The influence of carbon surface chemical composition on Dubinin - Astakhov equation parameters calculated from SF_6 adsorption data – grand canonical Monte Carlo simulation

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Abstract: Using GCMC simulation we show, for the first time, the influence of carbon porosity and surface oxidation on the parameters of the DA adsorption isotherm equation. We conclude that after carbon surface oxidation adsorption decreases for all studied carbons. Moreover, the parameters of the DA model depend on the number of surface oxygen groups. That is the reason why in the case of carbons containing surface polar groups SF_6 adsorption isotherm data cannot be applied for characterisation of porosity.

Keywords: adsorption, activated carbon, GCMC simulation

1. Introduction

In a recently published study Chiang and Wu [1] pointed out that the application of SF_6 in the electrical industry, semiconductor, aluminium smelting and magnesium industries, as well in medicine is due to its low toxicity, high thermal stability and high breakdown strength. SF_6 is also a common tracer gas for use in experiments or oceanography. According to the Intergovernmental Panel on Climate Change, SF_6 is the most potent greenhouse gas [1]. An SF_6 admixture to freons decreases the boiling temperature of halones, and this property is used in refrigeration engineering [2].

Due to the large amount produced annually and its long atmospheric lifetime (ca. 3200 years) the use of SF_6 has recently become a global environmental issue. SF_6 is a perfluorochemical (PFC) and there are several ways to reduce and eliminate PFC emissions from industrial processes. Different authors proposed abatement/destruction methods however, common techniques for recovery/recycling of SF_6 are cryogenic condensation, adsorption, and membrane separation. Regarding adsorption an SF_6 isotherm is often applied for characterization of carbons (see for example [2,3]).

In the current study we present the results of GCMC simulation of SF_6 adsorption on realistic Virtual Porous Carbon (VPC) model of activated carbon proposed by Harris *et al.* [4-6]. It was shown previously that using this model it is possible for simulated data to obtain the same correlations as observed in real experiments [7]. Moreover, using this model we explained the meaning of some empirical parameters occurring in models applied for theoretical description of methane adsorption on carbons [8]. Moreover, this model was also

successfully used for explanation of behaviour of carbons in adsorption of phenol from aqueous solutions [9].

For the reasons mentioned above we decided to check how the porosity and the chemical composition of the carbon surface layer determine the parameters obtained from description of SF_6 adsorption data by the most popular adsorption isotherm equation, namely the Dubinin - Astakhov one. Since it is impossible to check this experimentally we decided to use a realistic VPC model (where the geometric, i.e. absolute, porosity is exactly known), and a molecular simulation technique applying one of the most advanced models of the SF_6 molecule.

2. Calculations details

2.1. Simulation boxes

We used four series of VPCs generated based on the (above-mentioned) Harris model and described in detail previously [10,11]. The series were obtained by introduction of surface carbonyl groups (using, the so called "virtual oxidation" procedure developed by us [10]) into four generated VPCs [12], denoted as S00 (S0), S12, S20, S35. These structures differ in porosity (see [12]). This "absolute" (geometric) porosity was calculated using the method proposed by Bhattacharya and Gubbins [13] and described previously (see for example [10,11]). Structure S00 has the widest pores, and the average pore size decreases gradually down to structure S35. Structures are denoted as S*xx_yyy*, where S*xx* denotes starting structure and *yyy* denotes the number of carbonyl groups. We used following virtual carbons: (a) S00 series: S00_000, S00_036, S00_072, S00_108, S00_144, S00_180; (b) S12 series: S12_000, S12_050, S12_100, S12_150, S12_200, S12_250; (c) S20 series: S20_000, S20_058, S20_116, S20_174, S20_232, S20_290; and (d) S35 series: S35_000, S35_072, S35_144, S35_216, S35_288, S35_360. All structures were placed in cubicoid simulation box having dimensions 4.6 × 4.6 × 4.6 nm. As was shown in our previous papers [10,11] virtual oxidation practically does not change porosity (see below).

2.2. Grand Canonical Monte Carlo (GCMC) simulations

For all above-described structures the simulations of SF_6 adsorption at 298 K (in the range of pressures ca. 1 Pa up to ca. 2.32 MPa (p_s = 2.3568 MPa [14])) using the standard

GCMC method were performed [15]. The probability of attempts of changing of a state of a system by creation, annihilation, and rotation and displacement (the latter one is connected with the change in angular orientation) were equal to: 1/3, 1/3, 1/6 and 1/6. For each adsorption point 2.5×10^7 iterations were performed during the equilibration, and next 2.5×10^7 equilibrium ones, applied for the calculation of the averages (one iteration = an attempt to change the state of the system by creation, annihilation, rotation or displacement). Enthalpy of adsorption was calculated from the theory of fluctuations.

The SF_6 molecule was modeled by the seven-centre rigid model [16]. Each centre was the (12,6) Lennard-Jones one (LJ) as well as the point charge (q). We used the values of parameters of Strauss force field optimized by Dellis and Samios [16]. Values of parameters for the carbonaceous skeleton and atoms forming carbonyl groups were taken from [17]. The energy of interactions were calculated analogically as in our previous papers [10,18]. For all LJ-type interactions the cut-off is assumed as equal to $r_{cut,ij} = 5\times\sigma ij$. Tab. 1 collects all values of applied interaction parameters (we used the Lorentz-Berthelot mixing rules).

2.3 Description of simulated isotherms by the DA model

For a description of simulated adsorption isotherms we applied the Dubinin - Astakhov (DA) adsorption isotherm equation in the form:

$$a = a_0 \exp\left[-\left(\frac{A}{E}\right)^n\right] \tag{1}$$

where:

$$A = RT \ln\frac{p_s}{p} \tag{2}$$

and a and a_0 are the values of adsorption and maximum adsorption, respectively, p and p_s are the equilibrium pressure and saturated vapour pressure at a given temperature (T), E is the characteristic energy of adsorption (multiplied by the affinity coefficient), and R is the gas constant.

Data were described using genetic algorithms proposed by Storn and Price [19] and applied by us previously (see for example [11,12,20,21]). The goodness of the fit was

estimated using the values of the determination coefficients (*DC*) - for details see for example [11].

3. Results and discussion

Fig. 1 shows the geometric (absolute) pore size distributions of the studied structures. As mentioned above all structures are microporous, structure S00 has dispersed microporosity, and the average micropore diameter decreases passing from S00 down to S35. Figure 1 also shows one important feature of the studied structures, namely, that after "virtual oxidation" of structures the porosity remains almost unchanged. Therefore we can conclude that the changes in SF_6 adsorption value (for a given series) are caused only by the changes in chemical composition of carbon surface layer and not by porosity.

Fig. 2 shows adsorption isotherms. As one can see the number of molecules in the simulation box increases with increasing number of oxygen groups in VPC model. This effect is visible especially at low pressures. The isosteric enthalpy of adsorption increases at the same time, and this is due to electrostatic interactions between oxygen and SF_6 molecules. However, due to the rise in the VPC mass after oxidation, the differences in adsorption isotherms become strongly pronounced if absolute adsorption is considered. This is also the reason why we observe a decrease in adsorption (at larger pressures) with a rise in a number of surface oxygen groups in VPC model.

In Fig.3 we compare the number of molecules in a simulation box and adsorption isotherms for VPC models differing in porosity. One can observe that the number of SF_6 molecules in the simulation box increases at low pressures with the rise in micropore diameter of carbon and decreases at larger pressures due to the decrease in the volume of adsorption space. If absolute adsorption is considered we observe that the smaller the average micropore diameter the smaller is the adsorption, and exactly the reverse effect is seen if one compares the relative adsorption, or the enthalpy plotted as a function of relative adsorption.

The major conclusion of this part of the study is that the oxidation of activated carbon leads to a decrease in SF_6 adsorption.

Finally in Figs.4 and 5 we show the results of a description of simulated data using the DA adsorption isotherm equation (Eq.1 and Tab.2), plotted as a function of oxygen content (Fig.4) and the converse of average micropore diameter (Fig.5). Since there are negligibly small changes in porosity after carbon oxidation (see Fig.1) it is obvious that the correlations observed on Fig.4 are caused by the interactions of adsorbed molecules with oxygen. We see

that both the characteristic energy of adsorption as well as the parameter *n* of the DA model are affected by the number of oxygen groups present on carbon surface. Therefore as in the case of nitrogen [10] and/or carbon dioxide [10,11] adsorption, it can be concluded that SF_6 adsorption data on microporous carbon, described by DA model, cannot be applied for microporosity characterisation if carbon contains oxygen surface functionalities. On the other hand, Fig. 5 shows that in fact for carbons not containing oxygen *E* is related to the micropore diameter. Therefore the characteristic adsorption energy of the DA model can be applied for calculation of the average micropore diameter but only if the new relation between those two values is developed, since as can be seen from Fig.5 also the parameter *n* of this equation is correlated with the average micropore diameter. Therefore, the application of simple inverse relationship between characteristic energy and pore diameter is questionable.

CONCLUSIONS

We show, for the first time, the influence of carbon porosity and surface oxidation on the parameters of the DA adsorption isotherm equation. It is demonstrated that after carbon surface oxidation adsorption decreases for all studied carbons. Moreover, the parameters of the DA model depend on the number of surface oxygen groups. That is the reason why in the case of carbons containing surface polar groups SF_6 adsorption isotherm data described by DA model cannot be applied for characterisation of porosity. On the other hand if carbon does not contain polar surface groups a new relationship between E_0 and pore diameter should be proposed, since the parameter *n* also depends on the pore diameter.

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Table 1

The values of LJ parameters and point charges located on the centres of studied systems.

molecule/structure	**geometric parameters**	**centre**	**σ [nm]**	**ε/k_B [K]**	***q*/*e***	**reference**
SF_6	l_{SF} = 0.1564 nm	S	0.3228	165.14	+ 0.66	[16]
		F	0.2947	27.02	– 0.11	
adsorbent	l_{CO} = 0.1233 nm	C*)	0.3400	28.00	–	[17]
		C**)	0.3400	28.00	+ 0.50	
		O	0.2960	105.8	– 0.50	

*) - non-carbonyl group atom of C

**) - carbonyl group C atom

Table 2

The values of the best fit parameters obtained from the description of simulated isotherms using DA equation (Eqs. (1) and (2)).

System	a_0 [molecules/box]	E [kJ/mol]	n	DC
S00_000	452.0	7.215	1.370	0.9986
S00_036	452.6	7.479	1.410	0.9986
S00_072	452.5	7.750	1.439	0.9990
S00_108	451.3	8.050	1.479	0.9989
S00_144	449.8	8.324	1.507	0.9990
S00_180	449.5	8.556	1.524	0.9991
S12_000	377.7	9.706	1.861	0.9989
S12_050	374.3	10.09	1.928	0.9989
S12_100	374.6	10.43	1.937	0.9991
S12_150	370.1	10.83	1.991	0.9991
S12_200	367.3	11.23	2.049	0.9991
S12_250	368.3	11.56	2.094	0.9991
S20_000	333.4	10.74	1.952	0.9993
S20_058	331.0	11.21	2.006	0.9993
S20_116	329.2	11.74	2.074	0.9993
S20_174	330.2	12.02	2.101	0.9993
S20_232	326.0	12.49	2.171	0.9992
S20_290	323.1	13.04	2.262	0.9990
S35_000	272.2	11.58	1.925	0.9996
S35_072	271.0	12.10	1.988	0.9996
S35_144	265.7	12.66	2.043	0.9992
S35_216	260.9	13.20	2.135	0.9995
S35_288	259.2	13.79	2.170	0.9990
S35_360	253.7	14.41	2.269	0.9990

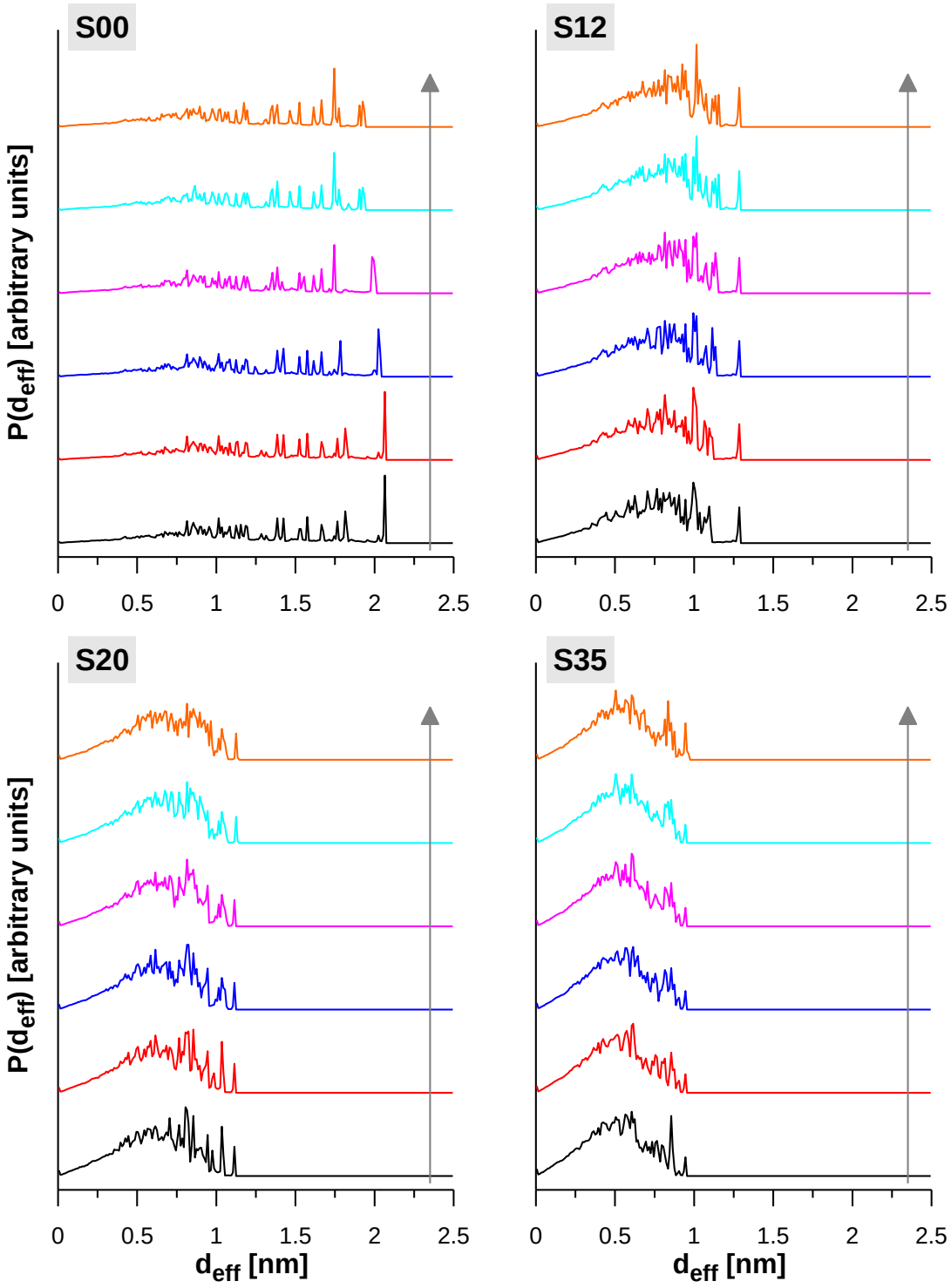

Fig. 1. The pore size distribution curves of studied VPC models calculated using Bhattacharya and Gubbins method (for details see [10,11]). Arrows shows the rise in the number of oxygen groups.

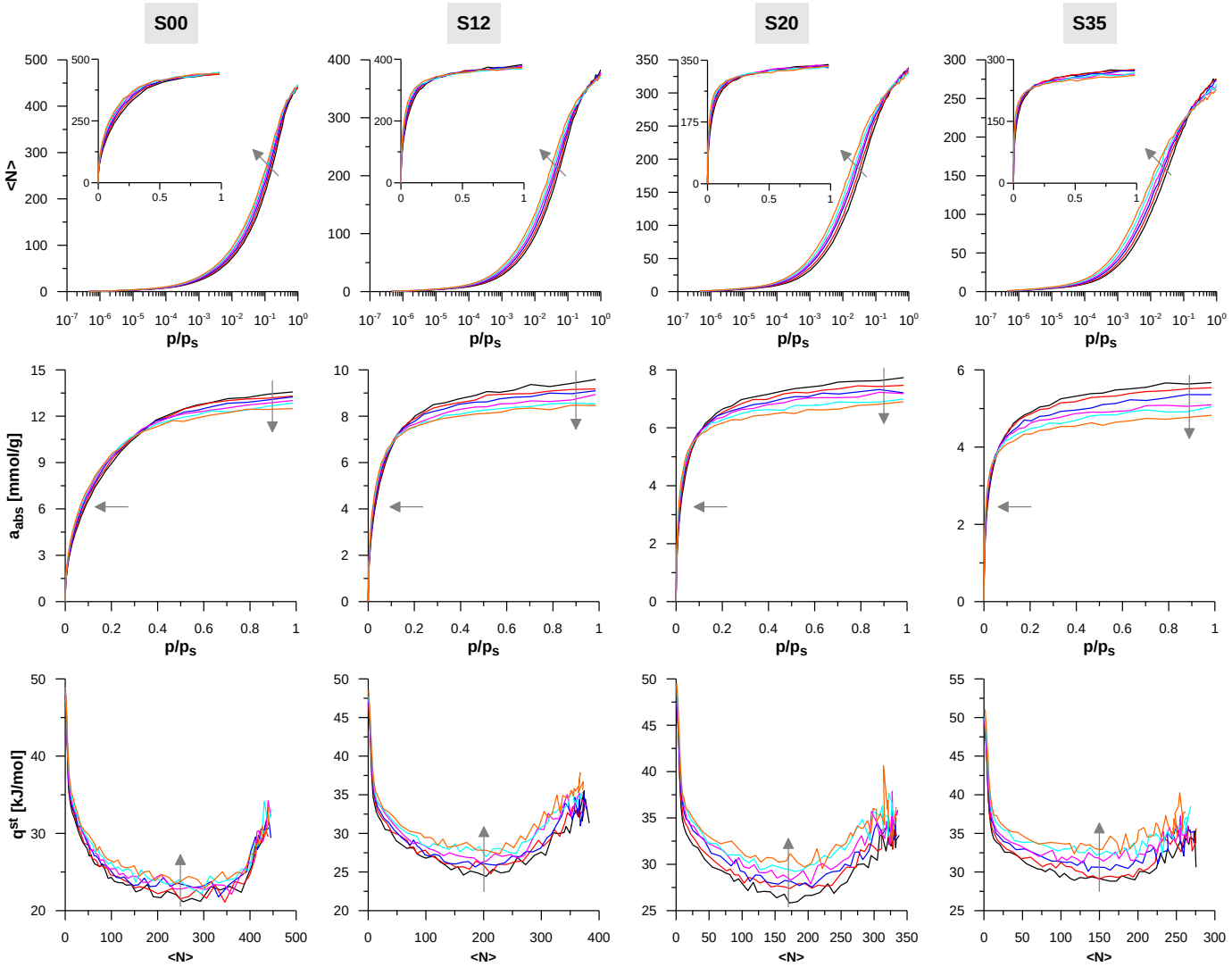

Fig. 2. The comparison of adsorption values (the average number of molecules in the box (<*N*>) and the absolute adsorption values (a_{abs})) and the isosteric enthalpy of adsorption for studied systems. Arrows shows the rise in the number of oxygen groups.

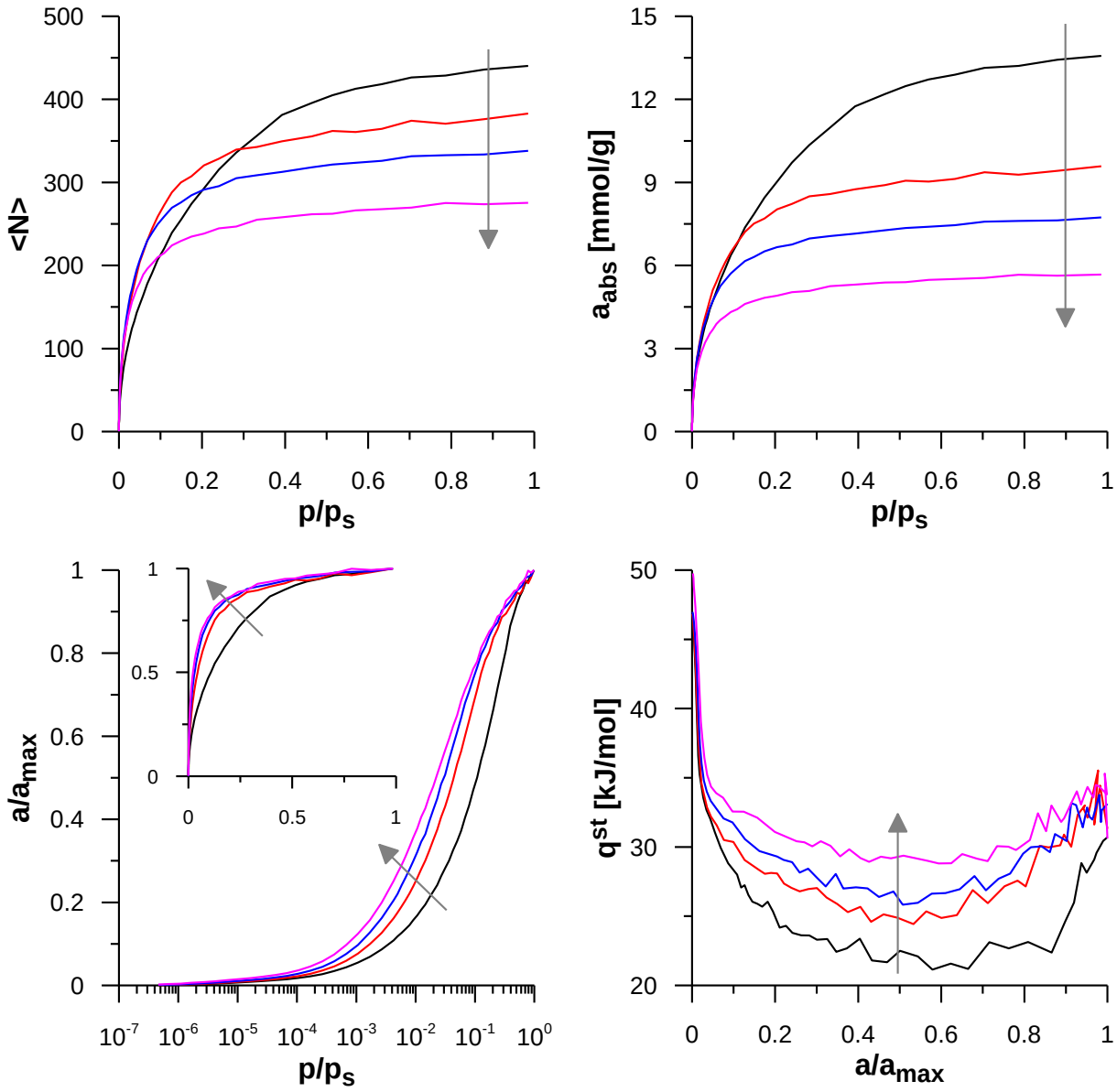

Fig. 3. The comparison of adsorption isotherms (the average number of molecules in the box (<*N*>)), the relative adsorption values and the isosteric enthalpy of adsorption for studied VPC do not containing oxygen (VPCs S00_000, S12_000, S20_000 and S35_000). Arrows shows the decrease in the average micropore diameter.

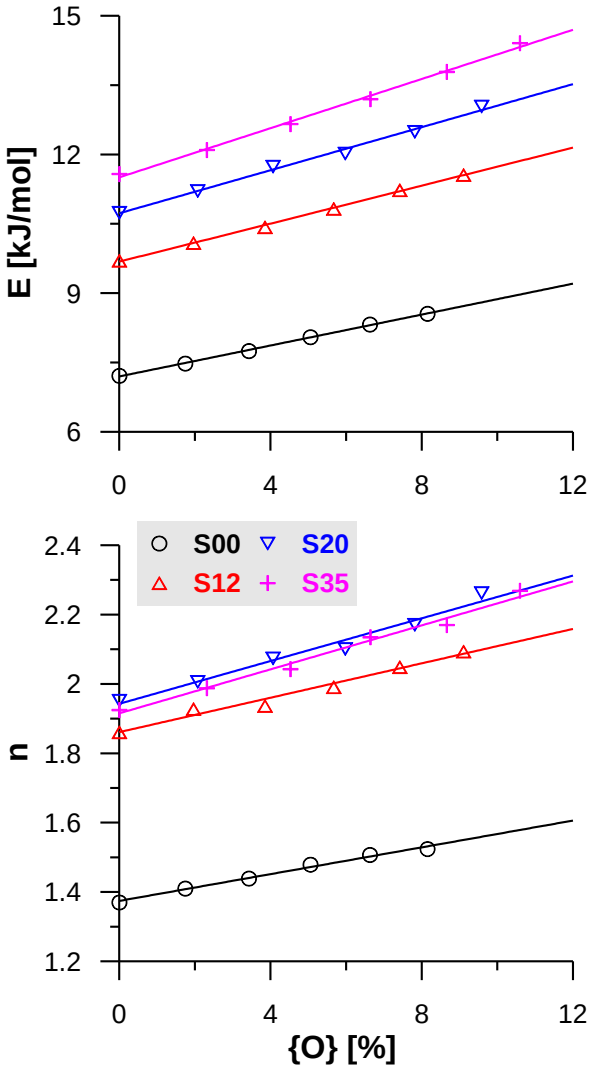

Fig. 4. The correlations between the DA equation parameters and the percentage contents of oxygen ({O}) for studied VPC models.

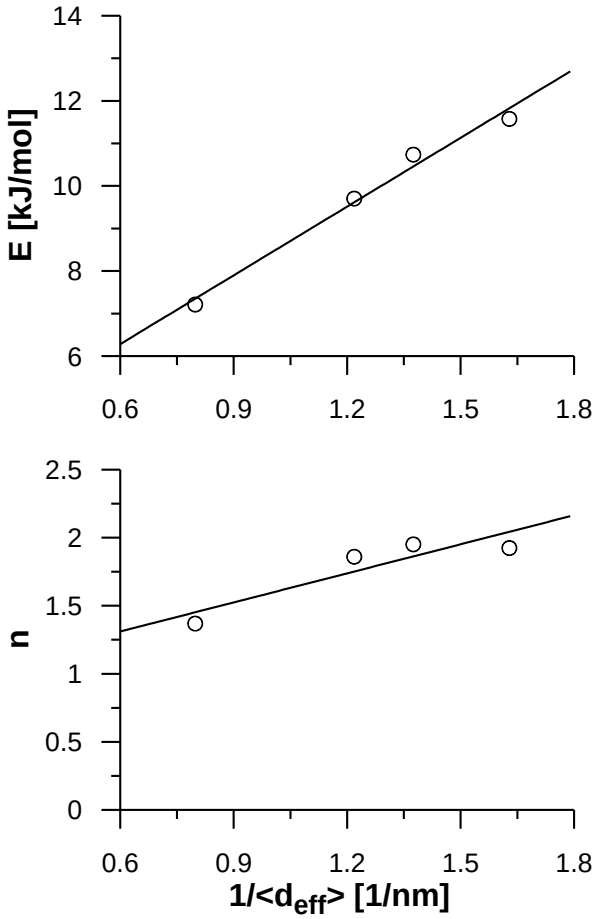

Fig. 5. The correlations between the DA equation parameters and the converse micropore diameter ($1/<d_{eff}>$) for the VPC models do not containing oxygen.