Description of benzene adsorption in slit-like pores. Theoretical foundations of the improved Horvath–Kawazoe method

Piotr Kowalczyk a, Eugene A. Ustinov b, Artur P. Terzyk c,*, Piotr A. Gauden c, Katsumi Kaneko a, Gerhard Rychlicki c

a Faculty of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan
b Department of Environment Protection, Saint Petersburg Technological Institute (Technical University), 26 Moskovsky Prospect, 198013 St. Petersburg, Russia
c Department of Chemistry, Physicochemistry of Carbon Materials Research Group, N. Copernicus University, Gagarin Street 7, 87-100 Toruń, Poland

Received 24 September 2003; accepted 21 January 2004

Abstract

The improved Horvath–Kawazoe method (IHKM) proposed by Ustinov and Do was studied by theoretical, numerical, and experimental approaches. The IHKM analysis was improved by incorporation of new numerical algorithms (REG and ASA). The benzene adsorption isotherms on carbon blacks and activated carbons at 293 K were measured for proving the new theoretical treatment. This theory gives a more better description of these observed adsorption isotherms. We can conclude that, presented theory can be applied to analyze others adsorption isotherms, proving reasonable pore structures for activated carbons.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: A. Activated carbon; C. Adsorption, Modeling; D. Porosity

1. Introduction

In recent years there has been considerable progress in the description of gas adsorption mechanism in micropores (i.e. pore width <2 nm according IUPAC classification). Nowadays, it is believed that not the classical Kelvin equation and its modifications but recently developed density functional theory (DFT), grand canonical Monte Carlo simulations (GCMC), molecular dynamic technique (MD) and the Nguyen and Do (ND) method are the most powerful tools applicable for the proper description of an adsorbate state in micropores. These promising techniques are mainly used for the estimation of primary source of surface heterogeneity i.e. pore size distribution function. For such a purpose, from the mentioned above techniques the local isotherms in micropores and mesopores of different geometries for supercritical and subcritical adsorption can be calculated. Here, it is worth to underline the limitations of DFT, GCMC, and MD i.e. these methods are relatively complicated and time-consuming (the last limitation is due to the power of present-time computes). On the other hand, as was shown recently, some simple methods—for example the ND method, leads to the same results as DFT and GCMC for carbons considerably differing in porosity [1–3]. However, the thermodynamical verification of this method showed that it also should be improved [3,4].

Considering the achievements on the ground of statistical mechanics and computer modeling of adsorption process it can be stated that the theoretical description of adsorption in heterogeneous system of pores is still far from complete [5,6]. For instance, pore size distributions evaluated from low-temperature nitrogen adsorption isotherm by the DFT method are quite similar for activated carbons obtained from different precursors and at different carbonization and activation conditions [7–10]. They usually posses a bi-modal structure of pores, characterized by a relatively small population of pores near 0.6 nm of width and a near absence of pores in the cooperative filling range centered around 0.9–1.0 nm. Moreover, the DFT calculations for some (supposing to be non-porous) carbon blacks show noticeable amounts of pores [11]. This raises the
question whether the PSD obtained by the DFT technique reflects the real micropore structure of activated carbons, or its multimodal character is just an artifact associated with the model assumptions. Agreeing with Olivier [12,13], Carroll et al. [14] the latter case seems the more probable. Consequently, modeling physical adsorption of non-symmetrical molecules in a wide range of surface coverage on porous and non-porous solids is not trivial and is still an unresolved problem.

Benzene is frequently used in adsorption studies. Dubinin and co-workers used the benzene adsorption on different porous solids at ambient temperature for the verification of widely known theory of micropore filling (TOMF). Moreover, benzene ring is a main component of different organic molecules, among them, the most dangerous dissolved organic matter, military agents and other toxic substances. The deeper insight into adsorption phenomena of benzene in micropores leads to the better understanding of macroscopic behavior of adsorbed organic molecules. Taking under consideration quoted examples we can say that the modern approaches (i.e. DFT, GCMC and MD) are not sophisticated enough to reproduce adequately the behavior of an adsorbed phase of simple molecules and, certainly, should be further developed. Moreover, it is questionable that the simple two-parametric Lennard–Jones model of adsorbate-adsorbate pair interaction can properly predict the behavior of unsymmetrical molecules, such as benzene and others [15].

In the light of arguments presented above it comes to no surprise that many scientists have been concentrated on developing of semi-classical approach, which are not so rigorous but do allow deeper insight into the phenomenon by relatively simple means. Among them, the Horvath and Kawazoe (HK) approach has been frequently used in adsorption studies for the extracting of the pore size distribution information of microporous materials from experimental adsorption isotherms [3,16–21]. This method based on the progressive pore filling of microporous materials with an increase in adsorbate pressure. Here it is worth to emphasize that in the light of recent studies the HK method seems to be very controversial [22]. Moreover, Dombrowski et al. [23] and Rege and Yang [24] reconsidered the main assumptions of original HK approach and have reveal all drawbacks introduced to the model. Clearly, the HK model seems to be very idealized in comparison with the modern methods of adsorption phenomena modeling.

An important step in the development of this theory was the thermodynamic verification of basic HK assumptions proposed by Ustinov and Do (so called “improved HK method”—IHKM) [25]. It is important to note that all features of local isotherms generated on the basis of improved HK method, for example, so-called 0→1 monolayer transition, are in agreement with the results obtained from the DFT and GCMC calculations [26]. We do realize that the proper description of the pore filling mechanism in small pores is still far from complete, and as a consequence, the novel approach should be still improved in the future.

In the first part of the present study, called “Modeling the System”, we concentrate on the main foundations of the improved HK method. Furthermore, we present some aspects of numerical modeling of benzene adsorption in heterogeneous structure of pores (i.e. characterized by the pore size distribution function). Advanced numerical algorithms (i.e. ASA (adsorption stochastic algorithm) [1,2,27–29] and REG (Hansen’s regularization tool)) [30] are used for the solution of the classical ill-posed problem (i.e. inverting of Fredholm linear integral equation of the first kind). In the second part of the paper, we adopt the modified HK method for the estimation of PSD function of carbonaceous materials from a single benzene adsorption isotherm measured at ambient temperature.

2. Modeling the system

The complexity of crystallographical and geometrical structure of many solids and their complex chemical composition are the main sources of adsorbent heterogeneity. As it was pointed out by Jaroniec and Brauer [31] the main sources of surface heterogeneity are the following: different types of crystal planes, growth steps, crystal edges and corners, various atoms and functional groups exposed at the surface and available for adsorption, irregularities in crystallographical structure of surface and impurities (i.e. mineral ash) strongly bounded with the surface. Clearly, surface heterogeneity plays generally very important role in adsorption on solids. The process of adsorption in micropores is strongly affected by the presence of small pores of different dimensions and geometrical forms [21,32–34]. Furthermore it is well known that uniform micropores are the source of the energetic heterogeneity in the sense that molecules adsorb in these micropores with different adsorption energies. This is caused by the change of adsorption potential field in the micropore volume. So, for microporous solids absolute heterogeneity should be identified as a superposition of non-uniformity of microporous structure and sources of, mentioned above, surface heterogeneity.

At the first sight the complete description of such three-dimensional complicated structure is very difficult [35]. Up to the present only simplified models have been developed. Clearly, different models rely on different assumptions in order to obtain relationships allowing the calculation of the main characteristics of adsorbent structural heterogeneity.
Let us consider the assumptions introduced by Ustinov and Do while developed the improved HK method [25]:

(1) The shape of the pores is assumed by simple slit-like. The effects of the connectivity can be neglected.
(2) The molecule–surface interaction obeys the equation of Steele.
(3) The adsorbed phase may be represented as one or two liquid-like layers between two parallel walls of a pore.
(4) The layer thickness is the distance between two parallel planes confining centers of molecules, with the density of the layer being constant over its thickness and equal to that of the corresponding liquid.
(5) The amount of the molecules of the bulk gas phase in a pore can be negligible; that is the absolute adsorption is almost equal to the surface excess adsorption [36].

Here, it is worth to point out the main weak points of the following assumptions. At first, the Steel’s potential function seems to be very idealistic and far from real cases. It does not take under considerations all mentioned above sources of structural heterogeneity. Moreover, the integration to infinity of the 10-4-3 potential function is also questionable. It is known that the number of graphite layers of the pore wall is limited to 3 or 4, corresponding to realistic pore wall thickness of about 1.1–1.5 nm [37]. Such a simple model of adsorbate–adsorbent interactions, also introduced in DFT, can lead to similar drawback observed on PSD calculated from a single adsorption isotherm by the DFT method. Secondly, as pointed out by different authors, the assumption of constant density inside thin layers is the most questioned. It is known that the density varies over the layer thickness. Besides the introduced simplifications, proposed mechanism of adsorption in modeled uniform silt-like pores is very similar to DFT or GCMC formalism.

According to Ustinov and Do [25], the following equations describe the mechanism of adsorption,

$$
\mu = \frac{dF_i}{di} \quad \text{(1)}
$$

$$
F_i - i\mu = \Omega \leq 0 \quad \text{(2)}
$$

Here, \( \Omega \) is the grand potential, \( \mu \) is the chemical potential, \( F_i \) is the Helmholtz free energy of \( i \) molecules in a pore. From such two main equations it can be seen that the adsorption is only possible when the grand potential functional is minimal and negative simultaneously. The grand potential, \( \Omega \), is defined by following formula,

$$
\Omega = q\Delta F_s + U - qRT \ln(p/p_0) \quad \text{(3)}
$$

where \( q \) is the number of molecules in the pore, \( \Delta F_s \) is the structural change of molar Helmholtz free energy due to adsorption, \( U \) is the potential of fluid–solid interaction, \( R \) is the universal gas constant, \( T \) is the temperature, and \( p/p_0 \) is the reduced pressure.

It is important to note here, that the final form of the equation describing the grand potential functional depends on the mechanism of adsorption. Such a mechanism is related to the size of a pore. In the very small pores having one minimum of the potential in the pore center or two symmetrical minima close to each other (see Fig. 1) only one adsorbate liquid-layer may exist. The thickness of the adsorbate layer (or adsorbed amount) depends on the relative pressure and as a consequence the local isotherm is a continuous function over a whole range of the relative pressure. In wider pores (i.e. two local minima of potential lie close the walls, see Fig. 2) the situation is more complicated. At small amount adsorbed in such type of pores two liquid-layers are formed. Further increase in the relative pressure leads to the increase of the layer thickness and, consequently, to the increase of the amount adsorbed.

When the distance between such two layers is small enough the mechanism of adsorption is identical to that in the small pores. So, for wider pores the first-order phase transition point should be expected. The criterion of first-order phase transition is the equality of the grand potential in the case of double and single layer mechanism. Detailed description of mentioned above mechanism of adsorption will be elaborated later. Now, we concentrate on the description of all terms in equation describing fundamental grand potential functional.

At first, as was mentioned in introduction the potential of fluid–solid interaction can be modeled by 10-4-3 Steel’s potential function given by the following equations:

$$
U(z) = \frac{5}{3} \varepsilon_{sf} [\phi(\xi + z) + \phi(\xi - z)] \quad \text{(4)}
$$

where

$$
\phi(x) = \frac{2\sigma_{sf}^0}{5x^{10}} - \frac{\sigma_{sf}^4}{x^4} - \frac{\sigma_{sf}^4}{3A(0.61A + x)^3} \quad \text{(5)}
$$

In this equation \( \xi = H/2 \), \( z \) is the distance from the pore center, \( H \) is the pore width, \( A \) is the distance between adjacent graphite layers, and,

$$
\varepsilon_{sf} = \frac{6}{5} \pi \rho_s \varepsilon_{sf} \sigma_{sf}^2 A \quad \text{(6)}
$$

where \( \rho_s \) is the number density of carbon atoms per unit volume, \( \varepsilon_{sf} \) is the potential well depth of solid–fluid interaction, \( \sigma_{sf} \) is the collision diameter of solid–fluid interaction given by Lorentz–Berthelot rule (\( \sigma_{sf} = (\sigma_s + \sigma_f)/2 \)); \( ss \) and \( ff \) denotes solid–solid and fluid–fluid interaction, respectively. The integration of Steel’s potential function with respect to \( z \) leads to:

$$
\int_0^z U(z) dz = \frac{5}{3} \varepsilon_{sf} [\varphi(\xi + z) - \varphi(\xi - z)] \quad \text{(7)}
$$
where
\[ \omega(x) = \frac{\sigma_{sf}^4}{3x^3} - \frac{2\sigma_{sf}^{10}}{45x^9} + \frac{\sigma_{sf}^4}{6D(0.61D + x)^2} \] (8)

Note that in the original paper [25] the power 3 in this equation was erroneously replaced by 2.

Ustinov and Do have introduced the correction of Helmholtz free energy for a thin layer. The resulting expression for \( \Delta F_s \) is given by,
\[ \Delta F_s = \frac{2\gamma \nu^* C}{h} \left[ s_1^3 - s_2^3 - \left( s_1^9 - s_2^9 \right)/30 \right] \] (9)

\[ s_1^3 - s_2^3 - (2/15)(s_1^9 - s_2^9) = 0 \] (10)

where:
\[ s_1 = \sigma_{sf}/h_0, \quad s_2 = \sigma_{sf}/(h + h_0) \] (11)

\[ C = (4/3)(2/15)^{1/3} \] (12)

In the above equations \( h \) is the film thickness, \( \gamma \) is the surface tension, \( \nu^* \) is the liquid molar volume, and \( h_0 \) is the lower boundary of integration of \( z \).

Using Eq. (9) we conclude that the behavior of a thin layer becomes quite close to that of macroscopic film when the layer thickness exceeds approximately five molecular layers (i.e. asymptotic region in Fig. 3). As a result, the mechanism of pore filling is different and depends on size of pores. In narrow pores (see low values of reduced the Helmholtz free energy presented in Fig. 3) the adsorption occurs without presetting on the pore walls (i.e. single layer mechanism). In the wider pores the formation of two thin layers on the walls is
followed by the first-order phase transition in the inner volume of the pore. For this reason it is necessary to consider the pore filling mechanism separately for small pores and relatively large pores [38].

In the case of narrow pores (i.e. small micropores, see Fig. 1) the potential energy distribution with respect to distance is characterized by one minimum located at the center of the pore or two symmetrical minima near the pore walls. As a consequence, only one liquid layer may exist in a pore. The grand potential functional at such a type of pores is given by following formula,

\[
Q_{\text{Narrow}} = S \rho \left\{ h \Delta F_s + \int_{-h/2}^{h/2} U(z) \, dz - hRT \ln(p/p_0) \right\}
\]

(13)

where \( \rho \) is the mean value of the molar density of the liquid-like adsorbed phase, \( S \) is the surface area of the pore wall. The adsorbed amount is given by,

\[
q = hS\rho
\]

(14)

Following the defined above conditions—see Eqs. (1) and (2) (i.e. \( Q_{\text{Narrow}} \) should be minimum and its minimum should be negative) the final two equations may be written as follows:

\[
RT \ln(p/p_0) = \frac{\partial h\Delta F_s}{\partial h} + U(h/2)
\]

(15)

\[
RT \ln(p/p_0) \geq \Delta F_s + \frac{2}{h} \int_{0}^{h/2} U(z) \, dz
\]

(16)

Fig. 2. Local isotherms (A) and distributions of reduced adsorption potential energy (B) for the system benzene and slit-like mesopores at 293 K. Local adsorption isotherms were generated for \( H_{\text{eff}} \) (nm) equal to 2.165, 2.665, 4.165, 4.665, 7.165, 8.665, 19.665, 49.665.
This set of equations defines the conditions of existence of a thermodynamically stable layer under the influence of an external potential field. Simultaneously solving Eqs. (15) and (16) will yield local isotherms in the case of single layer between two parallel walls (see Fig. 1). The shape of isotherms depends on the pore width and the variation of $\Delta F_s$ with layer thickness. This dependence should be continuous as it follows from the DFT and GCMC results [26]. The isotherms from IHKM are continuous and they are shifted to the higher values of the relative pressure with increasing of effective pore widths. Effective pore width is approximated as follows,

$$H_{\text{eff}} = H - \Delta; \quad \Delta = 0.335 \text{ nm} \tag{17}$$

In the case of pores, which are wide enough (i.e. mesopores and some micropores), there are two local minima close to the walls (Fig. 2). As a result, in this case, two liquid layers may exist in the same pore. Once appeared in the pore, these two liquid layers increase with the reduced pressure and the distance between them gradually decreases. As a consequence, these two liquid-like layers will coalesce into one liquid-like layer if a definite value of the reduced pressure is reached and the mechanism of pore filling changes into described above single layer.

For each liquid-like layer (both layers are symmetrical) the grand potential functional is defined as follows,

$$\Omega_{\text{Wider}} = S \rho \left\{ h\Delta F_s + \int_{z_1}^{z_2} U(z) \, dz - hRT \ln(p/p_0) \right\} \tag{18}$$

Here $z_1$ and $z_2$ are the coordinates of the internal and external boundaries of the adsorbed layer, respectively, with $h = z_2 - z_1$ being its thickness. Accounting for the two defined conditions (i.e. $\Omega_{\text{Wider}}$ should be minimum and its minimum should be negative) the final three equations are defined as follows,

$$RT \ln(p/p_0) = \left. \frac{\partial h\Delta F_s}{\partial h} \right|_{h=z_2-z_1} + U(z_2) \tag{19}$$

$$U(z_1) = U(z_2) \tag{20}$$

$$RT \ln(p/p_0) \geq \Delta F_s + \frac{1}{z_2 - z_1} \int_{z_1}^{z_2} U(z) \, dz \tag{21}$$

The condition of mechanical equilibrium is taken under consideration (i.e. $U(z_1) = U(z_2)$). It is very important that the coordinates $z_1$ and $z_2$ must be situated on different sides from the coordinate of the potential minimum. Simultaneous solving Eqs. (19)–(21) will yield only part of local isotherms for a double layer mechanism. When the distance between two parallel walls is relatively small, as a result of film thickness increasing, then the mechanism of single layer is thermodynamically favorable. The first-order phase transition corresponds to the equality of the grand potential for the case of single and double layer mechanism of pore filling (i.e. $\Omega_{\text{Narrow}} = \Omega_{\text{Wider}}$, as an example see Fig. 4). The detailed description of the generalization of local adsorption isotherms can be found in [25].

3. Results and discussion

3.1. Calculation of the theoretical adsorption isotherm and the PSD determination

Knowing the local isotherms for pores of various sizes, the global adsorption isotherm can be obtained by
summing the amounts adsorbed in all pores. Mathematically, for the patch-model of surface heterogeneity and at isothermal conditions, the global adsorption isotherm is given by linear Fredholm integral equation of the first kind of the general form [29]:

$$\theta_{\text{global}}(p/p_0) = \int_{\Xi(H_{\text{eff}})} \theta_{\text{local}}(p/p_0, H_{\text{eff}}) f(H_{\text{eff}}) \, dH_{\text{eff}}$$  (22)

Here $\Xi(H_{\text{eff}})$ defines physical boundaries of pore system in considered porous medium. As is known, such type of

---

**Fig. 5.** Results of the recovering of true PSD from generated and noised global adsorption isotherms (bars—true PSD; dotted line—PSD recovered by ASA algorithm, solid line—PSD recovered by the REG algorithm).

**Fig. 6.** (A) Fitting of theoretical noised global adsorption isotherms by ASA algorithm (dotted line) and REG algorithm (solid line); open triangles—(MS); open diamonds—(R); closed circles—(B); and open circles (SAC). (B) The comparison of $z_e$ plots for calculated for all modeled systems presented in (A).
integral equations is ill-posed (or ill-corrected), which is manifested by the fact that there exist an infinitely large of possible solutions, all satisfying Eq. (22) to within the experimental error. There is another difficulty associated with Eq. (22), reported by Setoyama et al. \[39\]. Experimentally we can measure adsorption isotherm only in a definite finite range of relative pressure (i.e. by small window, usually $10^{-7} - 0.99 ~ p/p_0$). For this reason, the reconstruction of the pore size distribution function, $f(H_{\text{eff}})$, is extremely hard problem especially for pores of $H_{\text{eff}} < 1.0$ nm. The reason is that all local isotherms generated by IHKM method for small micropores are characterized by a very similar shape in the measured range. They are continuous and high pore fillings occur quickly, thus the algorithm has problems with the choice of the proper isotherm.

Since the estimation of PSD from experimental data is a key problem in analysis of internal structure of carbonaceous materials, we decided to perform short numerical investigations. At first, we construct the global isotherms:

$$
\theta_{\text{global}}(p/p_0) = \sum_i \theta_{\text{local}}(p/p_0, H_{\text{eff},i}) f(H_{\text{eff},i})
$$

where $\theta_{\text{local}}(p/p_0, H_{\text{eff},i})$ is the local isotherm in a whole range of relative pressure for the effective pore width of $H_{\text{eff},i}$, and $f(H_{\text{eff},i})$ is the assumed form of PSD. The normalization condition for PSD is given by:

$$
\sum_i f(H_{\text{eff},i}) = 1
$$

(24)

Following Setoyama et al. \[39\] we assumed that all carbonaceous materials can be assigned to four basic classes: molecular sieve type (MS), representative type (R), bimodal type (B), super activated carbon type (SAC).

Next, we generated the benzene adsorption isotherms (the number of the values of the relative pressure is equal to 25) in the experimental range of relative pressure (i.e. $10^{-7} - 0.99 ~ p/p_0$) for defined four classes of carbonaceous materials. Next, for all four adsorption isotherms the Gaussian error was added following empirical assumption:

$$
\sum_{j=1}^N (\theta_{\text{True},j} - \theta_{\text{Noisy},j})^2 \approx 10^{-3}
$$

(25)

Generated adsorption isotherms are presented in Fig. 6(A) (together with the results of, described below, fitting procedures).
For the recovering of assumed PSD the ASA [1,2,27–29] and REG [30] algorithms were used (Fig. 5). There are three main reasons to apply REG algorithm. Firstly, the regularization method is usually used in adsorption studies and now it is believed that such a method is the most powerful. Secondly, the PSD of real heterogeneous solids is rather smooth and continuous than discreet, so regularization seems to be natural choice. Thirdly, the unknown level of noise in benzene adsorption measurements as well as relatively small measuring window can lead to high values of regularization parameter (i.e. there is necessary to take under considerations the smoothing effect on the estimated PSD). The base used in current studies consists of 152 benzene local isotherms non-uniformly distributed in the range of effective pore widths 0.531–99.665 nm (thus, \( N = 152 \)). The main quantity of benzene local isotherms are generated in the range of micropores i.e. \( H_{eff} < 2 \) nm. Notice, that considered two different methods of solution of ill-posed problem give very similar and good reconstruction of assumed PSD functions (see Fig. 5) and fit noisy global isotherms reasonably well (Fig. 6(A)). As we were expecting REG algorithm gives PSD more smoothed than ASA. Obviously, such a type of the regularization method seems to be very promising for estimation of continuous type of PSD (i.e. it is commonly known that regularization techniques fail to describe the PSD function in the case of discontinuous plots). However, the main disadvantage of the REG algorithm is the generating of negative parts of PSD (they occur in the range of the effective pore widths where PSD values should be equal to zero). ASA algorithm works well, but it does not take under consideration the smoothing effect [29]. As a result in some cases the unphysical sharp peaks may be observed. It is well known that to construct an algorithm with good properties a researcher should use all available information about the solution of the problem. When we know nothing about the solution, then we may find anything as an approximate solution. So in summary, we can state that such two algorithms in connection with intuition of researchers may be successfully applied for the proper solution of the considered ill-posed problem.

Additionally, the \( z_r \)-plots for all modeled systems were shown in Fig. 6(B). Simulated isotherm at \( H_{eff} = 3.56 \) nm was assumed to be a standard one. We obtained uncompleted \( z_r \)-plots. It is obvious since the values of adsorption on the standard isotherm starts from the relative pressure equal about \( 10^{-5} \). The main features of obtained \( z_r \)-plots agree with the GCMC results published by Setoyama et al. [39]. i.e. the \( z_r \)-plots are related to the assumed PSD function. The same

---

Fig. 8. The comparison of the experimental benzene adsorption isotherms measured at \( T = 293 \) K on activated carbon blacks and the PSD curves obtained from the IHKM model with ASA.

![Graphs showing pore size distribution and adsorption isotherms](image-url)
results were obtained recently by Terzyk et al. [40] basing on the method published by Nguyen and Do [4,41]. Applying this method the authors studied the relation between porosity and the type of $\alpha_s$-plot [40]. The $\alpha_s$-plots (Fig. 6(B)) progressively change with the range of pore width. The $\alpha_s$-plot for (MS) type of PSD is characterized by the rectangle rise and so-called filling swing occurs for $\alpha_s < 0.5$. For the R PSD type $\alpha_s$-plot is similar to (MS) one but the filling swing is not as steep as observed for the (MS) type. Bimodal type of PSD, (B), possesses filling as well as cooperative swings. Finally, (SAC) is characterized by a gradually rising cooperative swing.

4. The description of experimental data

In the current paper, the carbonaceous materials have been investigated on the basis of static measurements of benzene adsorption at 293 K and the low-temperature (77 K) nitrogen adsorption. All the necessary parameters used in the computations were taken from [25,42]. For the inverting of lineal Fredholm equation of the first kind (i.e. estimation of PSD from measured adsorption data) the ASA (ND and IHKM methods) and the regularization algorithm REG (IHKM) were applied. The regularisation parameter for all computations was chosen according to the L-curve criterion, i.e. optimal balance between norm and semi-norm of the solution.

The first group of studied adsorbents are carbon blacks. Benzene adsorption data for the first carbon black, called SAO, were reported by Choma and Jaro-
The second and third carbon blacks are Sterling FT and Elftex 120. The data were published by Carrott et al. [45] and have been also used as a reference for constructing $\alpha_s$-plots. Although all isotherms shown in Figs. 7–9 are of Type II according IUPAC classification and the reduced uptakes at any value of relative pressure are quite similar, the isotherms are evidently not identical. Moreover, both the obtained PSDs (Figs. 7–9) and the comparison of the $\alpha_s$-plots (Fig. 10), confirm the thesis of Carrott and others [45] that in the case of benzene adsorption it is not possible to define a universal standard benzene isotherm. For this reason the term ‘universal’ should be rather replaced by ‘reference’. The differences between reference benzene isotherms are particularly visible in the range of small and high values of $\alpha_s$ (Fig. 10). As mentioned above, the PSD curves shown in Figs. 7–9 were calculated applying two methods and two algorithms for solving the global adsorption isotherm equation (Eqs. (22) and (23)). The comparison of the REG and ASA algorithms with the

---

Fig. 11. Pore size distributions and the results of fitting of the experimental data (EXP) by theoretical models (IHKM with REG algorithm and ND with ASA algorithm).
IHKM kernel (Figs. 7–9) shows that REG method indicates the presence of small amount of micropores, while ASA does not. The remaining fragments of the PSD curves are similar. On the other hand, the comparison of ASA with IHKM and ND methods (Figs. 8 and 9) leads to the conclusion that the ND method shows negligibly small content of microporosity, and similar shapes of PSD curves is observed. Moreover, Fig. 9 shows the comparison of PSD form nitrogen and benzene adsorption data (for the Sterling FT carbon black the nitrogen adsorption data were unfortunately inaccessible). For Elftex 120 the same PSDs are observed. For another carbon black some differences occur in the range of the smallest and the largest pores. Summing up, all studied methods and procedures suggest that investigated carbon blacks possess very small amount of pores in comparison with activated carbons (see below discussion and Fig. 11), and the similar results for different carbon blacks were observed by others [46] (however, only nitrogen adsorption was studied). Many authors showed that carbon blacks are in fact heterogeneous. One can notice that the pore volumes calculated for studied carbon blacks are small. But it is important that nitrogen and benzene data measured on the same carbon blacks show porosity. Previous calorimetric studies showed that the surface of graphitized carbon Sterling NT is, in fact, heterogeneous [47]. Other authors also showed that on graphite surface different voids between crystalline regions are found and these voids play an important role in the surface energy calculation [48]. Graphitized carbons contain similar voids i.e. small cavities between microcrystalites [49]. It is also possible that during the preparation of carbon black under severe heating some of microcrystalites may break up into their original crystallites [50]. Other kind of heterogeneity can origin from the existence of surface heteroatoms [51].

The second group of adsorbents are activated carbons. It has been shown, basing on low-temperature nitrogen adsorption data, that carbonaceous films, C$_{ox}$ are microporous materials characterized by a very high homogeneity (i.e. they possess small dispersion of pore diameters) [20]. Benzene adsorption isotherm was measured in this study at 293 K using a gravimetric apparatus with Baratron pressure transducers (MKS Instruments, Germany). The data for the next studied

![adsorption plots](image-url)

Fig. 12. The $\alpha_s$-plots for investigated adsorbents (i.e. carbonaceous film C$_{ox}$, activated carbons ACS and WAK). The experimental isotherms on carbon black Sterling FT, Elftex 120, and SAO were used as references. Additionally the plots constructed basing on local isotherm from IHKM method is shown ($H_{eff} = 3.54$ nm).
adsorbent, namely carbon ACS, were taken from Dubinin’s work [52]. Finally, the last carbon was WAK obtained from pitch plums precursors [53].

Obtained results suggest that comparing to described above carbon blacks, studied carbons possess large amount of pores. IHKM and ND methods lead to similar results showing that studied adsorbents are microporous. The largest differences are visible for C_{\text{AC}}. In this case the REG method cannot describe the adsorption data adequately, and this leads to the differences in obtained PSD curves.

Finally, Fig. 12 shows the \( x_{s} \)-plots for all reference experimental isotherms on studied carbons. Additionally the plots constructed basing on local isotherm from IHKM method are shown (\( H_{\text{eff}} = 3.54 \) nm). It is seen that the carbons belongs to the group B following the classification of Setoyama et al. [39].

5. Conclusions

The IHKM method seems to be a promising tool for the description of adsorption in porous solids. Since DFT and GCMC methods are insufficient for the description of benzene adsorption in micropores, IHKM seems to be the most advanced and promising procedure of porosity characterization. Presented results show that the obtained pore size distribution curves depend on the type of algorithm applied for the inverting of global adsorption isotherm equation. In spite of the fact that REG leads to the smoother PSD curves than constructed by us ASA algorithm, it can sometimes generate negative parts of distribution what is without physical meaning. On the other hand, the PSD of real heterogeneous solids is rather smooth and continuous than discreet, so regularization method used in the REG algorithm seems to be natural choice (i.e. there is necessary to take under considerations the smoothing effect on the estimated PSD). Thus, we can state that such two algorithms in connection with intuition of researchers may be successfully applied for the proper solution of the considered ill-posed problem. The results of IHKM as well as ND methods show small amount of porosity in carbon blacks applied as reference materials for the construction of \( x_{s} \) plots. The comparison of the results from IHKM and ND for microporous carbons leads to the conclusion about similarity of the both methods.

References


