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Extension of the Theory of Volume Filling of Micropores to Adsorption in Supermicropores*

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Abstract. An enhancement in characteristic energy of adsorption in large micropores is analyzed. The effect is due to the overlapping of potential fields from opposite walls of pores and to reduction of the surface adsorption film on filling the micropore volume. The effects of both factors are comparable in magnitude and dependent on the micropore size.

Keywords: non-porous and supermicroporous adsorbents, characteristic energy of adsorption, adsorption potential, polymolecular adsorption

Introduction

The theory of volume filling of micropores (TVFM) developed by Dubinin has found a widespread application for calculating the values of equilibrium adsorption of various substances and estimating parameters that characterize adsorption properties and main varieties of micropore structure of activated carbons (Dubinin, 1965).

According to Dubinin's ideas, isotherms of adsorption by a microporous material are similar for different adsorbates. Based on this suggestion a general equation of the TVFM was put forward on the assumption of Gaussian distribution of the micropore filling over the differential molar work of adsorption A. The equation known as the Dubinin–Radushkevich (DR) equation can be written in a current form as (Dubinin, 1989):

$$W = W_0 \exp[-(A/\beta E_0)^2. \tag{1}$$

Herein, W is the amount adsorbed expressed as a liquid volume; W_0 is the limiting adsorption volume; E_0 is the characteristic energy of adsorption of vapor taken as standard (usually benzene); β is a scaling factor of characteristic curves; A is the differential molar work of adsorption. Equation (1) is valid for a description of isotherms of equilibrium adsorption over the range of low and moderate pressures (*P/Ps* from 10^{-4} to about 0.4) obtained with activated carbons that have a uniform microporous structure.

In addition to carbons with a homogeneous micropore structure, use is frequently made of activated microporous carbons with a heterogeneous collection of micropores. Activated carbons of this type are usually burnt off to higher extents (above 50%) by heating heterogeneous carbonized materials doped with inorganic activators. As the process of steam-to-gas activation of carbons proceeds, the characteristic energy of adsorption decreases with increasing micropore size. If the extent of activation is sufficiently high ($E_0 \leq 19\,\mathrm{kJ\,mol^{-1}}$) adsorption isotherms can-not be adequately described by Eq. (1). In these cases adsorption properties of carbons can be approximated by the adsorption isotherms equation DR-2 of TVFM (Izotova and Dubinin, 1965):

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

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*This work is devoted to memory of the professor W. Schirmer

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Equation (2) postulates that the microporous system of activated carbons comprises two sub-systems each with its own $W_{0,1}$, $E_{0,1}$ and $W_{0,2}$, $E_{0,2}$.This equation served as a basis to subdivide the micropore range into true micropores (micropore half-width $x_{0,1} < 0.6$–0.7 nm) and supermicropores (0.6–0.7 nm $< x_{0,2} <$ 1.5–1.6 nm).

In general, structural heterogeneity of micropores is characterized by a continuous pore size distribution. Stoeckli and Dubinin (Dubinin and Stoeckli, 1990) made a reasonable assumption on a continuous rather than a discrete pore size distribution and suggested an equation taking into account the normal pore size distribution. Integrating the thermal equation of adsorption suggested by the TVFM for adsorbents with a heterogeneous pore structure—based on the equation of normal micropore size distribution—, and Eq. (2) gives the equation of Dubinin–Stoeckli (DS):

$$W = \frac{W_0^0}{2\sqrt{1+2m'\delta^2 A^2}} \exp\left[-\frac{m' x_0^2 A^2}{1+2m'\delta^2 A^2}\right] \times \left[1+\operatorname{erf}\left(\frac{x_0}{\delta\sqrt{2(1+2m'\delta^2 A^2)}}\right)\right]. \quad (3)$$

This equation includes three parameters: the total micropore volume W_0^0, the half-width of micropore read from the maxima on the curve of micropore size distribution x_0, the spread δ of size distribution, and m' the constant that is characteristic of the given vapor. The model of slit-shaped pores with limited side dimensions (Gurianov et al., 1975) implies that the pore width ($2x_0$) is in inverse proportion to the values of the characteristic energy of adsorption $E_0^{2/3}$. The relation between parameters in Eqs. (2) and (3) was established (Dubinin, 1985). It was demonstrated that in the range of supermicropores which lies between ranges of micro- and mesopores the carbons gradually loose properties characteristic of micropores whereas those of mesopores become increasingly significant (Dubinin, 1974). It is therefore of interest to consider the differences between adsorption in large micropores (supermicropores) and a non-porous solid of the same chemical nature, and give an interpretation in quantitative terms.

Calculation of Energetic Characteristics of Adsorption on Supermicroporous Adsorbents

The abandonment of Eq. (1) in favor of Eqs. (2) or the DS Eq. (3), that involves spread values δ well in excess of zero, is explained by the energetic heterogeneity of micropore structure. It emerged from recent findings that a wider applicability of Eqs. (2) and (3) is caused not only by the occurence of additional pores in carbons but rather by a change in the nature of adsorption. The new feature is the multilayer character of adsorption caused by an enhanced spread of adsorption potential along the micropore size with increased linear dimensions. Some experimental findings tend to support this concept.

It was shown (Gurianov et al., 2001) that as the deep steam-to-gas activation of carbonized material proceeds both the number of micropores and their surface calculated to the unit of volume of microporous fragments remain unchanged. Recent experimental investigations of porous structure produced by activation of carbon sorbents prepared from different raw materials support this trend. Raw materials include woods, cellulose hydrate fibers, furfural, copolymer of 2-methyl, 5-vinylpyridine, and divinylbenzene. The adsorption isotherms were satisfactorily described by Eqs. (2) or (3) rather than by Eq. (1). Nevertheless the activation procedure led to micropores with. increased linear sizes and yielded no new variety of micropores. Furthermore, the values $E_{0,2}$ from Eq. (2) were markedly lower than the characteristic energy of adsorption ($E_m \sim 12\ \text{kJ mol}^{-1}$) which is associated with the monolayer coverage on non-porous carbons, non-graphitized and graphitized carbon blacks (Gurianov et al., 1978). Similarly, Dubinin and coworkers (Dubinin et al., 1988) found that for the adsorbents with a well-developed micropore volume the values of E_0 from the DS equation (8.5–8.8 kJ mol^{-1}) are also lower than E_m. In contrast to adsorption on non-porous adsorbent that in micropores is characterized, in particularly, by enhanced heats of adsorption and, accordingly, by a higher adsorption potential (Dubinin, 1974). Therefore, the use of Eq. (2) or DS instead of Eq. (1) stems from an essential change in the nature of the adsorption process that involves multilayer adsorption in large micropores. Examining Eq. (2) from this position it is possible to assume that the first term in Eq. (2) reflects adsorption in a monolayer while the second term describes adsorption in the remaining volume of supermicropores characterized by a much lower adsorption potential. Then the parameters of Eq. (2) serve to determine the number of adsorbate layers N in large micropores

$$N = 2\frac{W_{0,1} + W_{0,2}}{W_{0,1}}. \quad (4)$$

Table 1. Use of Dubinin-Stoeckli equation to calculate parameters of microporous structure of activated carbons from adsorption of substances with different molecular diameters

	W_0^0		x_0	δ
Adsorbate	(mmol g^{-1})	(cm^3 g^{-1})	(nm)	
	AG adsorbent			
C_6H_6	3.30	0.29	0.61	0.120
C_2H_5Cl	4.00	0.28	0.59	0.142
CCl_4	2.45	0.24	0.62	3.32×10^{-3}
	FAS adsorbent			
C_6H_6	11.5	1.02	1.22	0.555
C_2H_5Cl	12.2	0.87	1.06	0.358
CCl_4	9.88	0.93	1.11	0.289

The change in nature of adsorption is supported by a decrease in values of the spread in the DS equation with the size of the adsorbed molecules (Dubinin et al., 1990) and correspondingly with the ratio of the linear size of micropore to that of the adsorbed molecule.

Table 1 gives the parameters of micropore structure of two carbon samples AG and FAS with values of micropore half-width x_0 that differ two times as suggested by adsorption measurements. The parameters were estimated from adsorption isotherms using the DS Eq. (3). Three adsorbing species selected were EtCl, C_6H_6 and CCl_4 with the critical diameter ranging from 0.44 nm (EtCl) to 0.69 nm (CCl_4). The δ values derived from adsorption of EtCl and flat C_6H_6 molecule on active carbon AG are typical of usual heterogeneous micropore adsorbents. When CCl_4 molecule is adsorbed which has the largest critical diameters among the adsorbates of this group, the pores become completely filled avoiding monolayer formation. The spread values in this case are close to zero implying the validity of Eq. (1) for homogeneous micropores.

Reduced δ values are observed for the adsorbent FAS with larger pores although adsorption of carbon tetrachloride gives values other than zero. The reason is that the monolayer coverage in this carbon fails to completely fill the sorption volume of micropores.

Equation (2) serves to calculate weighted-mean values of C in large micropores (supermicropores) E_0. Use can be made of expression

$$E_0 = (E_{0,1} \times W_{0,1} + E_{0,2} \times W_{0,2})/(W_{0,1} + W_{0,2}). \tag{5}$$

On the other hand, E_0 values for supermicropores can be estimated from the number of layers N (Eq. 4) with allowance for the characteristic energy of monolayer adsorption of benzene on the carbon black $E_m \approx 12\,\mathrm{kJ\,mol^{-1}}$. This requires a qualitative estimation of the effect caused by the enhancement of adsorption energy due to overlapping fields of neighboring walls. The character of the force field over single wall can be accepted as similar to that over non-porous adsorbent of the same chemical nature.

To describe the process of multilayer adsorption on an energetically heterogeneous surface use can be made of Eq. (6) (Gurianova and Gurianov, 1989) that postulates that on non-porous adsorbents the filling of the first and higher layers can be described by the Dubinin–Radushkevich equation

$$\frac{a}{a_m} = \sum_{i=1}^{N} \exp\left(-\left[\frac{A}{E_m}\right]^2 2^{3(i-1)}\right) \tag{6}$$

where a is the value of the multilayer adsorption, a_m is the limiting capacity of the layer, E_m is the characteristic energy for adsorption in the first layer, i is the number of the given adsorption layer.

The expression $E_i = f(E_m, i)$ that describes the equation of the multilayer adsorption (6) can be written as

$$E_i = E_m/2^{\frac{3}{2}(i-1)}. \tag{7}$$

The appropriate form of this equation can be applied to calculate the mean values of the characteristic energy for adsorption of N layers on the flat surface:

$$\bar{E} = \left(\sum_{i=1}^{N} E_i\right) \Big/ N = \frac{E_m}{N} \sum_{i=1}^{N} 2^{-3(i-1)/2}. \tag{8}$$

For adsorption of N layers in large micropores the effect of the neighboring wall can likewisely be assessed by Eq. (8), and the mean values of the characteristic energy of adsorption can be taken as being equal to double $2\bar{E}$.

Another characteristic feature that serves to distinguish the mechanisms of adsorption on nonporous and porous adsorbents is that once the monolayer on the surface of a non-porous solid is formed the vapor-adsorbate interface originates. The area of the interface is equal to the adsorbent surface area. When the mechanism of volume filling is operative the interface disappears because adsorption films lining opposite pore walls coalesce. This should result in an enhancement in adsorption energy. To treat this difference in qualitative terms we can try to estimate the energy liberated

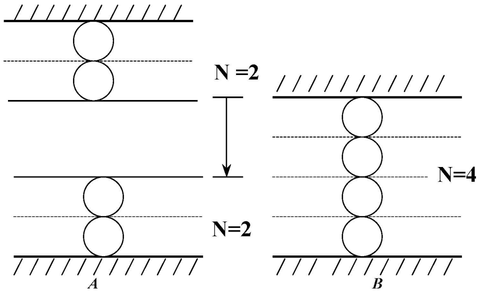

Figure 1. Transfer from multilayer adsorption (state **A**) to the volume filling of micropores (state **B**).

as a result of an imaginary transfer of the adsorption system (Fig. 1) from state **A** (adsorption on nonporous adsorbents) into state **B** (adsorption in micropores). In the state **A** the adsorption film is characterized by a free surface with the full energy per surface unit ε depending on surface tension σ and temperature T

$$\varepsilon = \sigma - T(d\sigma/dT). \tag{9}$$

As soon as the flat surfaces approach each other to a distance small enough to effect coalescence the energy 2ε evolves and the increment of the integral heat of adsorption ΔQ_σ must be in inverse proportion to the number of layers N and the number of adsorbate moles m per the surface unit

$$\Delta Q\sigma = 2\varepsilon/mN. \tag{10}$$

Evaluating the increment of the characteristic energy of adsorption, we assume that the different interaction energies on a flat surface and in micropores would not change the treatment of the adsorption isotherms. In both cases, adsorption in an i-th layer can be described by the Dubinin–Radushkevich equation. Accordingly, the equation developed for calculation of the differential molar work of adsorption (Bering and Serpinsky, 1957) can be applied. The integrated form can be written as:

$$\begin{aligned} Q_i &= \lambda + E_i \cdot \left[\int_{\Theta_i=0}^{\Theta_i=1} \left(\ln \frac{1}{\Theta_i}\right)^{1/2} d\,\Theta_i \right.\\ &\left. + \frac{\alpha_i T}{2} \int_{\Theta_i=0}^{\Theta_i=1} \left(\ln \frac{1}{\Theta_i}\right)^{-1/2} d\,\Theta_i\right]. \end{aligned} \tag{11}$$

Here Q_i is the integral heat of adsorption, α_i is factor of thermical expansion of the adsorbate in the i-th layer, λ is the molar heat of condensation of adsorbate vapor, $\Theta = W/W_0$ is the degree of volume filling of micropores by adsorbate. Taking the integral heat of adsorption as a mean value for all the N layers both for the states **A** and **B** and assuming in (11) that values α_i are equal to the integral heat of adsorption of bulk liquid α_0 we have

$$\bar{Q}_{A(B)} = \lambda + \left[\left(\sum_{i=1}^{N} E_i\right)\Big/ N\right] \cdot k = \lambda + k \cdot \bar{E}_{A(B)}, \tag{12}$$

where

$$\begin{aligned} k &= \int_{\Theta=0}^{\Theta=1} \left(\ln \frac{1}{\Theta}\right)^{1/2} d\Theta + \frac{\alpha_0 T}{2} \\ &\times \int_{\Theta=0}^{\Theta=1} \left(\ln \frac{1}{\Theta}\right)^{-1/2} d\Theta. \end{aligned} \tag{13}$$

Equation (12) leads to

$$\bar{Q}_B - \bar{Q}_A = k \cdot (\bar{E}_B - \bar{E}_A) = k \cdot \Delta E_\sigma. \tag{14}$$

Since $\bar{Q}_B - \bar{Q}_A = \Delta Q_\sigma$ we arrive at the following expression:

$$\Delta E_\sigma = 2 \times \varepsilon/m \times N \times k, \tag{15}$$

where for benzene $\varepsilon = 69.4\,\mathrm{erg\,cm^{-2}}$ (293 K), $k \approx 1.13$ (if Θ varies from 0.05 to 0.95); $m = 5.5 \times 10^{-10}$ mol cm^{-2} (molecular area calculated from the liquid density $\sim$40 Å^2). Values of ε and k were evaluated on the assumption that $\alpha_i = \alpha_0 = 1.237 \cdot 10^{-3}$ deg^{-1} and $\sigma_i = \sigma_0 = 28{,}9\,\mathrm{erg\,cm^{-2}}$, which in a strict sense can be crude approximations since the thermodynamic characteristics of the adsorbate as well as those of the adsorbent can be modified by adsorption (Bering and Serpinsky, 1957).

To estimate ΔE_σ values using Eq. (15) no concept on the course of the process is needed. The condition that the maximum energy is liberated in the vicinity of the saturation region is not necessary. On the contrary, based on a vague resemblance between adsorption in large micropores and mesopores, the suggestion can be made that adsorption films can loose their stability to coalesce in segments of micropores long before their width becomes equal to the half-width of the slit.

Discussion

In order to illustrate general validity of our approach we consider at first large micropores in which the number of adsorbate layers varies from 2 to 6. Use can be made of Eq. (4) to determine the $\frac{W_{0,2}}{W_{0,1}}$ ratio and to evaluate the mean values of the characteristic energy of adsorption $\bar{E}$ for N layers on a_flat surface, and finally the ΔE_σ values. Table 2 gives results of these calculations along with the combined values of the characteristic energy of adsorption E_0 that was evaluated considering both multilayer adsorption in micropores and coalescence of adsorption films from opposite pore walls

$$E_0 = 2\bar{E} + \Delta E_\sigma. \tag{16}$$

The cumulative values of the characteristic energy of adsorption of benzene vapor can be compared with the relevant weighted average values E_0 calculated with the help of equation

$$E_0 = 19,4 \cdot \left(1 + \frac{W_{0,2}}{W_{0,1}}\right)^{-1} + 4,65. \tag{17}$$

The equation resulted from treating extensive data sets (Gurianov, Petukhova and Polyakov, 2001) obtained by experiments with on a number of carbons made from furfural, wood, hydrated cellulose fibers and pyrolysed wood. It produces E_0, values in kJ mol^{-1}.

As evidenced by data given in Table 2 satisfactory agreement between calculated and experimental values is observed in spite of the tentative character of calculations. The highest divergence does not exceed 11%. In all cases ΔE_σ values prevail over the $\bar{E}$ ones. Accordingly, the effect of overlapping of the potential fields on the neighboring pore walls is not the only reason why the energy of adsorption in micropores is markedly higher than that on the flat surface. A reduction of the surface of the adsorption field makes a more considerable contribution to the adsorption energetics. An enhancement of the adsorption energy due to reduction of the adsorption field increases as the pore size increases.

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

		$\bar{E}$	ΔE_σ	E_0^{calc}	E_0^{exp}	
N	$W_{0,2}/W_{0,1}$	(kJ mol^{-1})				$\Delta 100$ (%)
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	11,9	12,4	10,5
6	2,0	3,08	3,76	9,9	11,1	10,6

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

Conclusion

It follows from the foregoing discussion that large micropores retain features typical to fine pores but show nevertheless signs of a "layer-to-layer" mechanism due to a considerable spread of the adsorption potential over their size. Considering these traits it is possible to clarify between adsorption on non-porous adsorbents and that in supermicropores.

Nomenclature

A	differential molar work of adsoeption (kJ mol^{-1})
a	amount adsorbed in a multilayer fashion (mol g^{-1})
a_m	limiting capacity of an adsorbed layer (mol g^{-1})
E_0	chracteristic energy of adsorption of a standard vapor (conventionally benzene) (kJ mol^{-1})
E_m	characteristic energy of adsorption in the monolayer (in the first layer (kJ mol^{-1})
$\bar{E}$	mean value of the characteristic energy of adsorption in a micropore conteaining N layers of adsorbate (kJ mol^{-1})
k	constant in Eqs. (12) and (13)
m'	constant in Eq. (13)
m	quantity of adsorbate (mol)
N	number of adsorbate layers in a micropore
ΔQ_σ	increment of the integral heat of adsorption (kJ mol^{-1})
Qi	integral heat of adsorption in i-th layer (kJ mol^{-1})
T	temperature (K)
W	amount adsorbed expressed as the molar volume (cm^3 g^{-1})
W_0	limiting adsorption volume (cm^3 g^{-1})
x_0	half-width of the micrpore (nm)

Greek letters

α_0	factor of thermical expansion of bulk liquid (deg^{-1})
α_i	factor of thermical expansion of adsorbate in i-th layer (deg^{-1})

β	similarity constant of characteristic curves
δ	spread (nm)
ε	total energy per surface unit (erg cm^{-2})
Θ	degree of filling of pore volume by adsorptive
λ	molar heat of condensation of adsorptive vapor (kJ mol^{-1})
σ	surface tension (erg cm^{-2})

Subscripts

$_{0,1}$	subscript denoting true micropores
$_{0,2}$	subscript denoting large micropores (supermicropores)
i	index of the adsorption layer.
A	adsorption on non-porous surface (Fig. 1)
B	adsorption in micropores

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