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Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures

M.M.Dubinin

Institute of Physical Chemistry Academy of Sciences of the USSR, Moscow, 117915, USSR

Abstract - The theory underlying the adsorption behavior of carbon adsorbents is discussed as a basis for quantitative analysis of their adsorption properties and microporous structure. The equations of the theory of volume filling of micropores for homogeneous and nonhomogeneous microporous structures are considered. Three principal parameters are proposed which describe the physical vapor adsorption and characterize the microporous structure.

As a rule carbonaceous adsorbents are microporous in structure and contain a relatively small proportion of mesopores. The adsorption potentials of dispersion forces are enhanced in micropores due to the overlap of the fields from the opposite pore walls and interactions between the adsorbed molecules. Physical adsorption of vapors in homogeneous micropores is described by the Theory of volume filling of micropores (TVFM) (Ref.1). The Dubinin-Radushkevich (DR) equation is the principal formula of the theory

$$W = W_0 \exp\left[- (A/\beta E_0)^2 \right] \qquad (1)$$

where A is the differential molar work

$$A = RT\ln(p_s/p) \qquad (2)$$

Using the small-angle X-ray scatering and adsorption techniques (C_6H_6, 293 K) we have obtained for a slit-shaped model of carbon micropores (Ref.2)

$$x_0 = k/E_0 \qquad (3)$$

where x_0 is the micropore half-width and E_0 - characteristic adsorption energy. Stoeckli and Krachenbuehl developed a method for determining the magnitude $2x_0$ involving calorimetric measurements of the heats of immersion into liquids with different molecular size (Ref.3). McEnaney has summarized all the results and obtained $k = 12.0 \pm 1.4$ kJ.nm/mol (Ref.4). Considering (1) and (3) the DR equation becomes (4)

$$W = W_0 \exp\left[- m x_0^2 A^2 \right] \qquad (4)$$

where $m = (1/\beta k)^2$ is a coefficient for a given vapor. According to eqn. (3) the constancy of E_0 means that the micropore size x_0 is

constant too. Therefore DR equation is applicable for carbonaceous adsorbents with homogeneous micropore structures. Generally carbonaceous adsorbents contain micropores of various size that are formed during activation process. Assuming a random formation of micropores we will have a normal distribution of microporous volume according to micropore half-width x for the slit-pore model

$$\frac{dW_o}{dx} = \frac{W_o^o}{\delta\sqrt{2\pi}} \exp\left[- \frac{(x_o - x)^2}{2\ \delta^2} \right] \qquad (5)$$

and the Dubinin-Stoeckli (DS) adsorption equation (6) (Ref.2)

$$W = \frac{W_o^o}{2\sqrt{1+2m\,\delta^2 A^2}} \exp\left[- \frac{m x_o^2\, A^2}{1+2m\,\delta^2 A^2} \right]\left[1+\mathrm{erf}\left(\frac{x_o}{\sqrt{2}\ \sqrt{1+2m\delta^2 A^2}} \right)\right] \qquad (6)$$

Equations (5) and (6) contains three identical parameters: W_o-the total micropore volume, x_o - micropore half with at distribution curve maximum and δ - variance characterizing the distribution range. The parameters are effective since carbon adsorbents contain larger mesopores and adsorption on their surface in weeker than in micropores. The effective values of W_o^o, x_o (or $E_o = 12.0/x_o$), δ determined from the experimental adsorption isotherm of the reference benzene vapor at 293 K allow one to estimate with reasonable accuracy the adsorption isotherms of other vapors within a temperature range of about 100 degrees. The real parameters for adsorption isotherms corrected for the adsorption in mesopores, i.e. the isotherms with the real parameters W_o^o, E_o and δ, can be used for calculating the geometric surface area of micropores and their volume within a given size range (Ref.2). Thus the effective micropore characteristics W_o^o, E_o and δ are, together with the specific surface area of mesopores S_{me} a quantitative characteristic of the adsorption properties and microporous structure each active carbon specimen. According to our research, an isotherm of vapor adsorption by a carbon adsorbent with a nonhomogeneous microporous structure can be accurately approximated with the sum of two adsorption isotherms for adsorbents with homogeneous microporous structures Therefore the micropore range include slit-shaped pores with $x < 0.6$-0.7 nm as well as larger sized pores with 0.6-$0.7 < x < 1.5$-1.6 nm called supermicropores. For a selected vapor the equation of such an isotherm after (4) will be

$$W = W_{01}\exp\left[- m x_{01}^2\ A^2 \right] + W_{02}\exp\left[- m x_{02}^2 A^2 \right] \qquad (7)$$

Equation (7) contains four parameters: W_{01}, x_{01} (or E_{01} after (4)) W_{02}, x_{02} (or E_{02}). For the homogeneous microporous structure $W_{02} = 0$ and (7) reduces to the single - term DR represented. The equation (7) is not a accidental one. The filling of micro- and supermicropores in adsorption are two independent events. Therefore the mathematical expectation for the two-term TVFM equation is represented by the sum of the corresponding values for the two pore types. Using the equation (7) we shall

obtain parameters of the DS equation

$$W_o = W_{01} + W_{02} \tag{8}$$

$$x_o = [1/(W_{01} + W_{02})][x_{01}W_{01} + x_{02}W_{02}] \tag{9}$$

$$\delta = [1/(W_{01} + W_{02})][(x_{01} - x_0)^2 W_{01} + (x_{02} - x_0)^2 W_{02}] \tag{10}$$

Using experiments and calculations we have shown that the two-term equation (7) is practically identical with the DS equation in how it described the adsorption isotherms for both different temperatures and different vapors. Yet, the characterisation of nonhomogeneous microporous structure by the parameters of two homogeneous structures is purely nominal and can give little, if any, information concerning the size distribution of micropores. The equation DRA by Dubinin, Radushkevich and Astakhov differs from the DR equation that instead of power n = 2 appearing in (1) it contains a variable parameter n

$$W = W_o \exp\left[-\left(\frac{A}{E}\right)^n\right] \tag{11}$$

It is assumed that the DRA equation (11) with three parameters W_o, E and n may describe nonhomogeneous structures of carbon adsorbents at $2 > n > 1$. In the limiting cases with n = 2 the DRA equation reduces to DR. Using experiments and calculation of all the three parameters by a computerized nonlinear optimization procedure we have found that the agreement between the adsorption values calculated by the DRA and DS equations respectively becomes rapidly the worse the more nonhomogeneous is the structure of the specimen. Comparison of the W_o^o and W_o parameters of the equations (11) and (6) shows that W_o are much greater the limiting adsorption values W_s at $p/p_s = 1$. Thus the parameters of the DRA equation lack a strict physical sense and rather represent effective values.

REFERENCES

1. M.M.Dubinin, Progr. Surface Membrane Sci., 9, 1-70 (1975)
2. M.M.Dubinin, Carbon 23, 593-598 (1985)
3. H.F.Stoeckli and F.Kraehenbuhl, Carbon 19, 353-356 (1981)
4. B.McEnaney, Carbon 25, 69-75 (1987)