Statistical interpretation of the Dubinin—Radushkevich equation

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A statistical approach was applied to describe the model of a homogeneous microporous adsorbent and obtain the dependences of the thermodynamic functions on the number of molecules and the temperature for molecular aggregates in discrete micropores over a wide region of fillings that lead to the Dubinin—Radushkevich equation. The energy nonuniformity of the adsorption space is the fundamental property of carbon adsorbents. In the region of small fillings, the statistical approach leads to Henry's law and the finite value of the initial differential energy of adsorption. The value of sorption corresponding to the saturated vapor pressure decreases with increasing temperature, but the decrease is considerably less than for the density of the corresponding liquid.

Key words: adsorption, equilibrium, active carbons, micropores, Helmholtz energy, entropy, statistical method.

The Dubinin—Radushkevich equation is widely used to describe the adsorption equilibrium of individual components on active carbons:[1-3]

$$a = (W_0/V^*)\exp[-A/\beta E_0)^2], \quad A = RT\ln(p_s/p), \qquad (1)$$

here a/mol kg^{-1} is the value of sorption; W_0/cm^3 g^{-1} is the total volume of the pore system; V^*/cm^3 g^{-1} is the amount adsorbed expressed as a liquid volume; $a_0 = W_0/V^*$ is the limiting value of sorption; E_0/kJ mol^{-1} is the characteristic energy; β is the similarity constant; A/kJ mol^{-1} is the differential molar work of adsorption; p and p_s are the pressures of the bulk phase and saturation vapor, respectively, at temperature T/K. In many cases, Eq. (1) gives an adequate description of the experimental isotherms when the pressure in the volume phase varies by several orders of magnitude, but it has an essentially empirical nature. Therefore, various methods for calculation of the parameters of the Dubinin—Radushkevich equation have been proposed at one time or another.[4-5]

The Dubinin—Radushkevich equation is commonly used to describe the adsorption on active carbons. According to the earlier works on the theory of the volume filling of the micropores,[6] a micropore size distribution exists, and as the pressure in the volume phase is increased, wider and wider micropores are progressively filled. It is accepted now that Eq. (1) describes the adsorption equilibrium on the adsorbent which has a narrow range of micropore sizes (with homogeneous collection of micropores). In subsequent

studies,[7] the concept of a close relationship between the size of micropores and the characteristic energy E_0 has been proposed by analogy with the Guinier formula for the small-angle X-ray scattering. Later Stoeckli[8] studied active carbons using molecular probes and found that the half-width of a micropore is in inverse proportion to the characteristic energy. Since Eq. (1) is valid for active carbons with identical micropores, it is possible to use the statistical method on the basis of the grand canonical distribution[9] assuming the discrete micropores as statistically independent subsystems. This method was first applied to the adsorption by zeolites by Bakaev,[10] and then it was frequently used for various systems, for instance by Ruthven,[11,12] who has arrived at a simple two-constant equation for the isotherm.

In this report, an attempt at statistical interpretation of the Dubinin—Radushkevich equation is made. Let us assume that the adsorption system of active carbon is presented by an array of identical micropores and each is a quasi-independent system. Then the adsorption equilibrium can be described by the grand canonical distribution, which can be reduced to the distribution function of the number of molecules in a micropore. The mean number of molecules in a micropore over an ensemble is proportional to the value of sorption. The probability of the presence of the specified number of molecules in the micropore, regardless of their kinetic energy, is related to the Helmholz energy of these molecules, since for this case the distribution over this parameter is neutral. Fur-

thermore, the experimental data are well approximated by the Dubinin—Radushkevich equation over a wide range of relative fillings. It is therefore necessary to find such dependences of the Helmholz energy for the adsorbate in a discrete micropore on the number of molecules and the temperature which reconcile the approaches outlined above.

After summing up all the corresponding states, the grand canonical distribution results in the following equation of the adsorption equilibrium:

$$a = \frac{a_m}{N} j = \frac{a_m}{N} \frac{\sum\limits_{j=1}^{N} j \exp[(j\mu - N_A F_j)/RT]}{\sum\limits_{j=0}^{N} \exp[(j\mu - N_A F_j)/RT]}. \qquad (2)$$

Here $a_m/\text{mol kg}^{-1}$ is the limiting value of sorption; N is the maximum number of molecules in the micropore; μ is the chemical potential; F_j is the Helmholz energy for j molecules in the micropore; j is the average number over the ensemble of molecules in the micropore; N_A is the Avogadro number. The grand statistical sum referred to one micropore serves as the denominator in this expression. As the bulk phase is nearly always ideal, then

$$\mu = \mu^{\circ}(T) + RT\ln p. \qquad (3)$$

Consider the state of a normal liquid at temperature T as the standard state. Assumption that the product $p_s V^{*}$ is negligible compared to RT leads to

$$N_A \Delta F_j = N_A F_j - j[\mu^{\circ}(T) + RT\ln p_s]. \qquad (4)$$

Equation (2) can be given by

$$a = \frac{a_m}{N} \frac{\sum\limits_{j=1}^{N} j \exp[j\ln(p/p_s) - \Delta F_j / k_B T]}{\sum\limits_{j=0}^{N} \exp[j\ln(p/p_s) - \Delta F_j / k_B T]}, \qquad (5)$$

where k_B is Boltzmann's constant. This equation can be used for approximation of the values of sorption as a function of the relative pressure and temperature calculated according to the Dubinin—Radushkevich equation for various E_0 values. Temperature dependence of free energy for fixed number of molecules was approximated by the function

$$N_A \Delta F_j = \alpha_j^{(1)} - \alpha_j^{(2)} RT - \alpha_j^{(3)} RT\ln(RT). \qquad (6)$$

The form of this relation is chosen to provide a linearity of the temperature dependence of the internal energy. The contribution of the latter term is small, and the temperature dependence of the Helmholz energy is also close to linear such as for many liquids. In this case, for the changes in the internal energy and entropy, we have:

$$N_A \Delta U_j = \alpha_j^{(1)} + \alpha_j^{(3)} RT, \qquad (7)$$

$$TN_A \Delta S_j = \alpha_j^{(2)} + \alpha_j^{(3)} RT[1 + \ln(RT)]. \qquad (8)$$

Each parameter α depends on the number of molecules in the micropore and is approximated by the polynom

$$\alpha_j^{(k)} = \sum\limits_{i=1}^{n} b_i^{(k)} j^i, \quad k = 1, 2, 3. \qquad (9)$$

Up to now, we have not introduced additional limitations. However, it is necessary to take into account the limited scope of Eq. (1): In particular, this equation is not valid in the region of small fillings, because it is not transformed into Henry's law and gives an infinite increase in the differential heat of sorption. According to this equation and taking into account the thermal expansion of the adsorbate, the differential heat of sorption also increases indefinitely in the range of fillings close to the maximum capacity. Therefore, the relative values of adsorption a/a_m ranged between 0.2 and 0.96 were chosen to determine the $b_i^{(k)}$ coefficients. This is rather arbitrary choice, but it considers an approximate range of applicability of the Dubinin—Radushkevich equation evaluated on the basis of processing numerous experimental data. In this search, each change in the p/p_s values by one order of magnitude up to 0.1 contained 10 values, and above 0.1, the step of the change in p/p_s was equal to 0.05. The family of isotherms was calculated according to Dubinin—Radushkevich in the temperature range of 20—150 °C with a step of 10°. The root-mean-square deviation of the calculated values of the natural logarithms of
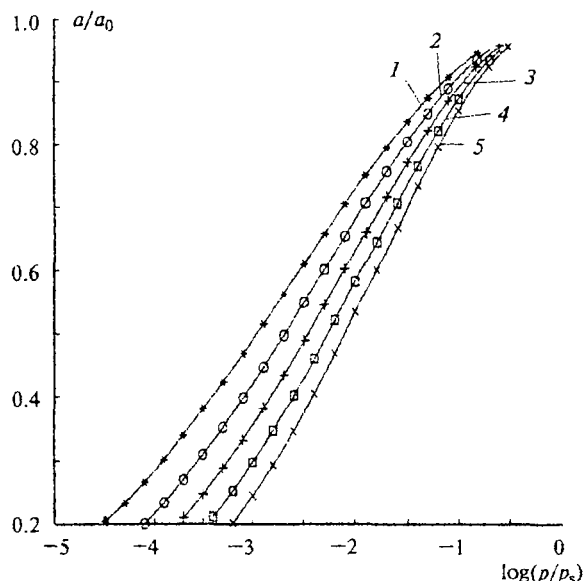

Fig. 1. Adsorption isotherms calculated according to Eqs. (1) (points) and (5) (lines) at $T/°C = 20$ (*1*), 50 (*2*), 80 (*3*), 110 (*4*), 140 (*5*) ($E_0 = 20$ kJ mol^{-1}; $N = 20$).

pressures from the experimental values was minimized. The power of each polynom in Exp. (8) was taken to be 6 to satisfy the required accuracy. Hence, the total number of the sought constants is equal to 18. On the basis of the coefficients found from Eqs. (6)—(8). It is possible to determine all the thermodynamic functions for the aggregate of j molecules in the micropore for the chosen values of the characteristic energy E_0 and the maximum value N of the molecules.

As an example, Fig. 1 shows a comparison of the isotherms (points) calculated according to Eq. (1) for $E_0 = 20$ kJ mol^{-1} and $N = 20$ at five temperatures in the temperature range of 20—140 °C and the curves calculated according to Eq. (5) for the values of the $b_i^{(k)}$ coefficients found by the root-mean-squares method. As can be seen in Fig. 1, both approaches give similar results. The root-mean-square deviation of the logarithms of pressures is only 0.4%. Figure 2 presents the calculated dependence of the change in the Helmholz free energy per one mole on the number of molecules in the micropore for various values of the characteristic energy E_0 and temperature 20 °C. The relative fillings of the micropore are plotted on the abscissa axis. Calculations show that the curves plotted in these coordinates are nearly independent of the chosen value of the maximum number of the molecules N in the micropore. The root-mean-square deviation also depends poorly on N. This means that it is impossible to determine the maximum number of molecules in the micropore and hence the volume of the micropore, taking into account only the parameters of the Dubinin—Radushkevich equation. The

dotted lines in this figure illustrate the change in the specific internal energy per one mole of molecules in a micropore as a function of the relative filling of the micropore volume. The main feature of this dependence at any values of E_0 is a monotonic increase in the specific (molar) internal energy with increasing number of molecules in the micropore. As the number of contacts between molecules increases with increasing size of a cluster, the internal energy of intramolecular interaction would decrease rather than increase. However, the potential of the interaction of molecules with the adsorption field is another constituent of the internal energy. Due to nonuniformity of the adsorption field, the mean potential of the adsorbent—adsorbate interaction increases with increasing number of molecules in the micropore, whereas the absolute value of the potential decreases. Probably as the number of molecules increases, larger fraction of them increasingly occurs in a zone of weaker interactions with the adsorbent. The domimant among these opposite trends would determine the resulting potential. Obviously, the physical model that serves as a basis of the theory of the volume filling of micropores assumes a very high energetic heterogeneity of the adsorption space. Each further molecule entering the micropore interacts with the adsorption field much weaker than the preceding molecule. As a result, the overall internal energy grows in spite of an increase in the intramolecular interactions.

As seen in Fig. 2, the difference between the Helmholz free energy and internal energy is small. Figure 3 shows a change in the product of entropy and temperature with the filling of the micropore for two values of the characteristic energy. The entropy of the adsorbate held in the micropore is less than that of a standard liquid over the whole range of fillings, but this difference decreases when the number of molecules in the micropore increases.

Known dependences of the internal energy on filling can be applied to calculate the pure differential heat of sorption corrected for the heat of evaporation. Use can be made of the following formula:[9]

Fig. 2. The Helmholz specific energy (solid lines) and internal energy (dotted lines) in the micropore as a function of the relative fillings of the micropore volume for E_0/kJ mol^{-1} = 16 (*1*), 20 (*2*), 24 (*3*), 28 (*4*) ($N = 20$, $T = 20$ °C).

$$q - \lambda = -\frac{\sum_{j=1}^{N} N_A \Delta U_j \left(j - \frac{Na}{a_m} \right) \exp\left[j \ln\left(\frac{p}{p_s} \right) - \frac{\Delta F_j}{k_B T} \right]}{\sum_{j=1}^{N} j \left(j - \frac{Na}{a_m} \right) \exp\left[j \ln\left(\frac{p}{p_s} \right) - \frac{\Delta F_j}{k_B T} \right]}. \quad (10)$$

For $a = 0$, $q - \lambda = -N_A \Delta U_j$. Figure 4 presents the calculated pure differential heat of sorption as a function of filling. The change in the value $A = RT\ln(p_s/p)$ with filling is shown by a dotted line in the figure. These two curves nearly coincide in a wide range of fillings. However, when the value of sorption decreases to 0, the differential value of sorption tends to some finite value, whereas the A value increases indefinitely.
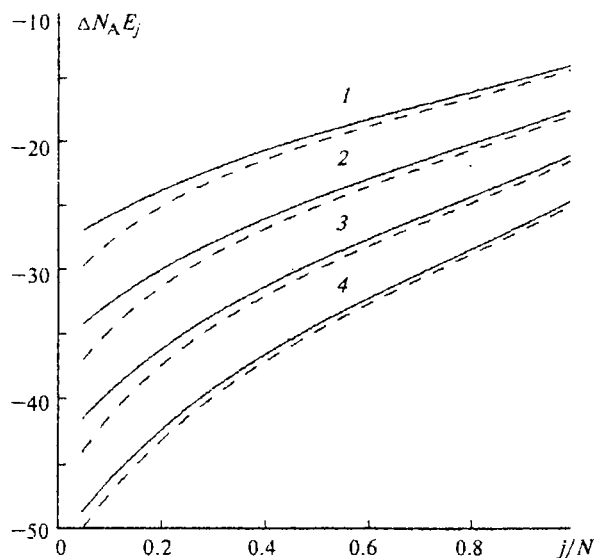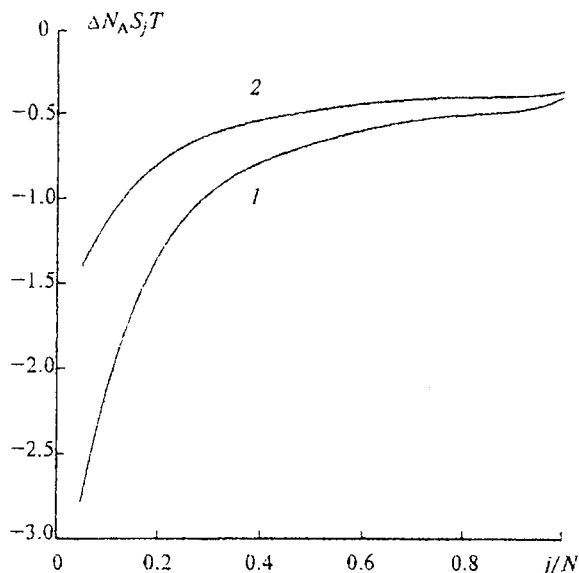
Fig. 3. The specific entropy in the micropore as a function of the relative filling of the micropore volume at E_0/kJ mol^{-1}: 20 (*1*), 28 (*2*); ($N = 20$, $T = 20$ °C).

Fig. 4. The pure differential heat of sorption as a function of filling ($E_0 = 20$ kJ mol^{-1}, $N = 20$, $T = 20$ °C). Dotted line, $A = RT\ln(p_s/p)$.

Results and Discussion

On the basis of the statistical approach, approximation of the Dubinin—Radushkevich equation with the aid of Eq. (5) was achieved for the model of the uniform microporous adsorbent with high accuracy. As Eq. (5) is valid within the framework of the model and is applicable over the whole range of the variation of the values of sorption, then the Dubinin—Radushkevich equation can be assumed to be a rational approximation in the range of medium fillings. In the range of small fillings, the more general Eq. (5) results in Henry's law and the finite value of the differential heat of sorption, whereas the Dubinin—Radushkevich equation gives unrealistic results such as a concave section of the isotherm and unrestricted growth of the differential heat of sorption. Statistical interpretation of the Dubinin—Radushkevich equation allowed us to find the dependences of the Helmholz energy, internal energy, and entropy for the guest molecules in the discrete micropore on the relative filling of its volume. Thus, the specific internal energy of the aggregate of molecules occurring in the micropore increases with increasing filling. This is possible when the extent of the energetic heterogeneity of the adsorption space is very high. This result seems to be due to the temperature independence of the characteristic curves followed from the Polanyi model. This model suggests that the adsorption space over the adsorbent is heterogeneous and the single elements of the micropores are progressively filled along the normal to the surface. For the microporous adsorbent, similar mechanism of succes-
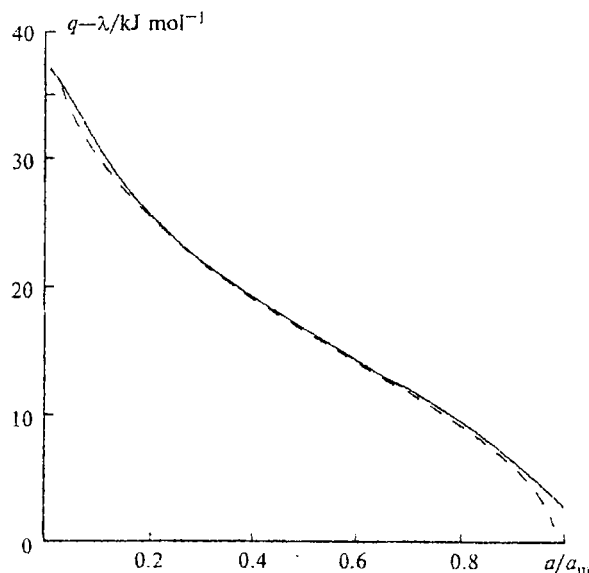
sive filling of the single units in the adsorption space is possible if the distribution of micropores with respect to the size and adsorption potential is fairly wide. When the potential within the volume of discrete micropores changes slightly, groups with identical micropores are filled at the characteristic pressure of the bulk phase that varies in a very narrow range. This explains the temperature independence of the characteristic curves. However, in our case, the micropores are assumed to be identical, and therefore the essential heterogeneity of the adsorption space should be assigned to the varying volume of micropores. This nonuniformity results in a smoother change in the value of sorption caused by the increasing equilibrium pressure in the gas phase.

In the range of small fillings, Eq. (5) results in a linearity of the isotherm. However, Henry's coefficient depends on the choice of the maximum number of molecules N in the micropore, *i.e.*, it is impossible to estimate this coefficient solely from the parameters of the Dubinin—Radushkevich equation. Therefore, additional experimental data on Henry's coefficients would be helpful for estimating N and, hence, the volume of the discrete micropore.

It was assumed upon approximation of the Dubinin—Radushkevich equation with Eq. (5) that a_0 equal to W_0/V^* is the value of sorption at $p = p_s$, therefore the term $a_m/(Na_0)$ is not a free parameter but a calculated value. The a_m/N ratio is the number of micropores in the weight unit of an adsorbent divided by Avogadro's number, and in a physical sense it should be constant at a specified temperature for each adsorbent. Therefore,

the found dependence of $a_m/(Na_0)$ on temperature determines the temperature dependence of the molar volume V^*. Calculations showed that the volume of an adsorbate actually increases with increasing temperature but the increase is substantially slower (approximately by one order in magnitude) than that of the corresponding liquid. Examination of the experimental data reveals[13] that the temperature coefficient of expansion of the adsorbate is essentially lower than that for the corresponding liquid due to high pressure (several hundred atmospheres) in the adsorption phase, however not so much lower as in the case under consideration. Apparently, this contradiction can be eliminated only by introducing the upper boundary of applicability of the Dubinin—Radushkevich equation even when the capillary condensation is absent. In this case, a_0 cannot be assumed as the calculated value of sorption at $p/p_s = 1$, because it will not give a correct extrapolation. The actual nature of the temperature dependence for a_0 will affect the thermodynamic functions of the adsorbate in micropores, and this requires further studies to obtain reliable experimental data.

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