

Improving fundamental ideas of Dubinin, Serpinsky and Barton - further insights into theoretical description of water adsorption on carbons*

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The purpose of the current study is the review the most important papers related to water adsorption on carbons, and published in four different fields, namely: computer simulations (CS), quantum methods (QM), analytical adsorption isotherm formulas (AF) and adsorption calorimetry (AC). The special attention is paid to the (AF) inspired by the pioneering papers of Dubinin, Serpinsky, Barton and co-workers. We present the concept of “the decrease in the number of adsorption sites” and we assign a physical meaning to $a_{c,B2}$ - the empirical parameter of Barton’s adsorption isotherm equation. Moreover, we discuss the applicability, advantages and defects of the most important (AF) presenting some new approaches in this field. Next, we solve some of the deficiencies of previous studies considering the mechanism of water adsorption on solids, by taking into account the possibility of the existence of various types of the hydrophilic centers. At the start we improve the original D’Arcy and Watt equation taking into account the dependence of the concentration of the surface primary sites on the amount of the secondary ones. Next, we assume that the surface of an adsorbent consists of regions of heterogeneity at the molecular level, and the multi-site generalized D’Arcy and Watt model is proposed. Finally we improve the Barton model and the original DW relationship, respectively. It can be noticed that for the both cases we propose to take into account the finite adsorption space via the term $(1-kGB1an)$. Moreover, the chemisorption of water molecules on the various types of the primary high-energy adsorption sites is considered. For all presented new models we show the corresponding adsorption enthalpy equations.

* The paper is dedicated to prof. M. Jaroniec on the occasion of receiving the title of Honorary Professor of UMCS.

1. INTRODUCTION

Water adsorption on carbons is still the subject of many experimental and theoretical studies. Recently, the progress in computer simulations (CS) and quantum methods (QM) led to very interesting results making possible the better understanding of the experimental observations and water adsorption mechanisms.

On the other hand, as it was mentioned by Cerofolini and Rudziński [1] despite the progress in computer simulations, it is still necessary to look for the elegant analytical formulas (AF) describing adsorption isotherms and being suitable for a wide range of scientist and engineers. Analytical approaches will always be competitive as far as the computational time is considered. The correctness of adsorption equations is easy for verification via the comparison with the results obtained from, for example, adsorption calorimetry (AC). This method is particularly important since allows to elucidate the thermodynamic state of the adsorbed molecules.

The purpose of the current study is to review the most important papers related to water adsorption on carbons and published in all mentioned above fields i.e. (CS), (QM), (AF) and (AC). The special attention is paid to the (AF) inspired by the pioneering papers of Dubinin, Serpinsky, Barton and co-workers. We present the concept of “the decrease in the number of adsorption sites” and assign a physical meaning to $a_{c,B2}$ - the empirical parameter of Barton’s adsorption isotherm equation. Moreover, we discuss the applicability, advantages and defects of the most important (AF) and show some new propositions in this field. Next we solve some of the deficiencies of previous studies considering the mechanism of water adsorption on solids, by taking into account the possibility of the existence of various types of the hydrophilic centers. At the start we improve the original D’Arcy and Watt equation taking into account the dependence of the concentration of surface primary sites on the amount of the secondary ones. Next, we assume that the surface of an adsorbent consists of regions of heterogeneity at the molecular level (i.e. the various functional groups and/or defect on the surface of the adsorbent). Moreover, water molecules can adsorb on all types of high-energy primary sites, obeying the Langmuir isotherm equation. Summing up, the multi-site generalized D’Arcy and Watt model is proposed. The final two sections are devoted to the improvement of the Barton model and the original DW relationship, respectively. It can be noticed that for the both cases the finite adsorption space is taken into consideration by the term $(1 - k_{GB}a^n)$. Moreover, the chemisorption of water molecules on the various types of the primary high-energy adsorption sites is taken into account. In next part we compare the new advanced theoretical models and finally, we present conclusions.

2. (CS) AND (QM) CALCULATIONS AND (AC) MEASUREMENTS

A lot of interesting information about the mechanism of water adsorption has been obtained from computer simulations [2-13] and quantum methods (QM) [3,11,14,15,16,17,18]. The adsorption process of water molecules on the hydrophobic surfaces has been widely investigated [4,10,11,14,15,19,20]. On the other hand, several types of polar oxygen-containing sites (e.g. carboxyl [3,5,6,17,18], carbonyl [4,5,8], hydroxyl [6,7,9] groups, and H-sites [10]) are placed on the surface of carbon with different densities and distributions in order to determine the influence of these factors on water adsorption. Computer simulations are still developed and more and more complicated systems have been analyzed. For example, Thompson and co-workers [8,12] in order to provide the realistic pore representation and the description of water adsorption, suggested recently the application of the model based on the reverse Monte Carlo method. In this model surface sites have been added at random points on the edges of the graphene microcrystals possessing random sizes and structures. Nevertheless, some advanced computer algorithms are computationally intensive and time-consuming. Therefore, uncomplicated analytic approaches are often favored in order to simplified consideration and cut down significantly the time of computations (for instance, the so-called local isotherms - obtained from computer simulations - are described by theoretical models as for example, by this proposed by Talu and Meunier)[9].

Very interesting paper dealing with the application of computer simulations to description of the mechanism of water adsorption on carbonaceous adsorbents has been published recently by Muller and Gubbins [13]. They showed, that for non-activated carbon slit-like pore, almost no adsorption occurs until a sharp vertical rise in the adsorption curve is seen and the pore fills suddenly (i.e. the capillary condensation occurs). If the surface is doped by active sites, adsorption isotherm changes drastically, strong bonds are formed between these sites and water molecules, and these adsorbed molecules become nucleation sites for other water molecules to adhere. Thus, these results confirm the role of primary surface sites in the enhancement of water adsorption. Furthermore, Jorge et al. [6] showed that the local distribution of primary sites (carboxyl, hydroxyl, and carbonyl groups) has a strong effect on the low-pressure part of the adsorption isotherm, while the overall site density affects mainly the vapor-liquid phase transition. The type of oxygen-containing groups was shown not to be of critical importance, since more complex groups can effectively be represented by simpler sites. On the other hand, McCallum et al. [9] proposed two alternative mechanisms for water adsorption onto activated carbon walls due to surface sites regularly arranged or in a random array (the same site density in both cases was assumed). The five stages are observed from the analysis of both types of

simulated adsorption isotherms. Moreover, their behavior is similar to experimental ones. Summing up, the results obtained from the computer simulations confirm the assumption of the complexity of water adsorption mechanism. However, further investigations are necessary in order to verify these models, for example, basing on the measurements of the enthalpy of adsorption.

A more complex problem considered by QM is the interaction of water with a graphite-like surface containing oxygenated hydrophilic groups. It is well-known that the adsorption is strongly dependent on the presence and arrangement of the hydrophilic groups. Tarasevich and Aksenenko [3] used the semiempirical PM3 method and studied the interaction of very few water molecules with a partially oxidized graphite surface. The main conclusion of this work is that water molecules are adsorbed at the hydrophilic center (i.e. the carboxyl) with the formation of microclusters consisting (at initial coverages) of 2 to 3 molecules. In the light of these results, Tarasevich and Aksenenko [3] suggested that water adsorption measurements cannot be used to determine the number of active centers even at hydrophobic, and, far less, at hydrophilic surfaces, and methanol was recommended for this purpose.

Hamad and coworkers [17] reported a quantum chemical characterization of a hydrophilic site modeled by a carboxyl group attached to one of the carbon atoms in the graphite layer. They supply values of point charges at the $-\text{COOH}$ sites that have been used to derive a pair potential for the water-active site interaction. Picaud et al. [18] presented molecular dynamics simulations based on a classical potential issued from QM calculations [17] to provide a view of the dynamics and the structure of a water adlayer on the model soot surface that consists of a planar graphitic layer plus different numbers of active carboxylic sites. The results of these simulations show that the $-\text{COOH}$ groups act as strong trapping sites for a few water molecules that then become nucleation centers for other water molecules that form larger aggregates tied to the $-\text{COOH}$.

It should be pointed out that one of the most spectacular methods to investigate the mechanism of water adsorption on activated or non-activated carbonaceous adsorbents is the calorimetry [21-36]. Careful measurements of the energetic effects accompanying water adsorption processes on carbon blacks and carbons were studied [21,24,25,28,29,31-36], especially, by scientists from the so-called "Russian school of adsorption" in the fifties [21,31] and the eighties [24-26,32,33]. Heats of adsorption of water indicate that adsorption is a strong function of surface chemistry. The primary high-energy sites have a significant influence on adsorption and the enthalpy of this process at low relative pressures (i.e. for low values of adsorption). A basic understanding of the mechanism of water adsorption on the carbonaceous adsorbents is far behind; in part because the study of interfaces requires extremely careful experimentation if meaningful

and reproducible results are to be obtained. Three components can be delineated according to measured differential heats of adsorption: (i) chemical adsorption, (ii) physical adsorption, and (iii) condensation and/or micropore filling. From the point of view of the thermodynamic verification of the theoretical models the first case is the most interested and important. Chemisorption of water on carbon surfaces has been previously reported [23,25-29,37,38]. In summary, the analysis of the experimental data points out that significant discrepancies exist between the role of specific surface groups (e.g. various type, location, density) and their energy of interaction with water molecules and a quantitative description of the isotherm over the entire relative pressure range that is universal for all carbons with low, medium, and high densities of surface groups.

On the basis of the mentioned above ideas it is seen that the mechanism of adsorption of water in porous carbonaceous solids is significantly different from that of simple, non-associating fluids, such as nitrogen, carbon dioxide, and hydrocarbons. The main underlying differences are caused by the strong water-water interactions, the weak water-carbon ones, and the formation of hydrogen bonds with oxygenated groups on the carbon surface. Although there have been numerous experimental and theoretical studies of water adsorption on carbonaceous adsorbents, the scientific community lacks consensus over the adsorption mechanism and the shape of the resulting isotherms. There is general agreement that adsorption occurs initially (at low relative pressures) via the formation of 3-D water clusters which is then followed by micropore filling behavior at high relative pressures. However, significant discrepancies exist in the details of pore filling and the role of the surface site type (primary ones, especially). Several predictive models have been proposed (the most important theories are discussed in the monographs [2,23,39]). Unfortunately, they do not describe the isotherms and corresponding differential heat of adsorption over the whole water relative pressure range.

3. (AF) - WATER ADSORPTION ISOTHERM EQUATIONS

The Dubinin and Serpinsky (DS) approach [21,40-42], leading to the explanation of the mechanism of water adsorption on carbonaceous materials, is still very attractive and often improved [22,23,37,43-46]. Although the fundamental assumptions of the resulting model were introduced fifty years ago it is still widely applied due to simplicity and giving reliable results [47]. In the mid-1950s Dubinin et al. [21,40,41] introduced a phenomenological model of adsorption of water molecules on energy privileged sites acting as primary adsorption centres for water on predominantly hydrophobic carbon surface. On the other hand, water molecules adsorbed on these sites create some new centres (called elsewhere the secondary ones) for adsorption of the subsequent

molecules via the cluster formation. The original DS1 equation can be written as [21,40,41]:

$$a = c_{DS1} (a_{0,DS1} + a) k_{DS1} h \quad (1)$$

where $a_{0,DS1}$ is the surface concentration of the energy privileged hydrophilic adsorption centers, h is water relative pressure ($= p/p_s$, where p and p_s are equilibrium and saturated vapour pressure, respectively), c_{DS1} is the ratio of the rate constants describing the kinetics of adsorption and desorption ($= k_{ads}/k_{des}$). On the other hand, k_{DS1} represents the loss of the secondary sites in the course of adsorption and thus the value of this constant affects the maximal adsorption capacity. In the original DS1 equation it is equal to unity, and it is treated as a part of the constant c_{DS1} (in other words, this parameter is always omitted in Eq. (1)). It should be noted that k_{DS1} is introduced in order to compare the decrease in the number of adsorption centers postulated by this simple model and by other models inspired by the Dubinin and Serpinsky concept (see Eqs. (2)-(4) and the legend in Figure 1). It is well known that Eq. (1) describes well only the data measured on non-porous adsorbents and on strongly hydrophobic carbons [21-24,39,45,48]. Therefore, the main disadvantage of this simple model is the assumption of unlimited adsorption space (or the lack of saturation of secondary adsorption centers). The applicability of the DS1 model is limited to the hyperbolic behavior of the adsorption isotherms (i.e. the water adsorption generated on the basis of Eq. (1) leads to infinity if the reduce pressure tends to $(1/c_{DS1})$).

So the original DS concept was improved by Dubinin et al. [41], and by Barton and co-workers [43,44]. The initial stages of water adsorption mechanism on carbonaceous solids are similar as assumed in the original DS1 equation (i.e. water molecules are initially strongly adsorbed via hydrogen bonding on surface sites considered as specific or active groups). However, further adsorption causes the creation of water clusters at larger relative pressures and this process decreases the number of secondary adsorption sites. Thus, Dubinin et al. [41,25,49] proposed the following equation:

$$a = c_{DS2} (a_{0,DS2} + a) (1 - k_{DS2} a) h \quad (2)$$

which is frequently called the DS2 adsorption equation. Moreover, Barton and co-workers [43] published an alternative modification of the DS1 isotherm. Resulting Barton's isotherm (B1) can be written as:

$$a = c_{B1} (a_{0,B1} + a) (1 - k_{B1} a^2) h \tag{3}$$

In the both equations the finiteness of the adsorption space is taken into account by the terms: $(1 - k_{DS2} a)$ and $(1 - k_{B1} a^2)$. It should be pointed out that these both terms take into account the decrease in the number of adsorption sites with increasing adsorption. Unfortunately, Eqs (2) and (3) do not describe satisfactorily the final parts of water adsorption isotherms measured for strictly microporous carbons [43]. Therefore, Barton et al. [44] postulated similar relationship introducing the term $(1 - \exp[-k_{B2}^2 (a - a_{c,B2})^2])$ and proposing the following adsorption equation (B2):

$$a = c_{B2} (a_{0,B2} + a) \left(1 - \exp \left[-k_{B2}^2 (a - a_{c,B2})^2 \right] \right) h \tag{4}$$

The values of the constant k (i.e. k_{DS2} - Eq. (2), k_{B1} - Eq. (3), and k_{B2} - Eq. (4), respectively) are calculated from the condition $a = a_s$ (where a_s is the maximum adsorption) if $h = 1$ [25,40,43,45,49].

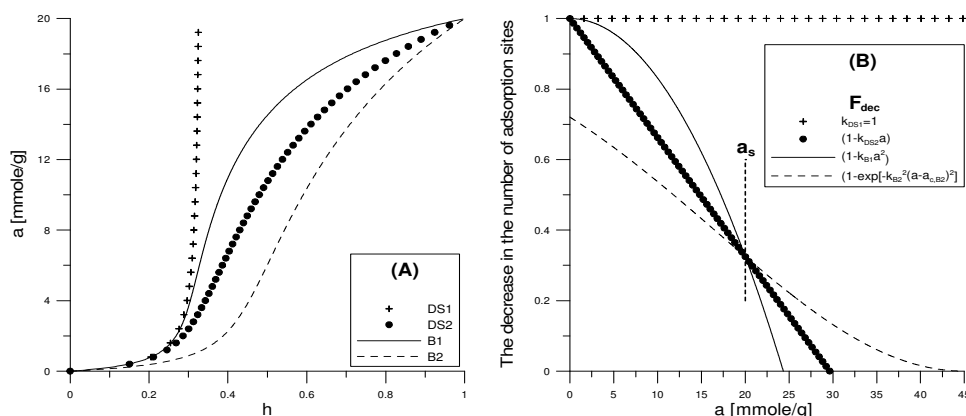


Fig. 1. (A) Generated numerically water adsorption isotherms and (B) the functions describing the decrease in the number of adsorption sites generated based on DS-like equations (Eqs. (1)-(4)). The parameters used in calculations: $c=3$; $a_0=0.5$ mmole/g; $a_s=20$ mmole/g; $a_c=45$ mmole/g. Additionally, in Figure 1B the hypothetical values of adsorbed amount greater than the maximum adsorption (a_s) are presented (they are limited by the vertical dashed line).

In the opinion of Barton and co-workers [44], the parameters k_{B2} and $a_{c,B2}$ serve to trigger the start of the decline in adsorptive power, and k_{B2} , as before (i.e. k_{B1} - Eq. (3)), governs the rate of this decline with increasing adsorption.

Obviously, both these parameters are associated with the Gaussian-like distribution of the adsorption sites or pore sizes of the carbon substrate. Barton et al. [44] observed that the values of $a_{c,B2}$ are all larger than those of $a_{s,B2}$. They also stated that it is difficult to assign a physical meaning to $a_{c,B2}$.

Therefore, in order to explain some of the doubts surrounding the interpretation of this parameter, water adsorption isotherms were generated on the basis of the original DS isotherm (Eq. (1)), and on the basis of the (presented above) three improvements of this equation (Eqs. (2)-(4)). The results are compared in Figure 1A. The values of the parameters are similar to those calculated from the fitting of Eqs. (1)-(4) to experimental data [22,43,44,23]. From Figure 1A it is seen that the DS1 equation (unlike the others) predicts infinite adsorption when h tends to $(1/c_{DS1})$. This result can be easily explained in view of the fact that the concentration of the secondary sites is constant during adsorption (i.e. $k_{DS1}=1$; Figure 1B). On the other hand, considering the improvements of the original DS1 model reported so far, one can generate the finite values of the adsorbed quantity (equal or very close to a_s) for relative pressures tending to unity, as a result of the gradual saturation of the secondary adsorption centers. Summing up, Eqs. (2)-(4) introduce the empirical factor $F(a,h)_{dec}$ (see legend to Fig. 1B), which describes the decrease in the concentration of adsorption sites. Additionally, Figure 1B shows hypothetical adsorbed quantities greater than the maximum adsorption (i.e. $a_s=20$ mmole/g). Analyzing the results shown in this figure, one can see that $a_{c,B2}$ is strictly linked to the decrease in the concentration of the secondary adsorption centers (the Gaussian-like shape). For adsorption equal to $a_{c,B2}$, $F(a,h)_{dec}$ is equal to zero. In other words, for $a=a_{c,B2}$ all active sites are saturated. In the original Gaussian function this parameter is the average value of a . For $a_{c,B2}>a_s$ we consider only the decreasing part of $F(a,h)_{dec}$ (the half of Gaussian-like function is considered). In the opposite case $F(a,h)_{dec}$ decreases to $a_{c,B2}$ and next increases tending to a_s (for $h=1$ the values of adsorption are smaller than a_s). In other words, from the analysis of the experimental data [44,50] it can also be noticed that the pore filling of the available adsorption space for water molecules occurs prior to the measurement of $a_{c,B2}$ (i.e. it is greater than $a_{s,B2}$). Therefore, this parameter represents the total (hypothetical) number of adsorbed water molecules (equal to or greater than $a_{s,B2}$) needed to saturate all possible secondary and primary adsorption centers [50] for the ideal arrangement (packing) of water molecules in the finite adsorption space.

Now we consider the less satisfactory aspects of the DS-like equations (Eqs. (1)-(4)). They do not treat molecules adsorbed directly on the primary centers as being different from the other adsorbed molecules, neither with regard to their

adsorption nor desorption (i.e. the DS-like models treat all molecules in the adsorbed phase as being of the same type). However, it is obvious that the nature of the primary sites will exert some influence on the adsorption of at least those molecules directly adsorbed on them. They do not consider the interactions between primary centers explicitly. In particular, they do not take into account the possibility that two or more adsorption centers can be situated very close on surface, for example as a part of a dibasic acid group. Although the functions describing the loss of adsorption sites in the course of adsorption are admirably concise, it should not be expected that a factor so simple could adequately treat all possible situations that could arise during water adsorption [42,46,50].

On the other hand, it is well known that the simplest method leading to the increase of the affinity of carbon surface for water vapor is, for example, the oxidation of this surface. In such a case, more hydrophilic surface chemical composition leads to the rise in adsorption, especially in the initial range of water isotherm (the increase in the value of enthalpy of adsorption and immersion is observed simultaneously [22,23,24,25,26,27,28,29,38]). Unfortunately, Eqs (1)-(4) are insufficient for description of water sorption on these hydrophilic surfaces [23,26,37,50]. It should be pointed out that the methods of the improvement of the DS-like models were recently proposed by Gauden and Terzyk [46,50] in order to experimental verification of water adsorption isotherms measured on strongly oxidized adsorbents. For water adsorbed on oxidized surfaces D'Arcy and Watt (DW) adsorption isotherm must be taken into account [51]. In the original DW model it is assumed that sorption of water takes place independently on strongly (high-energy) binding primary sites (which are the hydrophilic groups) and to a less extent on weakly (low-energy) binding primary sites (which are located elsewhere on the carbon surface). Moreover, the term describing multilayer adsorption on the so-called secondary centers (which need not be completely occupied before the monolayer formation) is assumed. However, it is simplified that there is only one type of secondary sites on which, for the adsorbate water, two- or three-dimensional hydrogen-bonded clusters can begin to build up even before all the primary sites are occupied. Summing up, in the considerations published by D'Arcy and Watt [51] the theoretical equation is composed of:

- (i) one or more Langmuir isotherms describing adsorption on high-energy sites
- (ii) a linear Henry's isotherm describing adsorption on low-energy sites,
- (ii) a component isotherm which accounts only for secondary adsorption.

$$a = \frac{a_{mL} K_L h}{\frac{1}{P_s} + K_L h} + K_H h + \frac{c_{DSI} a_{0,DSI} h}{1 - c_{DSI} h} \quad (5)$$

where a_{mL} is the total surface concentration of all Langmuir-type sites and K_L and K_H is the Langmuir and Henry's constants, respectively.

As shown by Evans [52,53], and many other authors [22,23,39,54,55] the DW model satisfactorily describes water adsorption data on various adsorbents (not only on carbonaceous). The simplest and most popular form of the original DW equation (Eq. (5)) is the sum of Langmuir (the adsorption on primary sites) and DS1 isotherms (describing the adsorption on secondary sites available for water molecules):

$$a = a_{prim} + a_{sec} = \frac{a_{mL} K_L h}{\frac{1}{P_s} + K_L h} + \frac{c_{DSI} a_{0,DSI} h}{1 - c_{DSI} h} \quad (6)$$

It should be pointed out that in the opinion of Barton and co-workers [53] it appears that the DW isotherm contains some inconsistencies. A serious flaw in this simple treatment is the implication that all the primary chemisorbed water molecules are not available to act as secondary centers for the adsorption of the subsequent water molecules. This is obvious since the DW equation reduces to the DS1 or to Langmuir ones only if a_{mL} or $a_{0,DSI}$ are equal to zero. Summing up, Langmuir and DS1 relationships describe independently adsorption of water molecules (i.e. this mechanism is connected with various centers).

3.1. The generalization of the D'Arcy and Watt (GDW) equation

It is well known that the difference in the shape of water isotherms is caused by the combined effects of carbon hydrophobicity (the low-energy centers) and the presence of different surface functional groups on carbon surface i.e. hydrophilicity (the high-energy centers). Water is known to have extremely low affinity toward the 'pure' graphite surface and high affinity toward polar sites causing chemisorption of some molecules on surface groups. Subsequently, those adsorbed molecules on primary sites (the both mentioned above types of centers should be considered) can become secondary ones and adsorption on them occurs following the original Dubinin - Serpinsky mechanism. Thus, the total adsorption is the sum of the adsorption on all, available for water molecules, primary (a_{prim}) and secondary sites (a_{sec}):

$$a = a_{\text{prim}} + a_{\text{sec}} \quad (7)$$

On the other hand, using the kinetic approach – at the equilibrium the rate of adsorption is equal to the rate of desorption. Thus, one can write:

$$a_{\text{sec}} = c_{\text{DSI}} (a_{0,\text{sec}} + a_{\text{sec}}) h = c_{\text{DSI}} (w a_{\text{prim}} + a_{\text{sec}}) h \quad (8)$$

where $a_{0,\text{sec}}$ is the total concentration of the secondary adsorption sites (a more general meaning of this parameter is given below). The meaning of other parameters (without w) is the same as in Eq (1). Ideally, all of the primary adsorbed water molecules should be available for multilayer formation, but mechanical constraints to swelling, and steric effects may prevent perfectly multilayer creation. Barton and co-workers [53] showed, analyzing the experimental data (water adsorption isotherm measured on oxidized nonporous carbon and described via the DW equation - Eq (6)) that only about 17% of the primary sites can be transformed into the secondary sites. Thus, it is seen that only some water molecules adsorbed on high-energy centers can be consider as the centers for the next adsorbing molecules. On the other hand, Carrott [42] and Pierce and Smith [57] considered the possibility that each molecule of water forms up to three bonds (due to the structure of the water molecules). Similar results were reported by Terzyk et al. [22,23], Venkataramani et al. [54,57] and Tarasevich and Aksenenko [3]. Moreover, Tarasevich and Aksenko [3] suggested that the water molecules are adsorbed at the hydrophilic center (i.e., the carboxyl) with the formation of microclusters consisting (at initial coverages) of 2 to 3 molecules. One can observe that the amount of the sum of all secondary adsorption sites significantly predominates in comparison with the primary ones (for example it can be observed that sometimes this amount is greater than 700% of the high-energy centers [22,23]). Summing up, considering these results, we decide to take into account the additional best-fit parameter in Eq. (8), w . It determines the amount of primary centers involved in the formation of the secondary sites. It should be pointed out that the values of w can be lower than unity [53] or close to three [22,23,42, 54,56,57].

After simple manipulation applying Eqs (7) and (8) one obtains the adsorption isotherm equation in the ‘global’ form:

$$a = \frac{a_{\text{prim}} (1 - c_{\text{DSI}} (1 - w) h)}{1 - c_{\text{DSI}} h} \quad (9)$$

or in the 'hybrid' one:

$$a = a_{\text{prim}} + \frac{wa_{\text{prim}}c_{\text{DSI}}h}{1 - c_{\text{DSI}}h} \quad (10)$$

It is obvious that Eqs (9) and (10) are equivalent. Moreover, for the cases of the chemisorption process we can assume that water molecules adsorb on the high-energy sites (the current considerations are limited to only one type of the primary centers) obey the Langmuir (Lng) isotherm:

$$a_{\text{prim}} = \frac{a_{\text{mL}}K_L h}{\frac{1}{p_s} + K_L h} \quad (11)$$

Finally, Eqs (9) and (10) can be rewritten assuming the explicit function describing the water adsorption:

$$a = \frac{a_{\text{mL}}K_L h}{\frac{1}{p_s} + K_L h} \frac{(1 - c_{\text{DSI}}(1 - w)h)}{1 - c_{\text{DSI}}h} \quad (12)$$

and

$$a = \frac{a_{\text{mL}}K_L h}{\frac{1}{p_s} + K_L h} + \frac{wa_{\text{mL}}K_L h}{\frac{1}{p_s} + K_L h} \frac{c_{\text{DSI}}h}{1 - c_{\text{DSI}}h} \quad (13)$$

In the current studies the above discussed model (Eqs. (12) or (13)) will be called the GDW (generalized D'Arcy and Watt) one.

The prime requirement for a theory of adsorption is that an experimentally correct isotherm and enthalpy of adsorption is obtained. The temperature dependence of the parameters of Eqs. (6), (12), and (13) are given as the following classical thermodynamics:

$$K_L = K_{0L} \exp\left(-\frac{q_L}{RT}\right) \quad (14)$$

$$c_{DSI} = c_{0,DSI} \exp\left(-\frac{q_{0,DSI}}{RT}\right) \quad (15)$$

where R is the gas constant; K_{0L} , and $c_{0,DSI}$ are entropic factors (slightly dependent on temperature); q_L and $q_{0,DSI}$ are the energies of adsorption on the Lng and DS - like sites, respectively.

The differentiation of Eq (13) with respect to the temperature [37,58,59] leads to the 'pure' isosteric enthalpy of adsorption:

$$q^{st} - L_c = \frac{\frac{a_{mL}p_s K_L}{(1+p_s K_L h)^2} (q_L - L_c) + \frac{c_{DSI} h}{1-c_{DSI} h} \frac{w a_{mL} p_s K_L}{(1+p_s K_L h)^2} (q_L - L_c) + \frac{c_{DSI}}{(1-c_{DSI} h)^2} \frac{w a_{mL} p_s K_L h}{1+p_s K_L h} q_{0,DSI}}{\frac{a_{mL} p_s K_L}{(1+p_s K_L h)^2} + \frac{c_{DSI} h}{1-c_{DSI} h} \frac{w a_{mL} p_s K_L}{(1+p_s K_L h)^2} + \frac{c_{DSI}}{(1-c_{DSI} h)^2} \frac{w a_{mL} p_s K_L h}{1+p_s K_L h}} \quad (16)$$

where L_c is water condensation enthalpy. On the other hand, analyzing the original D'Arcy - Watt equation (Eq. (6)) the corresponding enthalpy of adsorption is derived based on the same procedure as for Eq (16):

$$q^{st} - L_c = \frac{\frac{a_{mL} p_s K_L}{(1+p_s K_L h)^2} (q_L - L_c) + \frac{c_{DSI}}{(1-c_{DSI} h)^2} a_{0,DSI} q_{0,DSI}}{\frac{a_{mL} p_s K_L}{(1+p_s K_L h)^2} + \frac{c_{DSI}}{(1-c_{DSI} h)^2} a_{0,DSI}} \quad (17)$$

The typical plots of adsorption isotherms, generated from the DW (Eq. (6)) and GDW (Eqs. (12) or (13)) equations are compared in Figs. 2 and 3. The initial parameters of the GDW are similar to those taken by us previously [45]. To check the influence of the number of secondary centers on the adsorption isotherm and the enthalpy shape, the values of the parameters are assumed as fixed (without w (Fig. 2) or K_L (Fig. 3), respectively). Next, adsorption isotherms generated from the GDW are described using the DW equation. Thus, $a_{0,DSI}$ is only evaluated in order to find the correlation between this parameter and the product of w and a_{mL} .

Additionally, related enthalpies of adsorption for the both models (Eqs. (16) and (17), respectively) are presented in Figures 2 and 3. Both figures show that the adsorption isotherm shapes as well as the enthalpy plots are similar to those determined using adsorption calorimetry measurements [22,23,38,60].

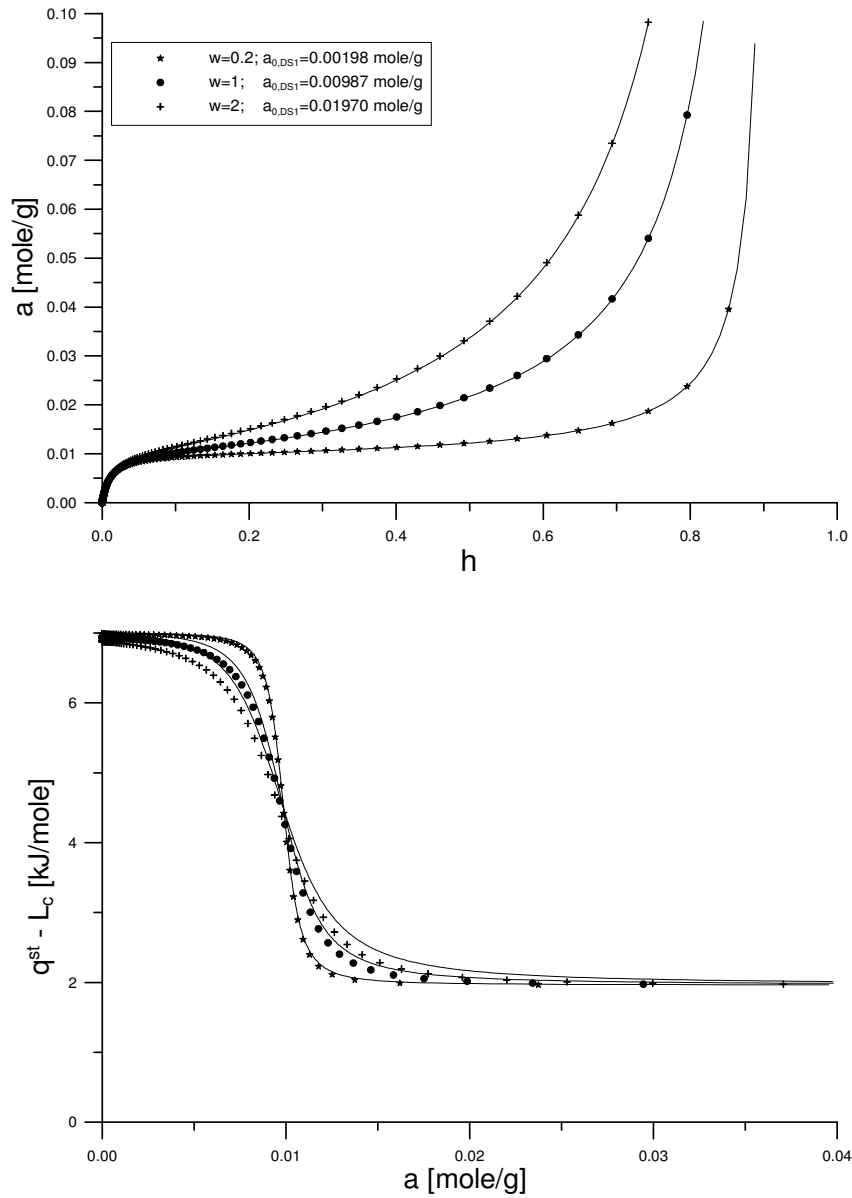


Fig. 2. Adsorption isotherms and corresponding enthalpy values, generated numerically on the basis of the generalized D'Arcy and Watt equation (Eq. (12), lines) for: $a_{mL} = 0.01$ mole/g, $K_L = 2.84$ 1/hPa, $q_L = 50.96$ kJ/mole, $c_{DSI} = 1.1$, $q_{0,DSI} = 1.96$ kJ/mole, $L_c = 43.96$ kJ/mole, $p_s = 31.672$ hPa. Additionally, for each system the results of fitting the DW equation (Eq. (6), lines) to generated numerically data are shown ($a_{0,DSI}$ is the only calculated parameter).

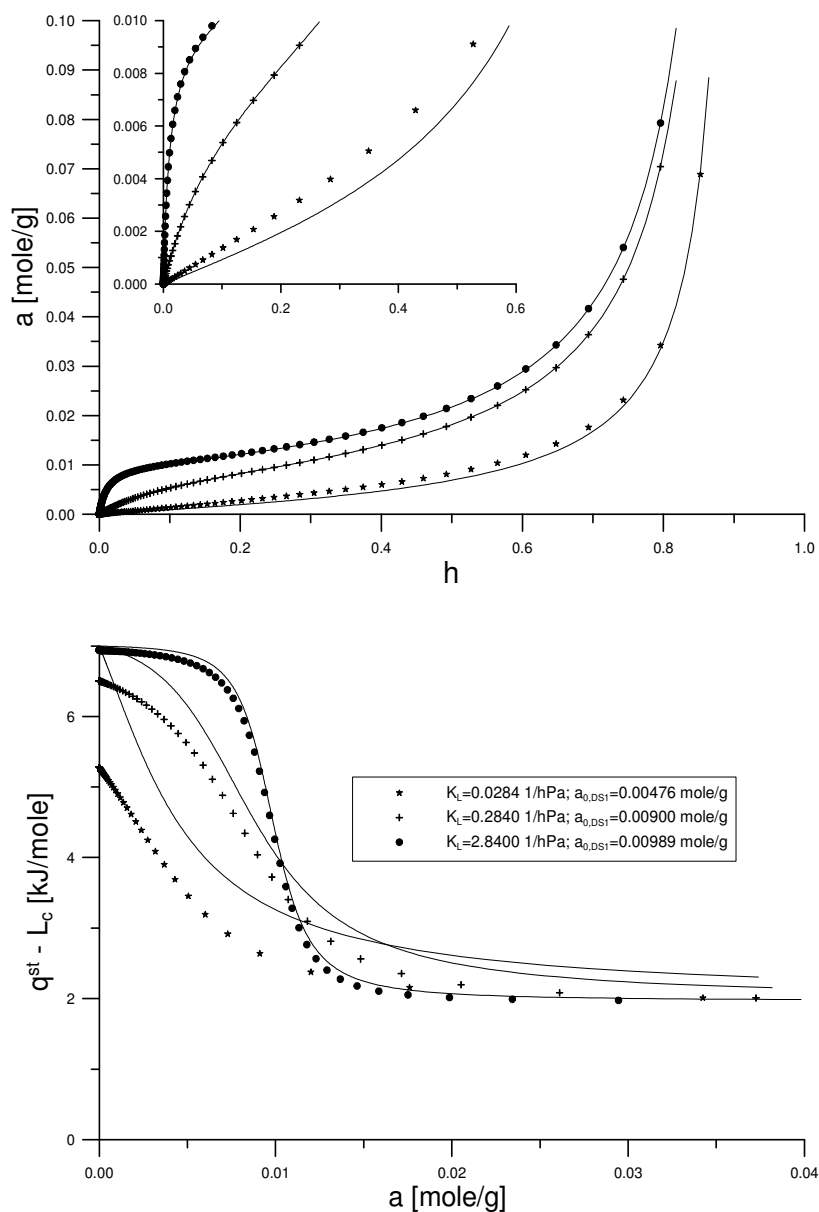


Fig. 3. Adsorption isotherms and corresponding enthalpy, values generated on the basis of the generalized D'Arcy and Watt equation (Eq. (12), lines) for: $a_{mL} = 0.01$ mole/g, $q_L = 50.96$ kJ/mole, $w = 1$, $c_{DSI} = 1.1$, $q_{0,DSI} = 1.96$ kJ/mole, $L_c = 43.96$ kJ/mole, $p_s = 31.672$ hPa. Additionally, for each system the results of fitting the DW equation (Eq. (6), lines) to generated numerically data are shown ($a_{0,DSI}$ is the only calculated parameter).

These results are not surprising since the superposition of the two theories assuming constant adsorption energetics leads to non-constant, depending on adsorption, enthalpy of adsorption. This behavior is typical for the so called “dual-site” models [59,61].

It is seen, from the analysis of data presented in Figure 2, that the increase in the value of the parameter determining the amount of primary centers involved in the formation of secondary sites (w) does not lead to the change of the shape of the generated isotherms (only the II BET type of IUPAC classification is observed). It can be noticed that for lower w the plateau region of the generated isotherm is more visible. The determination coefficients calculated from the comparison of the both types of adsorption isotherms are close to unity for all analyzed cases. On the other hand, the satisfactory fit occurring for the enthalpy equation developed from GDW and DW is observed (however, the insignificantly small differences between $(q^{st}-L_c)$ depend on the value of w).

The analysis of the influence of the Langmuir constant (K_L) on the generated adsorption isotherms and the enthalpy of adsorption is shown in Figure 3. The change of the shape of isotherm from II to III BET type is observed. Following that, the enthalpy plot changes from the typical observed for adsorption on oxidized and/or modified by an ionic-exchange method carbons, up to observed for adsorption of water on non-oxidized materials [22,23,38,60]. It can be noticed that almost the same plots of adsorption isotherms for the both models are achieved (the determination coefficients are close to unity). On the other hand, both Eqs. (6) and (13) predict different values of the enthalpy of adsorption over the whole range of adsorption amount. The greatest differences between started and fitted isotherms and $(q^{st}-L_c)$ are observed for low K_L values. It should be pointed out that the same values of heat of adsorption (close to q_L-L_c) at low coverages can be generated only basing on the GDW equation.

In order to explain the differences between $(q^{st}-L_c)$ shown in Figure 3, in spite of the similarities of the both types of adsorption isotherms (the same figure), the assumptions and properties of the original and the generalized D’Arcy and Watt equations should be analysed in details. Firstly, it should be pointed out that a_{prim} (GDW, Eq. (12)) changes gradually during the adsorption process. It can be treated as the temporary amount of occupied primary adsorption sites. Secondly, a_{prim} influences on the DS1 term of the GDW equation, and this term describes the formation of a multilayer on the primarily adsorbed monolayer. Thus, the amount of secondary adsorption centers is also a function of adsorption and/or relative pressure. Therefore, for w equal to zero (Eq. (12)) only the Langmuir type of theoretical adsorption isotherm is observed. Consequently, Eq. (16) simplifies to $q^{st}=q_L$ since the secondary adsorption sites are not created during the process of adsorption. Similar results can be obtained basing on Eqs (6) and (17) for $a_{0,DS1}=0$. On the other hand, the differences are observed for both types

of theoretical relationships if one assumes that the primary centers do not exist on the surface of the adsorbent, i.e. if one assumes that $a_{prim} = 0$. The opposite conclusions are drawn from the analysis of the original DW equation (Eq. (6)). In this model the parameter $a_{0,DSI}$ and a_{mL} are treated independently. Therefore, $a_{0,DSI}$ is not connected with the concentration of the primary adsorption centers (the significance of this behavior was discussed above in details).

On the other hand, it is easy to show (Figure 2 and 3) that Eqs. (6) and (12) (or Eq. (13)) can lead to almost the same results in the whole range of relative pressures. It is not surprising, especially taking into account, that the original DW equation can be converted into the GDW model. The maximum water capacity on the high-energy primary sites ($a_{prim,s}$) can be calculated from Eq. (11) by setting h equal to unity:

$$a_{prim,s} = \frac{a_{mL} K_L}{\frac{1}{p_s} + K_L} \quad (18)$$

Since primary adsorption centers (connected with the Lng model) are rapidly saturated at low water relative pressures it is reasonable to assume that the term a_{prim} (Eq. (12)) is constant, leading to the same form (i.e. $a_{0,DSI}$) as in Eq. (6). This statement is not true for all cases. The primary sites can become saturated at vapor pressure below the saturation vapor pressure when the affinity parameter K_L is larger. Thus, the Lng contribution should violently achieve the plateau. For smaller K_L values, the potential number of primary sites is only partially covered, below saturation vapor pressure and plateau region is not observed. These various cases are analyzed and presented in Figure 3.

Summing up, it is easy to formulate the new adsorption isotherm equation (Eq. (12)) from the simple kinetic or material balance relations describing primary and related secondary adsorptions. A serious advantage in this simple treatment is the implication that some primary adsorbed water molecules are available to act as secondary sites for the adsorption of subsequent water molecules and better prediction of the experimental enthalpy of adsorption data. Furthermore, it can be concluded that $a_{0,DSI}$ in the original DW model (Eq. (6)) gives information about the total amount of the primary adsorption sites (occupied and/or unoccupied). So, this parameter is independent from the relative pressure and/or adsorption amount. Moreover, $a_{0,DSI}$ is close to the amount of primary sites calculated from the Lng equation for the value of relative pressure equal to unity (the original and generalized DW models are compared). This case is only observed if the value of K_L is sufficiently high (the Lng relationship simplifies to the Henry's one for low values of K_L). Thus, the

available sites for water molecules are not completely saturated. Moreover, it can be pointed out that it is possible to present the generalized DW relationship (similar to the original one) as ‘no hybrid’ (‘no sum’) adsorption equation in contrast to the original one.

3.2. Langmuir-type adsorption on n-types of the primary sites (the multi-site generalized D’Arcy and Watt, MSGDW)

Some IR [62], calorimetry [21-24,26-36] as well as computer simulation [4-13] findings show that water molecules adsorbed at the beginning of the adsorption isotherm are very strongly bonded, even chemisorbed. On the other hand, it is well known that for the cases of chemisorption we can assume that water molecules adsorbed on all types of high-energy primary sites obey the Langmuir isotherm equation in the following form [51,53]:

$$a_{\text{prim}} = \sum_{i=1}^n \frac{a_{mL,i} K_{L,i} h}{\frac{1}{P_s} + K_{L,i} h} \quad (19)$$

The above equation represents the sum of independent, Langmuir-type adsorptions on n-types of the primary sites. The postulated model considers the adsorbent as a material which has the regions of heterogeneity at the molecular level (i.e. multi-site centers). It is well-known that the range of the interaction energy (affinity) between the surface sites (the functional groups) and water molecules is relatively wide. Thus for the purpose of taking the interactions with different groups into account it is important to assume the discrete distribution of the energetic heterogeneity. The differences in the shapes of measured experimentally isotherms are the result of the combined effects of carbon hydrophobicity and the presence of different surface functional groups acting as the primary adsorption centers. However, it is likely that the nature of the primary sites will exert some influence on the adsorption of at least those molecules directly adsorbed on them. For example, the energy of interaction is likely to be greater on acidic sites, interacting with the lone pairs on the oxygen atoms of water molecules, than with basic sites, which may prefer to interact with the hydrogen atoms. Thus, the approach developed in the current study involves the possibility of the existence of high-, medium- and low-energy sites (the interaction energy are significantly different in order to treat all centers independently) acting as the primary adsorption sites for water on predominantly hydrophobic carbon surface. In this mechanism it is probable that the additional sites on the carbon surface are induced by the adsorbed molecules (primary stage) promoting the entry of other molecules to adjacent sites. Summing up, the

sites existing on the surface of the adsorbent have different affinity for the adsorbate and involve a characteristic heat evolution when sorption occurs. Hence, the overall sorption process can be regarded as a number of constituent processes occurring on series homogenous substrates.

The GDW model (i.e. Eqs. (12) or (13)) postulated in the previous section differs remarkably from the original model proposed by D'Arcy and Watt (Eq. (6)) since it permits the existence of the relationship between primary and secondary adsorption processes. Both processes are simultaneously and continuously contributing to the overall adsorption in the whole vapor pressure range. Thus we can rewrite Eqs. (12) and (13) however, assuming in this case the explicit function describing water adsorption on the primary sites (i.e. the primary multi-site Langmuir model (Eq. (19)):

$$a = \sum_{i=1}^n \frac{a_{mL,i} K_{L,i} h}{1 + K_{L,i} h} + \frac{c_{DSI} h}{1 - c_{DSI} h} \sum_{i=1}^n \frac{w_i a_{mL,i} K_{L,i} h}{1 + K_{L,i} h} \quad (20)$$

where the temperature dependences of the parameters are given by Eqs. (14) and (15), respectively. Eq. (20) will be called MSGDW (the multi-site generalized D'Arcy and Watt). It can be noticed that the second term in the given above relationship is related to the concentration of the secondary adsorption sites ($a_{0,sec}$) equal to the sum of the multiplication of i -th Lng equation and w_i .

The differentiation of Eq. (20) with respect to T leads to the isosteric enthalpy of adsorption:

$$q^{st} - L_c = \frac{\sum_{i=1}^n \frac{a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} (q_{L,i} - L_c) + \frac{c_{DSI} h}{1 - c_{DSI} h} \sum_{i=1}^n \frac{w_i a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} (q_{L,i} - L_c) + \frac{c_{DSI}}{(1 - c_{DSI} h)^2} \sum_{i=1}^n \frac{w_i a_{mL,i} p_s K_{L,i} h}{1 + p_s K_{L,i} h} q_{0,DSI}}{\sum_{i=1}^n \frac{a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} + \frac{c_{DSI} h}{1 - c_{DSI} h} \sum_{i=1}^n \frac{w_i a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} + \frac{c_{DSI}}{(1 - c_{DSI} h)^2} \sum_{i=1}^n \frac{w_i a_{mL,i} p_s K_{L,i} h}{1 + p_s K_{L,i} h}} \quad (21)$$

It is easy to show that Eq. (21) simplifies to Eq. (16) if one assumes one kind of the surface centers (i.e. for the case $n=1$).

The exemplary plots of water adsorption isotherm (generated on the basis of Eq. (20)) and the corresponding enthalpy of adsorption (Eq. (21)) are shown in Figure 4. The considerations are limited to the study of the influence of q_L (the interaction energy between the surface sites and water molecules) on the isosteric heat of adsorption ($q^{st} - L_c$). From the analysis of the generated isotherms as well as the enthalpy plots it is seen that the generated curves are similar to those measured using adsorption calorimetry, and published elsewhere [22,23,25,32-34,60].

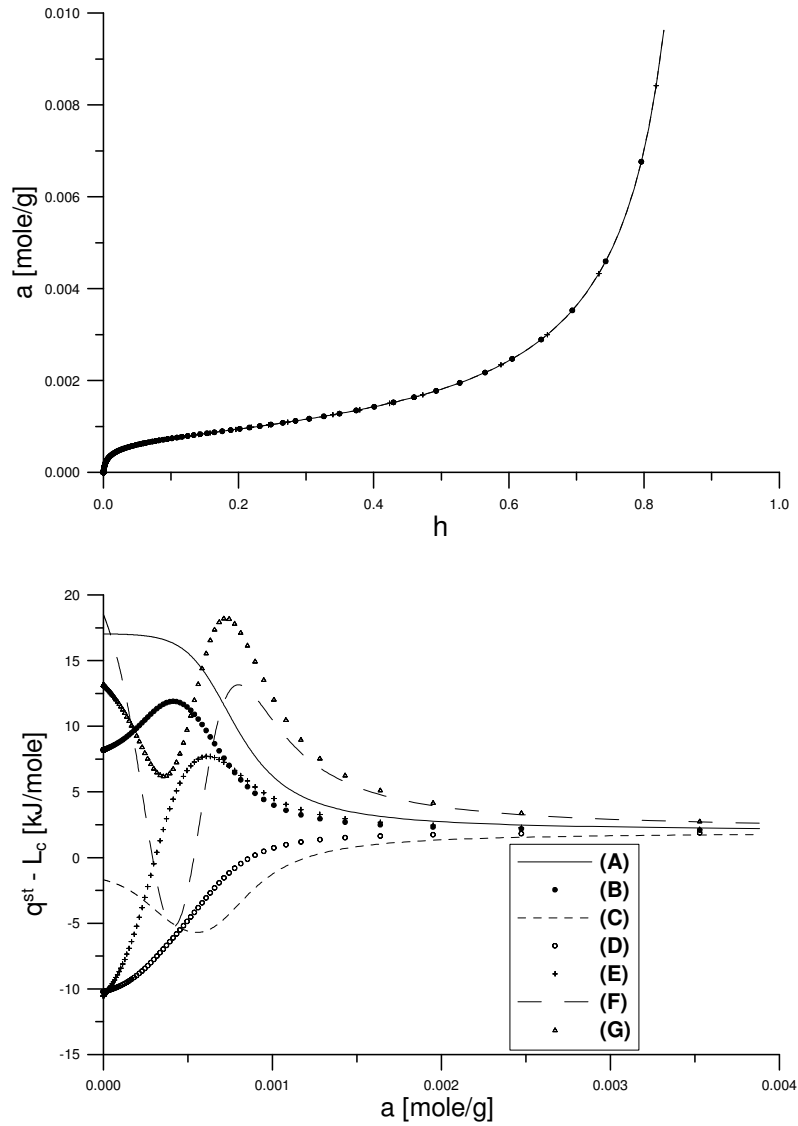


Fig. 4. Adsorption isotherms and corresponding enthalpy values generated on the basis of the multisite generalized D'Arcy and Watt equation, Eqs. (20) and (21), respectively (three types of primary sites are assumed); $c_{DS1} = 1.1$; $q_{0,DS1} = 1.96$ kJ/mole; $L_c = 43.96$ kJ/mole; $p_s = 31.672$ hPa; $T = 298.15$ K; $a_{mLi} = 0.0003$ mole/g, $w_i = 1$; $K_{L,1} = 11.6$ 1/hPa; $K_{L,2} = 1.54$ 1/hPa; $K_{L,3} = 0.205$ 1/hPa; (A) $q_{L,i} = 61$ kJ/mole; (B) $q_{L,1} = q_{L,2} = 51$ kJ/mole; $q_{L,2} = 56$ kJ/mole (C) $q_{L,1} = 43$ kJ/mole; $q_{L,2} = 38$ kJ/mole; $q_{L,3} = 33$ kJ/mole; (D) $q_{L,1} = 33$ kJ/mole; $q_{L,2} = 38$ kJ/mole; $q_{L,3} = 43$ kJ/mole; (E) $q_{L,1} = 30$ kJ/mole; $q_{L,2} = q_{L,3} = 56$ kJ/mole; (F) $q_{L,1} = 70$ kJ/mole; $q_{L,2} = 1$ kJ/mole; $q_{L,3} = 100$ kJ/mole; (G) $q_{L,1} = 60$ kJ/mole; $q_{L,2} = 30$ kJ/mole; $q_{L,3} = 100$ kJ/mole.

Moreover, from the results presented in this figure it is seen that the similar isotherm adsorption data give significantly different values of enthalpy of adsorption (increasing (A), decreasing (D) or mixed (B,C,E-G)). On the other hand, the main disadvantage of the MSGDW model is its limited applicability to the description of the experimental data in higher ranges of the relative pressures (i.e. similarly to the original and generalized D'Arcy and Watt equations (Eqs. (6) and (12)). Thus, the finite available adsorption space should be taken into account. As a consequence further development of the D'Arcy - Watt and Dubinin – Serpinsky theories is necessary and it will be discussed in next sections.

3.3. The generalization of the Barton adsorption isotherm equation (GB1)

As was discussed above the main disadvantage of Eqs (1), (6), (12) and/or (13) is the applicability only for the low range of water adsorption isotherms. Dubinin, Serpinsky and others tried to eliminate this disadvantage and these authors proposed to introduce the correcting terms taking into account the finite space available for water molecules (see Eqs (2)-(4) and Fig. 1). Unfortunately, these relationships do not describe satisfactorily the middle (i.e. the sudden upward rise in adsorption) and the final (i.e. the plateau region) ranges of water adsorption isotherms measured for strictly microporous carbons [22,23,43-45]. Thus, we propose in the current study the generalization of the terms proposed by Dubinin and Serpinsky (Eq. (2)) as well as by Barton and co-workers (Eq. (3)) to the following general form: $(1-k_{GB1}a^n)$. This improvement leads to the adsorption isotherm equation (called GB1):

$$a = c_{GB1} (a_{0,GB1} + a) (1 - k_{GB1} a^n) h \quad (22)$$

As in the case of the DS2, B1, and B2 equation it can be shown that k_{GB1} is related to the maximum adsorption (i.e. $h=1$):

$$k_{GB1} = \frac{c_{GB1} (a_{0,GB1} + a_{s,GB1}) - a_{s,GB1}}{c_{GB1} a_{s,GB1}^n (a_{0,GB1} + a_{s,GB1})} \quad (23)$$

It should be pointed out that Eq (22) can be simplified to the following expressions: DS1 (Eq (1); $k_{GB1} = 0$), DS2 (Eq (2); $n = 1$), or B1 (Eq (3); $n = 2$). Thus, the adsorption isotherms presented in Figure 5 show that if one takes into consideration the increase in the value of exponent n , the change of their shape is observed. Consequently, the plateau region and the upward rise are more and more visible.

As previously [22,23,37,45,63], one can assume (in order to derive $(q^{st}-L_c)$) that for microporous adsorbents the value of maximum adsorption of water changes with the temperature as:

$$a_{s,GB1} = a_{s,GB1}^0 \exp[-\alpha(T-T_0)] \quad (24)$$

where: $a_{s,GB1}^0$ and $a_{s,GB1}$ are the values of maximum adsorption at temperatures T_0 and T , respectively, and α is the water thermal expansion coefficient.

Finally, the equation defining the isosteric adsorption enthalpy can be derived from Eq. (22) assuming the temperature dependence of parameters (Eqs. (15) and (24)):

$$q^{st} - L_c = q_{0,GB1} + \Psi \frac{a^n}{k_{GB1} a^n - 1} \quad (25)$$

where

$$\Psi = \alpha RT^2 \left(\frac{n}{a_{s,GB1}^n} - \frac{(n-1)a_{0,GB1}}{c_{GB1} a_{s,GB1}^{n-1} (a_{0,GB1} + a_{s,GB1})^2} - \frac{na_{s,GB1}^{2-n}}{c_{GB1} (a_{0,GB1} + a_{s,GB1})^2} \right) + \frac{q_{0,GB1}}{c_{GB1} a_{s,GB1}^{n-1} (a_{0,GB1} + a_{s,GB1})} \quad (26)$$

If one considers the temperature dependence of maximum adsorption (while deriving the equation describing the enthalpy of adsorption) the obtained plots of enthalpy are convex and decreases. The constant $(q^{st}-L_c)$ close to zero is calculated only for $n = 0$. On the other hand, the similar behavior of the isosteric enthalpy curves is noticed for n tending to infinity ($(q^{st}-L_c)=q_{0,GB1}$). Therefore, the mathematical analysis of Eq. (25) with Eq. (26) leads to the conclusion about the differences between data generated by the GB1 equation and those reported on the basis of experimental measurements. Summing up, this simple modification of the original DS2 and/or B1 equation is unsatisfactory from the point of view of the further thermodynamic verification via the experimental data. In the other words, the description of adsorption data should be probably better in comparison with the differential heat of adsorption. On the other hand, similar plots of $(q^{st}-L_c)$ are observed for other models (Eqs. (1)-(4)) derived on the basis of the assumption of the Dubinin and Serpinsky theory.

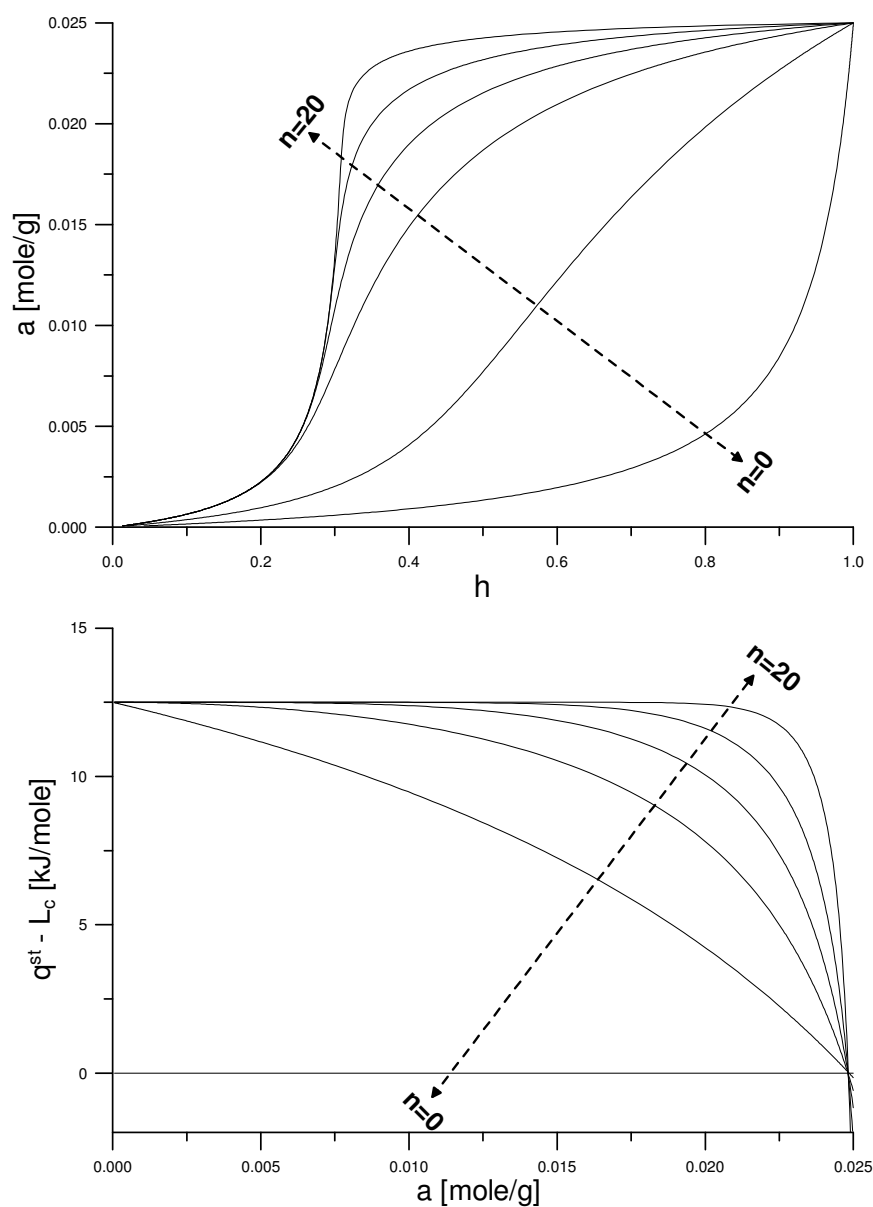


Fig. 5. Adsorption isotherms and corresponding enthalpy values, generated on the basis of the generalized Barton equation (Eqs. (22) and (25), respectively) for: $a_{0,GBI} = 0.0015$ mole/g; $a_{s,GBI} = 0.025$ mole/g; $c_{GBI} = 3$; $q_{0,GBI} = 12.5$ kJ/mole, $L_c = 43.96$ kJ/mole, $T = 298.15$ K; $\alpha = 18 \cdot 10^{-5}$ K⁻¹, and n equal to 0, 1, 2, 4, 8, or 20, respectively.

3.4. The multi-site generalized D'Arcy and Watt with the generalized Barton equation, MSDWGB – the limiting available adsorption space

As was mentioned in the previous part the generalized Barton model (Eq. (22)) gives unsatisfactory results from the thermodynamic analysis in spite of taking into account the correction term following the idea of Dubinin, Serpinsky and Barton et al. We take into account the adsorption process on i -th type of the primary (Eq. (19)) and one type of secondary centers (Eq. (22)). On the other hand, using the kinetic approach the following formula can be proposed for water adsorption on the secondary centers (see Eq. (7)):

$$a_{\text{sec}} = c_{\text{MSDWGB}} (a_{0,\text{sec}} + a_{\text{sec}}) (1 - k_{\text{MSDWGB}} a_{\text{sec}}^n) h \quad (27)$$

where the total concentration of the secondary centers is equal to

$$a_{0,\text{sec}} = \sum_{i=1}^n \frac{w_i a_{\text{mL},i} K_{\text{L},i} h}{\frac{1}{p_s} + K_{\text{L},i} h} \quad (28)$$

It should be pointed out that a_{sec} is a function of the concentration of the primary sites. Next, Eq. (27) can be rewritten taking into account Eq. (7) as follows:

$$a (\equiv a_{\text{prim}} + a_{\text{sec}}) = a_{\text{prim}} + c_{\text{MSDWGB}} (a_{0,\text{sec}} + a - a_{\text{prim}}) (1 - k_{\text{MSDWGB}} (a - a_{\text{prim}})^n) h \quad (29)$$

The parameter k_{MSDWGB} is connected with the finite pore volume:

$$k_{\text{MSDWGB}} = \frac{c_{\text{MSDWGB}} (a_{0,\text{sec},s} + a_s - a_{\text{prim},s}) - (a_s - a_{\text{prim},s})}{c_{\text{MSDWGB}} (a_s - a_{\text{prim},s})^n (a_{0,\text{sec},s} + a_s - a_{\text{prim},s})} \quad (30)$$

basing on the following assumptions:

$$h \rightarrow 1 \Rightarrow a \rightarrow a_s; \quad a_{\text{prim}} \rightarrow a_{\text{prim},s} = \sum_{i=1}^n \frac{a_{\text{mL},i} K_{\text{L},i}}{\frac{1}{p_s} + K_{\text{L},i}}; \quad a_{0,\text{sec}} \rightarrow a_{0,\text{sec},s} = \sum_{i=1}^n \frac{w_i a_{\text{mL},i} K_{\text{L},i}}{\frac{1}{p_s} + K_{\text{L},i}} \quad (31)$$

Assuming the temperature dependences of c_{MSDWGB} , $a_{0,\text{sec},s}$, $a_{\text{prim},s}$, and a_s and combining Eqs. (27) – (31) the isosteric enthalpy equation can be developed:

$$\begin{aligned}
q^{st} - L = & \frac{\sum_i \frac{a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} (q_{L,i} - L) + \frac{a - a_{prim}}{h} q_{0,MSDWGB} -}{\sum_i \frac{a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} + \frac{a - a_{prim}}{h} -} \\
& - c_{MSDWGB} \left(\sum_i \frac{(1 - w_i) a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} (q_{L,i} - L) \right) (1 - k_{MSDWGB} (a - a_{prim})^n) h + \\
& - c_{MSDWGB} \left(\sum_i \frac{(1 - w_i) a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i} h)^2} \right) (1 - k_{MSDWGB} (a - a_{prim})^n) h + \\
& + c_{MSDWGB} (a_{0,sec} + a - a_{prim}) \left(nk_{MSDWGB} (a - a_{prim})^{n-1} \sum_i \frac{a_{mL,i} p_s K_{L,i} h}{(1 + p_s K_{L,i} h)^2} (q_{L,i} - L) - B_{1,MSDWGB} (a - a_{prim})^n \right) \\
& + c_{MSDWGB} nk_{MSDWGB} (a_{0,sec} + a - a_{prim}) (a - a_{prim})^{n-1} \sum_i \frac{a_{mL,i} p_s K_{L,i} h}{(1 + p_s K_{L,i} h)^2}
\end{aligned} \tag{32}$$

where:

$$\begin{aligned}
B_{1,MSDWGB} = & \frac{n}{(a_s - a_{prim,s})^{n+1}} \left(RT^2 \alpha a_s + \sum_{i=1}^n \frac{w_i a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i})^2} (q_{L,i} - L_c) \right) + \\
& \frac{1}{c_{MSDWGB} (a_s - a_{prim,s})^n (a_s - a_{prim,s} + a_{0,sec,s})} \times \\
& \times \left[(a_s - a_{prim,s}) \left(\frac{RT^2 \alpha a_s + \sum_{i=1}^n \frac{(1 - w_i) a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i})^2} (q_{L,i} - L_c)}{(a_s - a_{prim,s} + a_{0,sec,s})} - q_{0,MSDWGB} \right) + (n - 1) \left(RT^2 \alpha a_s + \sum_{i=1}^n \frac{a_{mL,i} p_s K_{L,i}}{(1 + p_s K_{L,i})^2} (q_{L,i} - L_c) \right) \right]
\end{aligned} \tag{33}$$

The generation of the adsorption isotherm plots from Eq. (29) is possible applying the numerical procedure, although the equation describing the isosteric adsorption heat can be derived applying the analytical relationships (Eqs. (32) and (33)). The results are presented in Figure 6. The plots of adsorption isotherm and corresponding enthalpy are generated on the basis of the MSGDW (Eqs. (20) and (21), points, see Fig. 4) and MSDWGB (Eqs. (27)-(33), $n = 2$ (solid line) and $n = 20$ (dashed line)) models, respectively. Three types of primary sites and three sets of q_L (i.e. (A), (E), and (G) – see, Fig. 4) are considered. Moreover, for the MSDWGB equation the contribution of water amount adsorbed on the primary and secondary centers, to the total adsorption is taken into account. From the analysis of the adsorption data it is seen that the increase in the value of the parameter determining the amount of primary centers involved

in the formation of the secondary sites (w) leads to the change of the shape of the generated isotherms. However, the differences are observed only for higher values of the relative pressures. On the other hand, the langmuirian adsorption predominates in the low relative pressure region. It should be pointed out that parameters of the Lng equation ($p_s; a_{mL,i}, w_i, K_{L,1}, K_{L,2}, K_{L,3}$) are the same for the both models. Consequently, the insignificantly small influence of the value of w and of taking into account the assumption of limited adsorption space on ($q^{st}-L_c$) is observed (Fig. 6).

4. CONCLUSIONS

Several new models have been proposed on the basis of the Dubinin and Seprinsky approach. Unfortunately, none of them predicts satisfactorily the isotherms and the corresponding differential heat of adsorption over the whole pressure range, and further studies (as reported in this paper) are necessary. For example, it was shown previously that for typical microporous carbons the equations formulated previously by Dubinin and Serpinsky as well as by Barton et al. provide a good description of water adsorption isotherm data only for some water-activated carbon systems. In other words, satisfactory results are achieved only for carbons having low concentration of primary adsorption sites. It is well-known that the initial adsorption in carbon pores proceeds according to the mechanism described by the simple D'Arcy and Watt model. This means that for a correct description of water adsorption isotherm in this system, one has to take into account the partial chemisorption of water on sites with a very high energy of adsorption. Unfortunately, the original DW model does not describe the saturation region of experimental water adsorption isotherms. Moreover some fundamental aspects are not taken into account in theoretical considerations: i.e. the role of specific surface groups (e.g. various types, location, and density), their interaction with water molecules, and the structure of water confined in pores.

On the basis of the above considerations the following conclusions can be formulated. The concentration of "free" primary sites changes gradually during the adsorption process. Therefore, a_{prim} can be treated as the temporary amount of occupied primary adsorption sites. The amount of secondary adsorption centers is also a function of adsorption and/or relative pressure. On the other hand, some primary adsorbed water molecules are available to act as secondary sites for adsorption of second water molecules and better prediction of enthalpy of adsorption.

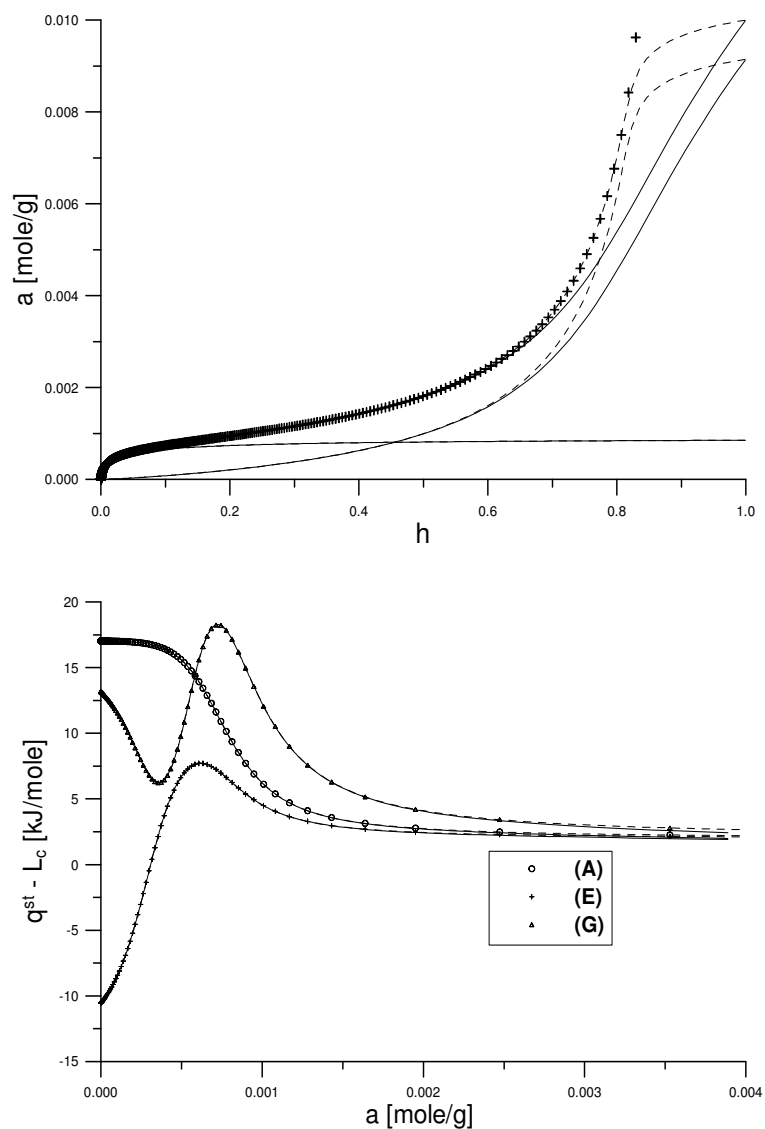


Fig. 6. Adsorption isotherms and corresponding enthalpy values generated on the basis of the MSGDW (Eqs. (20) and (21), points, see Figure 4) and MSDWGB (Eqs. (27)-(33), $n = 2$ (solid line) and $n = 20$ (dashed line)) models, respectively. Three types of primary sites are assumed. Moreover, for the MSDWGB model the contribution of adsorption on the primary and secondary centers to the total adsorption is taken into account. $c_{DSI} = 1.1$; $q_{0,DSI} = 1.96$ kJ/mole; $L_c = 43.96$ kJ/mole; $p_s = 31.672$ hPa; $T = 298.15$ K; $a_s = 0.01$ mole/g; $a_{mL,i} = 0.0003$ mole/g, $w_i = 1$; $K_{L,1} = 11.6$ 1/hPa; $K_{L,2} = 1.54$ 1/hPa; $K_{L,3} = 0.205$ 1/hPa; (A) $q_{L,1} = 61$ kJ/mole; (E) $q_{L,1} = 30$ kJ/mole; $q_{L,2} = q_{L,3} = 56$ kJ/mole; (G) $q_{L,1} = 60$ kJ/mole; $q_{L,2} = 30$ kJ/mole; $q_{L,3} = 100$ kJ/mole, $\alpha = 1.8 \cdot 10^{-4} \text{ K}^{-1}$.

Next, we assume that the surface of an adsorbent consists of regions of heterogeneity at the molecular level, and the multi-site generalized D'Arcy and Watt model is proposed. Finally we improve the Barton model and the original DW relationship, respectively. It can be noticed that for both cases we propose to take into account the finite adsorption space via the term $(1-k_{GB}a^n)$. Moreover, the chemisorption of water molecules on the various types of the primary high-energy adsorption sites is considered. For all presented new models we show the corresponding adsorption enthalpy equations. Summing up, the new adsorption isotherm equation (MSDWGB) should predict the plots of observed experimentally data (both adsorption and enthalpy) in the whole range of adsorption.

Since the basis of the DS-like or DW-like models is the existence of the primary adsorption sites, these equations are expected to fit experimental data for low relative pressures at least as well if not better than data for higher h . The validity of equating the value of a_0 with the quantity adsorbed at primary sites is therefore an open question. To solve this problem, the results of detailed investigations of water adsorption for a series of commercial active carbons, containing various surface groups will be reported and analyzed in the near future.

Acknowledgements. P.A.G. gratefully acknowledges the financial support from KBN Grant 4TO9A 077 24.

REFERENCES

- [1] W. Rudziński, W. A. Steele, G. Zgrablich, *Stud. Surf. Sci. Catal.* 104, 1 (1997)
- [2] J. K. Brennan, T. J. Bandosz, K. T. Thomson, K. E. Gubbins, *Colloids Surf. A* 187, 539 (2001)
- [3] Y. I. Tarasevich, E. V. Aksenenko, *Colloids Surf. A* 215, 285 (2003)
- [4] G. G. Malenkov, M. M. Dubinin, *Izv. AN SSSR* 6, 217 (1984) [in Russian]
- [5] A. V. Shevade, S. Y. Jiang, K. E. Gubbins, *J. Chem. Phys.* 113, 6933 (2000)
- [6] M. Jorge, C. Schumacher, N. A. Seaton, *Langmuir* 18, 9296 (2002)
- [7] E. V. Aksenenko, Y. U. Tarasevich, *Ads. Sci. Techn.* 14, 383 (1996)
- [8] J. K. Brennan, K. T. Thomson, K. E. Gubbins, *Langmuir* 18, 5438 (2002)
- [9] C. L. McCallum, T. J. Bandosz, S. C. McGrother, E. A. Muller, K. E. Gubbins, *Langmuir* 15, 533 (1999)
- [10] J. Galle, H. L. Vortler, *Surface Sci.* 481, 39 (2001)
- [11] H. Ruuska, T. A. Pekkanen, *Carbon* 41, 699 (2003)
- [12] K. T. Thompson, K. E. Gubbins, *Langmuir* 16, 5761 (2000)
- [13] E. A. Muller, K. E. Gubbins, *Carbon* 36, 1433 (1998)
- [14] D. Feller, *J. Phys. Chem.* 103, 7558 (1999)
- [15] D. Feller, K. D. Jordan, *J. Phys. Chem. A* 2000;104, 9971 (2000)
- [16] M. W. Feyereisen, D. Feller, D. A. Dixon, *J Phys. Chem.* 100, 2993 (1996)
- [17] S. Hamad, J. A. Mejias, S. Lago, S. Picaud, P. N. M. Hoang, *J. Phys. Chem. B* 108, 5405 (2004)

- [18] S. Picaud, P. N. M. Hoang, S. Hamad, J. A. Mejias, S. Lago, *J. Phys. Chem. B* 108, 5410 (2004)
- [19] T. Ohba, H. Kanoh, K. Kaneko, *J. Am. Chem. Soc.* 126, 1560 (2004)
- [20] T. Kiura, H. Kanoh, T. Kanda, T. Ohkubo, Y. Hattori, Y. Higaonna, R. Denoyel, K. Kaneko, *J. Phys. Chem. B* 108, 14043 (2004)
- [21] M. M. Dubinin, E. D. Zaverina, V. V. Serpinsky, *Trans. Far. Soc.* 1760 (1955)
- [22] A. P. Terzyk, P. A. Gauden, G. Rychlicki, *Colloids Surf. A* 148, 271 (1999)
- [23] P. A. Gauden, A. P. Terzyk, *The Theory of Adsorption of Gases and Vapours in Micropores of Carbonaceous Materials*. Warsaw: WICHiR; 2002 (in Polish)
- [24] R. S. Vartapetyan, A. M. Voloshchuk, *Usp. Khim.* 64, 1055 (1995) [in Russian]
- [25] R. S. Vartapetyan, A. M. Voloshchuk, M. M. Dubinin, L. A. Thekulina, S. G. Thepurnoy, *Izv. AN SSSR* 11, 2407 (1986) [in Russian]
- [26] M. M. Dubinin, A. A. Isirikyan, *Izv. AN SSSR* 10, 2183 (1989) [in Russian]
- [27] K. Tsutsumi, K. Mizoe, *Colloids Surf. A* 37, 29 (1989)
- [28] J. Philips, D. Kelly, L. Radovic, F. Xie, *J. Phys. Chem. B* 104, 8170 (2000)
- [29] K. Miura, T. Morimoto, *Langmuir* 4, 1283 (1988)
- [30] Y. I. Tarasevich, I. G. Polyakova, V. E. Polyakov, *Ads. Sci. Techn.* 20, 927 (2002)
- [31] I. I. Avgul, O. M. Dzigit, A. B. Kiselev, K. D. Sherbakov, *Izv. AN SSSR* 42,105 (1953) [in Russian]
- [32] M. M. Dubinin, *Izv. AN SSSR* 1, 9 (1981) [in Russian]
- [33] R. S. Vartapetyan, A. M. Voloshchuk, M. M. Dubinin, T. S. Yakubov, *Izv. AN SSSR* 9, 1934 (1987) [in Russian]
- [34] G. Rychlicki, *Role of Carbon Surface Chemism in Adsorption and Catalytic Processes*. Toruń: UMK; 1985 (in Polish)
- [35] H. Naono, M. Hakuman, M. Shimoda, K. Nakai, S. Kondo, *J. Colloid Interf. Sci.* 182, 1 (1996)
- [36] A. J. Groszek, *Carbon* 39, 1857 (2001)
- [37] R. P. Wesołowski, P. A. Gauden, A. P. Terzyk, S. Furmaniak, *Carbon* 42, 53 (2004)
- [38] G. Rychlicki, *Polish J. Chem.* 63, 255 (1989)
- [39] D. Mowla, D. D. Do, K. Kaneko, *Chem. Phys. Carbon* 27, 229 (2003)
- [40] M. M. Dubinin, V. V. Serpinsky, *Carbon* 19, 402 (1981)
- [41] M. M. Dubinin, V. V. Serpinsky, *Doklady AN SSSR* 285, 1151 (1981)
- [42] P. J. M. Carrot, *Ads. Sci. Techn.* 10, 63 (1993)
- [43] S. S. Barton, M. J. B. Evans, J. A. F. MacDonald, *Carbon* 29, 1099 (1991)
- [44] S. S. Barton, M. B. Evans, S. Liang, J. A. F. MacDonald, *Carbon* 34, 975 (1996)
- [45] S. S. Barton, M. J. B. Evans, J. A. F. MacDonald, *Carbon* 30, 123 (1992)
- [46] P. A. Gauden, *J. Colloid Interf. Sci.* 282, 249, 2005.
- [47] F. Stoeckli, T. Jakubov, A. Lavanchy, *J. Chem. Soc. Faraday Trans.* 90, 783 (1994)
- [48] H. F. Stoeckli, F. Kraehenbuehl, D. Morel, *Carbon* 21, 589 (1983)
- [49] M. M. Dubinin, K. M. Nikolaev, G. A. Petukhova, N. S. Polyakov, *Izv. AN SSSR* 4, 743 (1984) [in Russian]
- [50] A. P. Terzyk, P. A. Gauden, *The correctness of the equations describing the mechanism of water adsorption on activated carbons. 4th International Symposium Coal Structure - "Structure and Reactivity of Carbonaceous Materials"*, Gliwice, Poland, 2002
- [51] R. L. D'Arcy, I. C. Watt, *Trans. Far. Soc.* 66, 1236 (1970)
- [52] M. J. B. Evans, *Carbon* 25, 81 (1987)
- [53] S. S. Barton, M. J. B. Evans, J. A. F. MacDonald, *Langmuir* 10, 4250 (1994)
- [54] B. Venkataramani, *Langmuir* 9, 3026 (1993)
- [55] M. Sychev, R. Prihodko, A. Stepanenko, M. Rozwadowski, V. H. J. deBeer, R. A. vanSanten, *Microporous Mesoporous Mat.* 47, 311 (2001)

- [56] C. Pierce, R. N. Smith, *J. Phys. Chem.* 57, 64 (1953)
[57] D. Nandan, B. Venkataramani, A. R. Gupta, *Langmuir* 9, 3026 (1993)
[58] D. D. Do, *Adsorption Analysis: Equilibria and Kinetics*. London: ICP; 1998
[59] M. Jaroniec, R. Madey, *Physical Adsorption on Heterogeneous Solids*. Amsterdam: Elsevier; 1988
[60] G. Rychlicki, *Polish J. Chem.* 63, 255 (1989)
[61] R. Krishna, T. J. H. Vlugt, B. Smit, *Chem. Eng. Sci.* 54, 1751 (1999)
[62] J. Zawadzki, *Chem. Phys. Carbon* 21, 147 (1989)
[63] M. M. Dubinin, *Adsorption and Porosity*. Warsaw: WAT; 1975 (in Polish)

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