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A Simple Isotherm Equation for Describing Gas Adsorption on Heterogeneous Microporous Solids

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A simple isotherm equation for describing gas adsorption on solids showing heterogeneity of microporous structure is proposed. It is shown that this equation gives a good representation of the experimental data of argon, nitrogen and benzene adsorption on different types of activated carbons. Its parameters may be used to characterize heterogeneity of microporous structure of the solids.

(Keywords: Adsorption of gases; Adsorbent heterogeneity; Microporous adsorbents; Heterogeneity effects in adsorption; Isotherm equations in gas adsorption; Activated carbons)

Eine einfache Isotherme zur Beschreibung der Gas-Adsorption an heterogenen mikroporösen Feststoffen

Es wird eine einfache Isotherme zur Beschreibung der Gasadsorption an Feststoffen mit heterogener mikroporöser Struktur vorgeschlagen. Es wird gezeigt, daß diese Gleichung die experimentellen Daten für die Adsorption von Argon, Stickstoff und Benzol an verschiedenen Typen von Aktivkohle gut beschreibt. Die Parameter der Isotherme können zur Charakterisierung der Heterogenität der mikroporösen Struktur von Festkörpern herangezogen werden.

Introduction

Adsorption of gases and vapours on microporous solids is usually described by means of the *Dubinin-Radushkevich* (*DR*) equation[1—3]. The $\log a$—$\log^2 (p_0/p)$ linear form of this equation, where a is the adsorbed amount and p/p_0 is the relative equilibrium pressure, gives a good representation for many adsorption isotherms measured for microporous solids. However, there is a great number of adsorption data showing

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deviations from the log a—$\log^2(p_0/p)$ straight line predicted by the *DR* equation. To explain this fact *Izotova* and *Dubinin*[4] postulated that the *DR* equation applies only to the solids with an uniform structure of micropores. Thus, the observed deviation of adsorption data from the *DR* straight line may be due to heterogeneity of the microporous structure of the solids. The above idea has been successfully developed by *Stoeckli*[5] to formulate an integral equation describing gas adsorption on heterogeneous microporous solids. *Stoeckli*[5] derived an equation for the overall adsorption isotherm on heterogeneous microporous solids by solving the above mentioned integral equation for a *Gauss*ian distribution function characterizing the heterogeneity of the micropore volume with respect to the structural parameter appearing in the *DR* equation. His overall adsorption isotherm was used for characterizing several adsorption systems[5—7]. Other analytical solutions of the integral equation in question have been presented by *Rozwadowski* and *Wojsz*[8], and *Jaroniec* and *Piotrowska*[9]. The theoretical considerations of *Jaroniec* and *Piotrowska*[9] lead to a very simple equation of the overall adsorption isotherm, which may be easily applied for characterizing the adsorption systems with heterogeneous microporous solids. This isotherm equation will be discussed and examined experimentally in the present paper.

Theory

Generally, the overall single-gas adsorption on a heterogeneous microporous solid is represented by the following integral equation[5]

$$\theta_t(p) = a/a_0 = \int_{\Delta} \exp(-By)\,F(B)\,\mathrm{d}B \qquad (1)$$

where

$$y = [(T/\beta)\log(p_0/p)]^2; \quad p \leqslant p_0 \qquad (2)$$

In the above $\theta_t(p)$ is the relative adsorption at the equilibrium relative pressure p/p_0, a is the adsorbed amount, a_0 is the capacity of the micropores accessible for adsorbate molecules during the adsorption process, B is the structural parameter appearing in the *DR* isotherm equation[1], β is the affinity coefficient depending only on the adsorptive, T is the absolute temperature, $F(B)$ is the distribution function characterizing heterogeneity of the micropore volume with respect to the structural parameter B and Δ is the integration region.

Stoeckli[5] solved the integral Eq. (1) by assuming the normal *Gauss*ian distribution $F(B)$ and obtained the following overall adsorption isotherm:

$$a(p) = a_0 \exp(-\bar{B}y)\exp(0.5\,y^2\tilde{q}^2)\,[0.5(1-\mathrm{erf}(z))] \qquad (3)$$

where

$$z = (y - \bar{B}/\tilde{q}^2)(\tilde{q}/\sqrt{2}) \qquad (4)$$

and $\bar{B}$ is the average value of B, $\tilde{q}$ is the half-width of the *Gaussian* distribution, and erf(z) is the error function.

Assuming in the integral Eq. (1) the gamma-type distribution function:

$$F(B) = [q^{m+1}/\Gamma(m+1)]\,(B—B_0)^m \exp[—q(B—B_0] \qquad (5)$$

for representing $F(B)$, we have:

$$a(p) = a_0 \exp(—B_0 y)\,[q/(q+y)]^{m+l}; \quad q, m > 0 \qquad (6)$$

In the above B_0 is the minimum value of B, m and q are parameters of the distribution function $F(B)$ given by Eq. (5). The gamma-type distribution is widened in direction of high values of B and was successfuly used by severall authors to describe energetic heterogeneity of the solids[10—15]. The average value of B relating to this distribution is given by:

$$\bar{B} = B_0 + m/q \qquad (7)$$

It will be shown later that for many adsorption systems the minimum value of B may be safely replaced by zero and then Eqs. (5)-(7) become:

$$F(B) = [q^{m+1}/\Gamma(m+1)]\,B^m \exp(—qB) \qquad (8)$$

$$a(p) = a_0\,[q/(q+y)]^{m+l} \qquad (9)$$

$$\bar{B} = m/q \qquad (10)$$

Eq. (9) representing the overall adsorption isotherm for heterogeneous microporous solids has a very simple form and seems to be more convenient for describing adsorption data than Eq. (3).

Results and Discussion

To examine the adsorption isotherm equations discussed in the previous section we used the experimental data of argon, nitrogen and benzene adsorption on different types of activated carbons. A basic information concerning the above mentioned adsorption systems is given in Table 1. First, the adsorption isotherms mentioned in Table 1 were approximated by means of Eq. (6). In all cases the best-fit value of the parameter B_0 was very low (about 10^{-18}) and in consequence the term $\exp(—B_0 y)$ appearing in Eq. (6) approaches unity. This means that the lower limit of B of the integration region Δ may be assumed to be equal to zero. Then, Eq. (6), representing the overall adsorption isotherm, reduces to a very simple isotherm given by Eq. (9). This isotherm contains three parameters a_0, q and m, where the ratio m/q determines the average value of B. Similarly, Eq. (3) contains also three parameters: a_0, $\bar{B}$ and $\tilde{q}$ but its mathematical form is more complex than that of Eq. (9). Therefore, Eq. (9) seems to be more convenient for interpreting the adsorption data.

Table 1. *Adsorption systems used to examine the isotherm equations*

No. of system	Temp. K	Adsorbate	Adsorbent code	Source of adsorbent data	Ref.
b	77.3	Ar	BH	Bender-Hobein AG, Zurich	16
a	77.3	N_2	RKD-4	Norit	this work
d	293	C_6H_6	M 22	obtained from apricot kernels	17
c	293	C_6H_6	AC	Merck	this work
e	293	C_6H_6	AG 5	Hajnowka, PL	this work

Table 2. *Adsorption parameters characterizing the systems given in Table 1, calculated according to Eqs. (3) and (9)*

No. of system	Equation (9)					Equation (3)			
	a_0 mmol/g	$\bar{B}\cdot 10^6$ K^{-2}	$q\cdot 10^{-6}$ K^2	m	$\delta\%$	a_0 mmol/g	$\bar{B}\cdot 10^6$ K^{-2}	$\tilde{q}\cdot 10^6$ K^2	$\delta\%$
b	10.35	1.90	1.02	1.94	3.05	10.58	2.65	1.43	3.10
a	9.87	1.61	0.97	1.56	3.69	11.61	1.89	2.09	2.26
d	7.70	0.80	0.50	0.40	2.76	7.31	1.42	1.37	4.35
c	6.10	1.33	0.60	0.80	1.76	7.00	2.21	2.11	1.24
e	3.93	0.66	1.03	0.68	2.12	5.36	1.12	1.46	2.23

The best-fit parameters of Eqs. (3) and (9) relating to the systems mentioned in Table 1 are summarized in Table 2; the latter contains also the relative error values calculated according to the following expression:

$$\delta/\% = (100/n) \sum_{i=1}^{n} [(a_i^{\mathrm{exp}} - a_i^{\mathrm{cal}})/a_i^{\mathrm{exp}}] \qquad (11)$$

where a_i^{exp} and a_i^{cal} denote the experimental and calculated values of the adsorbed amount relating to the i-th experimental point and n is the total number of experimental points. Generally, Eqs. (3) and (9) give a good representation of the adsorption isotherms studied although Eq. (9) approximates these isotherms slightly better (see Figs. 1 and 2). The values of a_0 and $\bar{B}$ predicted by Eq. (3) are higher than those corresponding to Eq. (9). The differences between these parameters are not significant because the distribution functions $F(B)$ show similar behaviour (see Figs. 3 and 4).

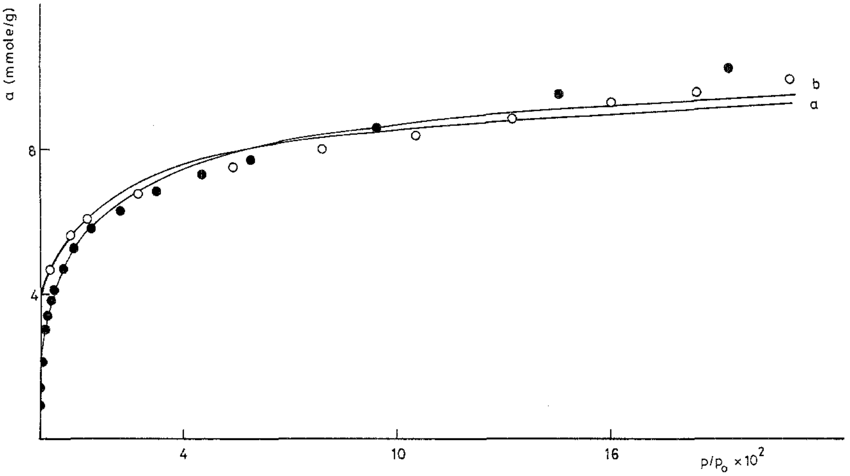

Fig. 1. Argon (●) and nitrogen (○) adsorption isotherms on activated carbons at 77.3 K. The solid lines are calculated according to Eq. (9) using the parameters summarized in Table 2; *a* and *b* refer to nitrogen and argon adsorption data

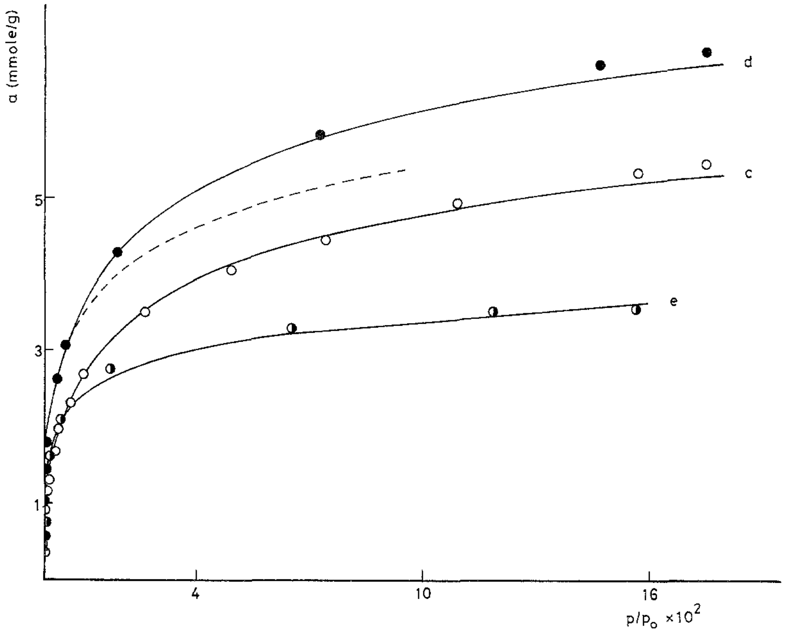

Fig. 2. Benzene adsorption isotherms on activated carbons: M 22 (●), AC (○) and AG 5 (◑) at 293 K. The solid lines are calculated according to Eq. (9) using the parameters summarized in Table 2. *d*, *c* and *e* refer to the systems given in Table 1. The dashed line denotes an adsorption isotherm calculated according to Eq. (3) for the system *d*

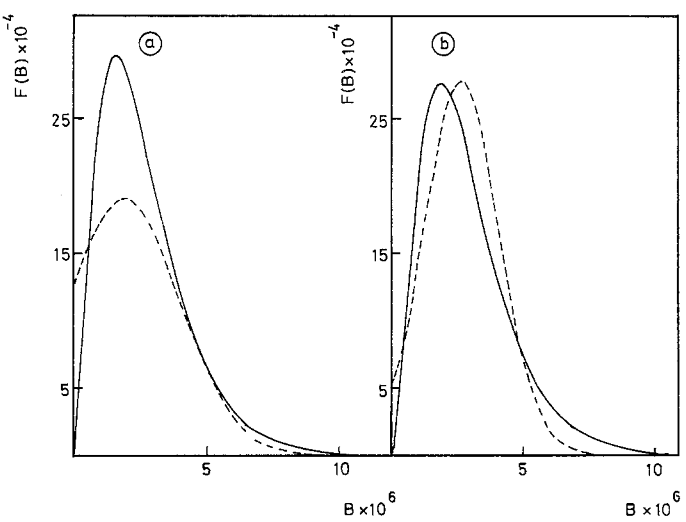

Fig. 3. Gamma-type (solid lines) and *Gauss*ian (dashed lines) distribution functions $F(B)$ calculated according to the parameters given in Table 2 for a and b

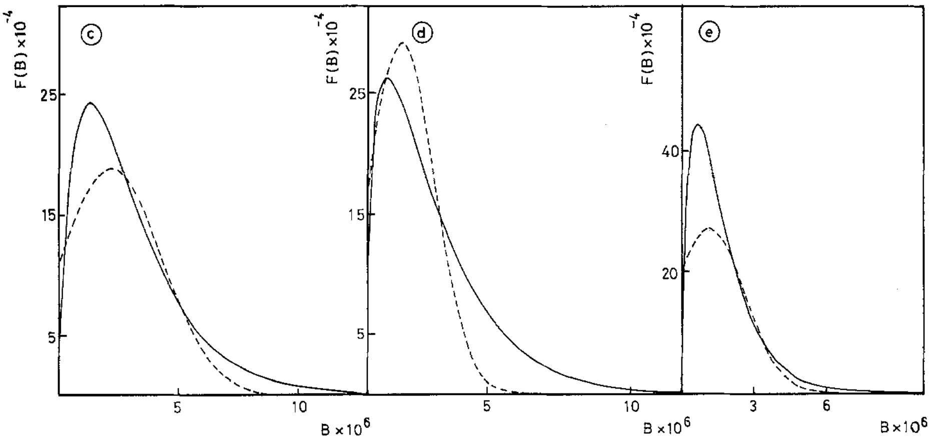

Fig. 4. Gamma-type (solid lines) and *Gauss*ian (dashed lines) distribution functions $F(B)$ calculated according to the parameters given in Table 2 for the systems c, d and e

The functions $F(B)$ calculated according to Eq. (8) are determined in the interval $(0, \infty)$ and are widened in the direction of higher values of B. This behaviour of the distribution functions is characteristic for heterogeneous adsorbents[3, 10—15]. However, the functions $F(B)$ calculated by using the parameters of Eq. (3) are "cut" *Gauss*ian distributions. It is difficult to explain the physical meaning of the value of $F(B)$ relating to $B = 0$. A such behaviour of $F(B)$ at $B = 0$ is a disadvantage of Eq. (3), which can produce the "cut" distributions at $B = 0$. Therefore, Eq. (9) seems to be better to determine the adsorption parameters characterizing the systems with heterogeneous microporous adsorbents.

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