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Consequence of Assuming Gamma-Type Distribution for Characterizing Structural Heterogeneity of Microporous Solids

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Extensive model studies were carried out for the gamma-type distribution, which was used to characterize structural heterogeneity of microporous solids. This distribution lead to a simple equation, which gave a good representation of many adsorption isotherms measured on microporous activated carbons. Assuming physically realistic values of the adsorption parameters, the gamma-type distribution curves were calculated together with curves of the adsorption isotherm, micropore distribution, adsorption potential distribution, enthalpy and entropy of adsorption.

(Keywords: Adsorption on microporous solids; Gas adsorption; Micropore distribution; Structural heterogeneity of solids; Thermodynamics of adsorption)

Die Konsequenz der Annahme einer Gamma-Typ-Verteilung bei der Charakterisierung der strukturellen Heterogenität von mikroporösen Feststoffen

Es wurden für die Gamma-Typ-Verteilung, die zur Charakterisierung der strukturellen Heterogenität von mikroporösen Feststoffen genutzt wurde, ausgedehnte Modellrechnungen durchgeführt. Diese Verteilung führte zu einer einfachen Gleichung, die eine gute Darstellung vieler Adsorptionsisothermen an mikroporös-aktiviertem Kohlenstoff erlaubt. Unter der Annahme von physikalisch realistischen Werten für die Adsorptionsparameter wurden die Gamma-Typ-Verteilungskurven zusammen mit Kurven für die Adsorptionsisothermen, der Mikroporenverteilung, der Adsorptionspotentialverteilung und der Enthalphie und Entropie der Adsorption berechnet.

Introduction

Several equations have been proposed to describe gas adsorption on heterogeneous microporous solids [1–4]. One of them has a simple mathematical form in comparison to other equations [2, 5] and gives a good representation of gas adsorption isotherms measured on microporous activated carbons [5–7]; it is [6]

$$\theta = [q\beta^2/(q\beta^2 + A^2)]^{m+1} \tag{1}$$

where

$$A = RT\ln(p_0/p) \tag{2}$$

Here θ denotes the relative adsorption in micropores at the equilibrium pressure p and absolute temperature T, p_0 is the saturation vapour pressure, A is the adsorption potential defined by Eq. (2), β is the similarity coefficient depending from the adsorptive, q and m are parameters of the distribution function which leads to the adsorption isotherm Eq. (1). The parameters q and $(m + 1)$ are greater than zero. The isotherm Eq. (1) is very promising for analysing the gas adsorption data on microporous solids [5–7]; this encouraged us for performing extensive model studies, which showed the influence of the parameters q and m on the behaviour of the adsorption isotherm, micropore distribution and other thermodynamic functions. Knowledge of physical and mathematical properties of the isotherm Eq. (2) facilitates its application for interpreting the experimental data of gas adsorption on heterogeneous microporous solids.

Theory

Equation (1) has been obtained by solving the following integral equation:

$$\theta(A) = \int_0^\infty \exp[-B(A/\beta)^2]\,F(B)\,\mathrm{d}B \tag{3}$$

with the gamma-type distribution $F(B)$, i.e.,

$$F(B) = [q^{m+1}/\Gamma(m+1)]\,B^m\exp(-qB) \tag{4}$$

Here B is the structural parameter appearing in the *Dubinin-Radushkevich* (*DR*) equation, which is the kernel in Eq. (3). The parameter B is proportional to the square of the micropore dimension x, i.e. [4],

$$B = cx^2 \tag{5}$$

The micropore distribution $J(x)$, which relates to the distribution function $F(B)$ given by Eq. (4), is [5]:

$$J(x) = [2(q^*)^{m+1}/\Gamma(m+1)]\,x^{2m+1}\exp(-q^*x^2) \tag{6}$$

where

$$q^* = cq \tag{7}$$

The condensation approximation method [8] enables calculation the adsorption potential distribution $X(A)$, which characterizes structural heterogeneity of a microporous solid by means of the adsorption potential A. The isotherm Eq. (1) corresponds to the following distribution $X(A)$:

$$X(A) = 2(m+1)(q\beta^2)^{m+1} A / [q\beta^2 + A^2]^{m+2} \tag{8}$$

This distribution function is useful for calculating the differential molar enthalpy of adsorption ΔH and entropy of adsorption ΔS; for adsorption in micropores these quantities are defined as follows [9]:

$$\Delta H = -A - \alpha T \theta(A)/X(A) \tag{9}$$

$$\Delta S = -\alpha\theta(A)/X(A) \tag{10}$$

where $\theta(A)$ denotes the so-called characteristic curve and $X(A)$ is the adsorption potential distribution associated with $\theta(A)$. The parameter α is the thermal coefficient of the limiting adsorption taken with a minus sign [10]. Combination of Eqs. (9) and (10) with Eqs. (1) and (8) gives:

$$\Delta H = -A - \frac{\alpha T(q\beta^2 + A^2)}{2A(m+1)} \tag{11}$$

$$\Delta S = -\frac{\alpha(q\beta^2 + A^2)}{2A(m+1)} \tag{12}$$

Equations (11) and (12) enable the plotting of ΔH and ΔS against A. To draw the enthalpy ΔH and entropy ΔS against θ, the function $A(\theta)$ should be defined; this function may be obtained from the isotherm Eq. (1):

$$A = \beta\sqrt{q}\,(\theta^{-1/(m+1)} - 1)^{1/2} \tag{13}$$

Substitution of Eq. (13) into Eqs. (11) and (12) leads to the expressions, which define ΔH and ΔS as functions of θ.

Results and Discussion

Equations (1), (4), (6), (8), (11), (12), and (13) were used to perform model studies, which showed the influence of the adsorption parameters m and q on the behaviour of the functions $F(B)$, $J(x)$, $X(A)$, $\theta(A)$, $\Delta H(A)$ and $\Delta S(A)$. The model studies were carried out for $m = 1$, $q = 100$; 500; $1\,000$ (kJ/mol)^2 and $q = 500$ (kJ/mol)^2, $m = 0.5$; 1.0; 2.0; Figs. 1–4 show these dependences. The parameters m and q used in the model calculations are similar to those obtained from the benzene adsorption isotherms on activated carbons [5–7]. The other parameters were assumed as follows [4]: $\beta = 1$, $c = 0.00694$ (kJ nm/mol)^2, $\alpha = 0.001\,\mathrm{K}^{-1}$ and $T = 293\,\mathrm{K}$.

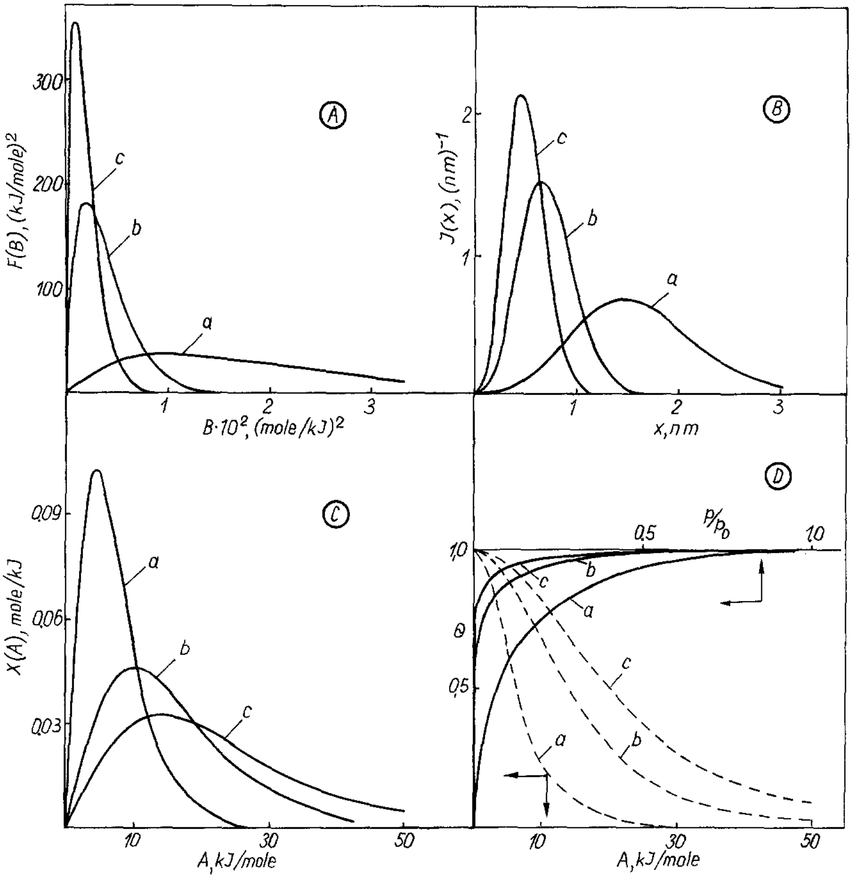

Fig. 1. Distribution functions $F(B)$, $J(x)$, $X(A)$ and adsorption isotherm $\theta(p/p_0)$ calculated according to Eqs. (4), (6), (8), and (1), respectively, for $m = 1$ and $q = 100$ (a), 500 (b) and 1 000 $(\mathrm{kJ/mol})^2$ (c); dashed lines denote the characteristic curves $\theta(A)$ for the above parameters

Thus, the theoretical curves presented in Figs. 1–4 are physically realistic and characterize the benzene adsorption on activated carbons of different structural heterogeneity. Figures 1 and 2 present the model calculations for $m = 1$ and different values of $q = 100$; 500; 1 000 $(\mathrm{kJ/mol})^2$, whereas Figs. 3 and 4 show analogous dependences for $q = 500$ $(\mathrm{kJ/mol})^2$ and different values of $m = 0.5$; 1; 2. It follows from these figures that the distribution functions $F(B)$, $J(x)$ and $X(A)$ show a maximum. The dependences $-\Delta H$ and $-\Delta S$ plotted as functions of A and θ show a minimum; this means that ΔH vs. A, ΔH vs. θ, ΔS vs. A and ΔS vs. θ show

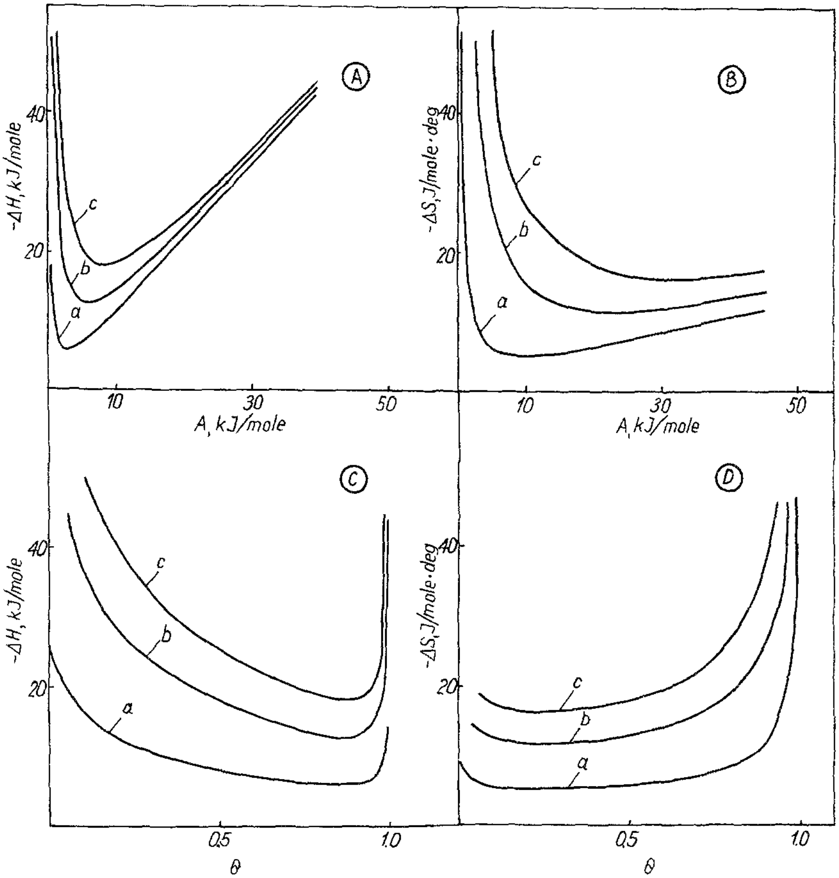

Fig. 2. Enthalpy and entropy of adsorption calculated according to Eqs. (11) and (12), respectively, for $m = 1$ and $q = 100$ (*a*), 500 (*b*), 1 000 $(\mathrm{kJ/mol})^2$ (*c*)

Table 1. *Equations defining values of the argument at which the functions $F(B)$, $J(x)$, $X(A)$, $\Delta H(A)$, $\Delta H(\theta)$, $\Delta S(A)$ and $\Delta S(\theta)$ reach the extreme points*

Function	Equation	Value of the argument at the extreme point
$F(B)$	(4)	$B_m = m/q$
$J(x)$	(6)	$x_m = [(2m + 1)/(2q^*)]^{1/2}$
$X(A)$	(8)	$A_m = \beta[q/(2m + 3)]^{1/2}$
$\Delta H(A)$	(11)	$A_m = \left[\dfrac{\alpha T\beta^2 q}{2(m + 1) + \alpha T}\right]^{1/2}$
$\Delta H(\theta)$	(11), (13)	$\theta_m = \left[\dfrac{\alpha T}{2(m + 1)\alpha T} + 1\right]^{-(m+1)}$
$\Delta S(A)$	(12)	$A_m = \beta\sqrt{q}$
$\Delta S(\theta)$	(12), (13)	$\theta_m = 2^{-(m+1)}$

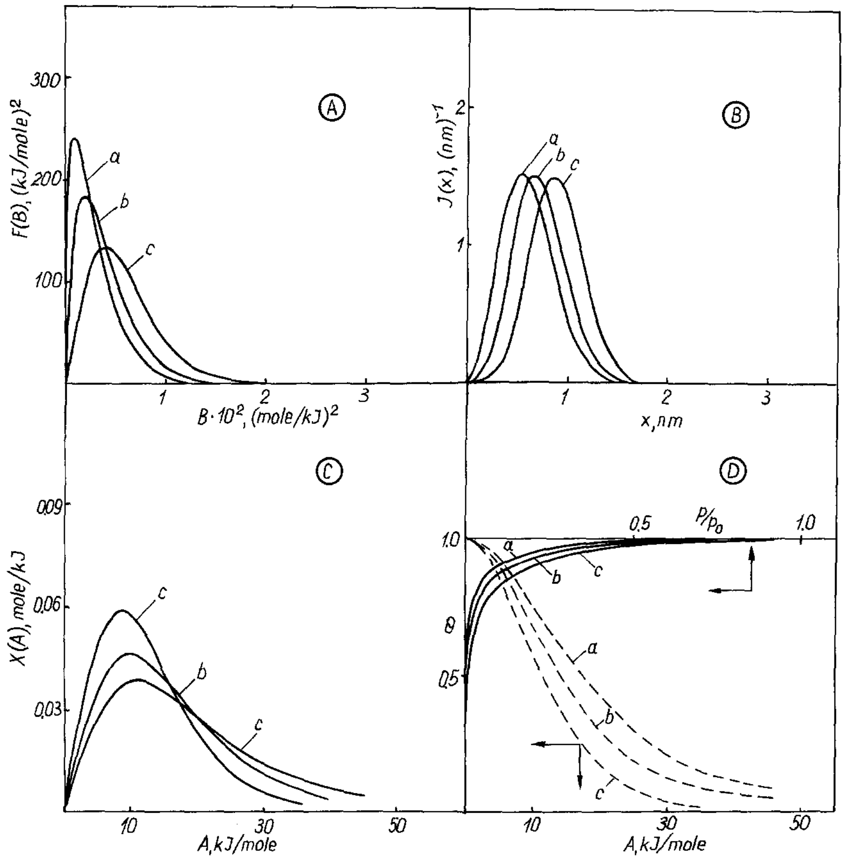

Fig. 3. Distribution functions $F(B)$, $J(x)$, $X(A)$ and adsorption isotherm $\theta(p/p_0)$ calculated according to Eqs. (4), (6), (8), and (1), respectively, for $q = 500$ (kJ/mol)^2 and $m = 0.5$ (*a*); 1 (*b*); 2 (*c*); dashed lines denote the characteristic curves $\theta(A)$ for the above parameters

Table 2. *Coordinates of the extreme points for distribution functions $F(B)$, $J(x)$ and $X(A)$ presented in Figs. 1 and 2*

		Function $F(B)$		Function $J(x)$		Function $X(A)$	
m	q (kJ/mol)^2	B_m (mol/kJ)^2	$F(B_m)$ (kJ/mol)^2	x_m (nm)	$J(x_m)$ (nm)$^{-1}$	A_m (kJ/mol)	$X(A_m)$ (mol/kJ)
1.0	100	0.01	36.79	1.47	0.68	4.47	0.104
1.0	500	0.002	183.94	0.66	1.53	10.00	0.046
1.0	1 000	0.001	367.88	0.46	2.16	14.14	0.033
0.5	500	0.001	241.97	0.54	1.55	11.18	0.038
2.0	500	0.004	135.34	0.85	1.51	8.45	0.059

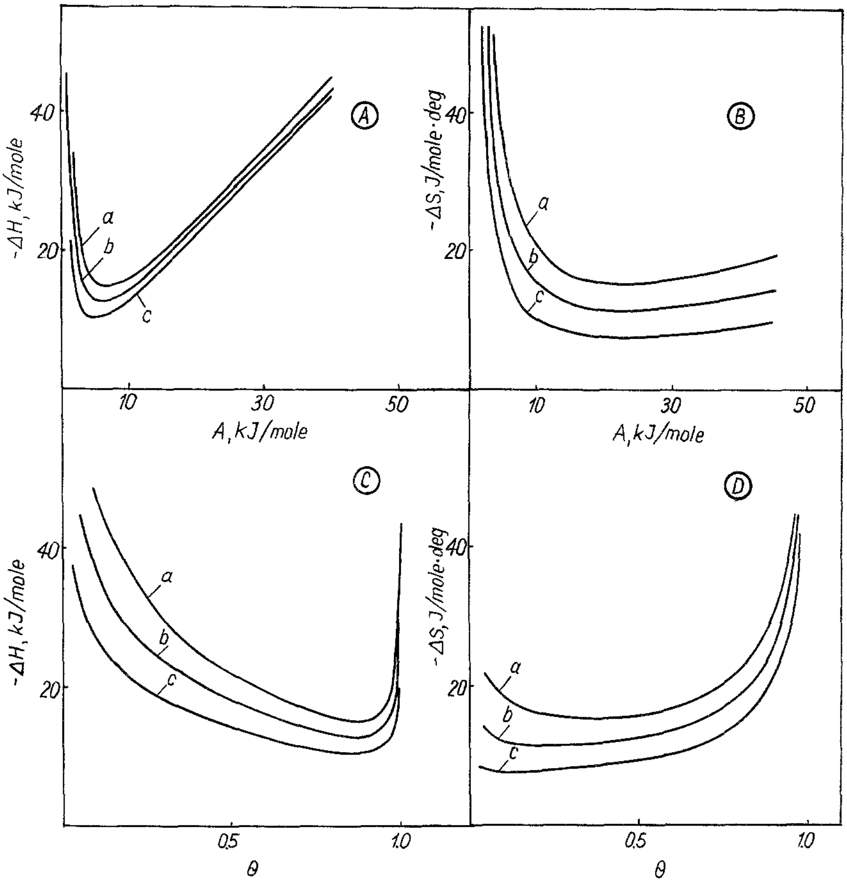

Fig. 4. Enthalpy and entropy of adsorption calculated according to Eqs. (11) and (12), respectively, for $q = 500$ (kJ/mol)^2 and $m = 0.5$ (*a*); 1 (*b*); 2 (*c*)

Table 3. *Coordinates of the extreme points for the enthalpy and entropy of adsorption plotted against A and θ in Figs. 1 and 2*

		Enthalpy ΔH			Entropy ΔS		
m	q (kJ/mol)^2	A_m (kJ/mol)	θ_m	$-\Delta H$ (kJ/mol)	A_m (kJ/mol)	θ_m	$-\Delta S$ (J/mol K)
1.0	100	2.61	0.88	5.61	10.00	0.25	5.0
1.0	500	5.84	0.88	12.54	22.36	0.25	11.2
1.0	1 000	8.26	0.88	17.73	31.62	0.25	15.8
0.5	500	6.67	0.88	14.64	22.36	0.35	14.9
2.0	500	4.82	0.87	10.12	22.36	0.13	7.5

a maximum. Table 1 presents equations defining values of the arguments at the extreme points for $F(B)$, $J(x)$, $X(A)$, ΔH and ΔS. Tables 2 and 3 contain coordinates of the extreme points for the curves presented in Figs. 1–4.

The distribution function $F(B)$ given by Eq. (4) is asymmetrical (see Figs. 1A and 3A). For greater values of q or smaller values of m this distribution becomes sharper and its maximum approaches to the $F(B)$-axis. The gamma-type distribution $F(B)$ generates the micropore distribution $J(x)$ given by Eq. (6), which is practically symmetrical (see Figs. 1B and 3B). It follows from Figs. 1B and 3B that the parameter q determines the distribution width and its maximum, whereas the parameter m determines mainly the value of the argument at the extreme point. For great values of q the values of the average micropore dimension $\bar{x}$ are small and these small micropores are a source of a strong energetic heterogeneity (broad distribution of the adsorption potential A) (see Fig. 1C).

The distribution $X(A)$ is obtained by differentiation of the characteristic curve $\theta(A)$; Figs. 1D and 3D present the characteristic curves θ vs. A for different values of q and m in comparison to the adsorption isotherms $\theta(p/p_0)$.

Figures 2 and 4 present the enthalpy ΔH and entropy ΔS against A and θ. A sudden increase of $-\Delta H$ at the values of θ close to unity results from the properties of the *Dubinin-Radushkevich* equation, in which the adsorption capacity is exponentially dependent on temperature [10]. For smaller values of θ the curves $-\Delta H$ vs. θ are decreasing because microporous solids are energetically heterogeneous; this decreasing becomes stronger for greater values of q (see Fig. 2C).

The above model studies show the physicochemical properties of the distribution functions $F(B)$, $J(x)$, $X(A)$ and the thermodynamic functions ΔH, ΔS, which characterize adsorption on heterogeneous microporous solids. Knowledge of these properties facilitate characterization of microporous adsorption systems.

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