

Homogeneous and Heterogeneous Micropore Structures in Carbonaceous Adsorbents—Twenty Years Later

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The major aim of this study is to show that, developed by Dubinin and Stoeckli, the relation between the parameters of DA (Dubinin–Astakhov) and DRS (Dubinin–Radushkevich–Stoeckli) equations is an approximation. It is shown that the parameter B_0 of DRS isotherm should be taken into account in such a relationship; strictly speaking, the parameter n_{DA} of DA adsorption isotherm equation is not only the function of the dispersion of the heterogeneity of carbon, it also depends on the location of the maximum of the distribution of this heterogeneity. Moreover, taking into account that the DR isotherm rather does not describe the adsorption in a homogeneous micropore system, the analogous relationship, however, for DA adsorption isotherm as a local equation in GAI (General Adsorption Isotherm) is proposed. © 2002 Elsevier Science (USA)

Key Words: adsorption; activated carbon; Dubinin–Radushkevich–Stoeckli and/or Dubinin–Astakhov–Stoeckli adsorption isotherm equation; heterogeneity; microporosity; theory of adsorption.

1. INTRODUCTION

The idea of the General Adsorption Isotherm (GAI) equation is one of the milestones in the theoretical description of adsorption on heterogeneous surfaces (1–7). Considering microporous carbons, Stoeckli and coworkers proposed extending the GAI concept and developing the equation that describes the process of adsorption on heterogeneous carbons (1, 9);

$$W_f(A) = W_{0,f} \int_{\Omega_B} F(B) \exp\left[-B \left(\frac{A}{\beta}\right)^2\right] dB, \quad [1]$$

where $W_f(A)$ is the global adsorption, $W_{0,f}$ is the total micropore volume, $F(B)$ is the distribution function of the structural parameter B ($\equiv E_0^{-2}$), A is the adsorption potential, β is the affinity coefficient, and Ω_B is the range of integration. They developed the so-called DRS (Dubinin–Radushkevich–Stoeckli) equation, assuming the Gaussian distribution of B , and the DR adsorption

isotherm equation as a local one in the GAI equation. This distribution of the micropore volume ($W_{0,f}$) with the parameter B can be given, for example, (1, 8)

$$\frac{dW_{0,f}}{dB} = F(B)_{BG} = \chi_{BG(i)} \exp\left[-\frac{(B - B_0)^2}{2\Delta^2}\right], \quad [2]$$

where B_0 is the value of B at the maximum of the function $F(B)_{BG}$; Δ is the parameter connected to the so-called dispersion of the above-mentioned distribution; and $\chi_{BG(i)}$ is the normalization factor. This factor can be easily calculated following the normalization conditions:

$$1 = \int_{\Omega_B} F(B)_{BG} dB. \quad [3]$$

Assuming the range of integration $\Omega_B \in (-\infty, \infty)$, the normalization factor is equal to (1)

$$\chi_{BG(-\infty, \infty)} = \frac{1}{\Delta\sqrt{2\pi}}. \quad [4]$$

Taking into account Eqs. [1], [2], and [4] (for integration in the range $\Omega_B \in (0, \infty)$), Stoeckli and Dubinin (1) developed the so-called DRS adsorption isotherm equation. Note that the contradiction exists between the ranges of normalization and of integration, and it was pointed out by many authors (2, 4–7). The final form of the equation generalized on an arbitrarily chosen n_{DA} can be written as (so-called DAS (Dubinin–Astakhov–Stoeckli adsorption isotherm equation (7)))

$$\theta_{DAS} = \exp\left[-B_0 \left(\frac{A}{\beta}\right)^{n_{DAS}} + \frac{\Delta^2}{2} \left(\frac{A}{\beta}\right)^{2n_{DAS}}\right] \frac{1 - \text{erf}(\bar{z})}{2}, \quad [5]$$

where

$$\bar{z} = \left[\left(\frac{A}{\beta}\right)^{n_{DAS}} - \frac{B_0}{\Delta^2}\right] \frac{\Delta}{\sqrt{2}} \quad [6]$$

and $\text{erf}(\bar{z})$ is the error function (10). It is obvious, for n_{DAS} equal to two, that the above-mentioned equation reduces to DRS one.

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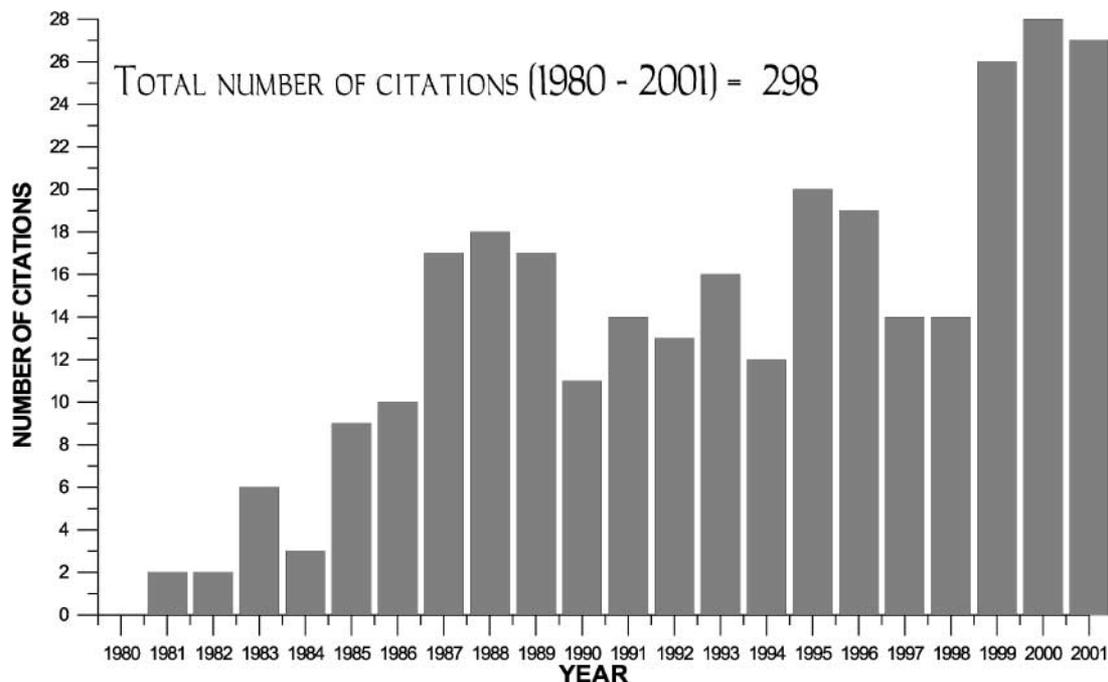


FIG. 1. The analysis of citations of the paper by Dubinin and Stoeckli (1) in the period 1980–2001, using “Science Citation Index” (1980–2000) and “Science Citation Index Expanded” (2001).

The idea and the main features of DRS isotherm were presented in the pioneering paper by Dubinin and Stoeckli (1). In this study, authors, using the experimental data, evaluated a very interesting relation between the parameter n_{DA} of DA equation and the parameter Δ of DRS one (see also in Fig. 2):

$$n_{DA} = 2.00 - 1.78 \times 10^6 \Delta. \quad [7]$$

Equation [7] has been widely applied in the study on heteroge-

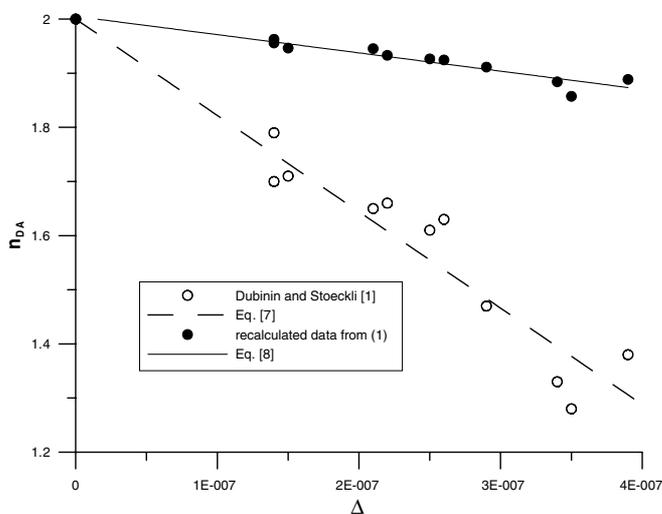


FIG. 2. The comparison of recalculated data (see details in text) based on results published by Dubinin and Stoeckli (1).

neous carbons. The significance of this relation was also indicated in the most important monographs dealing with the heterogeneity of surfaces by Jaroniec and Madey (4) and Rudziński and Everett (5). The study published by Dubinin and Stoeckli is still the inspiration for the experimental and theoretical research on surface heterogeneity. Figure 1 shows the analysis of the citations (excluding self-citations) of this paper for the period 1981–2001. The total number of citations is 298. What is interesting is that the number of citations per year has remarkably increased in the period of past 3 years.

Although the study of Dubinin and Stoeckli is very important in the area of adsorption on carbons, the main idea is rather hard to accept after 20 years. Both DR and DA adsorption isotherm equations possess limitations and are thermodynamically inconsistent (2, 11–13). Moreover, it is hard to accept that the DR equation describes the adsorption process in the system of homogeneous micropores (some authors are of the opinion that even the DA equation does not (14, 15)). The authors of the current study keep the point of view that DA equation can be applied as a local isotherm in the GAI equation (16), and the results showing that the DA equation do not describe the modeled or simulated adsorption data for systems assuming homogeneous microporosity should be treated with precaution. A very interesting paper dealing with this subject has recently been published by Valladares and coworkers (17). They concluded that the DS equation is not adequate for a microporous solid composed by ideal slit-shaped pores. However, the simulated isotherms do not take into account the basic and, what is important, experimentally observed features of activated carbons—for example the heterogeneity of

pore walls. Fundamental papers of Kelemen and Freund (18) where authors applied XPS spectroscopy showed that it is impossible to delete some heteroatoms from carbon surface even by heating at extremely high temperatures. It is obvious that these heteroatoms will influence the potential in the pore. A very interesting idea explaining the observations of Kelemen and Freund on the problems with desorption of heteroatoms from carbons was given by Rodriguez and coworkers (19), who postulate a special type of connection of carbonaceous microcrystallites via heteroatoms. On the other hand, van Slooten and coworkers (20) showed, using computer simulations, that the introduction of heteroatoms onto carbon surface (for example sulfur) remarkably changes the adsorption mechanism. A very important factor is also the pore structure assumed in modeling or simulations. A recent study of Bojan and Steele (21) as well as of Davies and Seaton (22) are pioneering papers where, slightly more complicated than typical slit-like, cylindrical or spherical geometry of micropores is considered. They support the very important study of Wickens (23), who presumed that the slits in porous carbons are rather wedge-like and the typical slit-like geometry (i.e., the pores are built from parallel graphite slabs) is overly simplified. Thus, typical computer simulations simplify the structure of carbons and usually neglect the effect of pore connectivity (24–27). On the other hand, the situation is more complicated since it is well known that there does not exist the model of the structure of microporous carbon that can successfully explain all experimentally measured physical and chemical features of this material (28–31). This was pointed out by Fitzer, Iwashita, Inagaki (28–31), and recently by Pesin and Baitinger (32). They stated that an extreme complexity of electronic structure and atomic arrangement of carbon is a firmly established fact. This is the main reason for the absence of a unique and commonly adopted carbon structural model nowadays. The most frequently used ones for data interpretations are those introduced by Jenkins and Kawamura and by Oberlin (28–31). Unfortunately, these models are entirely contradictory to each other. According to the first one, synthetic active carbon is a conglomerate of randomly twisted and highly anisotropic graphite-like fibrils whose width gradually increases due to high-temperature annealing. In contrast, the second model postulates the existence of practically spite isometric, but heavily crumpled graphite-like sheets (28–31). All these simplifications as well as different irregularities obtained on PSDs calculated from the DFT model led Jagieffo and Tolles to the statement that the pore model used in the DFT calculations does not adequately represent actual activated carbons (33). Thus, further refinements of the model is desired in order to describe the complex structure of activated carbons better. Summing up the methods of PSD determination from analytical equations using Dubinin's theory as well as computer simulations requires a solid experimental verification (17, 34–37).

Although all studies of simulation and modeling of carbons are very interesting and sometimes spectacular (17, 34, 35), it should be remembered that small changes in the values of fundamental parameters taken as constants in simulations can lead

to drastic changes in the results obtained, as it was shown in the important papers by McEnaney, Mays, and coworkers (38, 39). In our opinion, the results of computer simulations are uncertain as long as a satisfactory model of the structure of carbons is not evaluated.

Thus, taking all these factors into account allows the conclusion that as far as the models of carbon pores assumed in computer simulations do not approach the real (still unknown) ones, it is hard to decide definitely if the DA isotherm describes the adsorption in homogeneous pores.

2. THE AIMS OF THE STUDY, THE METHOD, AND RESULTS

The major aim of this study is to show that Eq. [7] is an approximation. Moreover, we want to demonstrate that the relationships between the parameters of theoretical local and global adsorption isotherm equations are more complicated than has been presumed up to the present. It will be shown that parameter B_0 of Eqs. [2] and [5] should be taken into account in Eq. [7]; strictly speaking, parameter n_{DA} of the DA adsorption isotherm equation is not only the function of the dispersion of the heterogeneity of carbon, it also depends on the location of the maximum of the distribution of this heterogeneity. Moreover, taking into account that the DR equation rather does not describe the adsorption in a homogeneous micropore system (40), the relationship analogous to Eq. [7] will be developed, however, for the DA adsorption isotherm as a local isotherm in the GAI equation (Eq. [1]).

Dubinin and Stoeckli, in their pioneering paper (1), analyzed the correlation between the DRS and DA equations for the series of 13 carbons and benzene adsorption data. To check the accuracy of the numerical methods they applied, we recalculated the data from their study (Table IV in (1) and Fig. 2 in the current paper). DRS isotherms were generated numerically using parameters for benzene adsorption tabulated by Dubinin and Stoeckli (1). The following conditions were assumed: $\beta = 1$, the range of p/p_s , 1×10^{-7} –1; and 1000 points on each isotherm. Next, generated isotherms were described applying DA equation. In the current study for searching of optimal parameters a modification of simple genetic algorithm (SGA) with real coding was developed (this algorithm was applied successfully by us previously (36, 41)). Such a novel optimization technique proposed by Holland (42) and developed by Goldberg (43) belongs to "special artificial intelligence techniques." The SGA maintains a population of individuals, $P(t) = \{x'_1, \dots, x'_n\}$ for iteration t (44). Each individual represents a potential solution to the problem at hand and is implemented as some data structure (i.e., structure, object, and so on). Each solution x'_1 is evaluated to give some measure of its "fitness." Then a new population (iteration $t + 1$) is formed by selecting of more fitting individuals (selection step by means of modified roulette wheel). Some members of the new population undergo transformations by means of "genetic" operators (simple crossover and classical mutation) to form new solutions. After some number of generations (stop condition) the algorithm converges. The best individual is hoped to represent

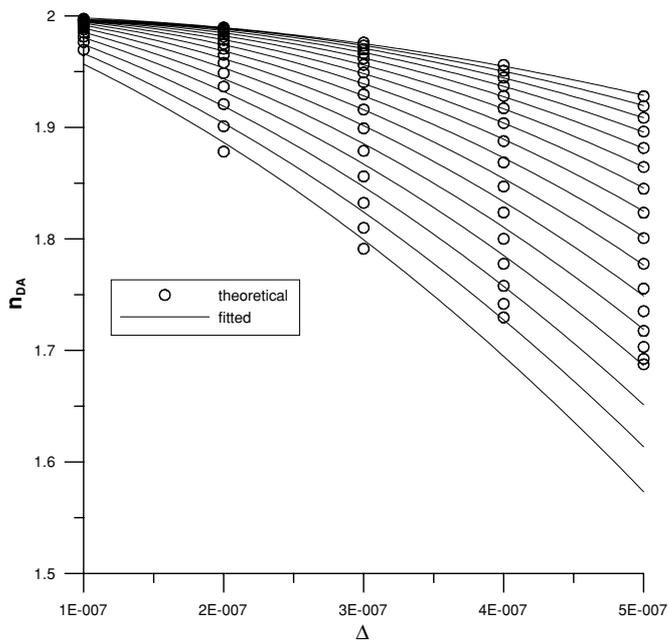


FIG. 3. The dependence of the correlation proposed by Dubinin and Stoeckli (Eqs. [7] and [8]) on the parameter B_0 . The value of this parameter was changed as follows (from bottom to top): from 5×10^{-7} up to 2×10^{-6} (with the step 1×10^{-7}). Open symbols were obtained from fitting of DA to DRS data. The comparison of n_{DA} values calculated by numerical fitting of DRS data by the DA equation with those calculated from Eqs. [9]–[12] are marked as solid lines. The average DC of lines to points is equal to 0.9979.

a near-optimum (reasonable) solution. The obtained data were fitted by line and we obtained

$$n_{DA} = 2.01 - 3.37 \times 10^5 \Delta, \quad [8]$$

and the fit of data to the straight line is equal to $DC = 0.9099$. The comparison of initial and recalculated data (closed circles and solid line, Eq. [8]) based on original results published by Dubinin and Stoeckli (open circles and dashed line, Eq. [7]) is shown in Fig. 2.

Although the differences between both equations occur (i.e., Eqs. [7] (dashed line in Fig. 2) and [8] (solid line in Fig. 2)), taking into account the progress in computer methods as well as the error of measurements (generated DRS isotherms are ideal, i.e., without any experimental error), one can conclude that Eq. [7] can be treated as a good approximation of experimental data considered in the Dubinin and Stoeckli paper. However, the question arises on the validity of the form of this relation. Taking into account the mathematical form of the assumed pore size distribution function (Eq. [2]) as well as the final isotherm equation (Eqs. [5] and [6]) it can be postulated that in Eqs. [7] and [8] the parameter B_0 should be taken into account. To check this we generated numerically 80 adsorption isotherms, using Eq. [5]. They were generated in the same range of relative pressure as mentioned above, i.e., $1 \times 10^{-7} - 1$ p/p_s (1000 points on each isotherm). We used the ranges of parameters of the DRS equation similar as determined experimentally by Dubinin and Stoeckli

(1). Therefore, Δ was changed from 1×10^{-7} up to 5×10^{-7} (with the step 1×10^{-7}), B_0 from 5×10^{-7} up to 2×10^{-6} (with the step 1×10^{-7}), and $n_{DAS} = 2$ in DRS equation, as it was assumed by Dubinin and Stoeckli (1). Again, the above-described

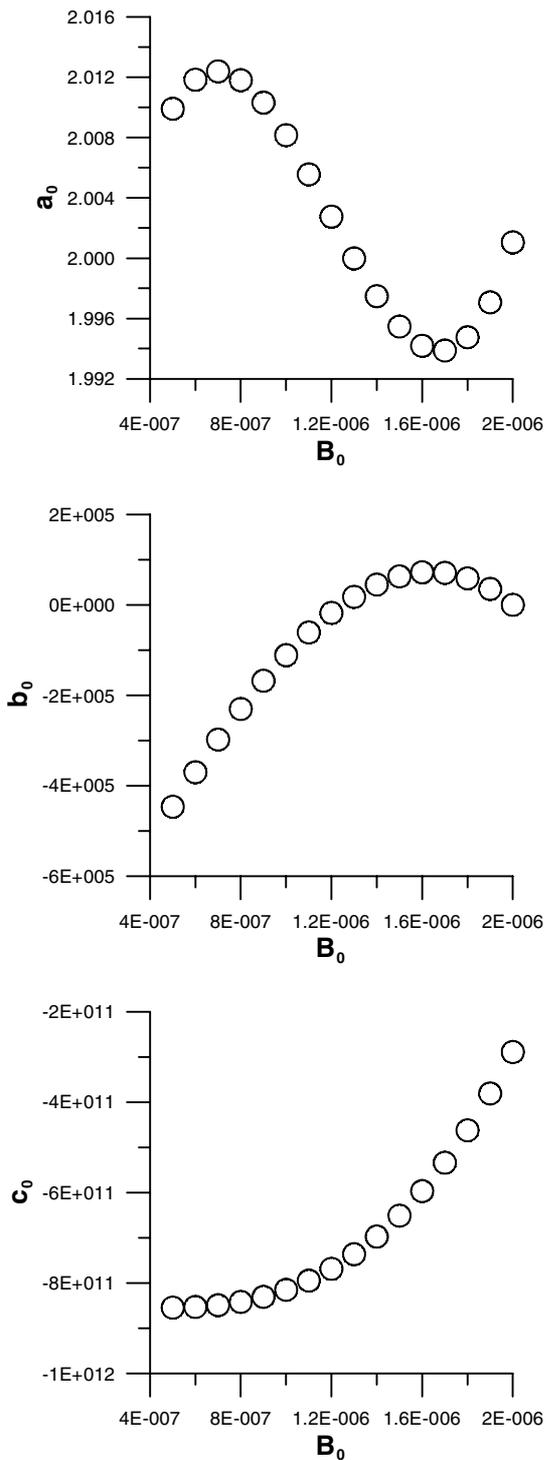


FIG. 4. The dependence of the parameters a_0 , b_0 , and c_0 of Eq. [9] on the value of B_0 in the studied range of the parameters of the DRS equation (Eq. [5]; $n_{DAS} = 2$).

fitting procedure (the simple genetic algorithm) was applied to obtain the parameters of the DA adsorption isotherm equation. The final results are shown in Fig. 3 (open points). It can be seen that in practice a strong dependence of the correlation between the parameter n_{DA} of the DA equation and Δ of the DRS one on the parameter B_0 is observed. This dependence cannot be neglected in Eqs. [7] and [8]; therefore, those relations are only very crude approximations. Therefore, in the next step we tried to correlate those parameters and to propose a new relationship between the parameters of the DA and DRS equations, instead of Eqs. [7] and [8]. Collecting the values of parameters from generated numerically DRS isotherms and from the description of these data using the DA equation, we noticed that n_{DA} is rather the quadratic function of Δ , contrary to the above-mentioned linear form of Eqs. [7] and [8]. Thus, it can be easily shown that

$$n_{DA} = a_0 + b_0\Delta + c_0\Delta^2, \quad [9]$$

where a_0 , b_0 and c_0 are constants, depending on B_0 . Describing the group of data n_{DA} vs Δ , with Eq. [9] for different B_0 values the dependence of the parameters of Eq. [9] on B_0 can be easily evaluated. The graphical representation of this dependence is shown in Fig. 4. Thus we postulated, analyzing some different types of equations and using numerical fitting procedure, that the form of this dependence is as follows:

$$a_0 = a_{0,1} + a_{0,2}B_0 + a_{0,3}B_0^2 + a_{0,4}B_0^3 \quad [10]$$

$$b_0 = b_{0,1} + b_{0,2}B_0 + b_{0,3}B_0^2 + b_{0,4}B_0^3 \quad [11]$$

$$c_0 = c_{0,1} + c_{0,2}B_0 + c_{0,3}B_0^2 + c_{0,4}B_0^3, \quad [12]$$

where $a_{0,1}, \dots, c_{0,4}$ are constants. They can be determined by a

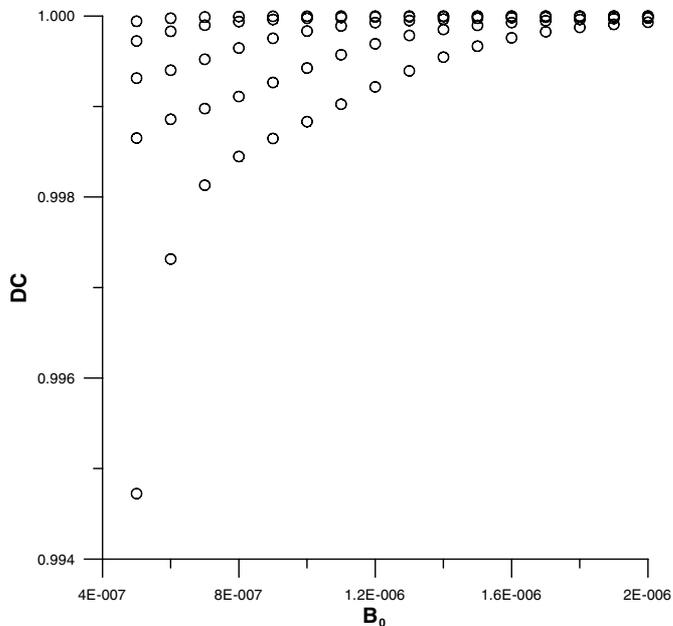


FIG. 5. The changes in the determination coefficient (DC) of the DA isotherm to the DRS one as the function of the value of B_0 parameter.

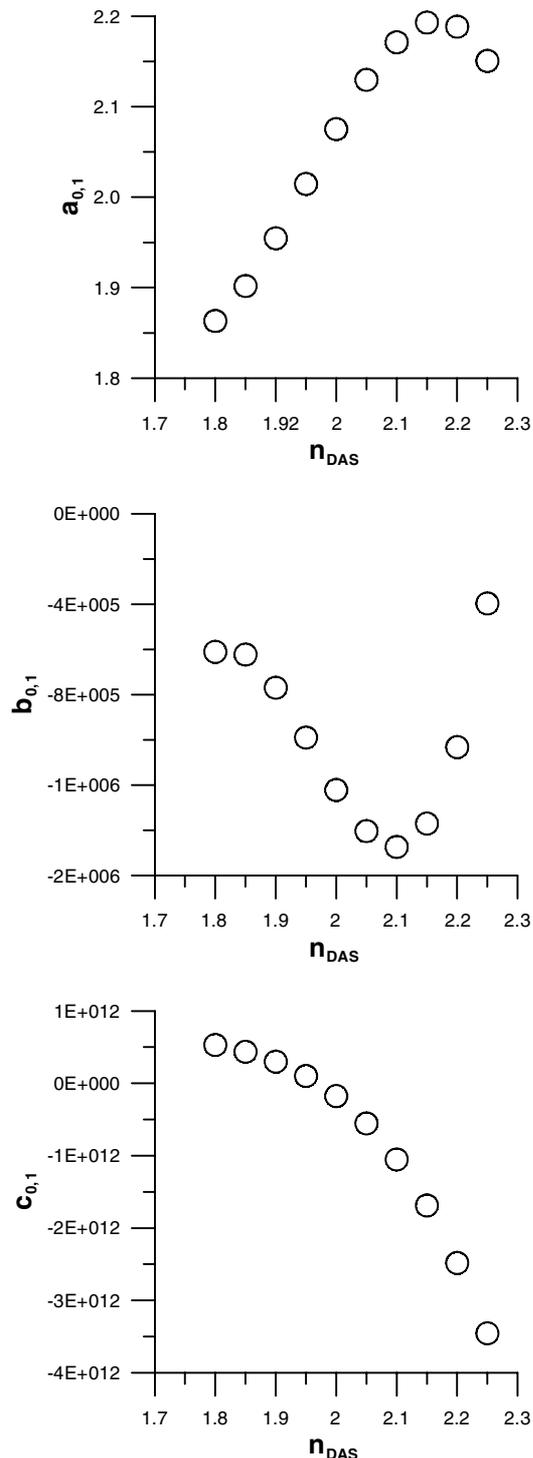


FIG. 6. The exemplary dependence of the parameters: $a_{0,1}$ of Eq. [10], $b_{0,1}$ of Eq. [11], and $c_{0,1}$ of Eq. [12] on the value of n_{DAS} in the studied range of the parameters of the DAS equation (Eq. [5] with n_{DAS} different than 2).

simultaneous numerical fitting procedure and are equal to $a_{0,1} = 1.972$, $a_{0,2} = 1.36 \times 10^5$, $a_{0,3} = -1.39 \times 10^{11}$, $a_{0,4} = 3.90 \times 10^{16}$, $b_{0,1} = -8.66 \times 10^5$, $b_{0,2} = 8.73 \times 10^{11}$, $b_{0,3} = -1.59 \times 10^{16}$, $b_{0,4} = -1.02 \times 10^{23}$, $c_{0,1} = -8.41 \times 10^{11}$, $c_{0,2} = -3.03 \times 10^{16}$,

TABLE 1
The Parameters of Eq. [13]

	$j \equiv a(i = 1, \dots, 4)$				$j \equiv b(i = 1, \dots, 4)$				$j \equiv c(i = 1, \dots, 4)$			
$j_{0,i,1}$	66.83	-3.41×10^7	-3.94×10^{13}	2.08×10^{19}	-6.11×10^8	6.97×10^{14}	-1.17×10^{20}	-4.17×10^{25}	1.40×10^{14}	-1.73×10^{20}	1.18×10^{25}	2.41×10^{31}
$j_{0,i,2}$	-101.96	5.32×10^7	5.96×10^{13}	-3.16×10^{19}	9.43×10^8	-1.07×10^{15}	1.74×10^{20}	6.60×10^{25}	-2.37×10^{14}	3.04×10^{20}	-2.97×10^{25}	-3.75×10^{31}
$j_{0,i,3}$	52.80	-2.78×10^7	-2.97×10^{13}	1.59×10^{19}	-4.84×10^8	5.45×10^{14}	-8.51×10^{19}	-3.48×10^{25}	1.35×10^{14}	-1.77×10^{20}	2.17×10^{25}	1.94×10^{31}
$j_{0,i,4}$	-9.01	4.86×10^6	4.91×10^{12}	-2.65×10^{18}	8.23×10^8	-9.19×10^{13}	1.37×10^{19}	6.10×10^{24}	-2.59×10^{13}	3.42×10^{19}	-4.84×10^{24}	-3.34×10^{30}

$c_{0,3} = -4.06 \times 10^{22}$, $c_{0,4} = 9.69 \times 10^{28}$. Figure 3 shows the comparison of numerical data (fitting of DA to DRS) with those calculated using Eqs. [9]–[12]. The average fit is equal $DC = 0.9979$. It can be noticed that Eqs. [9]–[12] describe the numerical data poor at higher values of Δ and low values of B_0 . However, we want to point out that this is resulted by the features of the DA equation and not by the methodological errors of the procedure applied in this study. Figure 5 shows how the determination coefficient (DC) values of fitting the DA equation to the DRS one change, and it can be noticed that they decrease for the larger values of Δ and low values of B_0 . Therefore, the differences in the data calculated from numerical procedure and from Eqs. [9]–[12] are caused by the properties of both studied isotherm equations.

At the next step, we tried to develop the relationship analogous to Eq. [9]; however, for the DA isotherm equation as a kernel in the GAI equation (Eq. [1]) (as mentioned above, the DRS equation with n_{DA} different than 2 is called DAS (Dubinin–Astakhov–Stoekli)). Therefore, it was necessary to generate some additional isotherms; however, in this case for n_{DAS} different than 2. For the same ranges of B_0 , Δ , and p/p_s , and changing n_{DA} from 1.80 up to 2.25 (with the step 0.05), 720 additional isotherms were generated and described using the DA equation. It is obvious that in this case, the values of the parameters $a_{0,1}, \dots, c_{0,4}$ (see Eqs. [10]–[12]) are now the function of n_{DAS} . The following forms of those functions are assumed:

$$j_{0,i} = j_{0,i,1} + j_{0,i,2}n_{DAS} + j_{0,i,3}n_{DAS}^2 + j_{0,i,4}n_{DAS}^3, \quad [13]$$

where j is assumed as a , b , and c (see Eqs. [10]–[12]), respectively, and i changes from 1 to 4. As an example, Fig. 6 shows how the parameters $a_{0,1}$, $b_{0,1}$, and $c_{0,1}$ change with n_{DA} (for other parameters similar shapes were observed). To find the values of the parameters $j_{0,i,1}, \dots, j_{0,i,4}$ we again used the numerical optimization procedure based on the SGA algorithm. One should realize that 48 best-fit parameters are searched at this stage. They are grouped together in Table 1. The value of determination coefficient, describing the fit of calculated data (using Eqs. [9]–[13] and applying the parameters from Table 1) to these generated numerically, is equal to 0.9964. This value is similar to the average fit ($DC = 0.9979$) achieved from fitting of the DRS equation to the DA one.

3. SUMMARY AND CONCLUSIONS

This article deals with the results of one of the most important papers in the area of physical adsorption in micropores of heterogeneous carbons. The correlation between the parameters of the DRS and DA adsorption isotherm equations was verified, and it is shown that this correlation is more complicated, as was presumed by Dubinin and Stoekli. Therefore, it was modified and extended in cases where the DA equation is applied as a local isotherm in the GAI equation. The obtained correlations suggest that the parameter n_{DA} of the DA adsorption isotherm

equation is not only the function of the dispersion of the heterogeneity of a carbon, but it also depends on the location of the maximum of the distribution of this heterogeneity.

It is unquestionable that the theory of volume filling of micropores is one of the most stimulating concepts occupying the principal position in adsorption science (45–54). Nevertheless, it seems that there are still two main unsolved problems connected with this equation. First is the applicability of the DA isotherm as the local one in the GAI equation. The second problem is the significance of the empirical parameter (n) of the DA equation. Some empirical data confirm the thesis that the DA equation can describe adsorption in an almost homogeneous microporous system and can be used as a local isotherm in the GAI equation (16). On the other hand, recent studies showed that the DA adsorption equation cannot describe the ideally homogeneous adsorption isotherms, i.e., the isotherms generated numerically for slits possessing the same pore diameters (55, 56). Therefore, the question arises as to what kind of pore size distribution is assumed in the Dubinin–Astakhov adsorption isotherm equation. We have recently tried to solve this problem (40). Two the most sophisticated methods of carbon porosity characterization (high-resolution α_s plot and the procedure proposed by Nguyen and Do (ND) (55, 56)) were utilized for the assessment of porosity from the series of generated numerically adsorption isotherms of nitrogen ($T = 77.5$ K) generated for constant E_0 and different n values and in contrast for constant n and different E_0 . The most important conclusion is that the DA equation can generate isotherms describing almost homogeneous structure of pores and/or bimodal heterogeneous structure. Therefore, the DA equation generates adsorption isotherms leading to all types of high-resolution α_s plots. Corresponding PSDs indicate the presence of homogeneous porosity, primary and/or secondary micropore filling, or both of them. Parameter n of the DA equation is responsible not only for the homogeneity of pores (i.e., the deviation of pores from the average size) but for the adsorption mechanism in micropores. In other words, lowering n leads to the change in this mechanism from primary to primary and secondary micropore filling simultaneously.

Taking all the obtained results into account suggests that the DA equation is probably the most universal isotherm applied for the description of adsorption in micropores. Recent studies of Carrott and coworkers (34) showed that the DRS equation (Eq. [5], $n = 2$) applied for the description of adsorption data of nitrogen on a series of activated charcoal cloths leads to almost the same PSD curves as obtained from computer simulations using GCMC. Therefore, the study of the features of this equation as well as of its modifications seems to be a very promising direction for the future.

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