Adsorption of vapors and gases by carbon sorbents with homogeneous microporous structures in the initial region of the adsorption isotherm

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Examination of the adsorption isotherm equation derived from the theory of volume filling of micropores (TVFM) showed that the region of low pressures of experimental isotherms is not always described by this equation. A method for describing the initial region of adsorption isotherms using the parameters of TVFM was proposed.

Key words: adsorption isotherm, theory of volume filling of micropores, equilibrium adsorption.

Adsorption of gases and vapors by microporous sorbents can be described with sufficient accuracy in most cases in terms of the theory of volume filling of micropores (TVFM). For sorbents with uniform microporous structures, the equation describing the isotherm of adsorption of vapors of substances has the following form[1]

$$a = a_0 \cdot \exp\{-[A/(\beta E_0)]^2\}, \qquad (1)$$

$$a_0 = W_0/V^*, \qquad (2)$$

where a and a_0/mmol g^{-1} are the amount adsorbed and its limiting value, respectively, V^*/cm^3 mmol^{-1} is the molar volume of the adsorbed phase, W_0/cm^3 g^{-1} is the limiting volume of the adsorption space in the micropores, $A = RT \cdot \ln(p_s/p)$/kJ mol^{-1} is the differential molar work of adsorption, E_0/kJ mol^{-1} is the characteristic energy of adsorption, and β is the coefficient of similarity.

Previously,[2] a method for the calculation of a unified characteristic curve based on adsorption isotherms both for gases and vapors has been proposed.

The molar volume of a substance in the adsorbed state at temperatures $T < T_{cr}$ can be calculated using the following relations:

$$V^* = M/1000\rho,$$

$$\rho = \rho_{boil} - [(\rho_{boil} - \rho_m)/(T_{cr} - T_{boil})](T - T_{boil}),$$

$$\rho_m = M/1000b,$$

while at $T > T_{cr}$,

$$V^* = b,$$

where b/cm^3 mmol^{-1} is the constant of the van der Waals equation, M/g mol^{-1} is the molecular weight of the substance; ρ_{boil}/g cm^{-3} is the density of the substance at the boiling point.

The differential molar work of adsorption is calculated from the equation $A = RT \cdot \ln(p_a/p)$; $p_a = p_s$ for vapors and $p_a = (T/T_{cr})^2 p_{cr}$ in the case of adsorption of gases.

It has been shown in a previous study[3] that Eq. (1) does not hold over the whole range of pressures. In the initial sections of adsorption isotherms, the experimental and calculated values of a differ appreciably (by factors of tens or higher). In some cases, adsorption occurs exactly in this region.

The purpose of this study is to identify the lower limit of applicability of the TVFM equation and to elucidate the possibility of describing adsorption isotherms at low coverages.

If we introduce the designations

$$x = p/p_a,\ \theta = a/a_0,\ k_1 = [RT/(\beta E_0)]^2,$$

equation (1) assumes the form

$$\theta = \exp(-k_1 \ln^2 x). \qquad (3)$$

Let us consider the graphical form of the dependence described by Eq. (3) (Fig. 1). This dependence contains an inflection point (see Fig. 1, point *B*); above this point, the curve of the $\theta(x)$ plot is convex, and below

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1778—1780, October, 1997.

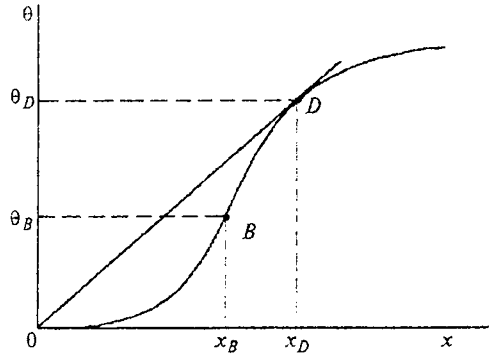

Fig. 1. Graphical form of the equation of the Dubinin—Radushkevich adsorption isotherm in the initial region.

this point, it is concave. It is known that at $x \to 0$ ($p \to 0$), adsorption systems are described by the equation $a = \mathrm{H}p$ (Henry's adsorption isotherm). To satisfy this requirement, let us draw a tangent from the origin of coordinates to the curve plotted using the TVFM equation and write the equation describing the straight line

$$\theta = k_2 x. \tag{4}$$

To ensure that the adsorption isotherm is continuously described by Eqs. (3) and (4), the right-hand sides of the equations and their derivatives must be equal at the point of tangency (see Fig. 1, point D). Let us write the following set of equations:

$$\begin{cases} \theta(x_D) = k_2 x_D \\ \dfrac{-2k_1\theta(x_D)\ln x_D}{x_D} = k_2 \end{cases}. \tag{5}$$

By solving this set of equations we obtain the coordinates of point D:

$$\ln x_D = -1/2k_1,\ \ln\theta_D = -1/4k_1.$$

Thus, we determined the coordinates of the point up to which the adsorption isotherm can be described by a linear equation and after which it is described by the TVFM equation:

$$\theta = p/p_a \exp[\beta^2E_0^2/(4R^2T^2)] \tag{6}$$
$$\text{at } p/p_a < \exp\{-[\beta^2E_0^2/(2R^2T^2)]\},$$

$$\theta = \exp\{-[R^2T^2/\beta^2E_0^2]\ln^2(p_a/p)]\} \tag{7}$$
$$\text{at } p/p_a \geq \exp\{-[\beta^2E_0^2/(2R^2T^2)]\}.$$

To make experimental verification more convenient, let us present Eq. (7) in the form

$$\ln\theta = -(A^2/\beta^2E_0^2),\ \text{at } A^2 \leq \beta^4E_0^4/4R^2T^2, \tag{8}$$

and let us write Eq. (6) as

$$R^2T^2\ln\theta = \beta^2E_0^2/4 - R^2T^2\ln(p_a/p) \tag{9}$$
$$\text{at } R^2T^2\ln(p_a/p) > \beta^2E_0^2/2.$$

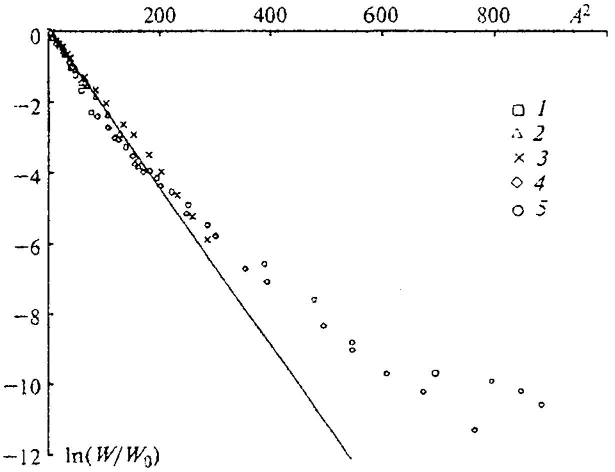

Fig. 2. Isotherms of adsorption of nitrogen on activated carbon (AG) in the coordinates of Eq. (1) at various temperatures (K): 77.4 (*1*), 101.2 (*2*), 126.2 (*3*), 233.2 (*4*), and 273.2 (*5*).

To verify the resulting relations, we used experimental data obtained previously.[2]

Figure 2 shows the adsorption isotherms of nitrogen on the AG activated carbon (parameters of the porous structure of the adsorbent: $W_0 = 0.32$ cm^3 g^{-1}, $E_0 = 18.5$ kJ mol^{-1}) at several temperatures plotted in the coordinates of the TVFM equation. The physicochemical properties of the adsorptive are listed in Table 1. It can be seen in Fig. 2 that in the region of low p values at $A^2 > 200$ the experimental points are poorly described by Eq. (1). The points in the plot constructed in $\ln(W/W_0)$—A^2 coordinates deviate from a straight line. This indicates that the TVFM equation does not describe the adsorption isotherms for the systems under study in the region of low relative pressures (concentrations). A similar examination of the experimental adsorption isotherms was carried out for the adsorption of a number of substances (krypton, xenon, tetrafluoroethylene) on the same adsorbent at several temperatures ranging from 120 to 323 K. The main physicochemical properties of the studied compounds are listed in Table 1.

At the same time, the isotherms plotted in $R^2T^2\ln(W/W_0)$—$R^2T^2\ln(p_a/p)$ coordinates (Fig. 3) fall rather well on a straight line in the region of low coverages. The straight line drawn through these points

Table 1. Physicochemical properties of the substances used for adsorption

Substance	M /g mol^{-1}	T_{boil}	T_{cr}	p_{cr} /atm	b /cm^3 mol^{-1}
		K			
N_2	28.02	77.4	126.1	33.5	38.6
Kr	83.7	120.3	210.2	54.0	39.8
Xe	131.3	166.1	289.8	58.2	51.1
C_2F_4	100.0	196.9	306.5	38.9	80.8

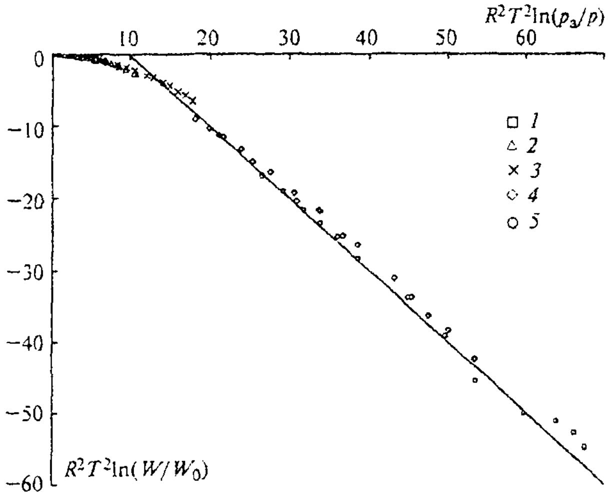

Fig. 3. Isotherms of adsorption of nitrogen on activated carbon (AG) in the coordinates of Eq. (9) at various temperatures (K): 77.4 (*1*), 101.2 (*2*), 126.2 (*3*), 233.2 (*4*), and 273.2 (*5*).

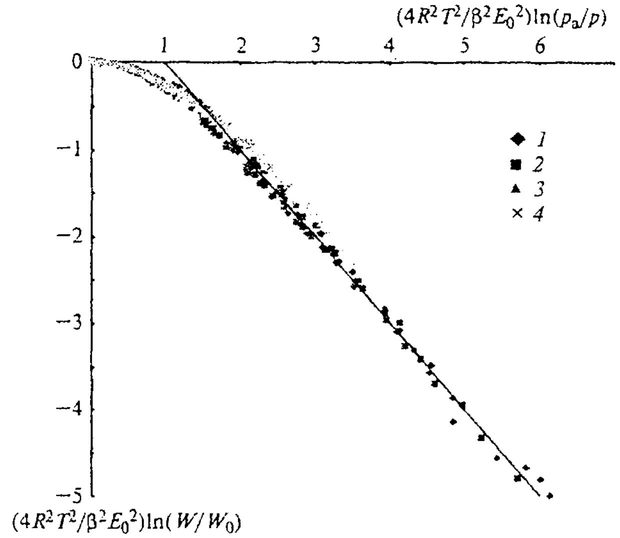

Fig. 4. Isotherms of adsorption of N_2 (*1*), Kr (*2*), Xe (*3*), and tetrafluoroethylene (*4*) on AG activated carbon at 120—323 K.

is inclined an angle of 45° with respect to the axes of the plot and intersects the abscissa axis at the point with the coordinates $\beta^2E_0{}^2/4$. The abscissa of point *D* (see Fig. 1) in the coordinates of Eq. (9) is equal to $\beta^2E_0{}^2/2$. Thus, by plotting an adsorption isotherm in the coordinates shown in Fig. 3, one can identify the regions described by linear adsorption isotherms (Henry's isotherms) and by the TVFM equation (the experimental points of the adsorption isotherms obtained at various temperatures are shown in the plot). The Henry coefficient can be calculated from the parameters of the adsorption isotherm plotted in terms of the TVFM, *i.e.*, using the parameters characterizing the porous structure of the adsorbent and the physicochemical parameters of the substance, which is convenient for practical purposes:

$$\mathrm{H} = a_0/p_a \cdot \exp(\beta^2E_0{}^2/4R^2T^2).$$

Figure 4 shows the points of the experimental isotherms of adsorption of nitrogen, krypton, xenon, and tetrafluoroethylene on the AG carbon measured at temperatures of 120—323 K in reduced (dimensionless) coordinates. It can be seen from the plot that all the isotherms are arranged in one line, in which a linear section can be reliably identified. The region of the adsorption isotherms described by Eq. (1) of the TVFM is located to the left of an abscissa coordinate of 2; the region of the adsorption isotherm described by a linear dependence is located to its right. To describe both isotherms, we used the parameters of the equation of the theory of the volume filling of micropores (W_0, E_0).

References

1. M. M. Dubinin and L. V. Radushkevich, *Dokl. Akad. Nauk SSSR*, 1947, 55, 331 [*Dokl. Chem.*, 1947 (Engl. Transl.)].
2. K. M. Nikolaev, and M. M. Dubinin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1958, 1165 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1958, (Engl. Transl.)].
3. M. M. Dubinin, V. A. Bakaev, and O. Kadlets, *Dokl. Akad. Nauk SSSR*, 1972, **205**, 628 [*Dokl. Chem.*, 1972 (Engl. Transl.)].

Received February 12, 1997;
in revised form April 18, 1997