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Comments on Correct Determination of Structural Parameters for Adsorbents of Heterogeneous Micropore Systems

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Summary. Different forms for functions determining the micropores volume after the structural parameter are given. It is stated that the accepted range of the variability of the structural parameter *k* can influence considerably the values of parameters determining the structural heterogeneity of microporous adsorbents. The lack of normalization can cause great errors in the micropore volume determination.

Keywords. Active carbons; Adsorption; Distribution function of heterogeneity; Microporous adsorbents.

Über die korrekte Bestimmung von Strukturparametern für Adsorbentien auf heterogenen, mikroporösen Systemen

Zusammenfassung. Es werden verschiedene Formen für Funktionen, die das Mikroporenvolumen bestimmen, gegenüber dem Strukturparameter angenommen. Man stellte fest, daß im angenommenen Bereich die Änderungen des Strukturparameters *k* die Werte der die Strukturheterogenität der mikroporösen Adsorbenten bestimmenden Parameter bedeutend beeinflussen. Der Mangel an Normalisierung kann große Fehler in der Bestimmung des Mikroporenvolumens verursachen.

Introduction

The determinations of the micropore volume distributions versus the characteristic dimension x [1–5] were used more and more often recently. This way, it was possible to define for the first time an approximate characteristics of micropores in micropore adsorbents. The most general form of adsorption isotherm for adsorbents of heterogeneous micropore system is

$$W(y) = \int_0^\infty \mathrm{f}(B)\exp(-B\cdot y)\,\mathrm{d}B, \qquad y = (T/\beta)^2\log^2(p_s/p), \tag{1}$$

where W is the volume of the liquid-like adsorbate filling the micropores at pressure p and temperature T; $\mathrm{f}(B)$ is the distribution function of the micropore volume with respect to B (B is the parameter from the DR equation [6, 7]) and β is the constant characterizing the adsorbate, affinity coefficient of the characteristic curves.

In order to obtain an analytical expression for the isotherm $W(y)$ as a first approximation Stoeckli [8] used the Gaussian function

$$\mathrm{f}(B) = \frac{W_0}{\Delta\sqrt{2\pi}} \cdot \exp\left[-\frac{(B - B_0)^2}{2\Delta^2}\right], \tag{2}$$

where B_0 represents the maximum; Δ is the distribution half-width and W_0 is the total volume of the micropores.

Discussion and Results

The condition of correctness for the value of the W_0 parameter [resulting from integration of the function $\mathrm{f}(B)$ within the range of the parameter B variancy] is to use the correct distribution of the micropore volume. However, the DRS equation [9] disregards the fact that a part of the distribution $\mathrm{f}(B)$ occurs within the range of negative values B not included in the calculation of the parameter W_0.

In a previous paper [10] we have shown that the correct function of the micropore volume distribution after the structural parameter has the form

$$\mathrm{f}(k) = \begin{cases} \dfrac{2W_0}{\Delta\sqrt{2\pi}\,\mathrm{erfc}\left(-\dfrac{k_0}{\Delta\sqrt{2}}\right)} \cdot \exp\left[-\dfrac{(k - k_0)^2}{2\Delta^2}\right], & k > 0, \\ 0, & k \leqslant 0, \end{cases} \tag{3}$$

$$B = k(R\ln 10)^2.$$

This expression satisfies the necessary condition:

$$\frac{1}{W_0} \cdot \int_0^\infty \mathrm{f}(k)\,\mathrm{d}k = 1. \tag{4}$$

Papers determining the distributions of micropore volume after their characteristic dimension x mention that in the case of benzene (and also other adsorbates of sizes equal or smaller than benzene when the moleculare sieve effect is absent) only the micropores of dimensions $0.25 < x < 1.6\,\mathrm{nm}$ [2, 9] have a physical sense. Since the dependence between x and k or B [9, 11] is

$$x = \mathrm{const} \cdot \sqrt{k}, \tag{5}$$

then the value $x = 0.25\,\mathrm{nm}$ yields the defined value k [minimum] $= 0.000789$ $\mathrm{mol^2/kJ^2}$ and the $x = 1.6$ – the value k [maximum] $= 0.0151$. For this reason in the plot of function $\mathrm{f}(k)$ one should consider [besides Eqs. (2) and (3)] also the other cases yielding different values of the normalized parameters:

$$\mathrm{f}(k) = \begin{cases} \dfrac{2 \cdot W_0 \exp\left[-\dfrac{(k - k_0)^2}{2\Delta^2}\right]}{\Delta\sqrt{2\pi}\,\mathrm{erfc}\left(\dfrac{k_{\min} - k_0}{\Delta\sqrt{2}}\right)}, & k > k_{\min}, \\ 0, & k \leqslant k_{\min}, \end{cases} \tag{6}$$

$$
\mathrm{f}(k)=\begin{cases}\dfrac{2\,W_0\exp\left[-\dfrac{(k-k_0)^2}{2\Delta^2}\right]}{\Delta\sqrt{2\pi}\left[\operatorname{erf}\left(\dfrac{k_0}{\Delta\sqrt{2}}\right)+\operatorname{erf}\left(\dfrac{k_{\max}-k_0}{\Delta\sqrt{2}}\right)\right]}, & 0<k<k_{\max},\\[2ex] 0, & k\leqslant 0 \text{ or } k\geqslant k_{\max},\end{cases} \tag{7}
$$

$$
\mathrm{f}(k)=\begin{cases}\dfrac{2\,W_0\cdot\exp\left[-\dfrac{(k-k_0)^2}{2\Delta^2}\right]}{\Delta\sqrt{2\pi}\left[\operatorname{erf}\left(\dfrac{k_0-k_{\min}}{\Delta\sqrt{2}}\right)+\operatorname{erf}\left(\dfrac{k_{\max}-k_0}{\Delta\sqrt{2}}\right)\right]}, & k_{\min}<k<k_{\max},\\[2ex] 0, & k\leqslant k_{\min} \text{ or } k\geqslant k_{\max}.\end{cases} \tag{8}
$$

Based on Eqs. (2), (3), (6), (7), and (8) Fig. 1 presents the curves of f(k) functions.

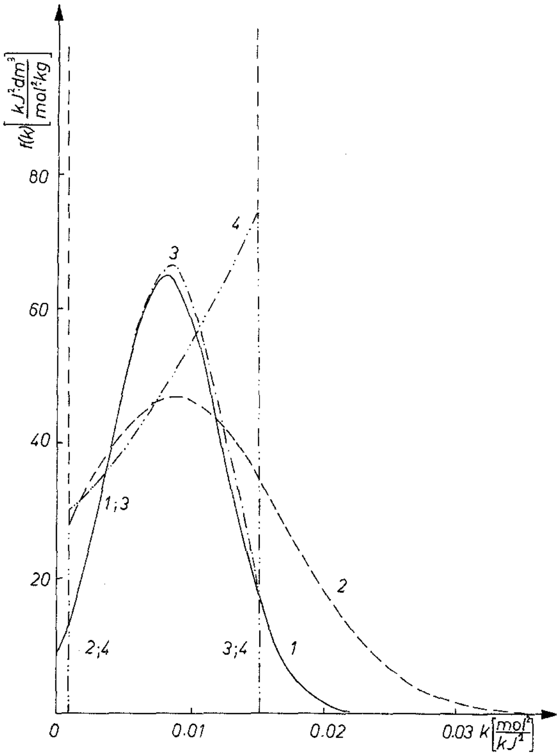

Fig. 1. Curves of f (k) functions for the data of ethanol adsorption on active carbon E; *1*: using Eq. (2) and (3); *2*: using Eq. (6); *3*: using Eq. (7); *4*: using Eq. (8)

The data are dealing with the adsorption isotherm of ethanol on active carbon E described previously [12, 13]. The value of parameters corresponding to the particular curves are given in Table 1.

The results show explicitly that the lack of normalization (Table 1) can cause relatively great error of the micropore volume W_0 determination for adsorbents of heterogeneous micropore system in all cases studied. The assumption of the physical sense of micropore dimensions ($0.25 < x < 1.6$ nm) gives the conclusion that the

Table 1. Parameters obtained from Eqs. (2), (3), and (6)–(8). ($[k, k_0, \Delta] = [\mathrm{mol}^2/\mathrm{kJ}^2]$; $[W_0, W_0^{NN}] = [\mathrm{dm}^3/\mathrm{kg}]$; $W_0^N = W_0$ normalized; $W_0^{NN} = W_0$ not-normalized; DC = determination coefficient)

Eq.	$k \in$	k_0	Δ	W_0^N	W_0^{NN}	DC
(2), (3)	$(0, \infty)$	0.00823	0.00420	0.669[a]	0.686[b]	0.99666
(6)	$(k_{\min}, \infty)$	0.00886	0.00808	0.799	0.950	0.99702
(7)	$(0, k_{\max})$	0.00845	0.00431	0.654	0.716	0.99660
(8)	$(k_{\min}, k_{\max})$	0.18052	0.05218	0.702	1477	0.99704

[a] From Eq. (3)
[b] From Eq. (2)

parameters most close to the real ones result from Eq. (8), to which the adsorption isotherm (9) is corresponding.

$$W = \frac{W_0 \exp\left(\frac{\Delta^2 Y^2}{2} - k_0 Y\right)\left[\operatorname{erf}\left(\frac{k_0 - k_{\min}}{\Delta\sqrt{2}} - \frac{\Delta Y}{\sqrt{2}}\right) + \operatorname{erf}\left(\frac{\Delta Y}{\sqrt{2}} + \frac{k_{\max} - k_0}{\Delta\sqrt{2}}\right)\right]}{\operatorname{erf}\left(\frac{k_0 - k_{\min}}{\Delta\sqrt{2}}\right) + \operatorname{erf}\left(\frac{k_{\max} - k_0}{\Delta\sqrt{2}}\right)},$$
$$Y = (A/\beta)^n, \tag{9}$$

where A is the differential molar adsorption work and n is the constant parameter equal to 2 or 3 in the case of very small micropores.

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