What kind of pore size distribution is assumed in the Dubinin–Astakhov adsorption isotherm equation?

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Abstract

Two most sophisticated methods of carbon porosity characterization (high resolution α_s-plot and the procedure proposed by Nguyen and Do, (ND)) were utilized for the assessment of porosity from the series of numerically generated adsorption isotherms. Basing on the Dubinin–Astakhov (DA) adsorption isotherm equation, two series of adsorption isotherms of nitrogen ($T = 77.5$ K) were generated for constant E_0 and different n values, and for constant n and different E_0. They were described by the both above-mentioned methods. The types of obtained α_s-plots as well as the pore size distribution curves (PSD) lead to suggestions about the basic features of the DA and the meaning of the parameters of this adsorption isotherm equation.
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1. Introduction

It is unquestionable that together with the concept of multilayer adsorption (leading to the BET equation) the theory of volume filling of micropores (TVFM) is one of the most stimulating concepts occupying the principal position in adsorption science. Developed formerly, and based on the Weibull distribution of adsorption potential, the Dubinin–Astakhov (DA) equation was considered to be a semi-empirical one [1–7]. However, Chen and Yang [8,9] developed it statistically, from the concept of hard disk fluid and applying the Reiss–Frisch–Lebowitz (RFL) equation of state [10]. Nevertheless, it seems that there are two main unsolved problems connected with the DA equation. The first one is the applicability of DA isotherm as a local one in general adsorption isotherm equation (GAI) [1–4,7,11]. Some empirical data confirm the thesis

that DA can describe adsorption in an almost homogeneous microporous system, and can be used as a local isotherm in GAI [12,13]. On the other hand, recent studies showed that this formula cannot describe ideally homogeneous adsorption isotherms, i.e., the isotherms generated numerically for slits possessing the same pore diameters [14–16]. Thus, some authors are of the opinion that DA equation describes only the primary micropore filling process and not the process of adsorption taking place in the whole microporous system [12,18]. Therefore, the description of the experimental adsorption isotherm by GAI with DA as a kernel cannot be extended into all micropores present in solid [18].

The second problem is the significance of the empirical parameter n of DA equation. Chen and Yang showed that n is really a structural parameter of carbon [8,9]. Dobrushkin [19], considering the physical meaning of the parameters of DA equation, noticed that n does not depend on the pore dimensions and it is determined only by the standard deviation of micropore sizes, hence, it characterizes the surface heterogeneity. Similar conclusion was also provided by Jagietto and Schwarz [20], Condon [21,22], as well as other authors. On the other hand, it has been

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widely accepted that for adsorbents there exists a direct connection between the values of the exponent n and the type of adsorbent [23–26]. For carbonaceous solids, the values of this parameter lie usually in the range 1–3, n approaching three is the most frequently found in literature for adsorbents with narrow micropores of small size range, while values of n approaching one are found for adsorbents with a wide range of pore sizes. Therefore, this parameter of the DA equation should be connected with the average size of micropores and the micropore-size distributions.

Another important question is connected with the problem of the determination of pore size distribution of microporous carbons. On the one side, assuming that DA equation describes adsorption process in a homogeneous pore system, the PSD can be implicit and the GAI solved analytically or numerically. Then, fitting GAI to experimental data, the parameters of PSD can be obtained. On the other hand, knowing an experimental isotherm, one can assume the DA equation as a local isotherm and calculate the PSD using, for example, advanced numerical procedures [18]. However, what we know is that the Weibull distribution of adsorption potential is associated with DA equation. Therefore, the following question can be posed at this point. What kind of PSD assumes DA equation itself? Does this distribution change if the parameters of DA isotherm change? A partial answer to this question has recently been given by Ohba et al. [27]. They studied the simulated nitrogen adsorption isotherms in heterogeneous carbons and Gaussian distribution of pores was assumed. It was shown that the simulated isotherms can be fitted by typical DR, although not in the whole range of relative pressures.

The authors of the current study are of the opinion that the interesting approach of Ohba et al. [27] can be extended, and the problem can be studied from the opposite point of view. The application of the new methods of porosity characterization can lead to the results answering in great extent the questions associated with DA equation. Recent studies in the modeling and computer simulations of adsorption in micropores guide some authors to the application of the DFT and/or GCMC methods for the calculation of PSD of carbons [28–32]. Although pore size distributions obtained from this method possess some artifacts, DFT and/or GCMC are considered to be the most sophisticated methods of porosity characterization. On the other hand, Nguyen and Do [16,33–35] proposed the new procedure of porosity calculation. It bases on the combination of BET and t-plot methods. Using the concept of local isotherms the mentioned authors [16,33–35], as well as the others [36–43] showed, that ND method leads to almost the same results as DFT and/or GCMC (the differences are small), thus the both procedures can be treated equivalently. Therefore, high resolution α_s-plot [27,44–47] and the ND, DFT and/or

GCMC methods can be treated as standard, newest and probably the most sophisticated methods of porosity characterization.

2. The aim of the study, applied methods and results

2.1. The aims and the procedure

The major aim of this study is to check what kind of pore size distributions and α_s-plots are associated with numerically generated 'ideal' DA adsorption isotherms. Basing on the equation proposed by Dubinin and Astakhov [5,48–50]:

$$\theta_{DA} = \exp\left[-\left(\frac{A_{pot}}{\beta E_0}\right)^n \right] \qquad (1)$$

where $A_{pot} = RT \ln(p_s/p)$, p/p_s is relative pressure, θ_{DA} is the degree of micropore filling, β is the affinity coefficient (for nitrogen equal to 0.32), E_0 is the characteristic energy of adsorption, n is the parameter of the above-mentioned equation, 12 adsorption isotherms were generated numerically (100 points each) in the range of relative pressure 1×10^{-6} up to 0.999 p/p_s ($T = 77.5$ K). Two groups of isotherms were generated. We studied the influence of n (0.5, 1.0, 1.5, 2.0, 3.0 and 5.0) at constant E_0 (the value 25.0 kJ/mol was chosen arbitrarily) and, in contrast, the effect of E_0 (10.0, 15.0, 20.0, 25.0, 32.0 and 40.0 kJ/mol) at constant n (the value 3.0 was chosen arbitrarily). Both groups of isotherms are shown in Figs. 1 and 2. The obtained curves were converted into the high-resolution α_s-plots. Since the analyzed isotherms were generated numerically, the nature of the surface is unknown, and it is hard to choose the reference system among the data published in literature. Thus, we decided to apply the procedure used recently for GCMC method by Kaneko and co-workers [27,46]. The reference isotherms were calculated, following the ND procedure, for three values of pore diameter (ca. 3.5-, 6- and 10-nm first diameter of pore was chosen by Kaneko and co-workers [27,46] for simulating from GCMC reference adsorption isotherm for construction of high-resolution α_s-plots). They are shown in Fig. 3, together with the GCMC isotherm simulated for the pore with diameter 6 nm (see Acknowledgement). We chose the same value of C_{BET} constant (i.e., 284) as applied by Nguyen et al. [16,33–39] during the construction of their procedure. Fig. 3 shows, that the isotherm generated for the pore with diameter 3.5 nm is strongly disordered by the effect of porosity, and this effect is almost invisible in the range 6–10 nm. Moreover, although the GCMC method leads to larger adsorption than ND method does, the shapes of the isotherms are practically the same. Therefore, we chose the isotherms generated from ND method (3.5 and
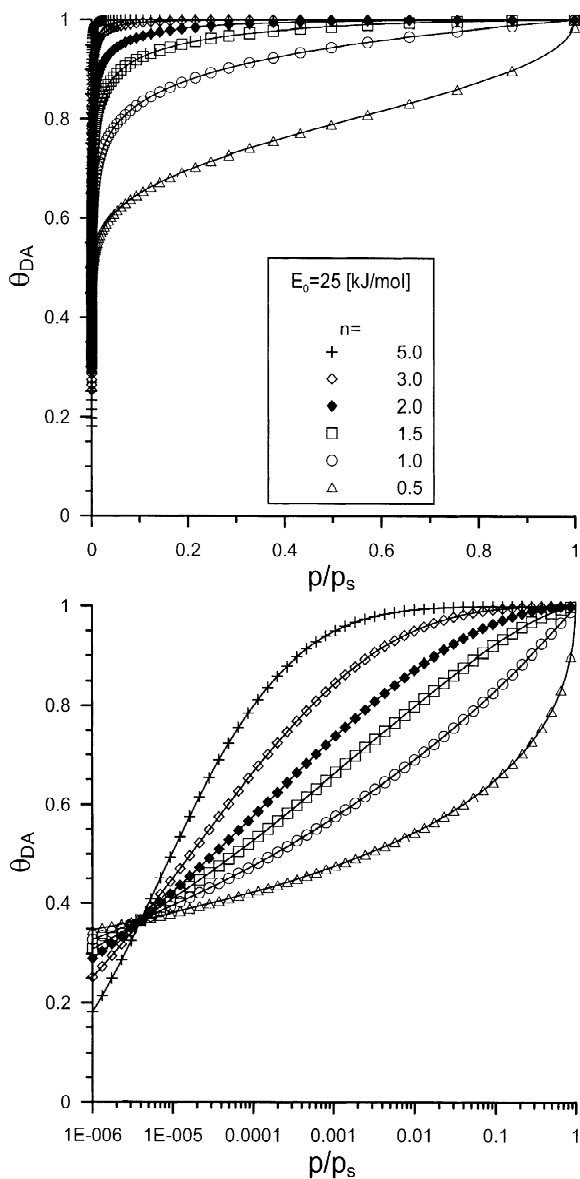
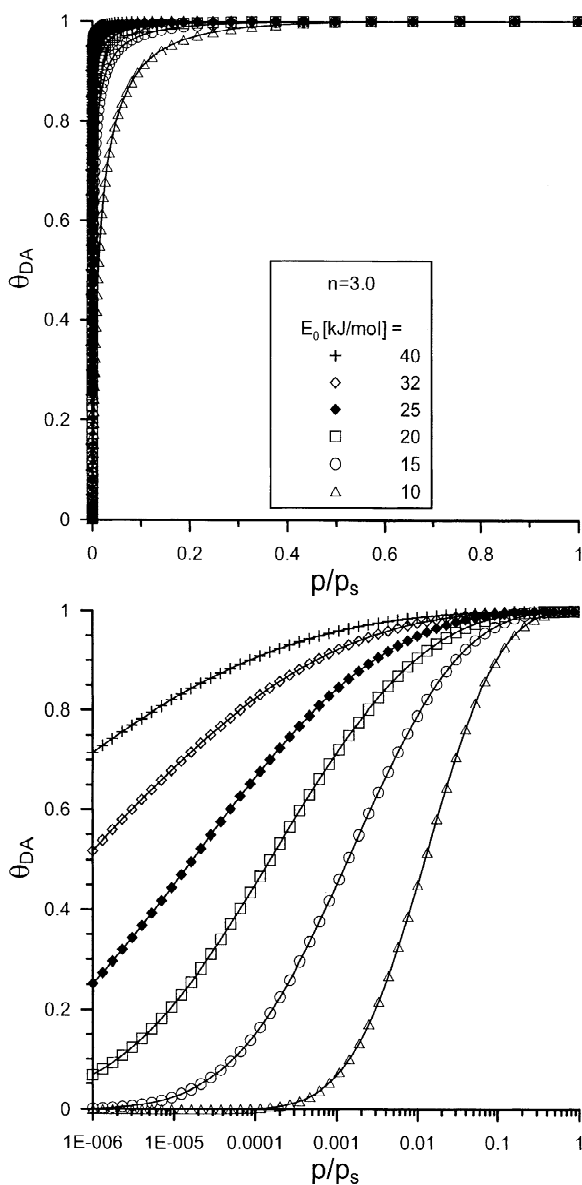Fig. 1. Numerically generated DA isotherms for group I.

Fig. 2. Numerically generated DA isotherms for group II.

10 nm) as the reference systems. The obtained high-resolution α_s-plots are shown in Figs. 4 and 5.

The basic procedure of the construction of local isotherms from ND method was the same as proposed by those authors [16,33–39]. However, in the presented paper the new algorithm is applied to solve the problem of fitting of an experimental isotherm with local ones, thus, we describe it in detail below. In general, we can define an expression describing a global adsorption isotherm as follows [33,51]:

$$\Psi_t(p_j) = \int_{x_{min}}^{x_{max}} g_{theor}(x_i, p_j) f(x) \cong \sum_{i=1}^{N} w_i g_{theor}(x_i, p_j) \qquad (2)$$

where $i = 1,2, \ldots ,N$; $j = 1,2, \ldots ,M$; x describes the structural heterogeneity of an adsorbent; $f(x)$ is the distribution function of the parameter x; $g_{theor}(x_i, p_j)$ is the discreet form of a local adsorption isotherm (i.e., kernel) that describes the adsorption process in homogenous pores; x_{min} is the smallest and x_{max} is the largest value of a
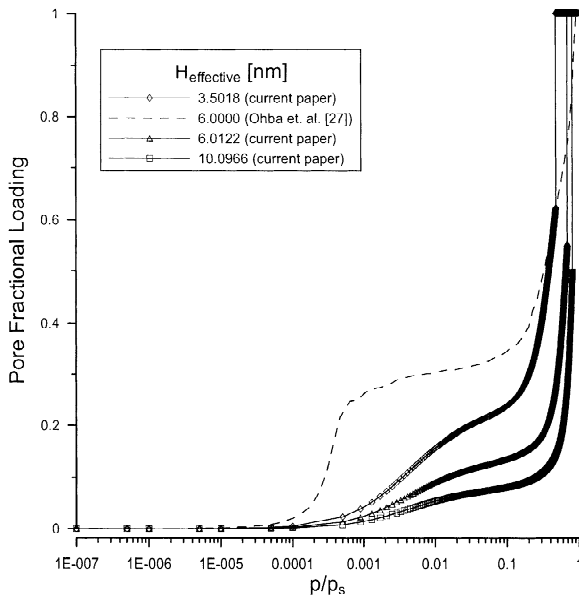
Fig. 3. Reference local nitrogen isotherms from ND method calculated for three pore diameters.

structural parameter (i.e., pore width, radius, half-width). Basing on both the theory of non-linear minimisation and static penalty function our task is to find $\bar{w}$ so as to minimise functional $\Omega(w)$. Mathematically:

Minimise $\Omega(w) =$

$$\begin{cases} \sum\limits_{j=1}^{M} \left(\Psi_t(p_j) - \sum\limits_{i=1}^{N} w_i g_{theor}(x_i, p_j) \right)^2 & \text{if } \bar{w} \epsilon \Xi \cap S \\ \sum\limits_{j=1}^{M} \left(\Psi_t(p_j) - \sum\limits_{i=1}^{N} w_i g_{theor}(x_i, p_j) \right)^2 + \sum\limits_{i=1}^{H} C_i \delta_i & \text{otherwise} \end{cases}$$

(3)

with respect to $\bar{w} = (w_1, w_2, \ldots, w_N) \in R^N$ and the normalisation condition $\Sigma_{i=1}^{N} w_i = 1$

where $\begin{cases} \delta_i = 1 & \text{if constraint '}i\text{' is violated} \\ \delta_i = 0 & \text{if constraint '}i\text{' is satisfied} \end{cases}$ (4)

here H is a number of constraints, $\bar{w} \in \Xi \cap S$. The set $S \subseteq R^N$ defines the search space and the set $\Xi \subseteq R^N$ defines a feasible search space. The search space S is defined as a N-dimensional rectangle in R^N (domains of variables defined by their lower and upper bounds)

$$l(i) \leq w_i \leq u(i) \quad 1 \leq i \leq N \tag{5}$$

The feasible search space Ξ was assumed outside the defined N-dimensional rectangle. One should notice that $\Omega(\bar{w})$ is the penalised objective function, and C_i is a constant imposed for the violation of the constraint i. We want to point out that such defining of a minimisation problem prevents from receiving unphysical solutions (i.e., negative value of distribution function $f(x)$, unphysical
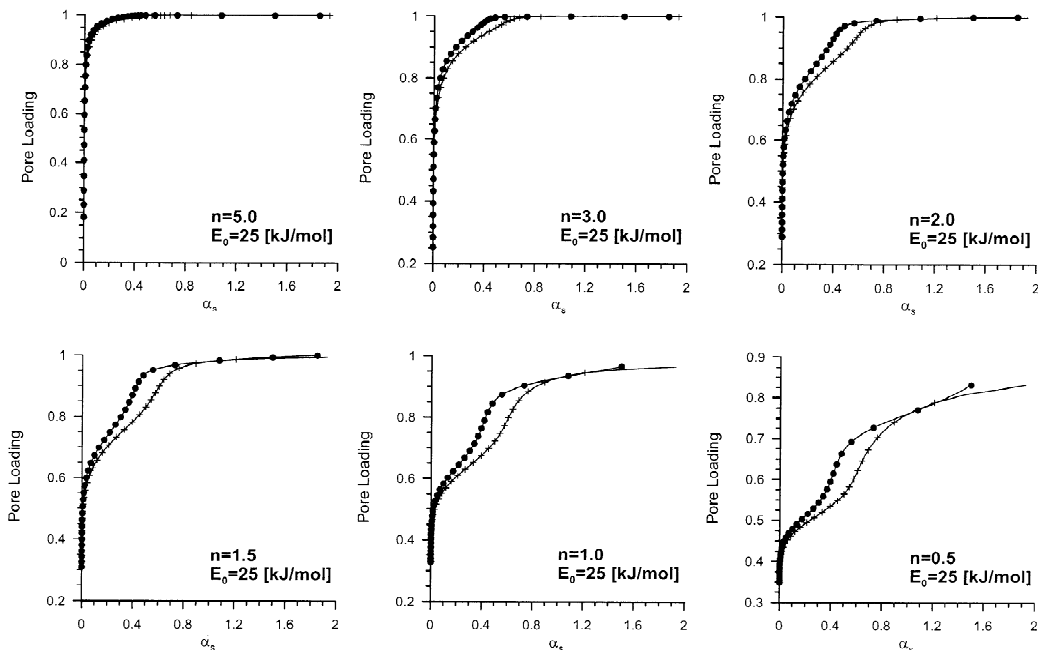

Fig. 4. High resolution α_s-plots calculated for the group I of isotherms and two reference systems (circles – $H_{effective} = 3.5018$ nm, crosses – $H_{effective} = 10.0966$ nm).
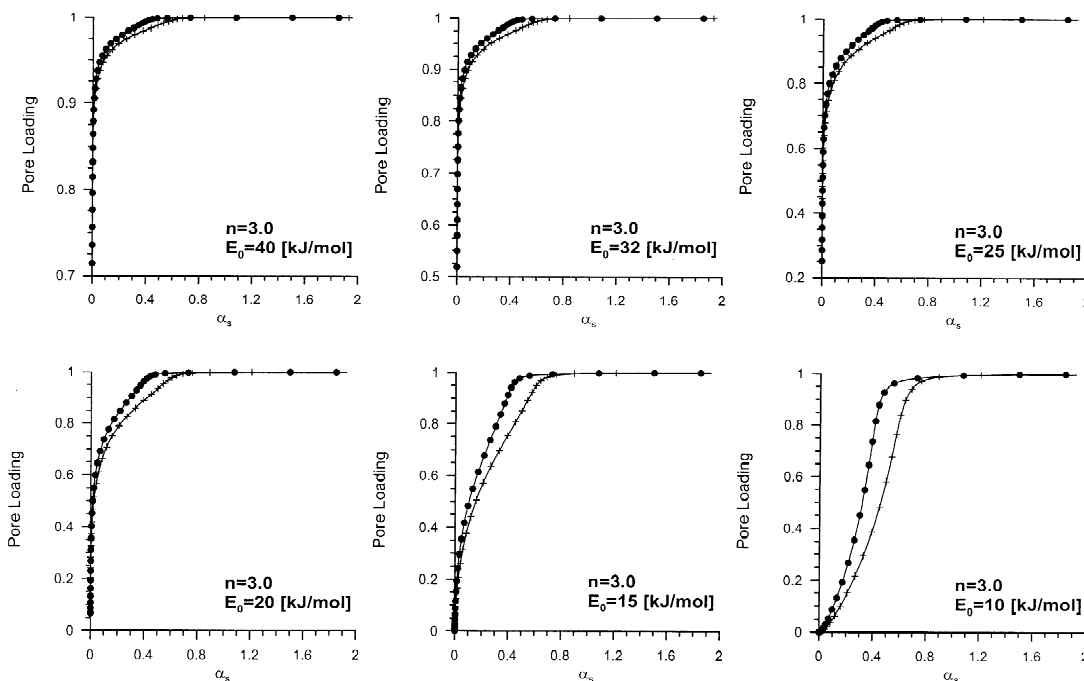
Fig. 5. High resolution α_s-plots calculated for the group II of isotherms and two reference systems.

oscillations of distribution function $f(x)$, and so on). Up till now we have defined only a minimisation problem of functional $\Omega(\bar{w})$ but we do not say anything about the construction of minimisation procedures. Obviously, for extracting $f(x)$ from a measured global adsorption isotherm we can use genetic algorithms, evolutionary algorithms, simulated annealing, taboo search, deterministic algorithms (i.e., simplex strategy of Nelder and Mead, strategy of Hook and Jeeves, and so on), gradient methods (i.e., simple gradient method and so on), and hybrid methods [52]. All the mentioned above techniques minimise all unknown variables, simultaneously. In developed by us and analysed in this study the new adsorption stochastic algorithm (ASA) [40], the well-known relaxation (successive variation of the variables, parallel axis search, Gauss–Seidel strategy, alternating variable search, sectioning method [53]) was applied. The main idea of such a minimisation procedure is successive minimisation in one dimension (i.e., minimise only one element from $\bar{w}$ vector). So the optimisation is first carried out by only optimising the first elements of optimisation variables $\bar{w}$ vector. Once w_1 is optimised, w_2 is then optimised until w_K has been optimised. Once this is completed, the process is then repeated until no further change in the functional is observed. In developed ASA program the well-known Rechenberg–Schwefel, Fibonacci division, and golden section procedures [54] were used for estimating relative minimum in one dimension. All such procedures give very similar results.

2.2. Analysis of the results for group I ($E_0 = const.$, n changes)

For the first group of isotherms (constant energy, different n values, Fig. 1) a decrease in n leads to the conversion of α_s-FS plots into FS/CS (Fig. 4) suggesting the transformation of the mechanism of adsorption in micropores from primary micropore filling into simultaneous primary and secondary micropore filling. It is seen that the choice of the reference isotherm has small influence on the shape of α_s-plots. From PSD curves (Fig. 6) one can notice that for high n almost a homogeneous pore system is observed (the dispersion of pore diameters is around the diameter of one nitrogen molecule). The decrease in n value leads to the decrease in the intensity of the peak and the second peak appears in the range of pores with diameters around 1.5 nm. Thus, the decrease in n value (at constant E_0) leads to the conversion of the PSD from one modal to bimodal. Moreover, a negligibly small amount of mesopores is present for $n = 1$ and in the case of $n = 0.5$.

2.3. Analysis of the results for group II ($n = const.$, E_0 changes)

From Fig. 5 it can be noticed that for the largest values of energy (40 and 32 kJ/mol) the obtained α_s-plots belong to the FS group, and the CS swing is almost absent. The decrease in energy value leads, however, to the creation of
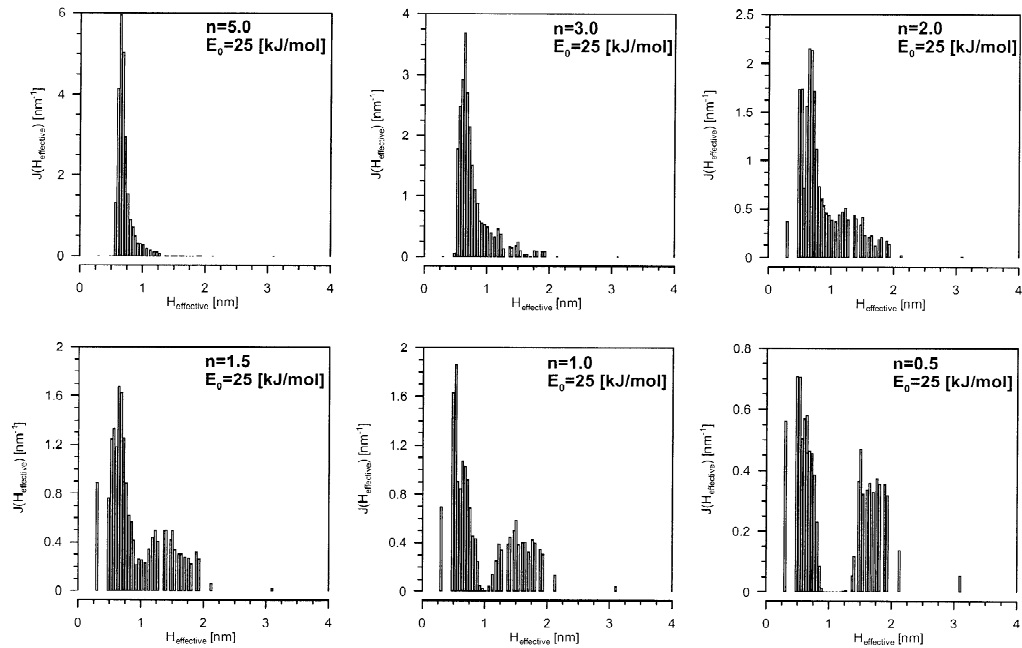
Fig. 6. PSD from ND method for the group I.

two swings, thus, for E_0 in the range 20–25 kJ/mol FS/CS-type α_s-plots are observed. For the smallest energies, the α_s-plots become the typical CS type. It can be noticed (Fig. 7) that for the largest energy value almost

homogeneous PSD is obtained from ND method. This distribution changes with the decrease in E_0 value. The same changes as those observed on α_s-plots occur also on PSD curves, and in the range of E_0 20–25 kJ/mol bimodal
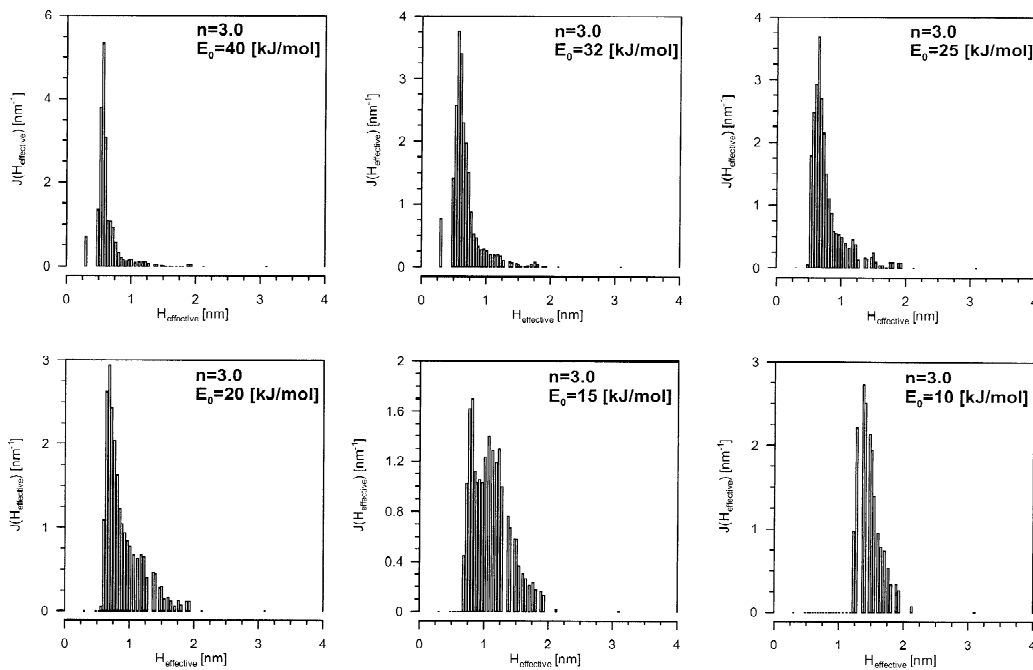

Fig. 7. PSD from ND method for the group II.

PSD is observed, as a result of the decrease in the intensity of the peak around 0.7 nm, and the increase in the intensity of the peak related to the adsorption in wider pores (ca. 1.2 nm). For the smallest analyzed value of energy the first peak vanishes completely and only the second is visible.

3. Conclusions

There is a consistency between the results obtained in this study from ND method and high resolution α_s-plots. The obtained results confirm the conclusions given by Kaneko and co-workers, i.e., the type of high resolution α_s-plot is strictly connected with the type of pore structure and the type of filling of this structure with adsorbate. Thus, the results of computer simulations obtained by Kaneko and co-workers are equivalent to these obtained from ND method. It is obvious, and independently confirms the equality of ND and DFT (and/or GCMC) methods. What is, however, the most important for the present study is that all types of porous structure can be obtained from the description of numerically generated data using DA adsorption isotherm equation. Therefore, DA equation generates isotherms describing almost a homogeneous structure of pores and/or bi-modal heterogeneous structure. Thus, 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. The parameter n of DA equation is responsible not only for the homogeneity of pores (i.e., the deviation of pores from average size) but for the adsorption mechanism in micropores. In other words, lowering n leads to the change in this mechanism from primary to simultaneous primary to secondary micropore filling.

Taking all obtained results into account allows suggesting that DA equation is probably the most universal one for the description of adsorption in micropores. Thus the question arises. Why does not this equation describe the experimental data in the whole range of relative pressure? This problem will be the subject of the forthcoming studies.

Acknowledgements

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