Impact of an adsorbed phase nonideality in the calculation of the filling pressure of carbon slit-like micropores

Piotr A. Gauden [a,b,*], Artur P. Terzyk [a], Sylwester Furmaniak [a], Radosław P. Wesołowski [a], Piotr Kowalczyk [c], Jerzy K. Garbacz [b]

[a] *Physicochemistry of Carbon Materials Research Group, Department of Chemistry, Nicolaus Copernicus University, Gagarin Street 7, 87-100 Toruń, Poland*
[b] *Department of Environment Protection, Academy of Humanities and Economics, Okrzei Street 9, 87-800 Włocławek, Poland*
[c] *Department of Chemistry, Faculty of Science, Chiba University, 1-3 Yayoi, Inage, Chiba 263, Japan*

Abstract

The influence of the model of an adsorbed phase on the pore-filling pressure and the pore-size distribution (PSD) curve is analysed for a carbon adsorbent possessing the slit-like micropores. Besides the Henry equation, applied previously in the original Horvath and Kawazoe (HK) approach, and the Langmuir one, studied in the improved HK method of Cheng and Yang, in this study we propose the application of the Dubinin–Astakhov (DA) adsorption equation. The reason is that this equation is more reliable for the description of the mechanism of adsorption in carbon micropores. The correction proposed by us leads to the change in the plot of the micropore filling pressure curve. It is shown that the type of the equation describing the behaviour of the adsorbate slightly modifies the shape of the pore-size distribution curves. Moreover, the improvement assuming the Langmuir equation of state does not predict the larger effective micropore widths than approximately 1.2 nm, contrary to the proposed in this study correction assuming DA-type behaviour of the adsorbed phase. Finally, we explain why the condensation approximation method can be effectively used for the calculation of the PSD of activated carbons where the process of primary micropore filling predominates.
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1. Introduction

The Horvath and Kawazoe (HK) method is widely used for determining the pore-size distribution (PSD) of microporous materials. Despite of criticism of the HK approach [1–3] the recent studies showed that it leads, for some microporous carbons, to similar results as those obtained from the most sophisticated methods of porosity calculation, namely the density functional theory (DFT) [4] and/or the Nguyen–Do (ND) [5,6] model. The similarity of the results is observed for carbons where the, so-called, "primary micropore filling" process predominates during adsorption [7–10].

Over the last couple of decades, different improvements of the original HK model (developed for the slit-like geometry of pores) have been suggested and the assumption of the cylindrical [11,12] and spherical [13–15] pore shapes was considered. Subsequently, Rege and Yang [15] corrected the HK model using an improved interaction potential in micropores for all three (discussed above) geometries. They proposed the new approach for determining the average potential of a molecule in the filled micropore. On the other hand, Lastoskie and co-workers [16,17] replaced the 10-4 solid–fluid potential in the original HK theory by the 10-4-3 potential with the same parameters as are used in the DFT model. Besides, they calculated the mean potential energy from a density weighted average over the adsorbed phase accounted for the density dependence on the distance from the pore walls. Recently, Ustinov and Do [18] reconsidered the mechanism of adsorption in micro and mesopores proposed by Horvath and

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[*] Corresponding author. Address: Physicochemistry of Carbon Materials Research Group, Department of Chemistry, Nicolaus Copernicus University, Gagarin Street 7, 87-100 Toruń, Poland. Tel.: +48-56-611-4512; fax: +48-56-654-2477.

E-mail address: gaudi@cc.uni.torun.pl (P.A. Gauden).

Kawazoe. They considered the change in the free energy of an adsorbate in the narrow slit-like pores (which has not been done in the original HK model) and applied thermodynamics more correctly. This model was shown to be applicable for the description of PSDs calculated from the benzene adsorption data for carbons with different porosity [19].

Very interesting papers dealing with the basic assumptions of the HK method have been published by Jaroniec et al. [20]. They showed, studying well characterised by the XRD method mesoporous materials, that the position of PSDs calculated by the HK approach depend strongly on the relationship used between the adsorption potential and the pore width. For instance, the pore widths at the maxima of PSDs obtained by the HK method with the Saito–Foley expression for cylindrical pores are underestimated by about 1.4 nm. However, the HK method with the relationship between adsorption potential and pore diameter established on the basis of good-quality MCM-41 materials provides an accurate estimation of the pore widths of mesoporous silicas. They also pointed out that the HK method leads to the appearance of an artificial small peak and tail in the micropore–mesopore transition range. In the opinion of the mentioned authors, these artefacts arise from the condensation approximation (CA) used in the HK method, which does not provide a good representation for the volume filling of micropores.

Summing up, it can be concluded that the basic idea of the HK approach is still very attractive and this is caused by its simplicity. The current models of evaluating the pore-size distributions should be easy to use for the wide group of scientists and moreover, they should giving the acceptable results (i.e. theoretical models should be successfully verified based on, for example, calorimetric data, or applying some independent from adsorption measurements experimental techniques). It is important especially for the carbonaceous materials where the detailed structure (geometry) of pores is still unknown, being difficult to investigate [21–23].

The experimental and theoretical studies allow to explain why the HK method gives for carbons possessing very narrow pores, the same results as the DFT and ND (or other advanced) models. Since this similarity has been observed only in the range of very small micropores, it will be interesting to study what should be done in order to obtain, without complicating the HK method, the similarity for the wider micropores, i.e. for those being filled via the mechanism of the secondary micropore filling. We believe that this can be achieved by the extensive mathematical and thermodynamic analysis of the basic ideas of the HK approach. In this study the first step is made, i.e. we show how to improve the pore-filling pressure curve. Moreover, the influence of

this curve on the pore-size distributions calculated based on the assumption of the condensation approximation is presented.

2. Theoretical

We start from the following relation proposed by Horvath and Kawazoe (other details were discussed elsewhere [13,15,24,25]):

$$RT \ln \left(\frac{p}{p_s} \right) + \left[RT - \frac{T\beta_{\text{surf}}}{\theta} \left(\frac{\partial \Pi}{\partial T} \right)_\theta \right]$$
$$= RT \ln \left(\frac{p}{p_s} \right) + K_{\text{impr}} = N_{Av} \Phi \qquad (1)$$

where R is the gas constant; T is the temperature; p and p_s are the equilibrium pressure of an adsorbate and its saturation pressure, respectively; β_{surf} is the surface occupied by an adsorbate molecule; θ is the fraction of surface occupied by molecules; K_{impr} is the so-called 'correction' term; N_{Av} is the Avogadros number; and Φ describes the adsorbate–adsorbate–adsorbent interactions being dependent on the pore geometry. Π is the spreading pressure that can be expressed in the following well-known form [26]:

$$\Pi(\theta) = \frac{RT}{\beta_{\text{surf}}} \int_0^\theta \left(\frac{\theta}{p} \frac{dp}{d\theta} \right) d\theta = \Pi_{\text{id}} \int_0^\theta \left(\frac{\theta}{p} \frac{dp}{d\theta} \right) d\theta \qquad (2)$$

Horvath and Kawazoe assumed that the adsorbed phase is a two-dimensional ideal medium, i.e. it obeys the Henry's law of adsorption [24,25]. Thus:

$$\theta_{\text{Hen}} = \frac{a}{a_{\text{m,Hen}}} = k_{\text{Hen}} p \qquad (3)$$

Hence the equation of state (derived from Eqs. (2) and (3)) is given by [27]:

$$\Pi_{\text{Hen}} = \frac{RT}{\beta_{\text{surf}}} \theta_{\text{Hen}} \qquad (4)$$

and the derivative of the spreading pressure with respect to the temperature is equal to

$$\frac{T\beta_{\text{surf}}}{\theta_{\text{Hen}}} \left(\frac{\partial \Pi_{\text{Hen}}}{\partial T} \right)_{\theta_{\text{Hen}}} = RT \qquad (5)$$

Substituting Eq. (5) into (1) and simplifying this relation leads to the original HK model [24,25]:

$$RT \ln \left(\frac{p}{p_s} \right) = N_{Av} \Phi \qquad (6)$$

and $K_{\text{impr,Hen}}$ is equal to zero (see Eq. (1)).

The assumption of linearity of the adsorption isotherm seems to be clearly inadequate. For that reason, Cheng and Yang [13] and Rege and Yang [14,15] proposed the use of the Langmuir-type equation of state instead of Eq. (4) due to the better mathematical representation for the first type of isotherms, following the

IUPAC classification. Therefore, the term omitted in the original HK derivation, was replaced with [27]:

$$\Pi_{\text{Lan}} = \frac{RT}{\beta_{\text{surf}}} \ln \left(\frac{1}{1 - \theta_{\text{Lan}}} \right) \tag{7}$$

which is derived based on the Langmuir adsorption isotherm equation and Eq. (2):

$$\theta_{\text{Lan}} = \frac{a}{a_{\text{m,Lan}}} = \frac{k_{\text{Lan}} p}{1 + k_{\text{Lan}} p} \tag{8}$$

Taking the derivative of Π_{Lan}:

$$\frac{T \beta_{\text{surf}}}{\theta_{\text{Lan}}} \left(\frac{\partial \Pi}{\partial T} \right) \theta_{\text{Lan}} = \frac{RT}{\theta_{\text{Lan}}} \ln \frac{1}{1 - \theta_{\text{Lan}}} \tag{9}$$

and substituting the above equation into Eq. (1), the 'improved' Horvath–Kawazoe model was obtained by Cheng and Yang [13] and Rege and Yang [14,15]:

$$RT \ln \left(\frac{p}{p_{\text{s}}} \right) + \left[RT - \frac{RT}{\theta_{\text{Lan}}} \ln \frac{1}{1 - \theta_{\text{Lan}}} \right] = N_{Av} \Phi \tag{10}$$

where the assumption of nonlinearity of the isotherm is introduced by the coverage dependent term:

$$K_{\text{impr,Lan}} = \left[RT - \frac{RT}{\theta_{\text{Lan}}} \ln \frac{1}{1 - \theta_{\text{Lan}}} \right] \tag{11}$$

From Eq. (11) it is seen that $K_{\text{impr,Lan}}$ is the function of the fraction of surface occupied by molecules and, consequently, of the relative pressure. Moreover, in order to calculate the differential pore-size distribution the values of parameters of the Langmuir equation should be known (i.e. obtained from the fitting procedure of this theoretical model to experimental data). It was discussed above that for the Henry adsorption isotherm equation $K_{\text{impr,Hen}}$ is equal to zero and, therefore, the description of the experimental data by the theoretical model is not necessary.

On the other hand, the choice of the Langmuir equation by Cheng and Yang [13] and Rege and Yang [14,15] must be questioned. Since the overall isotherm for a microporous material can be similar to Langmuir in shape, there is no reason to expect this equation as adequate for description of adsorption in the system of dispersed micropores. Therefore, there are some doubts connected with the application of simple Langmuir isotherm equation which can be useful only for homogeneous surfaces (or in the cases of chemisorption) since it postulates the constant enthalpy of adsorption. It is well-known that this situation is rarely observed for activated carbons. On the other hand, for the microporous solids the Polanyi–Dubinin [28] theory of volume filling of micropores usually describes well the experimental adsorption and the enthalpy of adsorption data. This is documented in many studies, especially for the data measured in the low-pressure range of an adsorption isotherm (the typical range is up to approximately $p/p_{\text{s}} < 0.1$). Despite of criticism of the Dubinin–

Astakhov (DA) adsorption isotherm equation, our model studies showed lately, that this equation describes very well the mechanism of the primary and secondary micropore filling of carbon micropores. We showed [29] that the changes in the shapes of modelled DA adsorption isotherms are accompanied by the simultaneous changes in the shapes of the high-resolution α_{s} plots and the shapes of the PSD curves calculated by means of the ND method (this approach leads to the same results as obtained from the DFT method [30]). Thus, it can be concluded that the DA equation is very powerful and the studies on its properties should be continued. Summing up, we propose to take into account the spreading pressure (Π) of an adsorbed phase [26] by the adsorption potential concept originally suggested by Polanyi as was described elsewhere [31–33]. It should be noticed, that a modern thermodynamic definition of Π is quite general as it was discussed by Ruthven [34] and it may be applied to both, adsorption in micropores and to surface adsorption. The spreading pressure analogue of the DR isotherm equation was developed by Sundaram [31], and the spreading pressure from the DA isotherm by Lavanchy et al. [32]. Thus the final result can be written as

$$\begin{aligned} \Pi_{\text{DA}} &= \frac{1}{\beta_{\text{surf}}} \frac{W_{0,\text{DA}} \beta E_{0,\text{DA}}}{n_{\text{DA}}} \gamma \left[\frac{1}{n_{\text{DA}}}, \ln \left(\frac{W_{0,\text{DA}}}{W} \right) \right] \\ &= \frac{1}{\beta_{\text{surf}}} \frac{W_{0,\text{DA}} \beta E_{0,\text{DA}}}{n_{\text{DA}}} \gamma \left[\frac{1}{n_{\text{DA}}}, -\ln \theta_{\text{DA}} \right] \end{aligned} \tag{12}$$

where $W_{0,\text{DA}}$ is the volume of micropores, $E_{0,\text{DA}}$ is the characteristic energy of adsorption, n_{DA} is the exponential parameter, β is the similarity coefficient, γ is the incomplete gamma function defined as $\gamma[a, z] = \int_z^\infty t^{a-1} \exp[-t] \, dt$. Assuming $n_{\text{DA}} = 2$ the spreading pressure analogue of the DR equation is obtained [31,33]. It should be pointed out that Eq. (12) is derived from Eq. (2) and the DA adsorption isotherm equation:

$$\theta_{\text{DA}} = \frac{W}{W_{0,\text{DA}}} = \exp \left[-\left(\frac{RT \ln (p_{\text{s}}/p)}{\beta E_{0,\text{DA}}} \right)^{n_{\text{DA}}} \right] \tag{13}$$

It is well-known that the DR and DA adsorption equations possess limitations; especially they do not describe the data measured in the low-pressure range of adsorption isotherm [35–37]. However, the authors of the current study keep the point of view that the change of adsorption data in this range of p/p_{s} insignificantly influences on the evaluated PSDs. We recently showed [38] that for the low and medium noise levels of generated adsorption isotherms (the Nguyen and Do model was analysed in the range of low-pressures) the reproducibility of perturbed isotherms was good. Summing up, it is apparent that the medium and high ranges of isotherms contain the sufficient information about the pore-size distribution (number of peaks, their location,

area, etc.). It should be pointed out that similar results were obtained by Gunko and Do [39].

Assuming the temperature dependence of $W_{0,DA}$ [28], taking the derivative of Π_{DA} ($\partial_z(\gamma[a,z]) = -\exp[-z]z^{a-1}$):

$$\frac{T\beta_{surf}}{\theta_{DA}}\left(\frac{\partial\Pi_{DA}}{\partial T}\right)_W = \frac{\alpha TW_{0,DA}\beta E_{0,DA}}{\theta_{DA}n_{DA}}\left\{\theta_{DA}\left(\frac{RT\ln(p_s/p)}{\beta E_{0,DA}}\right)^{1-n_{DA}}\right.$$
$$\left. -\gamma\left[\frac{1}{n_{DA}}, -\ln\theta_{DA}\right]\right\} \quad (14)$$

and substituting the above equation into Eq. (1), the following relationship is derived:

$$RT\ln\left(\frac{p}{p_s}\right) + \left[RT - \frac{\alpha TW_{0,DA}\beta E_{0,DA}}{\theta_{DA}n_{DA}}\right.$$
$$\times\left\{\theta_{DA}\left(\frac{RT\ln(p_s/p)}{\beta E_{0,DA}}\right)^{1-n_{DA}} - \gamma\left[\frac{1}{n_{DA}}, -\ln\theta_{DA}\right]\right\}\right]$$
$$= N_{Av}\Phi \quad (15)$$

where the 'correction' term is equal to

$$K_{impr,DA} = RT - \frac{\alpha TW_{0,DA}\beta E_{0,DA}}{\theta_{DA}n_{DA}}$$
$$\times\left\{\theta_{DA}\left(\frac{RT\ln(p_s/p)}{\beta E_{0,DA}}\right)^{1-n_{DA}} - \gamma\left[\frac{1}{n_{DA}}, -\ln\theta_{DA}\right]\right\} \quad (16)$$

and α is the adsorbate thermal expansion coefficient. From Eq. (16) it is seen that $K_{impr,DA}$ is the function of the fraction of surface occupied by molecules and, moreover, the relative pressure (similarly to $K_{impr,Lan}$ and contrary to $K_{impr,Hen}$).

In the original Horvath and Kawazoe considerations [7,24,25], the application of the Everett and Powl's formula for the potential energy between two carbon layers filled with adsorbate molecules (see Eqs. (1), (6), (10) and (15)) gives the following equation:

$$\frac{N_{Av}\Phi}{RT} = \frac{62.38}{(L-d)}\left[\frac{1.895\times10^{-3}}{(L-(d/2))^3} - \frac{2.7087\times10^{-7}}{(L-(d/2))^9} - 0.05014\right] \quad (17)$$

where the values of specific physicochemical constants are substituted for nitrogen, L is a slit-shaped pore width, and d (equal to 0.64 nm) is the sum of the diameter of an adsorbent atom and an adsorbate molecule (d_a).

Summing up, Eq. (17) with Eqs. (6), (10) or (15) connects the equilibrium gas phase relative pressure (p/p_s) with the effective pore diameter ($L - d_a$). Thus, measuring the adsorption isotherm as a function of reduced pressure the PSD can be directly calculated applying the transform $J(L - d_a) = d\theta/d(L - d_a)$.

3. The influence of the equation of state of an adsorbate on the pore-filling and PSD curves

In order to verify the influence of the nonlinearity of the relationship between $\Pi\beta_{surf}$ and θ on the pore-filling pressure and PSD curves the theoretical adsorption isotherms (presented in Fig. 1) are generated for the relative pressure range from 1×10^{-7} up to 0.99 p/p_s ($T = 77.5$ K). The Langmuir adsorption isotherm (Eq. (8)) is treated as the reference one. It is arbitrarily assumed that the monolayer capacity ($a_{m,Lan}$) is equal to 1 [unit of adsorption], the saturation pressure (p_s) is equal to 1 [unit of pressure], and the constant of above equation, k_{Lan} is equal to 100 [1/(unit of pressure)]. On the other hand, the values of the both parameters of the Henry equation (i.e. $a_{m,Hen}$ and k_{Hen}) are presumed to be the same as the responsible ones in the Langmuir equation (i.e. $a_{m,Lan}$ and k_{Lan}). This generalization is well justified in terms of the theoretical considerations for the fact that the Langmuir equation is simplified to Henry one for lower values of relative pressure. Moreover, the parameters of the Dubinin–Astakhov equation ($E_{0,DA}$, n_{DA} and $W_{0,DA}$) are calculated applying the fitting procedure of Eq. (13) to the earlier generated adsorption isotherm (Eq. (8)) in the whole range of the relative pressures (Fig. 1) for β equal to 0.32 (i.e. for nitrogen as the adsorbate). The following values of the parameters of the DA equation was obtained: $E_{0,DA} = 10.42$ kJ/mol, $n_{DA} = 3.06$, and $W_{0,DA} = 1.00$ [unit of adsorption] (the determination coefficient, DC = 0.9995). From the analysis of data presented in Fig. 1 it is seen that the
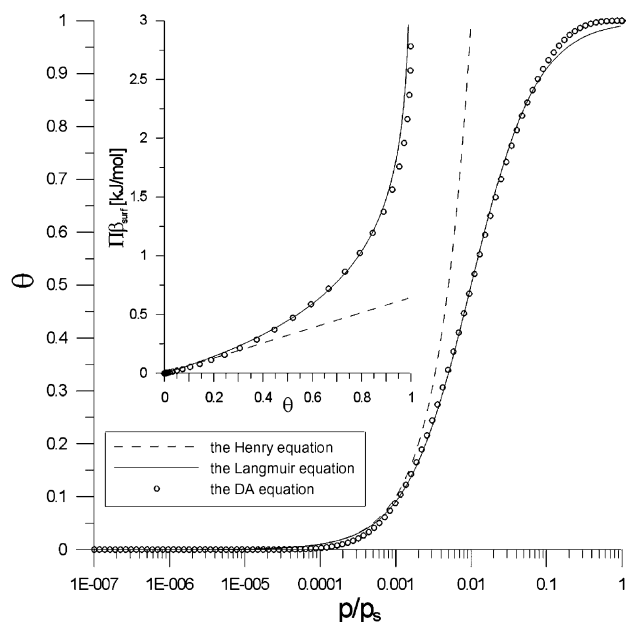

Fig. 1. The low temperature ($T = 77.5$ K) nitrogen adsorption isotherms generated based on the Henry (Eq. (3)), Langmuir (Eq. (8)) and Dubinin–Astakhov equations (Eq. (13)). Additionally, the relationship between $\Pi\beta_{surf}$ and θ is presented separately in the smaller figures.

evaluated DA and Langmuir adsorption isotherms belong to I type of IUPAC classification and thus these data should be successfully described by the original and improved Horvath and Kawazoe models. The excellent goodness between the both models is observed. The results are not surprising and they were predicted by Jaroniec and Marczewski [40] on the basis of the theoretical considerations. It should be mentioned here, that fitting the Langmuir isotherm by the DA equation almost always leads to the satisfactory results; however, not always the suitable fit can be obtained for the reverse situation, i.e. when the Langmuir equation is fitted to the DA isotherm. Thus, fitting by Eq. (8) the experimental data measured for microporous carbons can be the serious problem.

Additionally, the plots of $\Pi\beta_{surf}$ versus θ are presented separately as the inlet in Fig. 1. All relationships generate the increasing functions, i.e. linear for the Henry and increasing to infinity for the two remaining isotherm equations. This part of Fig. 1 clearly shows that there is the similarity between the results generated from Eqs. (7) and (12), since the adsorption isotherms almost coincide.

In all considered models (Fig. 2) it is assumed that adsorption of nitrogen molecules at 77.5 K in the pores is connected, among other things, with the pore-filling mechanism. Obviously, the relative pressure at witch pore filling occurs is lower for smaller pores in comparison with wider ones. The results shown in Fig. 2 are

limited up to 2 nm (this value of effective pore width is the upper limit of micropore diameters recommended by IUPAC and appropriate for the Horvath and Kawazoe method). As it was reported earlier [5,6,30] the agreement between ND theory [5,6] and the DFT method (data taken from [41]) is significant. It is worthwhile to mention that the original HK model shifts the pore filling for a fixed $(L - d_a)$ to the smaller values of the effective pore width (Fig. 2). For the micropores narrower than 0.8 nm the plots obtained based on the original HK model (Eq. (6)) and on the improvement proposed by Cheng and Yang [13] and Rege and Yang [14,15] (Eq. (10)) predict similar values of the relative pressure. On the other hand, the influence of the non-linearity of the Langmuir equation of state on the pore-filling pressure curves is considerable for higher pressures due to impossibility of calculating based on Eq. (10) the effective pore widths greater than 2 nm. Thus, this relationship allows evaluating the PSD curve in the limited range (i.e. for the studied case up to $(L - d_a)$ equal to approximately 1.2 nm). In order to explain these differences the relation between the coverage dependent term ($K_{impr,Lan}$; Eq. (11)) and the effective pore width should be analysed in details. For the original HK model (Eq. (6)) this relationship is not a function of the relative adsorption. Furthermore, the increase in p/p_s leads to the increase in $RT\ln(p/p_s)$ (the adsorption potential tends to zero if the relative pressure tends to unity (Fig. 3A and B)). On the other hand, the influence of θ_{Lan} on the 'correction' term in the improved HK (described by Eq. (11)) is significant for the higher values of relative pressure and/or adsorption, especially. Here, this term predominates. Summing up, the increase in p/p_s leads to plateau of the sum of ($RT\ln(p/p_s)$) and $K_{impr,Lan}$ (i.e. LHS in Eq. (10)), and this sum is close to -2.36 (Fig. 3A and B). The similar results were observed by Cheng and Yang [13] and Rege and Yang [14,15], however, they did not show that this behaviour of their methods leads to the limited values of $(L - d_a)$ (crosses; Fig. 2).

The opposite effect takes place when the Dubinin–Astakhov equation is analysed (Figs. 2 and 3). In order to generate the relationship between the pore-filling pressure and effective pore width based on Eq. (15), the values of the adsorbate thermal expansion coefficient should be considered. It should be pointed out that the choice of the values of the adsorbate thermal expansion coefficient is arbitrary (it is very difficult or impossible to find the experimental measured values of α for the nitrogen at 77.5 K). However, it is well-known that for N_2 (at $T = 77.5$ K) α is assumed to be very low [42]. Therefore, the lower values of this parameter are probably better to be acceptable. In spite of the fact, we decide to analyse three various values of α (1×10^{-2}, 1×10^{-4}, and 1×10^{-6} K^{-1}). The application of them leads to the similar curves of the pore filling for the fine
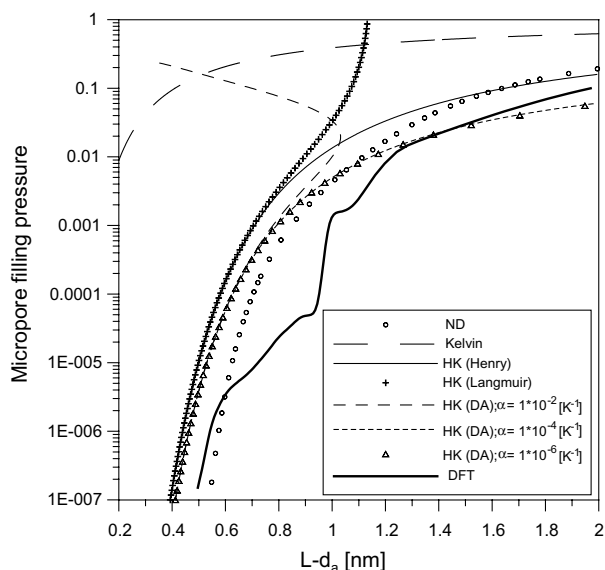

Fig. 2. Reduced pore-filling pressure for nitrogen at 77.5 K versus effective micropore widths. ND—the Nguyen and Do method [5,6]; DFT—density functional theory (data taken from Lastoskie et al. [41]); Kelvin—Kelvin equation; HK (Henry)—the original Horvath–Kawazoe method; HK (Langmuir) and HK (DA)—the improved HK models (for the Dubinin–Astakhov equation three various values of the adsorbate thermal expansion coefficient (α) are analysed).

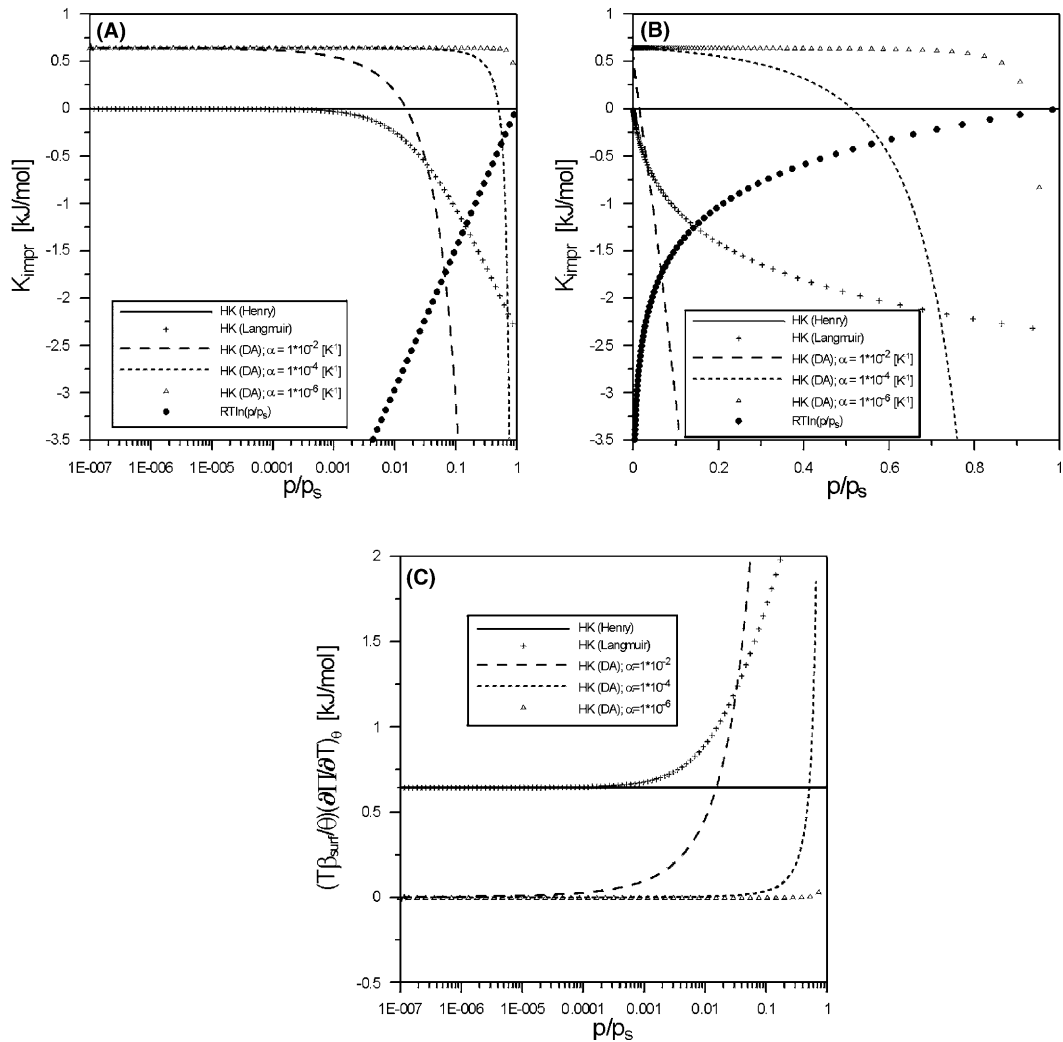Fig. 3. (A) and (B) The improvement terms calculated based on Eqs. (11) and (16). $K_{impr,Hen}$ is equal to zero. Additionally, the relationship between adsorption potential and relative pressure is analysed. (C) The derivative of the spreading pressure with respect to temperature calculated based on Eqs. (5), (9), and (14).

micropores (narrower than 0.8 nm) as it is shown in Fig. 2. The significant differences are observed for wider pores and for the adsorbate thermal expansion coefficient equal to 1×10^{-2} K^{-1}. From the point of view of the above mentioned considerations it has been found that the lower values of the thermal expansion coefficient than 1×10^{-4} K^{-1} give similar results. This result is not surprising and it can be treated as general. On the other hand, the similar behaviour of the curves describing the relationship between the micropore filling pressure and the effective pore width (for our method as for the improved by Cheng and Yang HK model) is observed for high values of α.

We observed that Eqs. (8) and (13) predict the same values of adsorption in the whole range of relative pressure (Fig. 1). Moreover, in this figure it is seen that the relationships between $\Pi\beta_{surf}$, and θ_{Lan} or θ_{Hen} give comparable results. The derivatives of the spreading

pressure with respect to the temperature for all models give values possessing positive signs (Fig. 3C). The analysis of more complicated equations of state than related to the Henry's law, change the simple relation described by Eq. (6). The LHS term (see Eq. (1)) is the sum of the original HK model and the 'correction' term (Eqs. (11) or (16); Fig. 3A and B). Therefore, LHSs are different than evaluated basing on the original HK approach. For the Langmuir model more negative values are evaluated comparing with the original HK theory, i.e. $K_{impr,Lan}$ is added to the adsorption potential term. For the DA equation the positive values of $K_{impr,DA}$ are added to the adsorption potential for lower p/p_s and α (Fig. 3A and B). Therefore, LHS is negative, but the values of sum are less negative than obtained based on the original HK theory. Summing up, the 'correction' factor $K_{impr,DA}$ is negligible at low relative pressure only for lower values of α, but it becomes considerable at the

greater pressures and α values, i.e. when the deviation from nonlinearity becomes significant. This divergence leads to the differences between critical pressures of pore filling for various values of the thermal expansion coefficient. It is important that remarkably wider range of the effective pore width values is usually calculated based on this improvement, contrary to the proposed by Cheng and Yang, and this is due to prediction of the wide range of the values of LHS (as mentioned above for the latter one the values are up to approximately -2.36 (Fig. 3B)).

It is very interesting to check how the behaviour of the plots drawn in Fig. 1 influences on the shapes of the PSD curves. Therefore, we compare the pore-size distributions generated based on the original and improved HK methods with the Nguyen and Do model (Figs. 4 and 5). In Fig. 4 the influence of the 'correction' terms on the plots of PSDs is analysed (basing on the Langmuir adsorption isotherm data shown in Fig. 1). Studied case corresponds to nitrogen adsorption in the carbon with relatively wide micropores. It is seen that all models lead to the similar monomodal bell-shaped functions. Two of them are truncated (see the data shown in Fig. 2). Moreover, the PSD curves for the HK models lead to the similar value of the pore diameter at the maximum, and this diameter is shifted to the smaller values, comparing with the results of the ND method. It can be seen the shape of PSD curve depends on the value of α, and for low values the shoulder is observed.

In order to discuss the effect of the pore structure on the similarity between HK and ND we generated the

model DA isotherms assuming different values of $E_{0,DA}$ and n_{DA}. As we showed previously [9,29] the values of the both parameters of the DA equation are strictly related to the mechanism of adsorption in micropores. Thus, in Fig. 5 the combinations of the parameters were chosen in order to generate the isotherms related only to the primary ($E_{0,DA} = 25$ kJ/mol, $n_{DA} = 5.0$), to the simultaneous primary and secondary ($E_{0,DA} = 25$ kJ/mol, $n_{DA} = 1.0$) and only to the secondary ($E_{0,DA} = 10$ kJ/mol, $n_{DA} = 3.0$) micropore filling processes. Since the HK - related methods based on the condensation approximation, it is interesting to compare the results of the PSD calculation with those obtained from the CA however, assuming different relations between pore diameter and the filling pressure. Therefore, in Fig. 5 we compare the PSDs obtained from the original and improved in this paper HK method and from the condensation approximation applying the relationships shown in Fig. 2 (DFT and ND). It is seen that the improved HK method with DA equation ($\alpha = 1 \times 10^{-6}$ K^{-1}) in comparison with the original one, slightly shifts the peaks to the larger pore diameters. The differences between all the methods increase with the rise in the amount of larger micropores, where the secondary micropore filling process predominates. Thus, it can be concluded that the CA can be successfully applied for the description of the primary micropore filling process and that the correction for the film thickness before condensation is very small for fine micropores. Summing up, for the carbons possessing pores with diameters up to approximately 1 nm all the methods lead to the similar results and the HK model can be successfully applied. Similar value of the micropore diameter was suggested by Kruk et al. [2] from the analysis of the model isotherms for slit-like graphite micropores obtained from nonlocal density functional theory. The authors concluded that the HK method can be used to calculate PSDs for pore of width up to 0.9 nm. Also other authors suggested the applicability of the CA approximation for description of the local isotherms in the range of finite micropores [43].

Finally, we decide to verify the original and improved by us the HK method based on the experimental data. We limited our considerations to two ashless strictly microporous polymeric carbons (called *A* and *B*) obtained from polyfurfuryl alcohol [44] and extensive studied elsewhere [7–9]. The parameters of the Dubinin–Astakhov and Dubinin–Radushkevich equations are calculated applying the fitting procedure of Eq. (13) in the range of adsorption which takes place in the pores where micropore filling and co-operative swing mechanism occurs (i.e. the relative pressure less than 0.1 p/p_s, i.e. all micropores were considered). The values of the optimized parameters were published elsewhere [7,9]. From Fig. 6 it is seen the satisfactory results of describing the experimental data using both theoretical
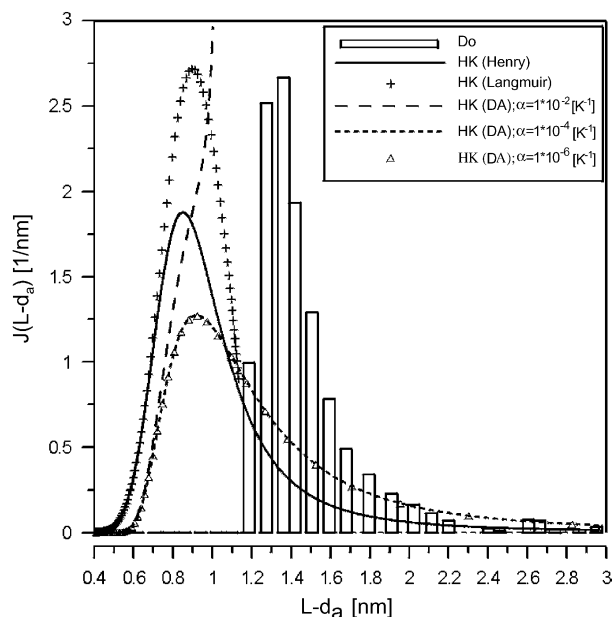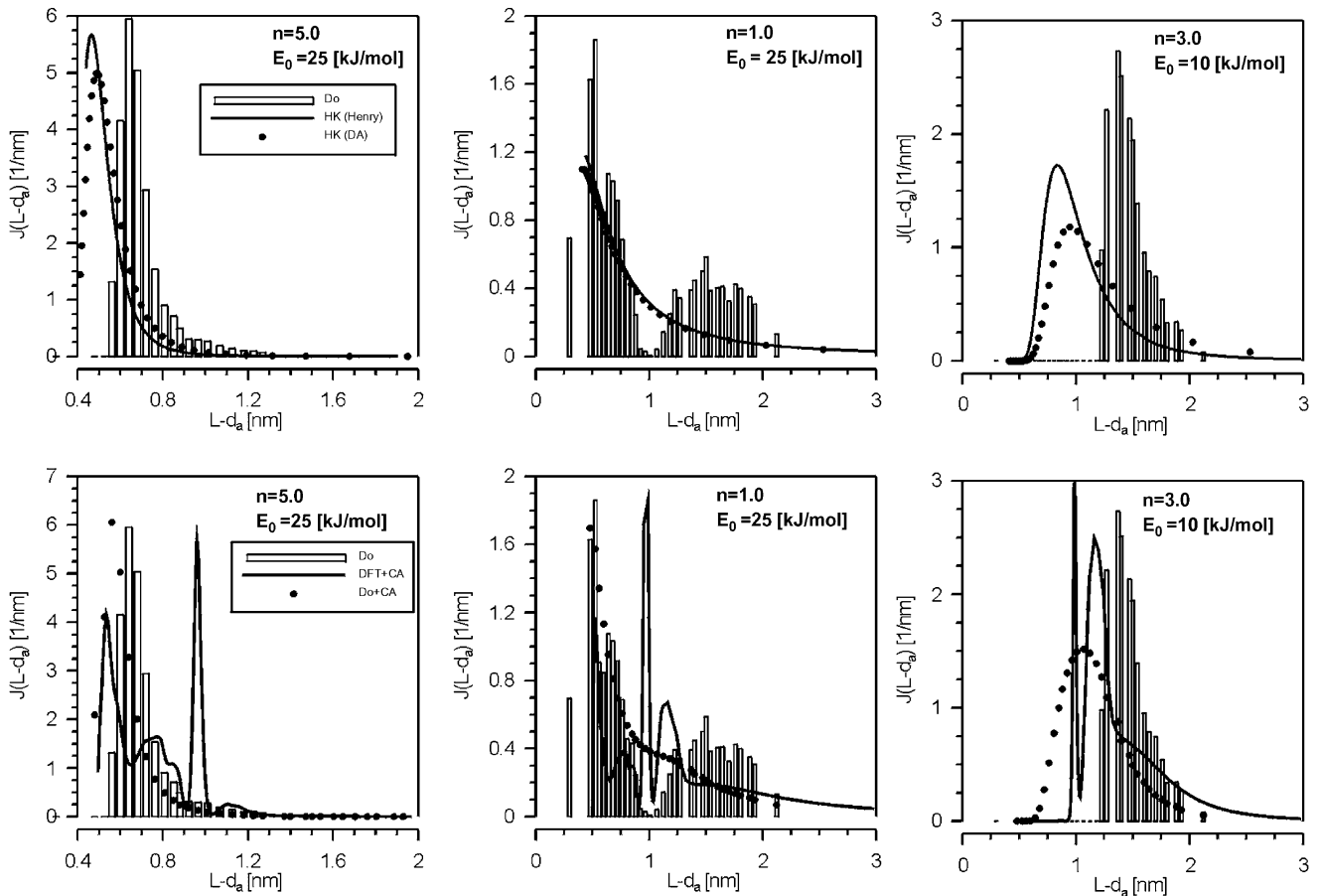

Fig. 4. The comparison of PSDs calculated based on three types of the HK method and based on the theory proposed by Do and co-workers. The Langmuir adsorption isotherm is treated as the reference.

Fig. 5. The influence of parameter E_0 on the $(J - d_a)$ calculated assuming different values of the both parameters of the DA equation which are strictly related to the mechanism of adsorption in micropores (related only to the primary ($E_{0,DA} = 25$ kJ/mol, $n_{DA} = 5.0$), to the simultaneous primary and secondary ($E_{0,DA} = 25$ kJ/mol, $n_{DA} = 1.0$) and only secondary ($E_{0,DA} = 10$ kJ/mol, $n_{DA} = 3.0$) micropore filling processes). Additionally, the pore-size distributions calculated based on the condensation approximation and the relationship between the pore-filling pressure and effective pore for the Nguyen and Do model or DFT (Fig. 2) are presented.
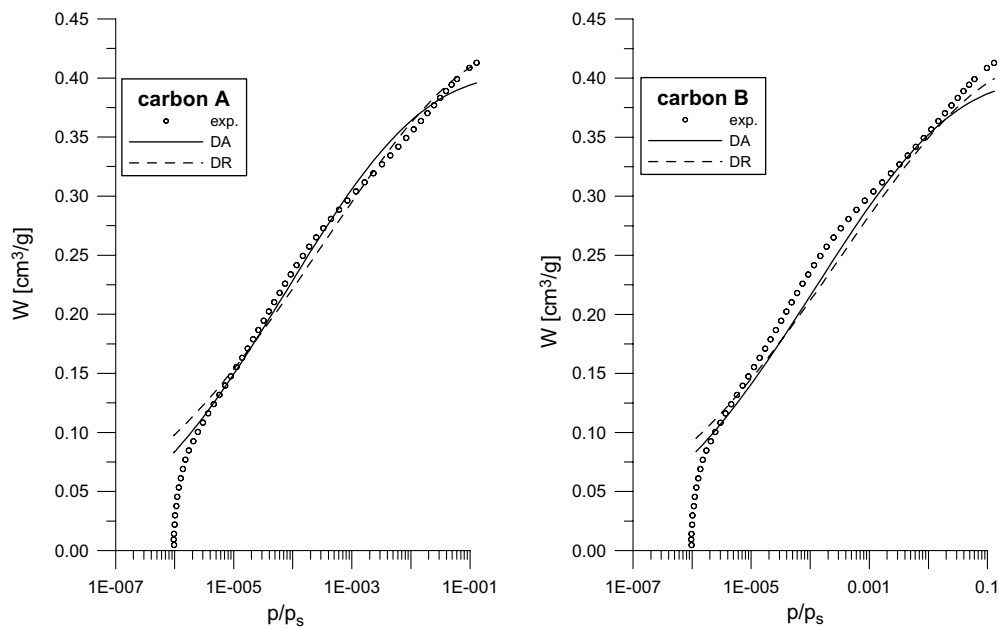

Fig. 6. The results of fitting of the Dubinin–Astakhov (DA) and the Dubinin–Radushkievich (DR) isotherm equations to the experimentally measured adsorption data (exp.). The values of the optimized parameters are published elsewhere [7,9].

models (the values of the determination coefficient are closed to 0.99 (DA) or 0.98 (DR) [7,9]). The significant differences are observed only for the low values of the relative pressures. On the other hand, in the next figure (i.e. Fig. 7) PSDs obtained on the basis Nguyen and Do (ND) method, DFT theory, and Horvath and Kawazoe (Henry–solid black line; DA and DR—dashed lines) method are compared for studied carbons. The considerations are limited to only the range of micropores.
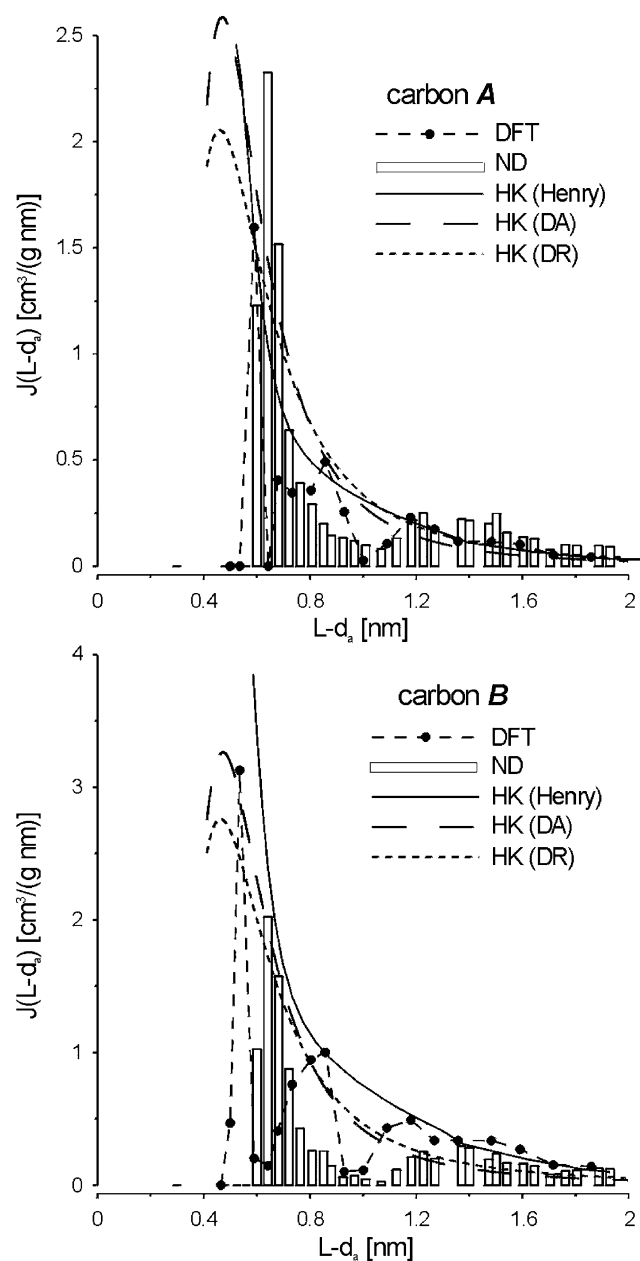

Fig. 7. Pore-size distributions for studied activated carbons obtained on the basis Nguyen and Do (ND) method, DFT theory, and Horvath and Kawazoe (Henry—solid black line; DA and DR—dashed lines) method. The considerations are limited to only the range of micropores.

DFT and ND methods suggest a polymodal structure of pores. Furthermore, one can notice that the method proposed by Nguyen and Do slightly shifts the dimension of pores to larger diameters in comparison with the DFT results. Contrary to the methods mentioned above, HK suggests an exponentially decreasing (the original HK method) or truncated bell-shaped (the improved HK models for the Dubinin–Astakhov equation) shapes of the PSD curves. It can be noticed that the HK method approximates the DFT and ND results reasonably well. Similar situation was observed for studied recently strictly microporous homogeneous carbon films [10]. The HK theories (original and improved ones) lead to similar PSDs for carbon *A* and *B* pore (moreover, also in comparison with the DFT and HK models). Summing up, we keep the point of view that adsorption data in low range of p/p_s insignificantly influences on the evaluated PSDs based on the corrected HK method. Thus, the experimental and theoretical results confirm the above mentioned conclusion.

4. Conclusions

It is shown that the assumption of an adsorbate nonideality influences on the relationships between the micropore filling critical pressure and the effective pore width. Contrary small influence on the shape of the pore-size distributions (the comparison of the original HK model and the proposed in the current considerations) is observed. We showed that for the improvement proposed by Cheng and Yang does not predict the effective pore widths greater than approximately 1.2 nm. Thus, this method allows evaluating the PSD curve in the limited range.

It is important to note that all local isotherms generated on the basis of the HK method describe so-called $0 \rightarrow 1$ transition where the precondensation film thickness is neglected. The results presented in the current work lead to the statement that for microporous carbons where primary micropore filling process predominates (especially, strictly microporous) the condensation approximation can be successfully applied. Obtained results explain why some authors observed the similarities and some differences between the PSD curves determined from the HK and DFT methods. Summing up, the HK method is effective for highly microporous carbons possessing the pores having similar width, i.e. with diameters smaller than 1 nm. We do realize that the proper description of the pore-filling mechanism in micropores is still far from complete, and as a consequence, the novel approach should be still improved in the future taking into the considerations of the entropy of adsorbed molecules and the film thickness for the range of secondary micropore filling. This will be the subject of our future correspondence.

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