Adsorption on nonporous and supermicroporous adsorbents

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The mean values of the characteristic energy of C_6H_6 adsorption in large micropores were calculated from the adsorption isotherms of benzene vapor on carbon blacks. The supermicropores are characterized by the significant dispersion of the adsorption potential resulted from the pore-size distribution, which imparts the polymolecular character to adsorption. The effect of enhancement of the characteristic energy of adsorption was analyzed, which was caused by the overlap of the force fields of the opposite pore walls and the reduction of the adsorption film surface with micropore volume filling. The both factors are comparable by magnitude and depend on the micropore sizes.

Key words: nonporous supermicorporous adsorbents, adsorption potential, characteristic energy of adsorption, polymolecular adsorption.

Microporous structures of active carbons are classified as uniform and nonuniform. According to the theory of the volume filling of micropores (TVFM), the adsorption isotherm on uniform microporous structures is described by the Dubinin—Radushkevich equation[1]

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

where W is the volume of the adsorbed substance, W_0 is the limiting adsorption volume, E_0 is the characteristic energy of adsorption of a standard vapor (usually benzene), β is the similarity coefficient of characteristic curves, and A is the differential molar work of adsorption.

During the progressive gas-vapor activation of the carbon adsorbents, the characteristic adsorption energies decrease due to an increase in the linear sizes of micropores. The model of slit-shaped pores with limited width[2,3] assumes that the pore width is inversely proportional to the characteristic adsorption energy $E_0^{2/3}$.

At a sufficiently deep activation of natural carbonized coals with a nonuniform structure ($E_0 \le 19$ kJ mol^{-1}), the accuracy of description of the adsorption isotherms by Eq. (1) decreases. This is explained by the development of size nonuniformity of micropores in the porous structure of active carbons. In these cases, the adsorption properties of the carbons are well approximated by the binomial equation of the adsorption isotherm of TVFM[4,5]

$$W = W_{0,1}\exp[-(A/E_{0,1})^2] + W_{0,2}\exp[-(A/E_{0,2})^2]. \qquad (2)$$

This equation reflects the superposition of two microporous structures with the $W_{0,1}$ and $E_{0,1}$ parameters for the true micropores and with $W_{0,2}$ and $E_{0,2}$ for larger supermicropores. According to Eq. (2), the structure of the active carbons is well described by the equation that assumes the presence of two uniform microporous structures, and which served as a basis for the classification of micropores as true micropores (micropore half-width $x_0 <$ 0.6—0.7 nm) and large supermicropores (0.6—0.7 nm $< x_0 <$ 1.5—1.6 nm).[6] Further, a more reasonable assumption about the continuous, instead of discrete, size distribution of pore volumes provided the Dubinin—Stoeckli (DS) equation[7] with three parameters: the total micropore volume $W_0{}^0$, the micropore half-width for the maximum of the size distribution curve of the micropore volume x_0, and the dispersion δ, which is the parameter characterizing the spread of size distribution of micropores. The interrelation between the parameters in Eq. (2) and the DS equation was established.[8] It was shown that supermicropores, which represent an intermediate region between micro- and mesopores, gradually lose the properties characteristic of micropores and attain those of mesopores.[9]

In recent years, a great body of data has been accumulated, indicating that the conversion of Eq. (1) to Eq. (2) is related to the appearance of additional pores and also to a change in the character of adsorption. Therefore, the purpose of this work is to study a possibility to establish a quantitative interrelation of adsorption processes in

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micropores to adsorption on nonporous adsorbents with the same chemical nature.

Method of calculation of energy characteristics of adsorption on supermicroporous adsorbents

The need for transition from the monomial equation (1) for the description of adsorption isotherms to Eq. (2) or to the DS equation with the dispersion values much higher than 0, is caused not only by the formation of large micropores resulting in an increase in the nonuniformity of the microporous structure. It is related, most likely, to the manifestation of the polymolecular character of adsorption induced by an increase in the dispersion of the adsorption potential across the micropore width with an increase in the micropore size. The first term in Eq. (2) reflects adsorption in the monolayer, and the second term describes adsorption in the rest micropore volume characterized by a substantially reduced adsorption potential. Then the number of the adsorbate layers N in large micropores can be expressed through the parameters in Eq. (2)

$$N = 2(W_{0,1} + W_{0,2})/W_{0,1}. \qquad (3)$$

It is shown[10—12] that the number of micropores in the volume unit of microporous fragments remains unchanged during the deep activation of carbons and the adsorption isotherms are described by Eq. (2) or the DS equation rather than by Eq. (1), although no new variety of large micropores is formed. In addition, the $E_{0,2}$ parameter values in Eq. (2) are much lower than the characteristic energy of adsorption ($E_m \approx 12$ kJ mol^{-1}) corresponding to monolayer coverage on the nonporous carbon adsorbents, *viz.*, nongraphitized and graphitized carbon blacks.[10] Similarly, the E_0 parameter (8.5—8.8 kJ mol^{-1}) in the DS equation for the adsorbents with the extremely developed micropore volume[13] is also substantially lower than E_m. However, one of the distinctive features of adsorption in micropores is much higher heats of adsorption compared to those for nonporous adsorbents and, hence, higher adsorption potentials.[9] Therefore, the transition from Eq. (1) to Eq. (2) or the DS equation is related to a qualitative change in the adsorption process. This is indicated by the experimental data, which show a decrease in the δ values in the DS equation with an increase in dimensions of adsorbed molecules.[14,15] Table 1 contains the parameters of the microporous structure of the active carbons,[14,15] one of which, *viz.*, AC-IV sample, is similar to domestic industrial carbons of the AG type and the second one, *viz.*, AC-IX carbon, was prepared from furfural (FAS type). The parameters were determined from the DS equation[7] using the adsorption isotherms of EtCl, C_6H_6, and CCl_4 molecules, whose critical diameter changes from 0.44 (EtCl) to 0.69 nm (CCl_4). The δ values obtained for the adsorption of EtCl and a planar benzene molecule on the AC-IV active carbon are characteristic of the typically nonuniform microporous adsorbents. The adsorption of CCl_4 with the largest critical diameter of the molecule in this group of adsorptives, does not lead to the formation of the monolayer and, most likely, the whole adsorption volume is filled. In this case, the dispersion value is virtually 0, *i.e.*, Eq. (1) for uniform microporous structures is fulfilled.

Table 1. Parameters of the Dubinin—Stoeckli equation

Vapor	$W_0{}^0$		x_0	δ
	mmol g^{-1}	cm^3 g^{-1}	nm	
	Adsorbent AC-IV			
C_6H_6	3.30	0.29	0.61	0.120
EtCl	4.00	0.28	0.59	0.142
CCl_4	2.45	0.24	0.62	$3.31 \cdot 10^{-3}$
	Adsorbent AC-IX			
C_6H_6	11.5	1.02	1.22	0.555
EtCl	12.2	0.87	1.06	0.358
CCl_4	9.88	0.93	1.11	0.289

Note. $W_0{}^0$ is the total micropore volume, x_0 is the micropore half-width for the maximum in the size distribution curve of the micropore volume, and δ is the dispersion.

The δ values for the larger-porous AC-IX carbon are also decreased. However, in the case of CCl_4 adsorption, this value differs from 0 because when the monolayer is filled the volume of the uptake is still below the whole sorption volume of micropores.

The weighted average values of the characteristic energy of C_6H_6 adsorption in large micropores can be estimated from the correlation

$$E_0 = (E_{0,1}W_{0,1} + E_{0,2}W_{0,2})/(W_{0,1} + W_{0,2}). \qquad (4)$$

To determine the E_0 values based on the characteristic adsorption energy $E_m \approx 12$ kJ mol^{-1} and on the number of layers N, one should quantitatively characterize the effect of increasing the adsorption energy due to the overlap of the fields of the neighboring walls. The character of the force field from each wall is accepted to be the same as that above the nonporous adsorbent of the same chemical nature.

To describe polymolecular adsorption, let us use Eq. (5),[16] which states that during adsorption on nonporous adsorbents with the energetically nonuniform surface, conformity to the Dubinin—Radushkevich equation occurs for the filling of the first and subsequent layers

$$\frac{a}{a_m} = \sum_{i=1}^{N} \exp\left[-\left(\frac{A}{E_m}\right)^2 \cdot 2^{3(i-1)}\right], \qquad (5)$$

where a is the amount adsorbed polymolecularly, a_m is the limiting capacity of the adsorption layer, E_m is the characteristic energy of adsorption in the first layer, and i is the number of the adsorption layer.

The dependence of the characteristic energy of adsorption of the substance in the ith layer (E_i) on E_m and i corresponding to the equation of polylayer adsorption (5) is described by the correlation

$$E_i = E_m/2^{3/2(i-1)}. \tag{6}$$

Using this equation, we obtain the following expression for the determination of the mean values of the characteristic adsorption energy of N layers on the plane

$$\bar{E} = \left(\sum_{i=1}^{N} E_i\right)/N = \frac{E_m}{N}\sum_{i=1}^{N} 2^{-\frac{3(i-1)}{2}}. \tag{7}$$

Evidently, in the case of adsorption of N layers in micropores, the influence of the neighboring wall is also determined by Eq. (7) and the mean value of the characteristic energy can be taken equal to $2\bar{E}$.

We have to take into account another characteristic that discriminates adsorption processes on the nonporous and microporous adsorbents. After the formation of the monolayer, nonporous solids are characterized by the vapor—adsorbate interface with the surface area equal to the adsorbent surface. When volume of micropores is filled, the surface of this interface disappears due to the junction of adsorption films of the neighboring pore walls, which can increase the adsorption energy. Let us estimate the energy evolved upon the conceivable transition of the system (Fig. 1) from position **A** (adsorption on nonporous adsorbents) to position **B** (adsorption in micropores). Case **A** is characteristic of the free surface of the adsorption film, whose total energy of surface unit (ε) depends on the surface tension σ and temperature T

$$\varepsilon = \sigma - T(\mathrm{d}\sigma/\mathrm{d}T). \tag{8}$$

When planes are brought together until the junction of the adsorption films occurs, the evolved energy is equal to 2ε, and the increase in the integral heat of adsorption ΔQ_σ should inversely be proportional to the number of layers N and the number of moles of the adsorbate m per surface unit of the closed films

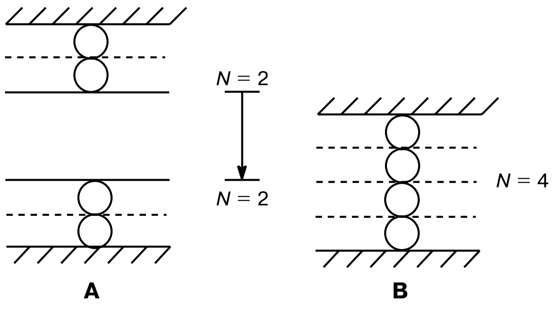

Fig. 1. Transition of polymolecular adsorption (position **A**) to volume micropore filling (position **B**).

$$\Delta Q_\sigma = 2\varepsilon/mN. \tag{9}$$

The difference in the energy of adsorption on the plane and in micropores does not change the character of description of the adsorption isotherms. In both cases, the Dubinin—Radushkevich equation is appropriate for any ith layer and, hence, the expression obtained for the differential molar work of adsorption[17] is valid. This equation in the integral form can be written as follows:

$$Q_i = \lambda + E_i\left[\int_{\Theta=0}^{\Theta=1}\left(\ln\frac{1}{\Theta}\right)^{1/2}\mathrm{d}\Theta + \frac{\alpha_i T}{2}\int_{\Theta=0}^{\Theta=1}\left(\ln\frac{1}{\Theta_i}\right)^{-1/2}d\Theta\right]. \tag{10}$$

Here Q_i is the integral molar heat of adsorption, α_i is the coefficient of thermal expansion of the adsorbate in the ith layer, λ is the molar heat of condensation of the adsorptive vapor, and $\Theta = W/W_0$ is the filling of the micropore volume with the adsorptive. Determining the integral heat of adsorption for N layers as the average of the sum for both cases **A** and **B** and assuming that in Eq. (10) α_i is equal to the coefficient of thermal expansion of the standard liquid (α_0), we obtain

$$Q_{\mathbf{A(B)}} = \lambda + \left[\left(\sum_{i=1}^{N} E_i\right)/N\right]\cdot k = \lambda + k\bar{E}_{\mathbf{A(B)}}, \tag{11}$$

$$k = \int_{\Theta=0}^{\Theta=1}\left(\ln\frac{1}{\Theta}\right)^{1/2}\mathrm{d}\Theta + \frac{\alpha_0 T}{2}\int_{\Theta=0}^{\Theta=1}\left(\ln\frac{1}{\Theta}\right)^{-1/2}\mathrm{d}\Theta. \tag{12}$$

It follows from Eq. (11) that

$$\bar{Q}_\mathbf{B} - \bar{Q}_\mathbf{A} = k\cdot(\bar{E}_\mathbf{B} - \bar{E}_\mathbf{A}) = k\cdot\Delta E_\sigma. \tag{13}$$

Taking into account that $\bar{Q}_\mathbf{B} - \bar{Q}_\mathbf{A} = \Delta Q_\sigma$, we obtain in the final form

$$\Delta E_\sigma = 2\varepsilon/mNk, \tag{14}$$

where for benzene $\varepsilon = 69.4$ erg cm^{-2} (293 K), $k \approx 1.13$ (for changing Θ from 0.05 to 0.95), and $m = 5.5\cdot10^{-10}$ mol cm^{-2} (using the molecular surface unit calculated from a density of the liquid of ~40 Å^2). The ε and k values were determined under the following assumptions: $\alpha_i = \alpha_0 = 1.237\cdot10^{-3}$ deg^{-1} and $\sigma_i = \sigma_0 = 28.9$ erg cm^{-2}, which, strictly speaking, can be crude because the thermodynamic characteristics of both the adsorbate and adsorbent change during adsorption.[18]

The estimate of ΔE_σ from Eq. (14) is independent of any concepts about the route of the process. It is not necessary to assume, as it follows from the accepted scheme, that the maximum of energy evolution should lie near the saturation region. On the contrary, when assuming a remote analogy between the adsorption processes in large micropores and mesopores, it can be supposed[19] that the adsorption films can lose their stability and merge in particular parts of micropores long before their thickness becomes equal to the slit half-width.

Results and Discussion

The results of calculation of the $\bar{E}$ and ΔE_σ values and total values of the characteristic energy obtained considering both effects, *viz.*, polymolecular adsorption in micropores and junction of adsorption films of the neighboring walls in them, are presented in Table 2

$$E_0 = 2\bar{E} + \Delta E_\sigma. \tag{15}$$

The calculations were carried out for different numbers of adsorbate layers N in large micropores from the $W_{0,2}/W_{0,1}$ ratios determined using Eq. (3). The total calculated E_0 values were compared to the weighted average values of the characteristic energy of adsorption of benzene vapor calculated from the equation

$$E_0 = 19.4 \cdot \left(1 + \frac{W_{0,2}}{W_{0,1}}\right)^{-1} + 4.65, \tag{16}$$

which was obtained by the generalization of the experimental data body[11] on active carbons prepared from different raw materials, including furfural, wood, hydrate-cellulose fiber, and products of wood pyrolysis, and it is valid for the E_0 values expressed in kJ mol^{-1}.

Table 2. Calculated $\bar{E}$ and ΔE_σ values and comparison of the calculated (E_0^{calc}) and experimental (E_0^{exp}) characteristic adsorption energies of benzene vapor on the supermicroporous carbon adsorbents

N	$W_{0,2}/W_{0,1}$	$\bar{E}$	ΔE_σ	E_0^{calc}	E_0^{exp}	$\Delta \cdot 100$ (%)
		kJ mol^{-1}				
3	0.5	5.90	7.51	19.3	17.6	9.7
4	1.0	4.55	5.63	14.7	14.3	2.8
5	1.5	3.68	4.50	11.1	12.4	10.5
6	2.0	3.08	3.76	9.92	11.1	10.6

Note. $\Delta = (E_0^{\mathrm{exp}} - E_0^{\mathrm{calc}})/E_0^{\mathrm{exp}}$.

Based on the data in Table 2, we can conclude that the calculated and experimental E_0 values demonstrate a satisfactory agreement despite the tentative character of calculations: the maximum divergence does not exceed 11%. It is important that the ΔE_σ values prevail over $\bar{E}$. Therefore, compared to adsorption on nonporous bodies, the adsorption energy in micropores is much enhanced and this is not only due to the effect of overlapping of the potential fields of the neighboring pore walls. This is caused, to a greater extent, by the fact that when the micropore volume is filled the adsorption film surface is sharply reduced, due to which the adsorption energy additionally increases: the smaller the pore size, the higher the increase.

Thus, large micropores, in which the considerable spread of the adsorption potential over the width of the pores is observed, can be considered as intermediate between micro- and mesopores. In these pores, the layer-by-layer character of adsorption already begins to appear. However, they are still inherent in the specific features characteristic of micropores. Taking into account these peculiarities, we can establish a quantitative correlation between the adsorption processes on the nonporous and supermicroporous adsorbents.

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