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# Determination of Microporous Adsorbents Heterogeneity with the Condensation Approximation Method

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Using the condensation approximation method the distribution function of adsorption energy for microporous adsorbents has been defined. Due to application of proper equations for the isotherm of global adsorption, the considerations include differencies in the shape of the distribution function of the structural heterogeneity for the microporous adsorbents studied.

*(Keywords: Adsorption; Condensation distribution function; Microporous adsorbents; Structural heterogeneity)*

*Die Bestimmung der Heterogenität mikroporöser Adsorbentien mit der Kondensationsnäherung*

Mit Hilfe der Methode der Kondensationsnäherung wurde die Verteilungsfunktion der Adsorptionsenergie für mikroporöse Adsorbentien bestimmt. Die Anwendung entsprechender Gleichungen für die Globalisotherme gestattet die Berücksichtigung von Differenzen in der Gestalt der Verteilungsfunktionen der Strukturheterogenität.

## Introduction

Although the concept of surface heterogeneity in the theory of physical adsorption had already been introduced by *Langmuir*[1], this is still one of the most important and still unsolved problems in adsorption investigations. The fundamental studies in this field are based on the integral equation of a global adsorption isotherm[2,3].

An alternative concept for the adsorbent heterogeneity description has been proposed by *Izotova* and *Dubinin*[4] and later developed by *Stoeckli*[5] and *Rozwadowski* and *Wojsz*[6,7]. This concept has been formulated for adsorption on microporous adsorbents with micropores of different dimensions i.e. heterogeneous adsorbents with respect to the microporous structure.

For such adsorbents the authors[6] have proposed the following isotherm equation:

$$W(A) = W_0^N \exp\left[\frac{\Delta^2}{2}\left(\frac{A}{\beta}\right)^{2n}\right]\exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right]\frac{\operatorname{erfc}\left[\frac{\Delta}{\sqrt{2}}\left(\frac{A}{\beta}\right)^n - \frac{k_0}{\Delta\sqrt{2}}\right]}{\operatorname{erfc}\left(-\frac{k_0}{\Delta\sqrt{2}}\right)} \quad (1)$$

where $W$ represents the volume of liquid-like adsorbate present in the micropores at temperature $T$ and relative pressure $p/p_s$; $W_0^N$ is the total normalized micropore volume; $A$ is the differential molar work of adsorption; $k_0$ represents the maximum of the distribution function of the micropores volume with respect to $k$; $k$ is a structural constant characterizing the solid; $\Delta$ is the half-width of the distribution which is a measure of the heterogeneity of micropore system; $\beta$ is the affinity coefficient.

The parameter $n$ in equ. (1) can achieve only integer values 2 or 3 and it is defined only by the sign of the second derivate $\mathrm{d}^2 \ln \mathrm{W}/\mathrm{d}(A^2)^2$. Therefore, equ. (1) can be accepted as equation with 3 parameters.

Equ. (1) allows to determine the texture parameters including the parameter $\Delta$ characterizing the structural heterogeneity for all microporous adsorbents without any limitations.

The aim of this paper is to apply the condensation approximation method (CA)[8—10] (commonly used in the determination of the adsorption energy distribution) for the microporous adsorbents heterogeneity determination including differencies in the shape of the condensation distribution function.

## Experimental

The investigations have been made on active carbons A, B, D and E prepared from chemically pure saccharose. The preparation method and texture of the carbons have been described previously[11—13]. Adsorption isotherms of spectroscopically pure aliphatic alcohols (*Me*OH, *Et*OH)[14,15], *n*-hexane[16] and chemically pure aliphatic amines (*Me*$NH_2$, *Me*$_2$NH, *Et*$NH_2$)[17,18] at different temperatures have been determined using a vacuum apparatus equipped with a *MacBain*'s balance. Adsorption isotherms of spectroscopically pure benzene[16,19] have been also measured at 298.2 K. All adsorption isotherms were determined up to a relative pressure of approximately 0.2.

## Results and Discussion

Assuming (after the procedure of the condensation approximation[8,9]) that the global isotherm is defined with equ. (1) as the result of the local *Langmuir*'s isotherm and accepting that:

$$f_c(Q) = -\frac{d\theta_{t,c}[p(Q)]}{dp}\frac{dp}{dQ} \tag{2}$$

where: $f_c(Q)$ is the condensation distribution function; $\theta_{t,c}$ is the global isotherm; $p$ is the equilibrium pressure; $Q$ is the adsorption energy, equ. (1) is transformed as follows:

$$f_c(Q) = \frac{n(Q-Q_0)^{n-1}}{\beta^{2n}\,\mathrm{erfc}\left(-\frac{k_0}{\Delta\sqrt{2}}\right)}\left\{[k_0\beta^n - \Delta^2(Q-Q_0)^n]\exp\left[\frac{\Delta^2(Q-Q_0)^{2n}}{2\beta^{2n}} - \right.\right.$$

$$\left.\left. -k_0\left(\frac{Q-Q_0}{\beta}\right)^n\right]\mathrm{erfc}\left[\frac{\Delta(Q-Q_0)^n}{\sqrt{2}\,\beta^n} - \frac{k_0}{\Delta\sqrt{2}}\right] + \sqrt{\frac{2}{\pi}}\,\beta^n\Delta\exp\left(-\frac{k_0^2}{2\Delta^2}\right)\right\} \tag{3}$$

The *Gauss*ian shape of the structural heterogeneity distribution function f$(k)$ assumed in equ. (1) is only one from many possible cases determining the global adsorption isotherms $W(A)$.

The *Rayleigh* and exponential distribution are also real forms from the physical view point[20]. Assuming the *Rayleigh* distribution[21] (*Gauss*ian distribution with a widening at the right or left-hand side) for the function f$(k)$ we obtain the following two equations for the global adsorption isotherm $W(A)$.

a) For the distribution f$(k)$ with a widening at the right-hand side

$$W = W_0^N\exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right]\left\{1 - \frac{\sqrt{\pi}}{2\Delta}\left(\frac{A}{\beta}\right)^n\exp\left[\frac{1}{4\Delta^2}\left(\frac{A}{\beta}\right)^{2n}\right]\mathrm{erfc}\left[\frac{1}{2\Delta}\left(\frac{A}{\beta}\right)^n\right]\right\} \tag{4}$$

Differentiation of equ. (4) with respect to $Q$ gives the following function of the energy distribution:

$$f_c(Q) = \frac{nq^{n-1}}{\beta^n}\exp\left(-\frac{k_0q^n}{\beta^n}\right)\left[k_0 - \frac{q^n}{2\Delta^2\beta^n} + \frac{\sqrt{\pi}}{2\Delta}\exp\left(\frac{q^{2n}}{4\Delta^2\beta^{2n}}\right)\cdot\right.$$

$$\left.\cdot\,\mathrm{erfc}\left(\frac{q^n}{2\Delta\beta^n}\right)\left(1 - \frac{k_0q^n}{\beta^n} + \frac{q^{2n}}{2\Delta^2\beta^{2n}}\right)\right] \quad \text{for } k_0 \geqslant 0 \tag{5}$$

where: $q = Q - Q_0$

b) For the distribution f$(k)$ with a widening at the left-hand side

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

$$\left.\left. + \frac{1}{4\Delta^2}\left(\frac{A}{\beta}\right)^{2n}\right]\operatorname{erfc}\left[\left[\frac{1}{2\Delta}\left(\frac{A}{\beta}\right)^n - k_0\Delta\right] - \operatorname{erfc}\left[\frac{1}{2\Delta}\left(\frac{A}{\beta}\right)^n\right]\right] - \exp(-\Delta^2 k_0^2)\right\} \tag{6}$$

Differentiation of equ. (6) gives:

$$f_c(Q) = \frac{nq^{n-1}}{\beta^n[1-\exp(-\Delta^2 k_0^2)]}\cdot\exp\left(-\frac{k_0 q^n}{\beta^n}\right)\left\{k_0 + \frac{\sqrt{\pi}}{2\Delta}\cdot\exp\left(\frac{q^{2n}}{4\Delta^2\beta^{2n}}\right)\cdot\right.$$

$$\cdot\left[\operatorname{erfc}\left(\frac{q^n}{2\Delta\beta^n} - k_0\Delta\right) - \operatorname{erfc}\left(\frac{q^n}{2\Delta\beta^n}\right)\right]\left(\frac{k_0 q^n}{\beta^n} - \frac{q^{2n}}{2\Delta^2\beta^{2n}} - 1\right) +$$

$$\left. + \frac{q^n}{2\Delta^2\beta^n}\left[\exp\left(\frac{k_0 q^n}{\beta^n} - k_0^2\Delta^2\right) - 1\right]\right\} \tag{7}$$

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

a) For the distribution with the decreasing exponential function f$(k)$ we obtain:

$$W = \frac{W_0^N}{1+\Delta\left(\frac{A}{\beta}\right)^n}\cdot\exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right] \tag{8}$$

Using the same procedure as above the next form for the energy distribution function is obtained from equ. (8):

$$f_c(Q) = \frac{n\cdot q^{n-1}\exp\left[-k_0\left(\frac{q}{\beta}\right)^n\right]}{\beta^n + \Delta q^n}\left(\frac{\Delta\beta^n}{\beta^n+\Delta q^n} + k_0\right) \tag{9}$$

b) For the distribution with the increasing exponential function f$(k)$

$$W = \frac{W_0^N\left\{\exp\left[-k_0\left(\frac{A}{\beta}\right)^n\right] - \exp\left(-\frac{k_0}{\Delta}\right)\right\}}{\left[1-\Delta\left(\frac{A}{\beta}\right)^n\right]\left[1-\exp\left(-\frac{k_0}{\Delta}\right)\right]} \tag{10}$$

Differentiation of equ. (10) with respect to $Q$ gives:

$$f_c(Q) = \frac{n \cdot q^{n-1}}{\beta^n - \Delta q^n} \cdot \frac{1}{1 - \exp\left(-\frac{k_0}{\Delta}\right)} \left\{ k_0 \exp\left(-\frac{k_0 q^n}{\beta^n}\right) - \right.$$

$$\left. - \frac{\beta^n \Delta \left[\exp\left(-\frac{k_0 q^n}{\beta^n}\right) - \exp\left(-\frac{k_0}{\Delta}\right)\right]}{\beta^n - \Delta q^n} \right\} \tag{11}$$

The heterogeneity curves for the studied adsorbents result from equs. (3), (5), (7), (9), and (11) as well as the DR and DA global isotherms. A characteristic example is presented in Fig. 1.

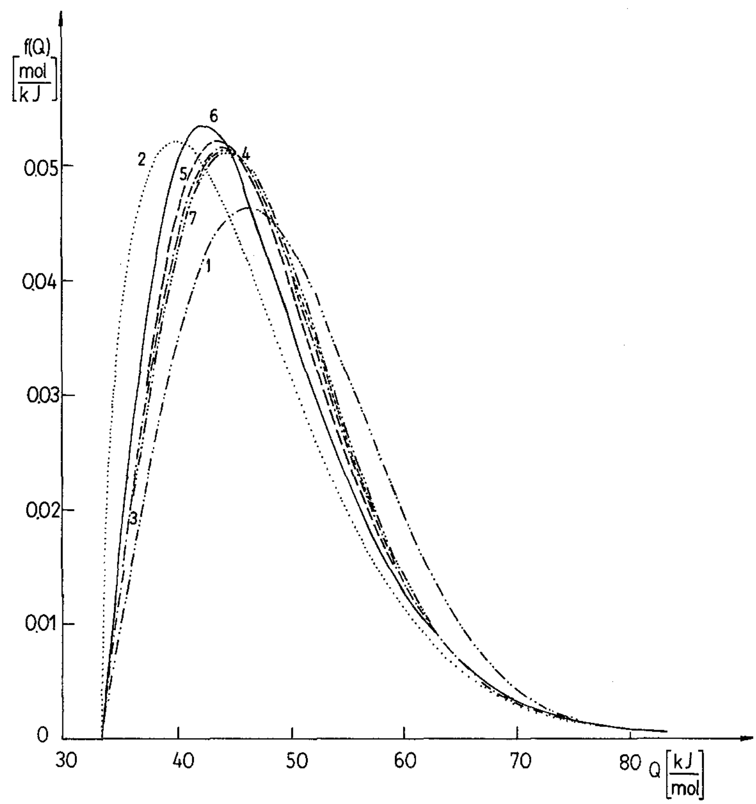


Fig. 1. Functions of the adsorption energy distribution for $C_6H_6$ adsorption on carbon D; *1* after equ. (DR); *2* after equ. (DA); *3* after equ. (3) for $n = 2$; *4* after equ. (5) for $n = 2$; *5* after equ. (7) for $n = 2$; *6* after equ. (9) for $n = 2$; *7* after equ. (11) for $n = 2$

The curves of the heterogeneity distribution (Fig. 1) give a very wide common range of the $Q$ values in spite of differencies in the form of the global adsorption isotherm. In general every applied distribution $f(Q)$ except the distribution resulting from the DA equation (often open distribution), can be used for the determination of the microporous adsorbents heterogeneity.

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