The influence of the 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 grand canonical Monte Carlo simulation we show, for the first time, the influence of the carbon porosity and surface oxidation on the parameters of the Dubinin–Astakhov (DA) adsorption isotherm equation. We conclude that upon carbon surface oxidation, the adsorption decreases for all carbons studied. Moreover, the parameters of the DA model depend on the number of surface oxygen groups. That is why in the case of carbons containing surface polar groups, SF$_6$ adsorption isotherm data cannot be used for characterization of the porosity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In a recently published study, Chiang and Wu [1] pointed out that the application of SF$_6$ in the electrical, semiconductor, aluminium smelting and magnesium industries, as well as in medicine, is a result of its low toxicity, high thermal stability and high breakdown strength. SF$_6$ is also a common tracer gas, finding use in experiments and oceanography. According to the Intergovernmental Panel on Climate Change, SF$_6$ is the most potent greenhouse gas [1]. SF$_6$ admixture into 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 (about 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 have proposed various abatement/destruction methods however; common techniques for recovery/recycling of SF$_6$ include cryogenic condensation, adsorption, and membrane separation. As regards 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 grand canonical Monte Carlo (GCMC) simulation of SF$_6$ adsorption on a realistic virtual porous carbon (VPC) model of activated carbon proposed by Harris *et al* [4–6]. It was shown
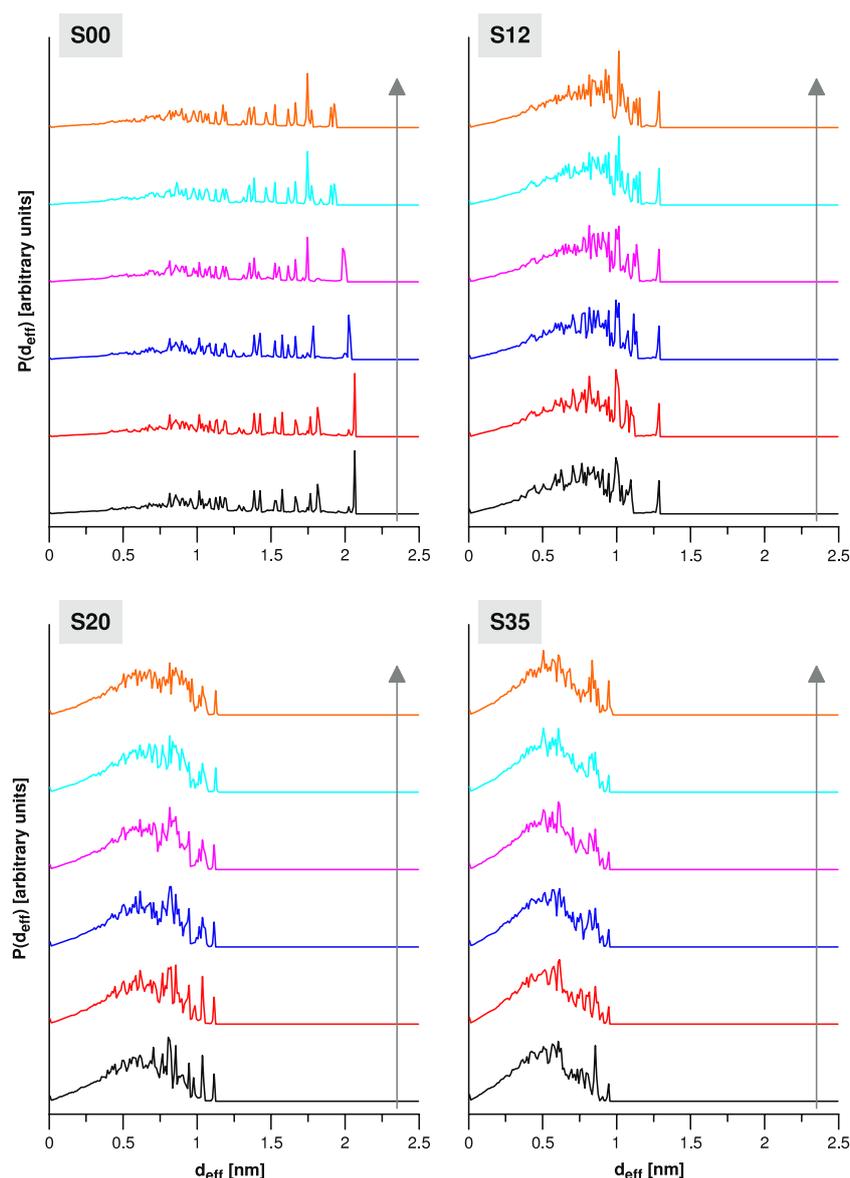
Figure 1. The pore size distribution curves of the VPC models studied calculated using the Bhattacharya and Gubbins method (for details see [10, 11]). Arrows show the rise in the number of oxygen groups.

previously that using this model it is possible for simulated data to obtain the same correlations as are observed in real experiments [7]. Moreover, using this model we explained the meaning of some empirical parameters occurring in models applied for the theoretical description of methane adsorption on carbons [8]. Moreover, this model was also successfully used for the explanation of the behaviour of carbons in the 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 the description of SF_6 adsorption data using the most popular adsorption isotherm equation, namely the Dubinin–Astakhov (DA) 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 on the basis of the (above-mentioned) Harris model and described in detail previously [10, 11]. The series were obtained by the 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
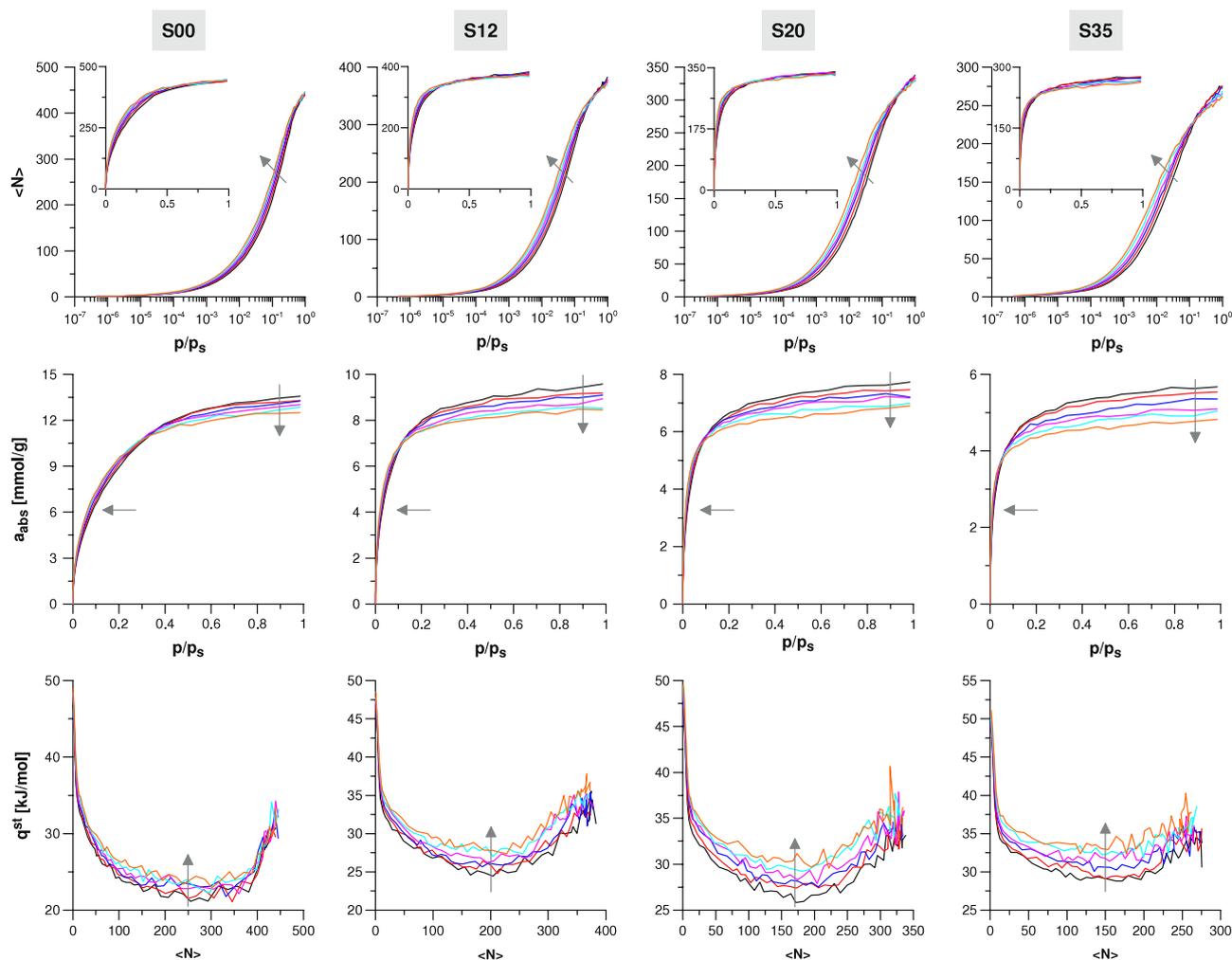
Figure 2. The comparison of the adsorption values (the average numbers of molecules in the box ($\langle N \rangle$), the absolute adsorption values (a_{abs})) and the isosteric enthalpies of adsorption for the systems studied. Arrows show the rise in the number of oxygen groups.

has the widest pores, and the average pore size decreases gradually down to structure S35. The structures are denoted as S*xx*_*yyy*, where S*xx* denotes starting structure and *yyy* denotes the number of carbonyl groups. We used the 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 a cubicoid simulation box having dimensions 4.6 nm × 4.6 nm × 4.6 nm. As was shown in our previous papers [10, 11], virtual oxidation leaves the porosity practically unchanged (see figure 1).

2.2. Grand canonical Monte Carlo (GCMC) simulations

For all above-described structures, simulations of SF_6 adsorption at 298 K (in the range of pressures from about 1 Pa up to about 2.32 MPa (p_s = 2.3568 MPa [14])) using the standard GCMC method were performed [15]. The

probabilities of attempts at changing a state of a system by creation, annihilation, rotation and displacement (the latter one is also 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 then 2.5×10^7 equilibrium ones, applied for the calculation of the averages (one iteration is one attempt to change the state of the system by creation, annihilation, rotation or displacement). The enthalpy of adsorption was calculated from the theory of fluctuations.

The SF_6 molecule was modelled using the seven-centre rigid model [16]. Each centre was a (12, 6) Lennard-Jones (LJ) one, with a point charge (q). We used the values of the parameters of the Strauss force field optimized by Dellis and Samios [16]. The values of the parameters for the carbonaceous skeleton and the atoms forming carbonyl groups were taken from [17]. The energies of the interactions were calculated analogously to those in our previous papers [10, 18]. For all LJ-type interactions, the cut-off is assumed as equal to $r_{cut,ij} = 5 \times \sigma ij$. Table 1 collects all values of the interaction parameters applied (we used the Lorentz–Berthelot mixing rules).
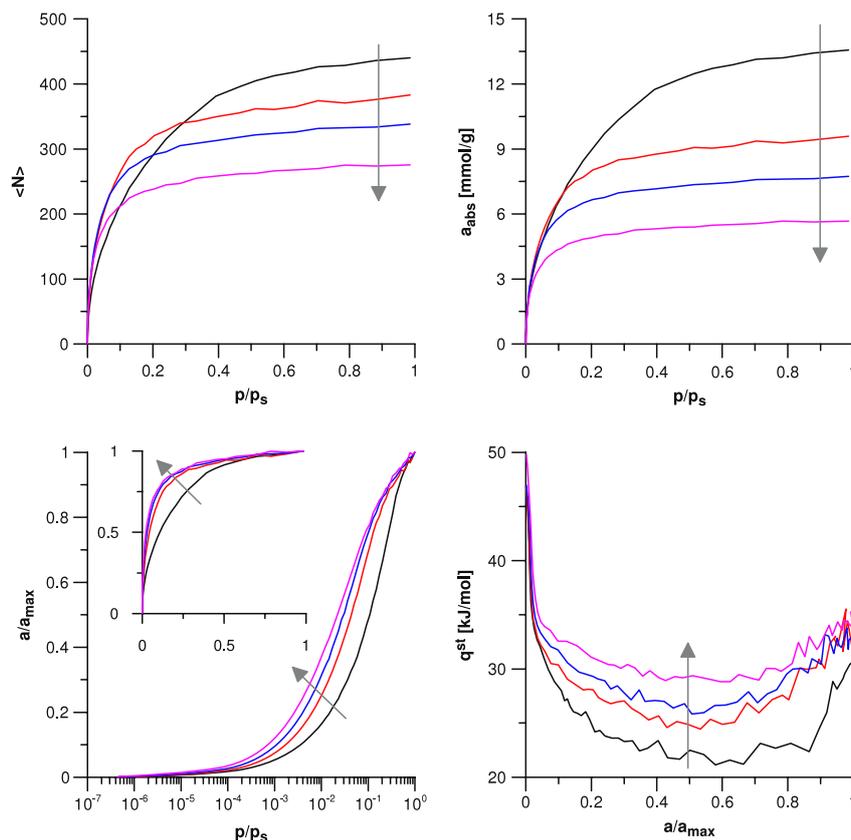
Figure 3. The comparison of adsorption isotherms (the average numbers of molecules in the box ($\langle N \rangle$)), the relative adsorption values and the isosteric enthalpies of adsorption for the VPCs studied not containing oxygen (VPCs S00_000, S12_000, S20_000 and S35_000). Arrows show the decrease in the average micropore diameter.

Table 1. The values of the LJ parameters and point charges located at the centres of systems studied.

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[a]	0.3400	28.00	—	[17]
		C[b]	0.3400	28.00	+0.50	
		O	0.2960	105.8	−0.50	

[a] Non-carbonyl group atom of C.

[b] Carbonyl group C atom.

2.3. Description of the isotherms simulated by the Dubinin–Astakhov model

For a description of simulated adsorption isotherms we applied the DA adsorption isotherm equation in the form

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

where

$$A = RT \ln \frac{p_s}{p} \qquad (2)$$

and a and a_0 are the values of the 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.

The 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 fit was estimated using the values of the determination coefficients (DC)—for details see for example [11].

3. Results and discussion

Figure 1 shows the geometric (absolute) pore size distributions of the structures studied. As mentioned above, all structures are microporous, structure S00 has dispersed microporosity, and the average micropore diameter decreases on passing from S00 down to S35. Figure 1 also shows one important feature of the structures studied, namely, that upon 'virtual oxidation' of structures, the porosity remains almost unchanged. Therefore we can conclude that the changes in the
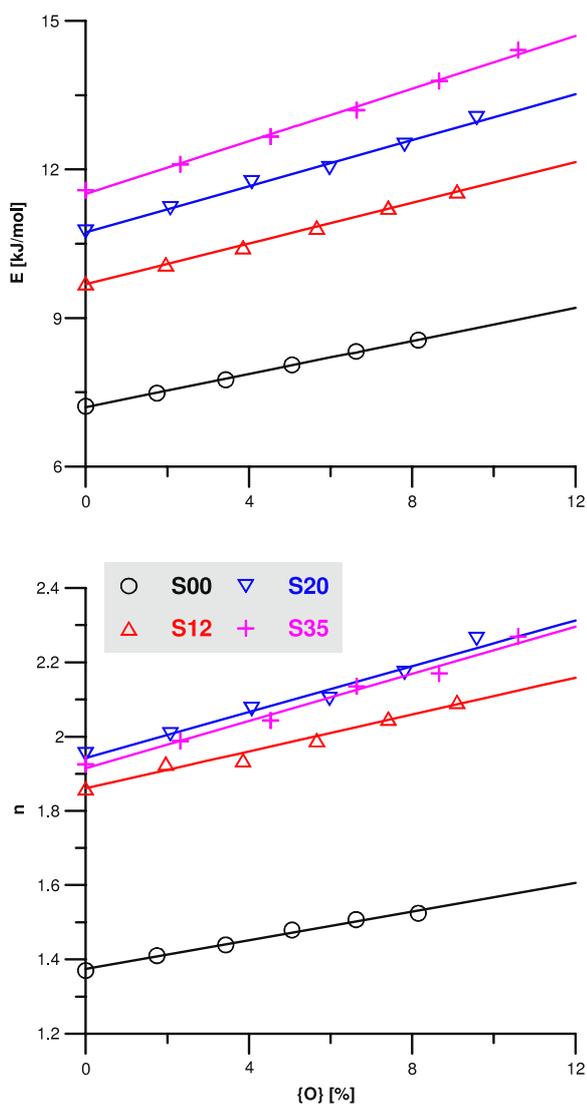
Figure 4. The correlations between the DA equation parameters and the percentage contents of oxygen ({O}) for the VPC models studied.

Figure 5. The correlations between the DA equation parameters and the inverse average micropore diameter ($1/\langle d_{eff}\rangle$) for the VPC models not containing oxygen.

SF_6 adsorption value (for a given series) are caused only by the changes in chemical composition of the carbon surface layer and not by the porosity.

Figure 2 shows adsorption isotherms. As one can see, the number of molecules in the simulation box increases with increasing number of oxygen groups in the 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 the SF_6 molecules. However, due to the rise in the VPC mass upon oxidation, the differences in the adsorption isotherms become strongly pronounced if the absolute adsorption is considered. This is also why we observe a decrease in the adsorption (at larger pressures) with increase in the number of surface oxygen groups in the VPC model.

In figure 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
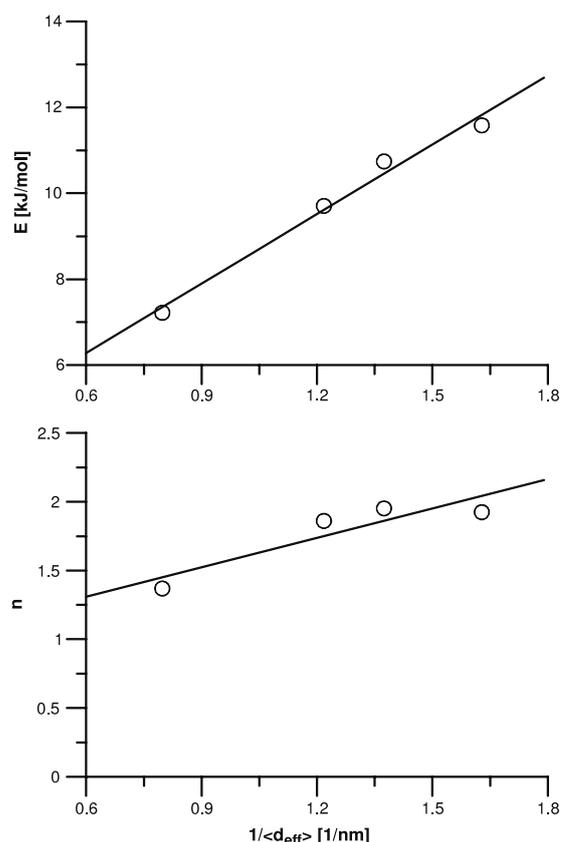
of SF_6 molecules in the simulation box increases at low pressures with the rise in the micropore diameter of carbon and decreases at larger pressures due to the decrease in the volume of the adsorption space. If the absolute adsorption is considered, we observe that the smaller the average micropore diameter, the smaller 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 figures 4 and 5 we show the results of a description of simulated data using the DA adsorption isotherm equation (equation (1) and table 2), plotted as a function of the oxygen content (figure 4) and the inverse of the average micropore diameter (figure 5). Since there are negligibly small changes in porosity upon carbon oxidation (see figure 1), it is obvious that the correlations observed in figure 4 are caused by the interactions of adsorbed molecules with oxygen. We see that both the characteristic energy of adsorption and the parameter *n* of the DA model are affected by the number of oxygen groups present on the 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 using the DA model, cannot be applied for microporosity

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

System	a_0 (molecules/box)	E (kJ mol^{-1})	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

characterization if the carbon contains oxygen surface functionalities. On the other hand, figure 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 figure 5, the parameter n of this equation is also correlated with the average micropore diameter. Therefore, the application of a simple inverse relationship between the characteristic energy and pore diameter is questionable.

4. Conclusions

We show, for the first time, the influence of the carbon porosity and surface oxidation on the parameters of the DA adsorption isotherm equation. It is demonstrated that upon carbon surface oxidation, the adsorption decreases for all carbons studied. Moreover, the parameters of the DA model depend on the number of surface oxygen groups. That is why in the case of carbons containing surface polar groups, SF$_6$ adsorption isotherm data described using the DA model cannot be applied for the characterization of the porosity.

On the other hand, if carbon does not contain polar surface groups, a new relationship between E_0 and the pore diameter should be proposed, since the parameter n also depends on the pore diameter.

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