Adsorption on nonporous and supermicroporous adsorbents

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The mean values of the characteristic energy of C 6 H 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 supermicroporous 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

\[ W = W_0 \exp\left(-\frac{A}{\beta E_0}\right)^2 \],

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), \( \beta \) 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 \( \delta \) 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 (\( E_0 \leq 19 \text{ kJ} \text{ mol}^{-1} \)), 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

\[ W = W_{0,1} \exp\left(-\frac{A}{E_{0,1}}\right)^2 + W_{0,2} \exp\left(-\frac{A}{E_{0,2}}\right)^2. \]

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 \( x_0 < 0.6—0.7 \text{ nm} \)) and large supermicropores (0.6—0.7 nm < \( x_0 < 1.5—1.6 \text{ nm} \)). 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 \( \delta \), 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
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)

\[
N = 2(W_{0,1} + W_{0,2})/W_{0,1}.
\]  

(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 (\( E_m = 12 \) 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 \( \delta \) 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 using the adsorption isotherms of EtCl, \( \text{C}_6\text{H}_6 \), and \( \text{CCl}_4 \) molecules, whose critical diameter changes from 0.44 (EtCl) to 0.69 nm (\( \text{CCl}_4 \)). The \( \delta \) 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 \( \text{CCl}_4 \) 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.

The \( \delta \) values for the larger-porous AC-IX carbon are also decreased. However, in the case of \( \text{CCl}_4 \) 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 \( \text{C}_6\text{H}_6 \) adsorption in large micropores can be estimated from the correlation

\[
E_0 = (E_{0,1}W_{0,1} + E_{0,2}W_{0,2})/(W_{0,1} + W_{0,2}).
\]  

(4)

To determine the \( E_0 \) values based on the characteristic adsorption energy \( E_m = 12 \) 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

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

(5)

where \( a \) is the amount adsorbed polymolecularly, \( a_m \) is the limiting capacity of the adsorption layer, \( E_m \) is the

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**Table 1. Parameters of the Dubinin—Stoeckli equation**

<table>
<thead>
<tr>
<th>Vapor</th>
<th>( W_{0}^{0} ) mmol g(^{-1})</th>
<th>( x_0 ) cm(^3) g(^{-1})</th>
<th>( \delta ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent AC-IV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>3.30</td>
<td>0.29</td>
<td>0.61</td>
</tr>
<tr>
<td>EtCl</td>
<td>4.00</td>
<td>0.28</td>
<td>0.59</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>2.45</td>
<td>0.24</td>
<td>0.62</td>
</tr>
<tr>
<td>Adsorbent AC-IX</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>11.5</td>
<td>1.02</td>
<td>1.22</td>
</tr>
<tr>
<td>EtCl</td>
<td>12.2</td>
<td>0.87</td>
<td>1.06</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>9.88</td>
<td>0.93</td>
<td>1.11</td>
</tr>
</tbody>
</table>

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 \( \delta \) is the dispersion.