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ADSORPTION EQUILIBRIUM AND HYSTERESIS IN OPEN SLIT-LIKE MICROPORES

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For qualitative and quantitative description of adsorption equilibrium and hysteresis in open slit-like micropores, theoretically rigorous equations are proposed based on the theory of volume filling of micropores which imply the physical and formal analogy between the volume filling of micropores and capillary condensation. The applicability of the proposed equations for description of the hysteresis in such systems is demonstrated for water adsorption/desorption isotherm on the fibrous carbon material AUVM-Dnepr which possesses micro- and mesoporous structure.

Keywords: adsorption, hysteresis, slit-like pores, carbon material, porous bodies

INTRODUCTION

In the general case of porous bodies which possess micro- and mesopores, the adsorption should be considered as a stage-by-stage process. Within pore range with a characteristic size lower than the adsorbate molecular diameter σ , the adsorption occurs on the external surface. If the characteristic size of the slit-like pore, i.e. the ratio of the pore width to the adsorbate molecular diameter is in the range $1 < h/\sigma < 2$, then the adsorption process is governed both by the interaction between the adsorbate molecules and by the interaction of adsorbate molecules with the force field of very narrow pore, having in mind the overlapping of the pore walls potential. For the pores with characteristic size above 2σ filmwise condensation occurs [1].

The irreversibility of the adsorption process in porous bodies, which results in adsorption hysteresis, also should be considered with regard to the characteristic size of the porous space. If the pore width $h > 5\sigma$, then the hysteresis description should assume the filmwise condensation and capillary evaporation process, governed by the Kelvin equation [1, 2]. On the other hand, if the pore width is in the range $\sigma < h < 2\sigma$, the adsorption process should be treated according to the theory of volume filling of micropores (TVFM) [1]; in this case the adsorption hysteresis is caused by the ‘memory effect’ of the adsorption system [1, 3]. The adsorption hysteresis theory based on

TVFM was developed in [3]. It should be noted that, while the scope of the publications related to the adsorption hysteresis theory is vast, these refer to the hysteresis in mesopores, while the adsorption hysteresis in micropores was studied only experimentally. The authors are unaware of any theoretical publications in this specific field.

It was reported recently by one of the authors in [4] that the classic TVFM equations do not correspond exactly to the basic TVFM principle, and a new equation was proposed to describe the volume filling of cylindrical pore. In the proposed study the approach developed in [4] is presented in more detail (having in mind that the short publication [4] is quite hard-to-reach), and is applied to the description of the adsorption equilibrium and hysteresis in a slit-like pore.

THEORY

To begin with, we recapitulate some statements considered in [4]. The TVFM developed by Dubinin [5] and (independently) by Pierce, Wiley and Smith [6] was based on the assumption that the adsorption in the pores should be treated as their volume filling (similar to the capillary condensation process) rather than their layer-by-layer filling. The physical analogy between both processes implies their formal analogy, i.e. the volume filling of pores and the capillary condensation could be expected to obey similar mathematic treatment.

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All the TVFM equations currently used were derived on the basis of the Polanyi theory [1, 7]. The adsorption isotherm equation proposed here is also based on the Polanyi's characteristic curve [7]:

$$\theta = f(\beta A), \quad (1)$$

where, according to the TVFM, θ is the relative coverage, i.e. the ratio of the current adsorption value to its maximum possible value which corresponds to the rightmost boundary of the micropores range; note that $\theta < 1$. In Eq. (2) A is the Polanyi adsorption potential which by its physical meaning determines the variation of Gibbs potential during the adsorption: $A = -\Delta G$:

$$A = RT \ln(p_0/p), \quad (2)$$

where p and p_0 are the adsorbate pressure in the bulk phase and the saturation pressure, correspondingly, at temperature T ; β is the affinity parameter as introduced by Dubinin [8], R is the universal gas constant.

Various adsorption isotherm equations (Dubinin-Radushkevich [9], Dubinin-Astakhov [10, 11], Dubinin-Stoeckli [8, 12]) can be obtained based on the characteristic curve, using the equation of the thermodynamic perturbation theory for polymolecular adsorption, see [7, 13, 14]:

$$\theta_n = \int_A^\infty f(\varepsilon_k) d\varepsilon_k, \quad (3)$$

where θ_n is the n -th layer relative coverage, ε_k is the local value of the pore wall potential, $f(\varepsilon_k)$ is the fraction of adsorption space which corresponds to this ε_k value. The total coverage then is:

$$\theta = \sum_{n=1}^{\infty} \theta_n. \quad (4)$$

Equations (3) and (4) were used mostly to describe the polymolecular adsorption. However, assuming $\theta_n = 0$ for all $n > 1$, the integration in Eq. (4) with the modified Gaussian distribution for $f(\varepsilon_k)$ yields the Dubinin-Radushkevich equation [8, 13]. If the Weibull-Gnedenko distribution is chosen for $f(\varepsilon_k)$, then the integration in Eq. (4) results in the Dubinin-Astakhov adsorption isotherm [1].

It should be stressed here that the Polanyi theory [7], upon which all presently known TVFM equations essentially rely, is in fact the special case of the Gibbs surface thermodynamics [7].

Therefore, the theoretical approach on which the TVFM adsorption isotherm is based, does not involve the basic postulate of TVFM about the analogy between the volume filling and capillary condensation.

For the pore width range $\sigma < h < 2\sigma$, the quasi-one-dimensional phase (molecular associate, cluster which does not exhibit any surface tension) is formed in the pore.

The capillary evaporation process is described by the Kelvin equation [1,2]:

$$x = \frac{p}{p_0} = \exp\left(-\frac{\gamma V_l}{RTt_k}\right). \quad (5)$$

Here γ and V_l are the surface tension and molar volume of liquid adsorbate; t_k is the core width, which is the difference between the pore width and the thickness of the condensate film on the pore walls [1]. The governing parameter in Eq. (5) is the surface energy γ , which for the molecular associate could be zero or even negative [15].

The molecular theory of spherical drops in vapor phase was developed by Yu. Tovbin [15]. In particular, the expression analogous to the Kelvin's equation was proposed where the governing parameter ϕ is the molecular associate energy in the potential field of pore walls. For the slit-like pores the equation derived in [15] becomes:

$$x = \frac{p}{p_0} = \exp\left(-\frac{\phi z_0}{RTh}\right), \quad (6)$$

where h is the pore width. In [15] the parameter z_0 is rigorously determined analytically; however, in practical applications its calculation is too complicated. On the other hand, within the transition region thermodynamics for low-molecular substances [15–17] the approximation $z_0/h \approx \sigma/h = \theta$ provides reasonable accuracy.

The potential energy of molecular associate ϕ in very thin pores was theoretically studied in [18, 19]. In particular, the ratio of the potential energy of molecular associate in a slit-like pore to the potential energy of molecules relative to their interaction with open plane surface ϕ_0 was calculated in [20]; this dependence plotted vs h/σ is shown by solid curve in Fig. 1. It is seen that the influence of the overlapping potentials created by the opposite walls remains essential even for slit-like pore width of 1.5σ . The potential function shown in Fig. 1 was analytically approximated in [20] using the Kirkwood-Muller formula; however,

as was mentioned in [4], it could be deduced that for practical calculations a simpler dependence shown in Figure 1 by dashed curve:

$$\frac{\bar{\varphi}}{\varphi_0} = \frac{\varphi}{\varphi_0} = \frac{h/\sigma}{-m + h/\sigma} \quad (7)$$

provides a good approximation (with maximum relative error $\pm\delta = 5.5\%$) within the relative pore width range $1 < h/\sigma < 2$. Here

$$m = 1 - \left(\frac{\varphi_0}{\varphi} \right)_{h/\sigma \rightarrow 1} \quad (8)$$

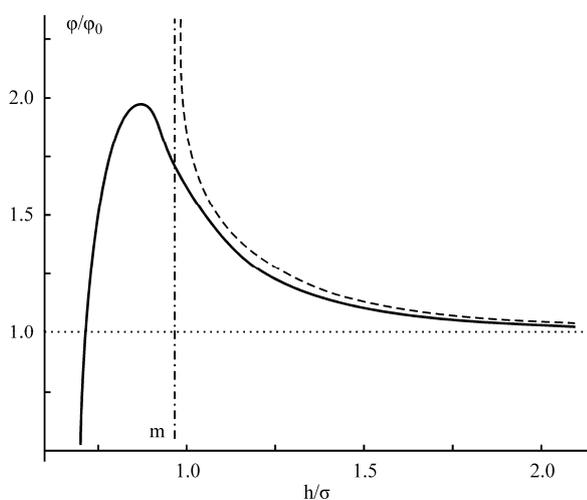


Fig. 1. The excess of the potential energy of adsorbate molecules in a pore φ with respect to the potential energy of molecules over the infinite plane φ_0 vs the relative pore size h/σ (solid curve). Also shown are: the analytical approximation, Eq. (7) (dashed curve); the schematic asymptotic of this analytical approximation at $(h/\sigma) \rightarrow m$ (vertical dash-dotted line); and the asymptotic at high h/σ (horizontal dotted line)

In what follows, the assumption commonly adopted in the adsorption theory is used: the relative pore width h/σ is taken equal (within the accuracy sufficient for practical calculations) to the pore filling value θ [1], i.e. to the ratio of the current adsorption value to its value which corresponds to monolayer formation. This definition of θ is more reliable than that adopted in TVFM, because the rightmost boundary of the micropores range cannot be precisely determined due to the fact that a quite large transition range exists between the micropore and mesopore regions. Then Eq. (7) becomes:

$$\frac{\bar{\varphi}}{\varphi_0} = \frac{\theta}{-m + \theta} \quad (9)$$

The solution of combined Eqs. (7) and (9) with respect to θ yields:

$$\theta = m - \frac{\varphi_0}{RT \ln x} \quad (10)$$

Introducing the adsorption potential $A = RT \cdot \ln(1/x)$, one obtains from Eq. (10):

$$\theta = m + \frac{A_0}{A} \quad (11)$$

Here A_0 is the adsorption potential corresponding to the relative pore range where the influence of the opposite pore walls becomes negligibly small, i.e. $A_0/RT = \varphi_0/RT = -\ln(x_0)$, where x_0 is the relative pressure at which $\bar{\varphi} \rightarrow 1$. Therefore, Eq. (11) is obtained here in the framework of the basic TVFM postulate.

Comparing Eq. (8) and Fig. 1 one can see that the m value is approximately equal to 1. However, in practical calculations it is more convenient to determine the parameters in Eq. (11) from the analysis of the specific isotherm considered.

Next we apply Eq. (11) to describe the adsorption hysteresis in a quasi-one-dimensional pore. The adsorption hysteresis is defined as the difference between the adsorption potential values at the direct and reverse branches of the hysteresis loop at the same value of adsorption value considered as the process coordinate.

From Eq. (11), the expressions for the process coordinates of adsorption $a^{(a)}$ and desorption $a^{(d)}$ follow:

$$a^{(a)} = a_m^{(a)} \theta = a_m^{(a)} \left(m^{(a)} + \frac{A_0^{(a)}}{A^{(a)}} \right), \quad (12)$$

$$a^{(d)} = a_m^{(d)} \theta = a_m^{(d)} \left(m^{(d)} + \frac{A_0^{(d)}}{A^{(d)}} \right). \quad (13)$$

In what follows, the superscripts (a) and (d) refer to the process parameters for the adsorption and desorption hysteresis branches, respectively; in Eqs. (12) and (13) the values $a_m^{(a)}$ and $a_m^{(d)}$ are the maximum adsorption values for the adsorption and desorption, respectively. Then the adsorption potential at the desorption branch of the hysteresis loop for equal coordinates of the adsorption and desorption processes is:

$$A^{(d)} = A_0^{(d)} \left[\frac{a_m^{(a)}}{a_m^{(d)}} \left(m^{(a)} + \frac{A_0^{(a)}}{A^{(a)}} \right) - m^{(d)} \right]^{-1} \quad (14)$$

and the adsorbate relative pressure in the bulk phase for the desorption branch of the hysteresis loop $x^{(d)}$ is given by the expression:

$$x^{(d)} = \exp \left\{ - \frac{A_0^{(d)}}{RT} \left[\frac{a_m^{(a)}}{a_m^{(d)}} \left(m^{(a)} + \frac{A_0^{(a)}}{A^{(a)}} \right) - m^{(d)} \right]^{-1} \right\}. \quad (15)$$

In what follows, Eqs. (12) and (15) are used to describe the adsorption equilibrium and hysteresis in open slit-like micropores.

EXPERIMENTAL RESULTS AND DISCUSSION

Isotherms of water vapor adsorption on fibrous carbon materials were reported in several publications, see e. g. [21]. In this study, the water vapor adsorption/desorption isotherm on the fibrous carbon material AUVM-Dnepr (AYBM-Днепр) which possesses micro-mesoporous structure in which the slit-like and cylindrical micropores prevail. The physicochemical characteristics of the material are extensively summarized in [22]; in particular, the specific surface area (BET) is 1375-1680 m²/g, the micro-, meso- and macroporous volumes are 0.26, 1.17 and 0.44 cm³/g, respectively. The isotherms were measured by the authors using the vacuum adsorption device with McBain-Bakr quartz helix balance at T = 294.15 K [23].

The initial analysis of the isotherm shown in Fig. 2 by its fitting to the BET equation [1] yields the monolayer adsorption value $a_m^{(a)} = 3.85$ mmol/g. Therefore, even at $x \rightarrow 1.0$ the coverage value $\theta < 1.9$, and therefore the adsorption process within the range $0.1 < x < 1$ obeys the volume filling mechanism.

To apply Eq. (11) for the description of the adsorption isotherm, the isotherm was re-plotted in the coordinates $\theta^{(a)} = f(A^{(a)})^{-1}$. The result is shown in Fig. 3; it is seen that the isotherm consists of two straight intervals. For the first interval the parameters (the m value and the slope) were obtained using the standard procedure; it was found that (to within the experimental error) $m = 1$. From Fig. 3, an interesting feature of the quasi-one-dimensional adsorption regime becomes obvious: for low adsorbate density in the bulk the adsorbate in the pore exists as the molecular associate, while with the increase of the bulk adsorbate density

above the value which corresponds to $x = 0.9$ clusterisation of the associate takes place. This behaviour resembles the transition from gaseous phase to condensed phase; however, any exact analogy with the phase transition cannot be drawn because the one-dimensional system is incapable to undergo any phase transition [24].

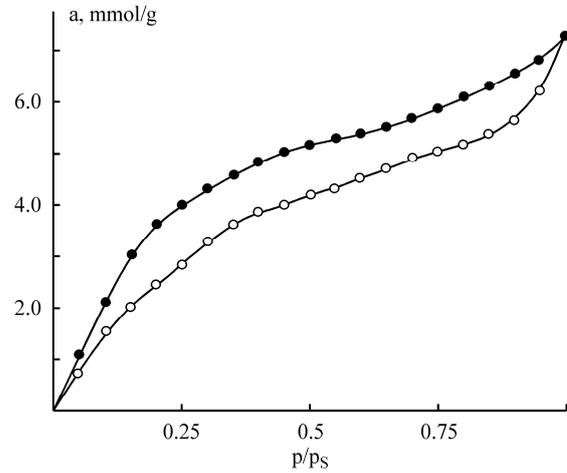


Fig. 2. The adsorption (○)/desorption (●) isotherm for water vapors on the fibrous carbon material AUVM-Dnepr

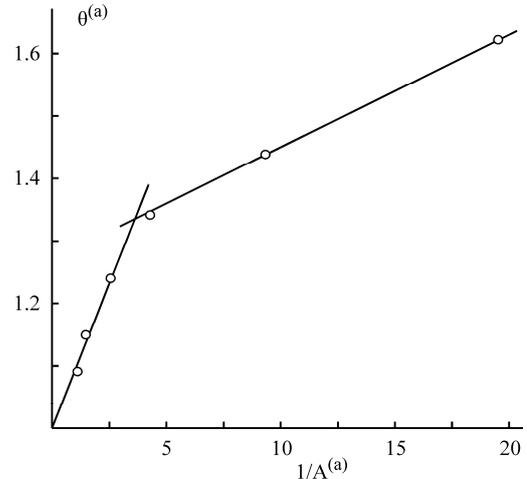


Fig. 3. The water vapor adsorption isotherm on fibrous carbon material AUVM-Dnepr plotted in the coordinates $\theta^{(a)} = f(A^{(a)})^{-1}$

It was noted above that the adsorption process is characterised by two stages with different process parameters. Assuming the decreasing power function as the approximation, one obtains for the adsorption isotherm equation:

$$\theta^{(a)} = 1 + \left(\frac{A_0^{(a)}}{A^{(a)}} \right)^{\alpha_1}, \quad (16)$$

where the values $A_0^{(a)} = 0.032 RT$, $\alpha_1 = 0.68$ were obtained from the fitting. With these parameters, Eq. (16) describes the adsorption isotherm shown in Fig. 2 to within the maximum relative deviation $\pm\delta = 7.5\%$.

Next the desorption isotherm was analysed. The monolayer adsorption as determined from BET equation is $a_m^{(d)} = 4.28$ mmol/g. In Fig. 4 the desorption isotherm re-plotted in the coordinates $\theta^{(d)} = f(A^{(d)})^{-1}$ is shown; it is seen that the desorption process also takes place in stages. However, it is obvious from the adsorption/desorption isotherm plot that for the calculation of the hysteresis loop only the range $0.4 < x < 0.9$ is relevant. Similarly to the adsorption process, the equation for the desorption branch in the framework of the formalism involved in Eq. (12) should read:

$$\theta^{(d)} = 1 + \left(\frac{0.06 \cdot RT}{A^{(d)}} \right). \quad (17)$$

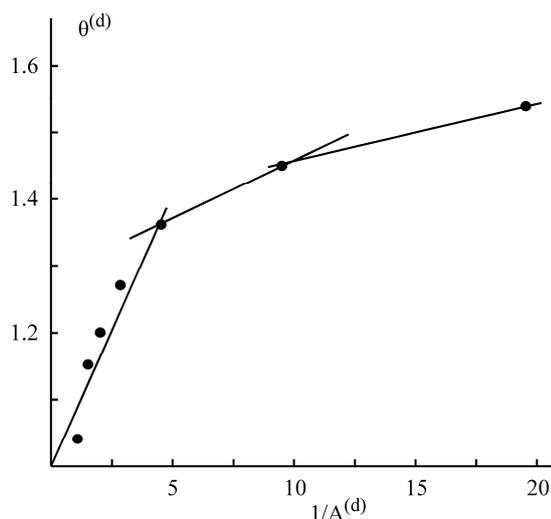


Fig. 4. The water vapor desorption isotherm on fibrous carbon material AUVM-Dnepr plotted in the coordinates $\theta^{(d)} = f(A^{(d)})^{-1}$

Eq. (17) describes the desorption branch of the hysteresis loop in the range $0.4 < x < 0.9$ with maximum relative error $\pm\delta = 5.7\%$.

To calculate the hysteresis loop, the expression for the relative adsorbate pressure in the bulk phase should be derived, in which the process coordinates should be equal to each other. Similarly to Eqs. (14) and (15), one obtains:

$$\frac{A_0^{(d)}}{A^{(d)}} = \left\{ \frac{a_m^{(a)}}{a_m^{(d)}} \left[1 + \left(\frac{A_0^{(a)}}{A^{(a)}} \right)^{\alpha_1} \right] - 1 \right\} \quad (18)$$

which yields the relation for the calculation of $x^{(d)}$ value:

$$x^{(d)} = \exp \left\{ -A_0^{(d)} \left[\frac{a_m^{(a)}}{a_m^{(d)}} \left(1 + \frac{A_0^{(a)}}{A^{(a)}} \right)^{\alpha_1} - 1 \right]^{-1} \right\}. \quad (19)$$

In Fig. 5 the values $x_{\text{calc}}^{(d)}$ calculated from Eq. (19) are compared with the $x_{\text{exp}}^{(d)}$ values determined from the experimental isotherm. This clearly demonstrates the validity of the proposed approach.

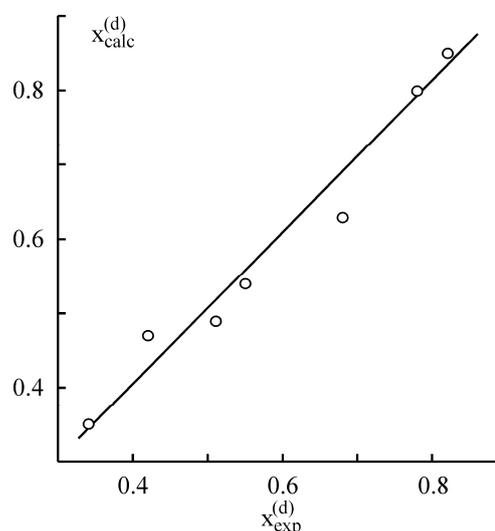


Fig. 5. The comparison of values $x_{\text{calc}}^{(d)}$ calculated from Eq. (19) (straight line) with $x_{\text{exp}}^{(d)}$ values determined from the experimental isotherm (points)

CONCLUSIONS

Within the framework of the basic postulate involved in the TVFM, which implies the physical and formal analogy between the volume filling of micropores and the capillary condensation, the rigorous new equations are proposed for the description of adsorption equilibrium and hysteresis in open slit-like micropores. The applicability of the developed approach is demonstrated using the isotherm of water vapor adsorption/desorption on fibrous carbon material AUVM-Dnepr which possesses micro- and mesoporous structure.

Адсорбційна рівновага і гістерезис у відкритих щілиноподібних мікропорах

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Для якісного і кількісного опису адсорбційної рівноваги і гістерезису у відкритих щілиноподібних мікропорах запропоновані теоретично строгі рівняння, засновані на постулаті теорії об'ємного заповнення мікропор щодо фізичної і формальної аналогії між процесами об'ємного заповнення мікропор і капілярною конденсацією. На прикладі ізотерми адсорбції-десорбції парів води волокнистим вуглецевим матеріалом АУВМ-Днепр, який має мікро-мезопористу структуру, показана придатність одержаних рівнянь для опису гістерезису в таких системах.

Адсорбционное равновесие и гистерезис в открытых щелевидных микропорах

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Для качественного и количественного описания адсорбционного равновесия и гистерезиса в открытых щелевидных микропорах предложены теоретически строгие уравнения, основанные на постулате теории объемного заполнения микропор о физической и формальной аналогии между процессами объемного заполнения микропор и капиллярной конденсацией. На примере изотермы адсорбции-десорбции паров воды волокнистым углеродным материалом АУВМ-Днепр, имеющим микро-мезопористую структуру, показана применимость полученных уравнений для описания гистерезиса в таких системах.

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