The volume of micropores and the Dubinin—Radushkevich equation

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The substantiation and the area of applicability of the Dubinin—Radushkevich equation for determination of the micropore volume in microporous systems from experimental data on adsorption isotherms were examined. It was shown that the micropore volumes found using the standard procedure are overestimated. A more accurate method for determining the micropore volumes based on the pressure of filling of micropores was proposed.

Key words: adsorption, isotherm, micropore volume, Dubinin—Radushkevich equation, lattice-gas model.

In the classical work by Dubinin and Radushkevich,1 an equation for determination of the volume of micropores \( W_0 \) in active carbons was proposed:

\[
W = W_0 \exp(-kz^2/\gamma^2),
\]

(1)

where \( k \) is a parameter characterizing the system, \( \gamma \) is the affinity coefficient that connects the "adsorption potentials" of the given and standard adsorbates (for benzene, \( \gamma = 1 \)), and \( z = RT \ln(p_0/p) \) is the "adsorption potential," i.e., the work needed to compress a vapor from equilibrium pressure \( p \) to the saturated vapor pressure \( p_0 \) under isothermal conditions. The \( p_0 \) values needed for calculations are taken from experimental data obtained for liquid—vapor equilibria at the experimental temperature \( T \). This equation was derived based on the concept of volume filling of micropores and the Polanyi potential theory.1,2,3 This equation is still widely used for determining the micropore volumes for various substrates.

It has been mentioned repeatedly5,6 that the first attempt to substantiate Eq. (1) was undertaken by Radushkevich4 based on the idea of inhomogeneous adsorption systems and on the search for the density of the distribution function corresponding to Eq. (1) (more recent studies dealing with justification of this equation were surveyed in Refs. 7 and 8). Later, Eq. (1) was extended to polydisperse microporous adsorbents.9—14 However, in none of the studies cited above, was the role of intermolecular interactions taken into account.

The problem of determining the density of the distribution function \( \Phi(e) \), provided that \( W = W_0 \phi(x)dx \), is easily solved4 using the known distribution function (1):

\[
\Phi(e) = 2ke^{\gamma^2/2kz^2}.
\]

(2)

Previously, the function \( \Phi(e) \) was represented as \( \Phi(e) = f(e)q(e) \), where \( f(e) \) is the normalized density of the distribution function of the "adsorption potential" in unit

weight of the adsorbent, \( q(e) \) is the weight of the liquefied gas that fills the micropore volume \( \nu(e) \): \( q(e) = \rho \nu(e) \), \( \rho \) is the density of the liquid at the experimental temperature, and \( \nu(e) \) is the volume of the micropores possessing the "adsorption potential" \( e \). To elucidate the dependence \( q(e) \), the result obtained by DeBour—Custer\(^{17} \) (\( e = b/\nu \)) was used; this means that in the middle of a cavity having a regular geometric form, the "adsorption potential" is inversely proportional to the volume of this cavity and depends on its shape. This dependence is taken into account by the coefficient \( b \). In addition, the coefficient \( b \) includes molecular constants for the adsorbent and the adsorbate. It follows from Eq. (2)\(^4 \) that

\[
q(e) = \frac{(4k^3/2/\pi^{1/2})e^2\exp(-ke^2)}{b^3Vb^{3/2}}.
\]

The normalized Maxwell distribution of the "adsorption potentials." This \( f(e) \) distribution corresponds to a normalized distribution of the micropore volume in the range from \( \nu \) to \( \nu + d\nu \): \( dW/e = (4k^3/2/\pi^{1/2})b^3Vb^{3/2}\exp(-ke^2) \). Analysis of this formula in which the parameters \( k \) and \( b \) correspond to the experimental systems described by Eq. (1) led to the conclusions that the volumes of micropores lie in a narrow range surrounding the maximum value \( \nu_{\text{max}} = b(k/2)^{1/2} \) and that, for example, active carbons can be regarded as virtually monodisperse materials.

**Nonhomogeneous adsorption systems**

The molecular theory of adsorption in nonhomogeneous systems gives the following equation for the adsorption isotherm\(^7,8,15 \) relating the degree of filling of the micropore volume \( \theta \) to the equilibrium pressure \( p \)

\[
\theta(p) = \int_{\nu_{\text{min}}}^{\nu_{\text{max}}} \theta(p; Q) F(Q) dQ, \quad \frac{\nu_{\text{max}}}{\nu_{\text{min}}} = 1, \quad (3)
\]

where \( \theta(p; Q) \) is the local filling of the adsorption sites with bond energy \( Q \) at a given gas pressure \( p \); \( F(Q) \) is the normalized density of the probability to find a group of adsorption sites with a bonding energy from \( Q \) to \( Q + dQ \). (As the upper and lower limits, \( Q_{\text{max}} = \infty \) and \( Q_{\text{min}} = 0 \) are often used.)

Within the framework of the lattice-gas model,\(^15 \) Eqs. (3) are applicable to both nonporous and porous sorbents. According to this simple molecular model, the volume of the adsorption space (the multilayer region over the surface or the volume of the pores) is broken up into unit cells (sites) having the size of the sorbate. The lattice model takes into account the following main properties of the condensed phase: the proper volume of the molecule and interparticle interactions. The proper volume of the molecule is taken into account by assuming that a lattice site can contain not more than one molecule of the sorbate, and the interparticle interactions are taken into account by using the parameter of local interaction \( E \) (the average energy of interaction between the particles occupying neighboring sites of the lattice). Below we will restrict ourselves to the simplest variant of this theory according to which the pore walls are considered to be homogeneous and the pores themselves are shaped as slits with width \( H \) (the width is expressed in the number of monolayers). We will notice only interactions between the closest neighbors. In the general case, the lattice model makes it possible to take into account all the main properties of real adsorption systems, namely, intermolecular interactions, nonhomogeneous pore walls, different characteristic pore sizes, the presence of capillary condensation, etc. The sets of equations derived using the cluster approach\(^1 \) make it possible to analyze numerically all characteristics of a porous system based on known model potentials of interaction of the adsorbate molecules with the walls and with one another and on a specified porous structure model.

To calculate local coverages, the space in a pore is divided into monoatomic layers parallel to the walls of the slit-like pore. The lattice of sites is characterized by fixed numbers of closest neighbors \( q_n \) is the number of closest neighbors corresponding to the first coordination sphere for a site in a layer \( q \). Let us denote by \( z_{qk} \) the number of closest neighbors, located in a layer \( k \), for a site in a layer \( q \). \( k = q, q \pm 1 ; z_{q-1} + z_{q+1} + z_q = z \). All the sites in the layer \( q \) possess identical properties, because the energy of the sorbate—sorbtion interaction varies from layer to layer \((1 \leq q \leq H)\) but remains constant within the same layer. Using the known equations,\(^15 \) which take into account the energetic inhomogeneity of lattice sites and the interaction between the closest sorbate molecules, it can be shown that the isotherm of multilayer adsorption has the following form:

\[
\theta(p) = \sum_{q=1}^{q_{\text{max}}} f_q \theta_q(p),
\]

\[
a_q = a_q^0 \exp(\beta Q_{q_\text{f}}),
\]

where \( f_q \) is the fraction of type \( q \) sites in the lattice, \( \theta_q \) is the mole fraction of particles that occupy sites of type \( q \); \( a_q^0 \) is the preexponential factor for the local Langmuir constant for a lattice site with the number \( q \) and bonding energy \( Q_q \), and \( a_q^0 \) is the preexponential factor for the local Langmuir constant, and \( \beta = (kT)^{-1} \). The energy of bonding for a site in a layer \( q \) was calculated as \( Q_{q\text{f}} = U(q) + 1/(H - q + 1) \), where \( U(q) \) is the potential of interaction of the adsorbate with the pore wall; \( U(q) = U(q)/q^2 \) corresponds to the 3—9 Mie potential in which the repulsive branch of the potential is taken into account by the lattice structure, \( \Lambda_q \) is the term taking into account the lateral interactions between the particles located in the neighboring sites. In the quasi-chemical approximation

\[
\Lambda_q = \prod_{p=1}^{q} (1 + x \delta_{qp}),
\]

where \( \delta_{qp} = 2q^0/\{q^0 + b_{qp} \} \), \( x = \exp(-\beta E) - 1 \), \( \delta_{qp} = 1 + x(1 - q^0 - \theta_q) \), \( b_{qp} = (q^0 + 4x\theta_q^0)/q^{1/2} \). In the mean-field approximation