



BET surface area of carbonaceous adsorbents—Verification using geometric considerations and GCMC simulations on virtual porous carbon models

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ABSTRACT

The applicability of BET model for calculation of surface area of activated carbons is checked by using molecular simulations. By calculation of geometric surface areas for the simple model carbon slit-like pore with the increasing width, and by comparison of the obtained values with those for the same systems from the VEGA ZZ package (adsorbate-accessible molecular surface), it is shown that the latter methods provide correct values. For the system where a monolayer inside a pore is created the ASA approach (GCMC, Ar, $T = 87$ K) underestimates the value of surface area for micropores (especially, where only one layer is observed and/or two layers of adsorbed Ar are formed). Therefore, we propose the modification of this method based on searching the relationship between the pore diameter and the number of layers in a pore. Finally BET; original and modified ASA; and A, B and C-point surface areas are calculated for a series of virtual porous carbons using simulated Ar adsorption isotherms (GCMC and $T = 87$ K). The comparison of results shows that the BET method underestimates and not, as it was usually postulated, overestimates the surface areas of microporous carbons.

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1. Introduction

In 2008 we celebrated the 70th Anniversary of the publication of the BET equation—the model applied mainly for calculation of the surface area of solids from gas sorption data. Although more sophisticated methods have been developed, the BET model is still a standard (recommended by IUPAC [1,2]) and the most widely used procedure to characterize various adsorbents [3–7]. Of course, the concept of the surface area for a microporous carbon is very useful unless one is operating at low pressures during adsorption. At high pressures where pore filling dominates it is the pore volume that is a more important characteristic. On the other hand, the BET surface area is provided in almost each paper where activated carbons are applied, since it is a standard parameter.

The main advantage of the BET equation is its simplicity and this is the reason why, in spite of its success, this equation is also one of the most criticized theories since its origin [3–10]. In the light of the problematic assumptions of the original BET equation, the key question about this relationship is whether the surface area it provides is the “true” and “correct” value. Therefore, in our opinion information about its accuracy can be quite useful. Recent developments in the field of computer modelling and molecular

simulations make it possible to check the validity of different assumptions and concepts applied in the field of physical adsorption. The assumption of the atomistic structure of heterogeneous adsorbents offers, for example, the possibility to test the BET method and the limitations of its application reported in literature [8–18]. From the analysis of published results it can be seen that for different types of adsorbents the overestimation, the underestimation and/or the similarity of the surface area calculated by the BET method (in comparison with the geometrical considerations) can be observed [8–18]. Therefore, it is very difficult to correlate the differences between both types of surface areas with that of an adsorbent, the structural heterogeneity, and porosity.

Considering activated carbons a crucial role in checking of different adsorption concepts and models has been played by the so called Virtual Porous Carbon models (VPC). One of them i.e., the VPC model proposed by Harris and developed in our previous reports [19–27] is considered in this study. It was obtained from the analysis of HRTEM images of carbon samples; however, as recently shown by Powles et al. [28] the quenched MD simulations of carbon structures using sophisticated carbon–carbon potential provided a very similar structure, so the model seems to be realistic. In this study, known molecular structure of a series of VPCs having various average pore sizes and porosity is used for calculations of both the BET (from the low-temperature simulated adsorption isotherms of Ar) and the accessible surface areas (the

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geometrical considerations). To calculate the latter, the method identified with the centre of mass of the spheres rolling along the surface of the investigated adsorbents is considered (VEGA ZZ package was applied for this purpose [29,30]). It should be noted that by application of VPCs and the proposed procedure we avoid the problem of imperfection of the materials (occurring in real experiments) and their unknown structure and porosity.

2. Methods

To test the reality of the surface areas obtained from the VEGA ZZ package [29,30] a carbon slit-like pore composed of 1440 carbon atoms was constructed (Fig. 1) (note that some figures (i.e. Figs. 1 and 5) were created using the VMD program [31,32]). For slit with a gradually changed width (H) the surface area from VEGA ZZ (with periodic boundary conditions in all three directions) was calculated (S_{VEGA}). We considered the van der Waals and adsorbate-accessible molecular surface (VdW). The probe radius ($0.5\sigma_{\text{adsorbate}}$) was assumed to be equal to 0.17 nm (related to Ar). VEGA ZZ uses two methods to generate the surfaces: (i) *the fast double cubic lattice method* and (ii) *the method called marching cubes*

(the surface facet approximation to an isosurface through a scalar field sampled on a rectangular 3D grid). Both methods give comparable results. Therefore, we limited our studies to the former one. In this method the target sphere is systematically inserted into all accessible pores of the investigated structure using the cubic lattice approach. The surface areas are calculated for each dot and its distance from the geometric centre of the molecule (the surface dot density is equal to 100 for Å^2).

The geometric surface area of the slit (S_G) was calculated by the method analogous to this proposed by Kaneko et al. [33]. Knowing the coordinates of carbon atoms forming the slit one can construct the cuboid(s) (restricted by red lines in Fig. 1) and easily calculate the geometric surface area.

To compare S_G and S_{VEGA} (calculated by the above-mentioned methods) with those obtained from adsorption data molecular simulations were applied. In the case of carbon slit-like model Ar adsorption isotherms (87 K) were simulated by the classical GCMC method using the same procedure and parameters as previously (65 adsorption isotherms in the range of H varying from 0 up to 1.4 nm). For all slits the same dimensions of simulation box (L_x , L_y , and L_z) were assumed, i.e. 5.8959 nm \times 5.8005 nm \times 4.000 nm,

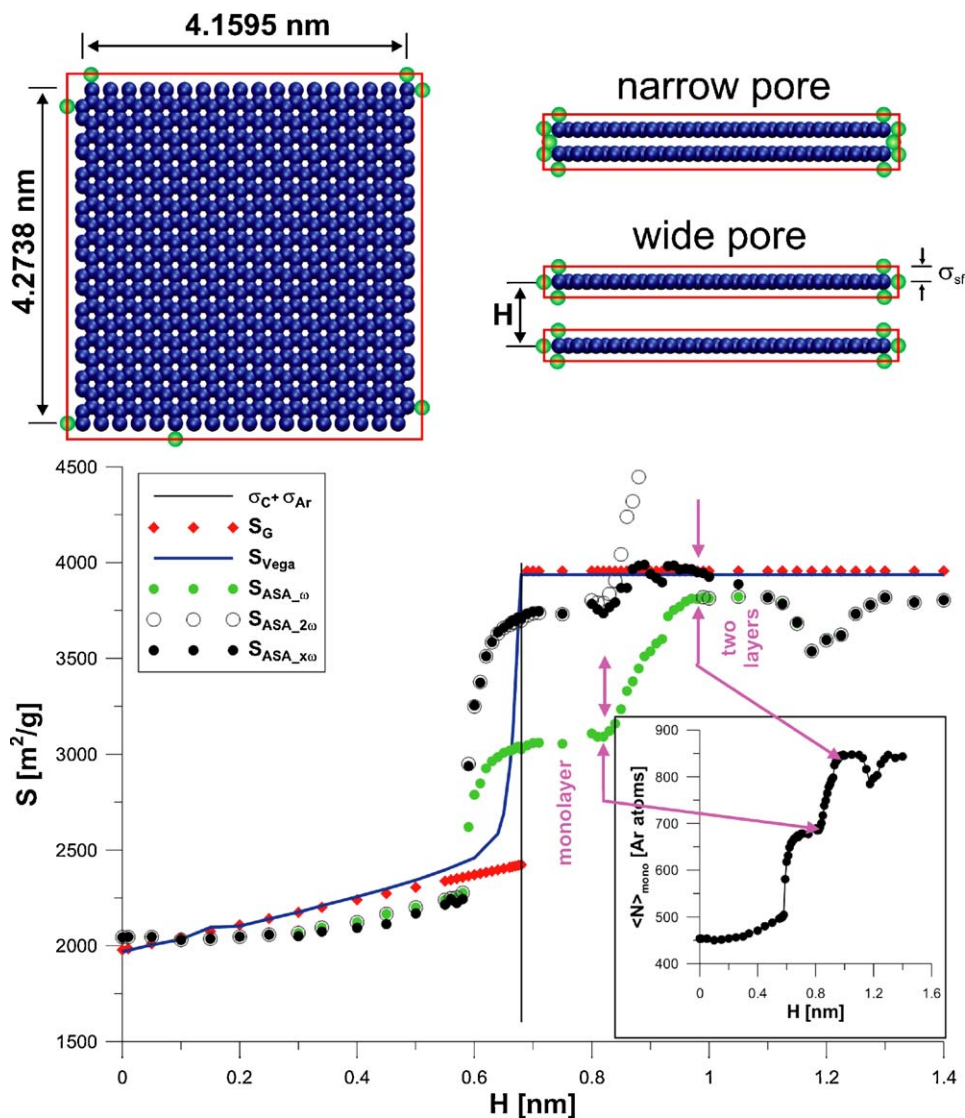


Fig. 1. Studied slit-like carbon pores and the values of S_G , S_{VEGA} and S_{ASA} calculated for three ways of the application of the values of cross section area ω (S_{ASA_ω}), 2ω ($S_{ASA_{2\omega}}$), and $x\omega$ ($S_{ASA_{x\omega}}$) plotted as the function of pore width (H). The values of the pore widths related to the start and the end of formation of the second layer (0.82 and 0.98 nm, respectively) inside the pore are shown by arrows. The inset shows the influence of H on the number of Ar atoms adsorbed in the monolayer inside and outside the pore.

respectively. Adsorption isotherms of Ar were also simulated (by the same method, $L_x = L_y = L_z = 4.6$ nm) for a series of VPCs composed of the fullerene-like fragments and generated from the Monte Carlo insertion of two types of carbon fragments into the initial structure [24]. The details of the MC procedure can be found in Ref. [24]. Pore size distributions of this series of VPCs were calculated using the method proposed by Bhattacharya and Gubbins and described in detail previously [24,25,34].

From those isotherms the Active Surface for Adsorption (S_{ASA}) was calculated by the method proposed by Pellenq et al. [13] and applied in a recent study [18]. In order to calculate the values of these surface areas, one can assume that the Ar atom is in the monolayer if the distance between carbon and argon atoms is smaller than the critical value, $\sigma_{crit,mono}$. In our previous paper [18] the correct value was found empirically (analysing the GCMC adsorption isotherms on graphite) to be equal to 0.51 nm for Ar. All simulated adsorption data were additionally analysed using the “adsorption type” methods of surface area calculation i.e. A, B, C-point [3], $S_{ABC-point}$, to obtain the surface area values. Formally the C-point is related to the point on the II type adsorption isotherm where adsorption starts to deviate from the linear range. Since in the case of studied microporous VPCs adsorption isotherms are of I type we call them *pseudo* C-point. Additionally, the original BET equation [1–7] was fitted to the adsorption data using two ranges for description of simulated adsorption isotherms: ca. 0.05–0.35 p/p_s (widely used in literature and the surface area obtained for this range is labelled as (S_{BET})) and the second one determined from the procedure proposed by Rouquerol et al. [35] (calculated by this method surface area is labelled as $S_{BET,R}$).

3. Results and discussion

From the results shown in Fig. 1 one can observe the slow rise in the value of geometric slit-like pore surface area (S_G) with the increase in the width of narrow pores. The abrupt rise in S_G is obtained at the value of H approaching 0.68 nm. At this pore width the internal space inside a pore is completely accessible for spheres with a diameter equal to 0.34 nm. The differences between S_G and S_{VEGA} (in the range of H from 0.58 up to 0.68 nm) are connected with the method of the calculation of the adsorbate-accessible molecular surface area on the basis of the VEGA ZZ package (connected with the possibility of the insertion of the target sphere into the internal edges of the narrow slit-like pore and into the pore at the position of the centre benzene rings of the opposite pore walls). For pores larger than 0.68 nm the influence of H on both types of geometrical surface area is not observed due to the maximum accessibility of adsorbed atoms to entire pore space. For the low values of H (up to 0.58 nm) only external monolayer adsorption occurs and this is why we observe a relatively good agreement between values of the surface area calculated in different ways (i.e. S_G , S_{VEGA} , S_{ASA}). For this range of H (similarly to that for the largest studied pores, i.e. from 0.98 nm) the insignificant differences between the adsorption and geometrical S values are related to (i) the imperfect packing of the adsorbed atoms in the respective layers (and on the edge C atoms) and (ii) to the assumed value of the cross-sectional area (ω) equal to 0.13 nm² (estimated previously [18] from the data simulated for Ar on graphite). Since at $H = 0.68$ nm we observe a monolayer of Ar inside a pore, the S_{ASA} value for such a slit is smaller by approximately 25% from S_G and/or S_{VEGA} . Of course, doubling the value of ω for Ar atom (in fact each Ar atom has the contact with two carbon walls inside a slit with the size up to ca. 0.82 nm) leads to a better agreement between the obtained in this way surface area ($S_{ASA,2\omega}$) and the remaining geometric areas (Fig. 2(a)). It should be noted that it is very difficult to estimate the number of layers formed inside a pore for the H in the range from 0.82 up to 0.98 nm (in Fig. 1 this range is

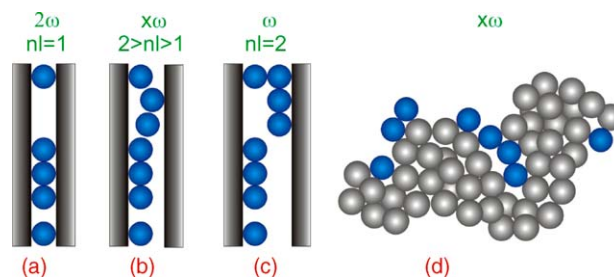


Fig. 2. Schematic representation of the application of cross-sectional area ω values in the case of the ideal slit-like pores (a–c, the influence of H) and disordered adsorbents (blue balls – adsorbate atoms, grey walls or balls – an adsorbent structure). nl is the number of layers and $x = 3 - nl$.

marked by arrows). Calculated for this range S_{ASA} taking into account the normal ($S_{ASA,\omega}$) and doubled ($S_{ASA,2\omega}$) the value of ω leads respectively to under- and overestimation. Therefore it is obvious that the intermediate values of ω should be considered (Fig. 2(b)) in order to observe the discontinuous plot of S_{ASA} vs. H . For pores larger than 0.98 nm the differences between the above-mentioned surface area values disappear due to the complete formation of two layers on the opposite walls inside the slit-like

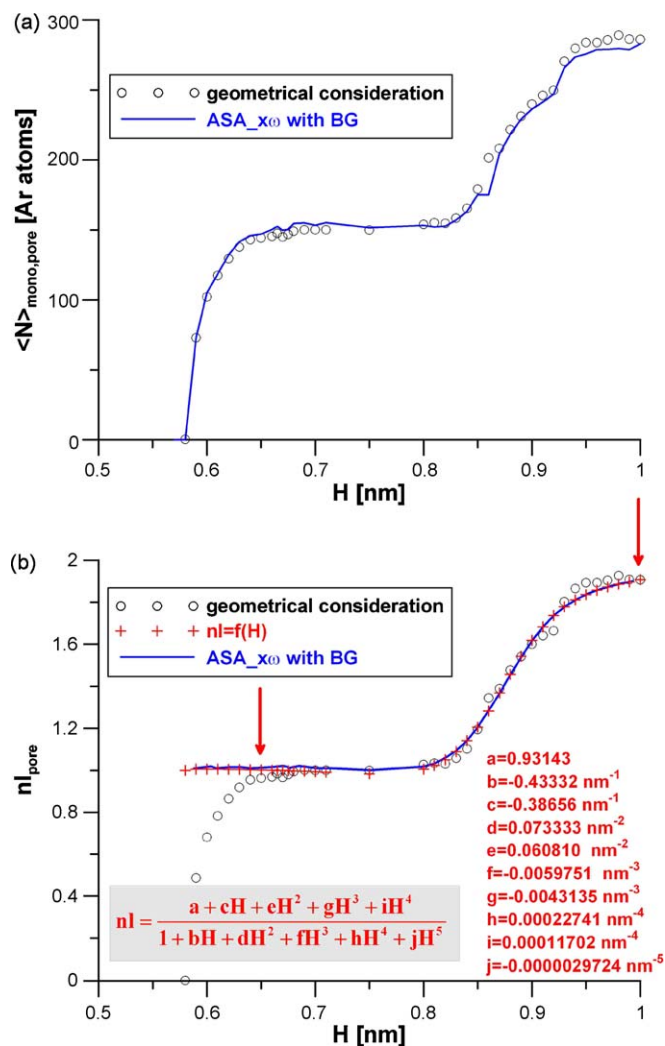


Fig. 3. (a) The number of Ar atoms adsorbed in a monolayer inside a slit-like pore calculated from geometric considerations and using ASA connected with the BG method. (b) Shows the procedure applied for calculation of the number of layers inside a slit-like pore with a diameter H in the range limited by arrows.

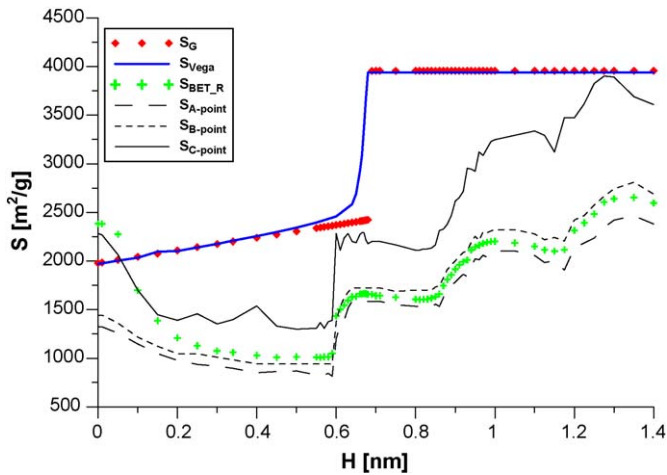


Fig. 4. Surface area values of slit-like pore calculated from different “adsorption” methods compared with the S_G and S_{VEGA} values.

pore (Fig. 2c). The minima observed at larger H (ca. 1.1–1.3 nm) for the ASA type methods (Fig. 1) are due to the adsorbate-induced rearrangement of molecules adsorbed in pores (formation of the third layer). The irregular trend is also observed in the inset of Fig. 1 where the relationship between the number of monolayer Ar atoms and H is plotted.

According to the schematic representation shown in Fig. 2(b), it is necessary to determine the value x (related to a number of neighbouring walls) for the cases where we observe the intermediate situation between the number of layers equal to one and two (H in the range 0.82–0.98 nm, Fig. 1). To do this we paid attention to Ar atoms adsorbed inside those slits using geometrical considerations and the ASA method. In Fig. 3(a) the number of Ar atoms adsorbed in a monolayer inside pores from this range is shown. One can observe two ranges of constant (i.e. almost independent of H) number of atoms. The first one (around

151) is responsible for the creation of a monolayer (i.e., the situation shown in Fig. 2(a)) whereas the second one (around 300) is due to creation of two layers (i.e. the situation shown in Fig. 2(c)). Therefore, the number of layers (nl) in a pore can be simply obtained dividing the number of adsorbed atoms by the number of atoms in a monolayer (i.e. 151 for this case). The final results are shown in Fig. 3(a). Next the curve describing obtained nl (for H in the range of 0.65–1.0 nm marked as red arrows) was fitted by the function described by equation shown in Fig. 3(b). In the case of VPCs analysed below we must apply the BG method to calculate the pore diameter (that according to the results published previously [25] small correction should be applied because the method applied for carbon slits detects some “pores” located inside benzene rings forming the graphite walls.). In the current study, this method was used not only in its original form (where the grid of nodes is formed inside porous structure) but we also used this method replacing the nodes by the centres of mass of adsorbed Ar atoms. In this way for each Ar atom adsorbed in monolayer a pore diameter can be calculated. Using the equation shown in Fig. 3(b) nl and x values were evaluated, knowing that $x = 3 - nl$. The latter value is crucial because it determines the number of contacts of an adsorbed atom with the walls. Therefore, it imposes how many times the specific surface area (ω) should be multiplied [15]. It can be pointed out that in all typical adsorption-based methods the value of x is assumed to be equal to unity. The obtained results (line in Fig. 3(a)) show a good agreement with the values calculated from the geometrical considerations, and the surface area values calculated using this approach are shown as black points in Fig. 1. Summing up, the application of this method leads to avoiding the problem of abrupt rise in S value observed for $S_{ASA, 2\omega}$ in the considered range of H .

Fig. 4 shows the comparison of S_G , S_{VEGA} and the values calculated from the simulated isotherms using the BET, A, B and C-point methods. One can observe similarity in the shapes of the plots and the ranges of covering especially between $S_{C-point}$ and geometric surface areas, but generally S values calculated by means of adsorption methods are underestimated. This is caused,

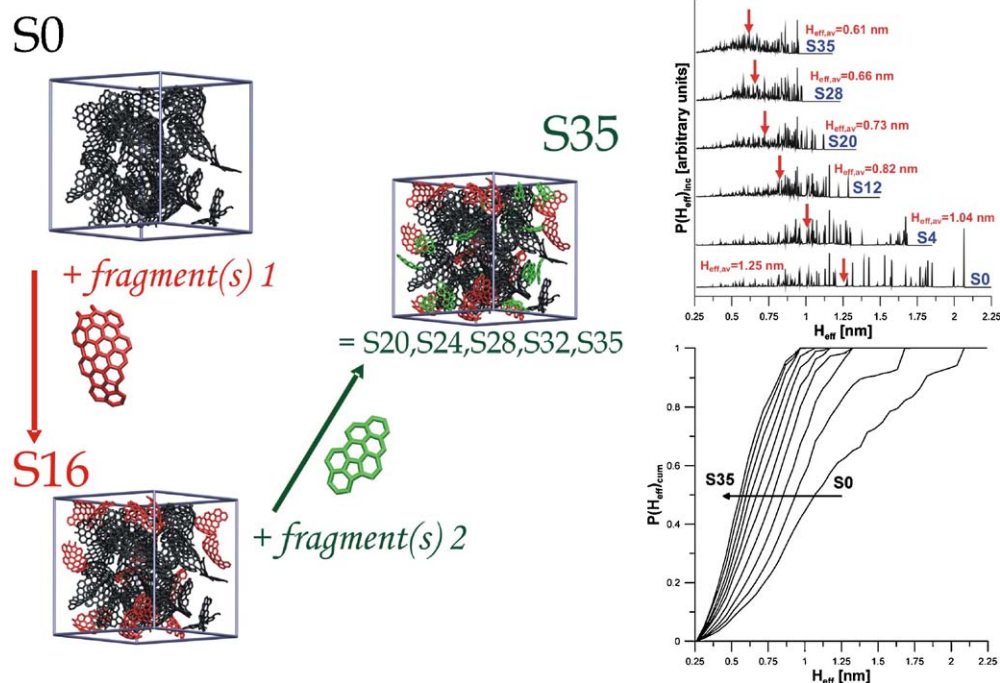


Fig. 5. Schematic representation of Monte Carlo method applied for creation of VPCs together with the differential and cumulative PSDs calculated from the BG method. The values of the average effective pore widths ($H_{eff,av}$) are shown by arrows.

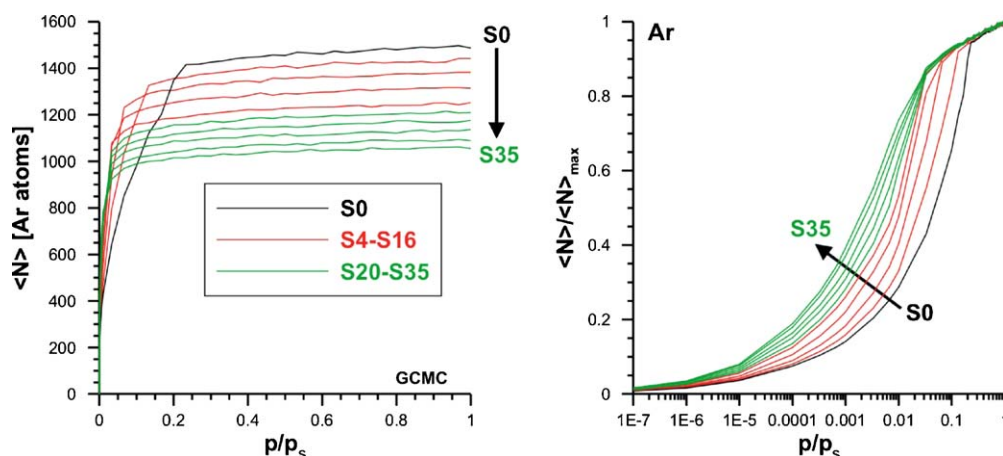


Fig. 6. Simulated Ar adsorption isotherms ($T = 87$ K) for studied VPCs.

among other things, by the above-mentioned assumption that $x = 1$, questionable method of linearization, and more complex mechanism of creation of a monolayer than assumed in the model.

Fig. 5 shows that a series of VPCs has gradually changed porosity and one can observe the development of microporosity from the structure S0 up to S35. The average effective micropore diameter ($H_{\text{eff}} = H - \sigma_{\text{CC}}$, where σ_{CC} is equal to 0.34 nm) decreases from 1.25 up to 0.61 nm, respectively. Since all structures are microporous we observe that simulated Ar adsorption isotherms are of I Type according to the IUPAC classification (Fig. 6). One can also observe the decrease in maximum adsorption with the crowding of the structures, and the rise in adsorption at low pressures due to the decrease in micropore widths.

Fig. 7 collects the values of surface areas calculated using all considered methods. In Fig. 7(a) there can be seen the progressive decrease in S_{VEGA} with the rise in microporosity of studied carbons. It can be surprising that generally all applied methods underestimate the values of surface area (carbon S8 is the only exception where the agreement between the surface areas from VEGA ZZ and BET_R is observed). The method of BET equation linearization modified by Rouquerol et al. [35] leads to more reliable values of surface areas than the original model applied in the typical range of linearization; however, the differences between S_{VEGA} and S_{BET} increase with the progress in microporosity. Since simulated isotherms have more or less pronounced I type character we observe larger or smaller differences between the surface areas calculated from the application of A, B and the *pseudo* C-point methods; however, the latter leads to the best results. Fig. 7(b) compares the geometric surface area with those obtained from original and modified ASA approaches. As one can observe, the neglecting of the multiplication of the ω value causes that too small surface areas are obtained from the original ASA approach. A better agreement is observed for the approach proposed in this study; however, since we use the slit-like pore model during determination of the number of layers this approach is not perfect. Moreover, the assumption of constant for each systems ω value is also questionable.

4. Conclusions

It was shown that for the case of ideal carbon slit-like pore, large values of surface areas are possible. In this way, using molecular simulations and geometric considerations we confirm the validity of the results obtained by Kaneko et al. [33]. Taking into account the multiplication of the specific surface area of adsorbed molecules leads to a better agreement between the geometric and “adsorption” types of surface areas. For realistic carbon models the BET type methods provide, generally, too small values of S , and a better agreement is observed for the results obtained from the linearization method proposed by Rouquerol et al. [35]. The original ASA method was modified leading to the values of S being more realistic; however, the presented approach is not perfect yet. Further studies are necessary and the results will be reported.

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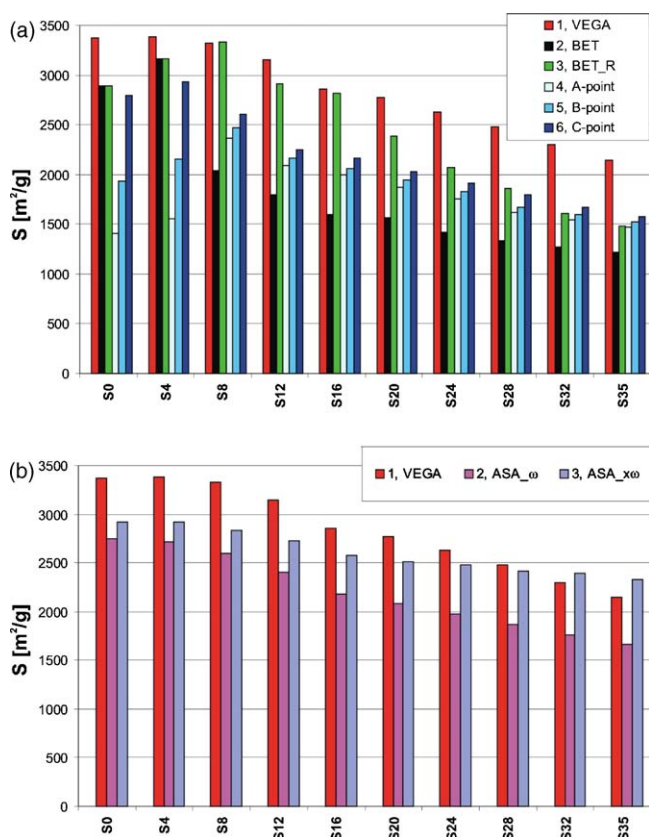


Fig. 7. The comparative plot of obtained surface areas for VPCs.

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