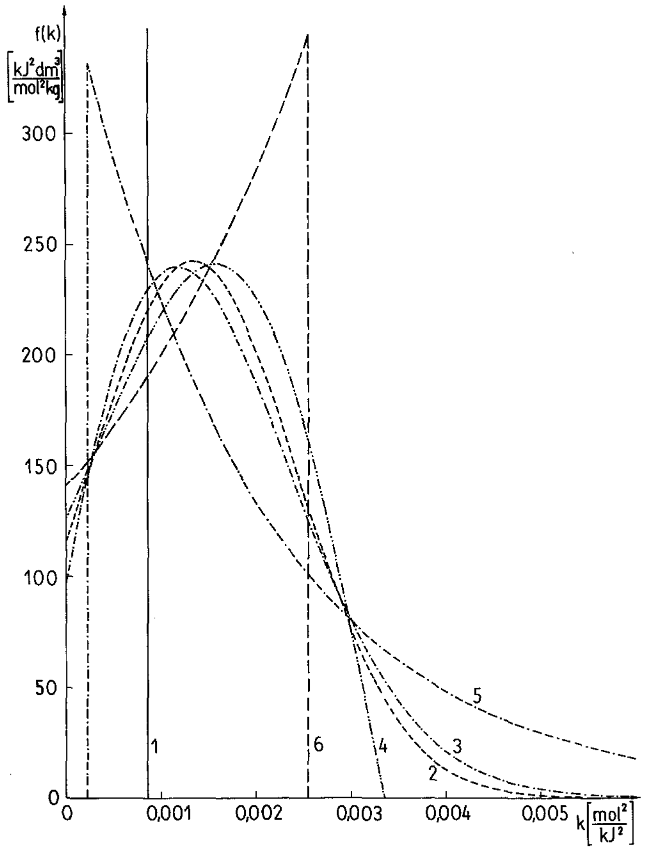

Fig. 4. Functions of the structural parameter distribution for *Me*NH_2 adsorption on the carbon B: *1* the distribution resulting from the *DR* equation; *2* the distribution resulting from Eq. (3) described with Eq. (4); *3* the distribution resulting from Eq. (6) described with Eq. (5); *4* the distribution resulting from Eq. (8) described with Eq. (7); *5* the distribution resulting from Eq. (10) described with Eq. (9); *6* the distribution resulting from Eq. (12) described with Eq. (11)

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