New equation of adsorption for the calculation of parameters of microporous structure

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A new equation describing the equilibrium adsorption of vapors of substances with different physicochemical properties was obtained on the basis of the lognormal distribution of pore volume within the theory of volume filling of micropores. Unlike the existing equations, this equation is more general since it is not related to a specific geometrical model of pores. Adsorption isotherms described by this equation for active carbons with wide pore-size distributions have smaller mean square deviations than those calculated using the Dubinin—Stoeckli equation.

Key words: lognormal distribution of micropore volume, active carbon, benzene, sulfur dioxide, Freon 114B2, carbon disulfide.

The theory of volume filling of micropores (TVFM) developed by M. M. Dubinin and co-workers is widely used for describing the equilibrium adsorption of vapors of substances with a wide variety of physicochemical properties. Active carbons (ACs) manufactured in industrial quantities and under laboratory conditions are certified and classified on the basis of this theory.

The bases of TVFM have been elaborated for carbon adsorbents with relatively homogeneous microporous structures. The equation obtained is known as the Dubinin—Radushkevich equation[1]:

$$a = a_0 \cdot \exp[-(A/(\beta E))^2]. \qquad (1)$$

However, real carbon adsorbents are characterized by heterogeneous microporous structures. In such cases, in addition to the limiting adsorption volume or total micropore volume $W_0 = a_0 \cdot V$ (where V is the molar volume of the adsorbed substance) and characteristic adsorption energy E, the size distribution of micropore volumes is also a rational characteristic of microporous structure. Dubinin and Stoeckli have obtained an equation (DS) that describes the continuous normal size distribution of micropore volumes[2]:

$$W = \frac{W_0^0}{\delta\sqrt{1+2m\delta^2A^2}} \cdot \exp\left[-\frac{mx_0^2A^2}{1+2m\delta^2A^2}\right] \times$$
$$\times\left[1+\operatorname{erf}\left(\frac{x_0}{\delta\sqrt{2\pi}\cdot\sqrt{1+2m\delta^2A^2}}\right)\right], \qquad (2)$$

where δ is the dispersion characterizing the size distribution of micropore volumes, $m = (1/(\beta k))^2$, $k =$ 10÷12 kJ nm mol^{-1}.

The pore size can be estimated rather approximately by small angle X-ray scattering. In this method, the radii of gyration of the pores are generalized sizes. The transition from radii of gyration to geometrical sizes of micropores is rather arbitrary. An attempt to find a correlation between micropore sizes and values inversely proportional to characteristic adsorption energies has been made. In this case, the normal size distribution of micropore volumes acquires the following form:

$$\frac{\mathrm{d}W_0}{\mathrm{d}(1/E)} = \frac{W_0^0}{\Delta\sqrt{2\pi}}\exp\left[-\frac{(1/E_0-1/E)^2}{2\Delta^2}\right], \qquad (3)$$

where Δ is the dispersion (mol J^{-1}).

The following equation was obtained by Dubinin for adsorbents with heterogeneous microporous structures [3]:

$$W = \frac{W_0^0}{2\sqrt{1+2(\Delta A/\beta)^2}}\exp\left[-\frac{1}{1+2(\Delta A/\beta)^2}\left(\frac{A}{\beta E_0}\right)^2\right] \times$$
$$\times\left[1+\operatorname{erf}\left(\frac{1}{\sqrt{2}\ E_0\Delta}\frac{1}{\sqrt{1+2(\Delta A/\beta)^2}}\right)\right]. \qquad (4)$$

In this equation, the dimensionality of Δ is not quite logical, although Δ is taken as a parameter indirectly characterizing the size of micropores. In addition, Eq. (4) does not describe the equilibrium adsorption more precisely than Eq. (2).

The modern technology of AC production makes it possible to vary the parameters of porous structure over a wide range and synthesize samples with developed supermicroporous structures. However, it is difficult to get reliable information about the micropores in these

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adsorbents, since the experimental data deviate from the calculated ones by more than 20 % when the adsorption isotherms for a series of samples are described by TVFM equations. It was of interest to derive a new equation which would describe more precisely the adsorption in micropores.

We started with a lognormal distribution of pore volumes over characteristic adsorption energies E without any specific geometrical model of a micropore. The equation proposed can be used for describing equilibrium adsorption by adsorbents with micropores of crevice-like, hemispherical, V-shaped, and other forms.

In a general case, the function of normal distribution has the form:

$$\frac{\mathrm{d}W_0}{\mathrm{d}x} = \frac{W_0^0}{6\sqrt{2\pi}}\exp\left[-\frac{(x-x_0)^2}{2\delta^2}\right], \qquad (5)$$

$\int_{-\infty}^{+\infty} f\mathrm{d}x = 1$, where x is the half width of the micropores (x changes from $-\infty$ to $+\infty$).

When passing from x to $\ln E$, the value of E changes from 0 to $+\infty$ (x may have any value from $-\infty$ to $+\infty$). If $\phi\Delta E$ is the fraction of the volume of micropores, whose characteristic energy lies from E to $E+\Delta E$, then $f\mathrm{d}x = \phi\mathrm{d}E$, and, taking into account that $\mathrm{d}x = \mathrm{d}\ln E = \mathrm{d}E/E$, we obtain $\phi = f(1/E)$.

The fraction of filling for every group of micropores with characteristic energy E is determined by the factor

$$Z = \exp\left[-\left(\frac{RT\ln(p_s/p)}{E}\right)^2\right] = \exp\left[-\left(\frac{A}{E}\right)^2\right]. \qquad (6)$$

Then the fraction of filling for the total volume of micropores may be expressed by the integral:

$$W = W_0^L\int_0^\infty \varphi\cdot\exp\left[-\left(\frac{A}{E}\right)^2\right]\mathrm{d}E = \frac{W_0}{\sigma\sqrt{2\pi}}\int_0^\infty \frac{1}{E}\exp\left[-\frac{\ln^2 E/E_0^L}{2\sigma^2}\right] \times$$
$$\times \exp\left[-\left(\frac{A}{E}\right)^2\right]\mathrm{d}E.$$

Rearrangement of Eq. (7) results in the following expression:

$$a = \frac{W_0^L}{V}\frac{2}{\sigma\sqrt{2\pi}\cdot A^2}\int_0^1 E^2\exp\left[-\left(\frac{\ln E/E_0^L}{\sigma\sqrt{2\pi}}\right)^2\right]\mathrm{d}Z. \qquad (8)$$

The value of adsorption in Eq. (8) depends on three parameters: $W_0{}^L$, $E_0{}^L$, and δ.

Experimental

Adsorption isotherms were obtained for benzene, sulfur dioxide, Freon 114B2 (1,1,2,2-tetrafluorodibromoethane), and carbon disulfide at 293 K under equilibrium conditions. Carbons with different porous structures were used as adsorbents. They were prepared on the basis of hard coal, except AC-VI, which was prepared from furfural.

Results and Discussion

Table 1 presents the parameters of microporous structure for different types of ACs. The parameters were obtained from the experimental adsorption isotherms of benzene using the lognormal Eq. (8) and Eq. (2). The mean square deviation of calculated isotherms from the experimental ones was chosen as a criterion of adequacy of the description of adsorption on AC by the normal and lognormal distribution laws. Table 1 also presents the mean deviations (MD) of the calculated isotherms from the experimental ones at relative pressures within $p/p_s = (1\cdot10^{-6}$—$0.4)$. As can be seen from Table 1, the adsorption isotherms described by Eq. (8) have lower MD than those calculated using the DS equation. The limiting volumes of adsorption space and characteristic adsorption energies calculated according to Eqs. (2) and (8) are practically equal. The dispersion σ of Eq. (8) defines the distribution of micropore volumes over characteristic adsorption energy and has the dimensionality of this adsorption energy, which depends on the size of the pores available for adsorbents.

The adsorption isotherms of benzene and other substances were calculated using lognormal Eq. (8) and Eq. (2). The mean deviations of these results from the experimental data are given in Tables 2 and 3. The model of lognormal size distribution of pore volume is in

Table 1. Parameters of microporous structure of active carbons

Sample	Lognormal equation (8)				Equation (2)				
	$W_0{}^L$ /cm^3 g^{-1}	$E_0{}^L$ /kJ mol^{-1}	σ /kJ mol^{-1}	$\bar{D}$* (%)	$W_0{}^0$ /cm^3 g^{-1}	E_0 /kJ mol^{-1}	x_0 /nm	δ /nm	$\bar{D}$* (%)
AC-III	0.403	16.43	0.478	3.7	0.396	16.03	0.624	0.251	9.5
AC-IV	0.265	20.82	0.307	2.7	0.260	20.57	0.486	0.124	3.0
AC-V	0.367	16.68	0.323	2.5	0.363	16.06	0.622	0.188	4.8
AC-VIII	0.455	11.11	0.496	4.1	0.446	10.79	0.927	0.364	7.8

* $\bar{D}$ is mean deviation.

Table 2. Deviations of calculated values for adsorption of benzene vapor from experimental data

Sample	p/p_s	Deviation of a_{theor} from a_{exp} (%) for equation	
		(2)	(8)
AC-III	$1.19 \cdot 10^{-6}$	16.0	6.6
	$3.64 \cdot 10^{-6}$	−9.9	−5.4
	$1.25 \cdot 10^{-5}$	−12.1	−6.9
		9.5*	3.7*
AC-V	$6.20 \cdot 10^{-6}$	10.8	1.9
	$1.06 \cdot 10^{-5}$	7.6	2.8
	$3 \cdot 10^{-5}$—0.15	1—8	1—4
		4.8*	2.5*
AC-VI	$1.22 \cdot 10^{-6}$	−12.1	−1.1
	$2.46 \cdot 10^{-5}$	−13.4	−2.6
	$1 \cdot 10^{-3}$—0.1	0.3—8	0.2—5
		6.8*	3.8*
AC-VIII	$8.90 \cdot 10^{-6}$	24.1	7.5
	$2.16 \cdot 10^{-6}$	18.6	7.9
	$8 \cdot 10^{-5}$—0.3	1—7	0.2—3
		8.8*	4.1*

* Mean deviation.

better agreement with experiment practically in all cases. Equation (8) describes most precisely the equilibrium adsorption of vapors in the region of small pressures ($p/p_s < 0.01$), *i.e.*, in the region which is of most interest from the practical viewpoint.

Hence, we obtained an equation based on the log-normal distribution of micropore volume over characteristic adsorption energies, unrelated to any specific form of micropores. The equation describes the adsorption of vapors on the different types of AC with high accuracy.

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Table 3. Deviations of calculated values for adsorption from experimental data

System	p/p_s	Deviation of a_{theor} from a_{exp} (%) for equation	
		(2)	(8)
AC-VI—SO$_2$	$5.31 \cdot 10^{-4}$	−18.7	−8.2
	$1.91 \cdot 10^{-3}$	13.4	5.3
	$3.10 \cdot 10^{-3}$	14.0	4.6
	$5 \cdot 10^{-3}$—0.15	5—10	0.1—5
		16.9*	3.0*
AC-VII—SO$_2$	$1.65 \cdot 10^{-4}$	47.2	10.2
	$3.79 \cdot 10^{-4}$	16.9	2.8
	$8.79 \cdot 10^{-3}$	20.6	−4.7
	$1.44 \cdot 10^{-3}$	−28.9	−5.67
	$1 \cdot 10^{-2}$—0.3	2—17	1—6
		25.1*	4.6*
AC-VIII—CS$_2$	$2.30 \cdot 10^{-4}$	19.5	4.8
	$3.11 \cdot 10^{-4}$	14.4	2.2
	$5 \cdot 10^{-3}$—0.4	0.5—9	1—5
		8.8*	4.6*
AC-VI—Freon 114B2	$2.16 \cdot 10^{-4}$	−12.4	−1.3
	$3.60 \cdot 10^{-4}$	−5.4	2.3
	$1 \cdot 10^{-3}$—0.2	0.3—4.0	0.1—1
		3.5*	0.8*

* Mean deviation.

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