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The influence of carbon surface oxygen groups on Dubinin–Astakhov equation parameters calculated from CO₂ adsorption isotherm

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Abstract

We present the results of a systematic study of the influence of carbon surface oxidation on Dubinin–Astakhov isotherm parameters obtained from the fitting of CO₂ adsorption data. Using GCMC simulations of adsorption on realistic VPC models differing in porosity and containing the most frequently occurring carbon surface functionalities (carboxyls, hydroxyls and carbonyls) and their mixtures, it is concluded that the maximum adsorption calculated from the DA model is not strongly affected by the presence of oxygen groups. Unfortunately, the same cannot be said of the remaining two parameters of this model i.e. the heterogeneity parameter (n) and the characteristic energy of adsorption (E_0). Since from the latter the pore diameters of carbons are usually calculated, by inverse-type relationships, it is concluded that they are questionable for carbons containing surface oxides, especially carboxyls.

 Supplementary data files are available from stacks.iop.org/JPhysCM/22/085003/mmedia

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

1. Introduction

In our previous study the influence of the type of adsorbate on the pore size distribution curve of activated carbon was tested, using virtual porous carbon (VPC) models proposed by Harris *et al* (and developed previously) together with grand canonical Monte Carlo (GCMC) simulations of adsorption isotherms [1]. From simulated data it was concluded that the carbon surface chemical composition strongly influences the

obtained pore size distribution (PSD) curves, especially for adsorbates possessing permanent electric moments. It was also shown that carbon dioxide adsorption data should be treated with care, especially if they are applied for estimation of the PSD of carbons containing oxygen surface functionalities.

On the other hand, in the field of experimental characterization of microporous carbons a very important role is played by the Dubinin–Astakhov (DA) approach (this was also the subject of our previous studies [2–4]) due to its simplicity. Moreover, many researchers apply CO₂ adsorption data for the characterization of microporosity of activated carbons, completely neglecting the existence of a

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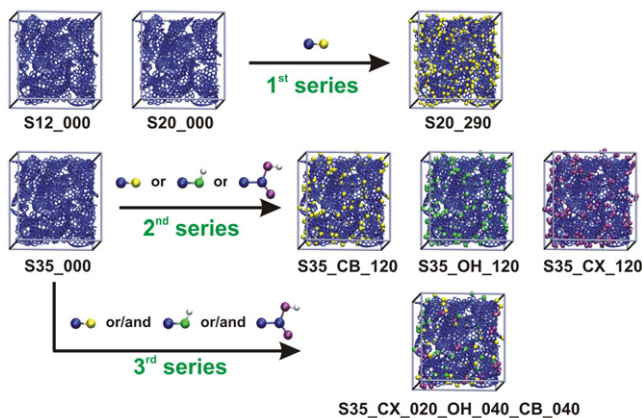


Figure 1. Schematic representation of the creation of VPC series 1–3 studied in this paper. This figure and movie 1 (supplementary data available at stacks.iop.org/JPhysCM/22/085003/mmedia) were created using the VMD program [14, 15].

permanent electrostatic moment in the CO₂ molecule (see discussion and references from our previous study [1]). In a recent review, Marsh and Rodrigues-Reinoso [5] presented an excellent discussion on the applicability of carbon dioxide in the characterization of the porosity of carbons, based mainly on the analysis of adsorption data by the formalism of the

DA model. However, a discussion of the possible influence of electrostatic interactions on the DA model parameters obtained (from analysis of experimental data) has been neglected. Therefore the question arises of the influence of carbon surface chemical composition on the DA equation parameters. The estimation of this effect is the major purpose of the current study. Using the VPC models of Harris *et al*, in conjunction with GCMC simulations of carbon dioxide adsorption, we discuss the effect of the chemical composition of the carbon surface on the parameters obtained from fitting of DA model to simulated carbon dioxide isotherms. In a previous study, the influence of surface functionalities on PSD was discussed for VPCs containing only surface carbonyl groups. Since in activated carbons different types of surface groups are usually present, in this study we consider a more realistic situation than studied previously, i.e. we take into account the presence of three of the most frequently occurring groups. Moreover, adsorbents containing a mixture of all groups are also considered.

2. The method

2.1. Simulation boxes

Three series of microporous structures were analysed, based on the VPC model proposed by Harris *et al* [6–8] and applied

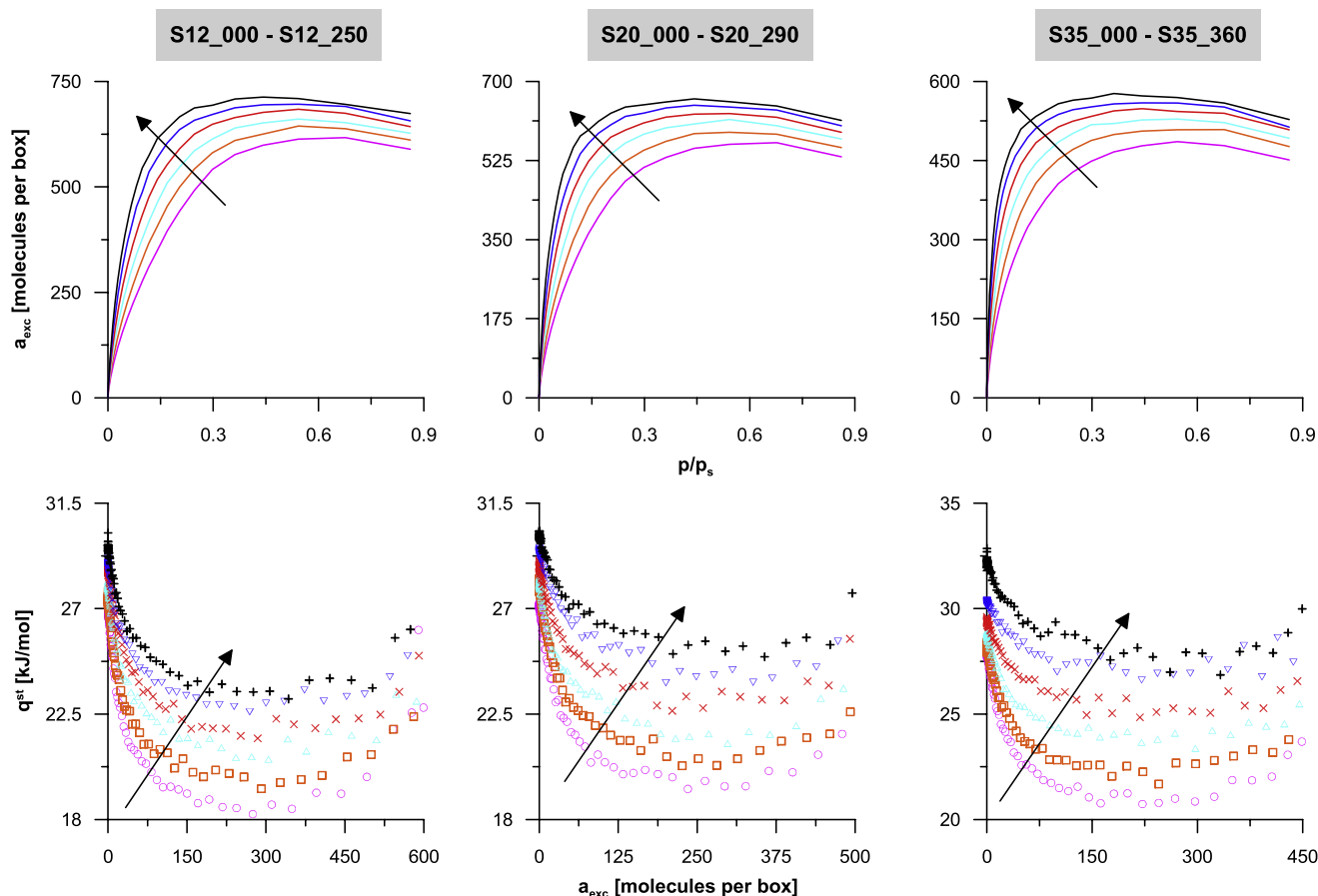


Figure 2. The comparison of adsorption isotherms (and isosteric enthalpy— q^{st}) simulated for the first series (only carbonyl groups present). Arrows show the direction of changes from the structure without carbonyls up to the structure with a maximum number of those groups.

Table 1. Characteristics of studied simulation boxes.

Notation	The number of groups			
	Carboxyl	Hydroxyl	Carbonyl	{O} ^a _%
	First series			
S12_000	0	0	0	0.00
S12_050	0	0	50	1.96
S12_100	0	0	100	3.85
S12_150	0	0	150	5.67
S12_200	0	0	200	7.42
S12_250	0	0	250	9.10
S20_000	0	0	0	0.00
S20_058	0	0	58	2.08
S20_116	0	0	116	4.07
S20_174	0	0	174	5.98
S20_232	0	0	232	7.82
S20_290	0	0	290	9.59
S35_000	0	0	0	0.00
S35_072	0	0	72	2.32
S35_144	0	0	144	4.53
S35_216	0	0	216	6.64
S35_288	0	0	288	8.66
S35_360	0	0	360	10.60
Second series				
S35_CX_024	24	0	0	1.55
S35_CX_048	48	0	0	3.03
S35_CX_072	72	0	0	4.44
S35_CX_096	96	0	0	5.81
S35_CX_120	120	0	0	7.11
S35_OH_024	0	24	0	0.78
S35_OH_048	0	48	0	1.55
S35_OH_072	0	72	0	2.31
S35_OH_096	0	96	0	3.06
S35_OH_120	0	120	0	3.79
S35_CB_024	0	0	24	0.78
S35_CB_048	0	0	48	1.56
S35_CB_072	0	0	72	2.32
S35_CB_096	0	0	96	3.06
S35_CB_120	0	0	120	3.80
Third series				
S35_CX_060_OH_000_CB_000	60	0	0	3.74
S35_CX_040_OH_040_CB_000	40	40	0	3.76
S35_CX_040_OH_030_CB_010	40	30	10	3.76
S35_CX_040_OH_020_CB_020	40	20	20	3.76
S35_CX_040_OH_010_CB_030	40	10	30	3.76
S35_CX_040_OH_000_CB_040	40	0	40	3.76
S35_CX_020_OH_080_CB_000	20	80	0	3.78
S35_CX_020_OH_060_CB_020	20	60	20	3.78
S35_CX_020_OH_040_CB_040	20	40	40	3.78
S35_CX_020_OH_020_CB_060	20	20	60	3.78
S35_CX_020_OH_000_CB_080	20	0	80	3.78
S35_CX_000_OH_090_CB_030	0	90	30	3.79
S35_CX_000_OH_060_CB_060	0	60	60	3.80
S35_CX_000_OH_030_CB_090	0	30	90	3.80

^a Percentage mass contents of oxygen in studied structures.

in our previous studies [1–4, 9–11]. We use the method of construction of boxes, leading to progressive changes in surface oxygen complexes concentration, and/or the type of the groups.

The first series (series 1) is based on the microporous VPC models: S12, S20 and S35 (containing 3328, 3644 and 4049

Table 2. Geometric characteristics of CO₂ and surface groups introduced in structures.

Molecule/group	Bond type	Length of the bond (nm)	Angle type	Value of the angle (deg)	References
CO ₂	CO	0.1160	—	—	[12]
Carbonyl	CO	0.1233	—	—	[13]
Hydroxyl	C ^a O	0.1364	C ^a OH	110.5	[13]
	OH	0.0960	—	—	—
Carboxyl	C ^a C	0.1520	C ^a CO	111.0	[13]
	C=O	0.1214	OCO	123.0	—
	CO	0.1364	COH	107.0	—
	OH	0.0970	—	—	—

^a An atom of the carbon structure bounding the groups.

Table 3. The values of LJ potential parameters and point charges applied in simulations.

Molecule/group	Site	σ (nm)	ϵ/k_B (K)	q (e)	References
CO ₂	C	0.280	27.0	+0.70	[12]
	O	0.305	79.0	-0.35	—
C ^a	C ^a	0.340	28.0	— ^b	[13]
	—	—	—	—	—
Carbonyl	C	0.340	28.0	+0.50	[13]
	O	0.296	105.8	-0.50	—
Hydroxyl	C ^c	0.340	28.0	+0.20	[13]
	O	0.307	78.2	-0.64	—
Carboxyl	H	— ^d	— ^d	+0.44	—
	C ^c	0.340	28.0	+0.08	[13]
	C	0.375	52.8	+0.55	—
	=O	0.296	105.7	-0.50	—
	O	0.300	85.6	-0.58	—
H	— ^d	— ^d	+0.45	—	

^a An atom of carbon structure non-bounded with hydroxyl and/or carboxyl.

^b LJ-type centre without charge.

^c An atom of carbon structure bounding a group.

^d A centre treated only as a point charge and not as a LJ centre.

carbon atoms, respectively) with dimensions 4.6 nm × 4.6 nm × 4.6 nm. The detailed description of the creation procedure can be found in [3]. Those structures possess decreasing average pore diameters (S12: 0.82 nm, S20: 0.73 nm and S35: 0.61 nm [3]). To the structures of this series only carbonyl surface groups were introduced by so called ‘virtual oxidation’ procedure proposed previously [1]. In this procedure at the first stage almost the maximal possible number of carbonyl oxygen atoms is introduced randomly (avoiding overlaps), and next, oxygen atoms are progressively deleted and in this way boxes with a progressively decreasing number of oxygen groups are created. For the structures S12, S20 and S35 the maximum possible number of surface carbonyl groups is equal to ca. 250, 290 and 360. Starting from this number of groups, in each attempt 20% of the starting number of functionalities was deleted and finally, three groups of structures were obtained (each containing six structures) where the oxygen content ranged from maximal down to zero (i.e. in this case we have the initial structure). For the VPCs from the first series we applied the notation: ‘Sxx_yyy’, where ‘Sxx’ denotes the type of initial structure, and ‘yyy’ is the number of carbonyl groups (see table 1).

Table 4. The values of the best fit parameters obtained from the description of simulated CO₂ isotherms (in the range $p/p_s < 0.5$) using DA equation (equation (5)) (the values of a_0 are in molecules per box, E_0 in kJ mol⁻¹).

First series					Second series					Third series				
Structure	a_0	E_0	n	DC	Structure	a_0	E_0	n	DC	Structure	a_0	E_0	n	DC
S12_000	795.3	16.06	1.387	0.9989	S35_CX_024	561.4	26.16	1.862	0.9993	S35_CX_060_OH_000_CB_000	576.2	31.40	2.011	0.9996
S12_050	770.0	18.39	1.558	0.9988	S35_CX_048	568.7	29.89	1.929	0.9997	S35_CX_040_OH_040_CB_000	571.6	29.46	1.978	0.9994
S12_100	764.7	20.34	1.697	0.9987	S35_CX_072	581.8	33.26	2.036	0.9993	S35_CX_040_OH_030_CB_010	570.2	29.72	2.055	0.9990
S12_150	765.8	22.13	1.847	0.9987	S35_CX_096	588.8	36.66	2.143	0.9994	S35_CX_040_OH_020_CB_020	575.7	29.72	1.962	0.9995
S12_200	762.0	24.15	2.047	0.9986	S35_CX_120	594.5	40.25	2.299	0.9994	S35_CX_040_OH_010_CB_030	575.6	29.06	1.942	0.9991
S12_250	769.1	25.66	2.190	0.9984	S35_OH_024	550.0	22.66	1.807	0.9992	S35_CX_040_OH_000_CB_040	569.1	29.77	2.114	0.9992
S20_000	672.3	18.79	1.548	0.9990	S35_OH_048	549.4	23.48	1.864	0.9995	S35_CX_020_OH_080_CB_000	570.9	27.57	1.948	0.9990
S20_058	676.7	20.90	1.707	0.9989	S35_OH_072	553.3	24.15	1.934	0.9993	S35_CX_020_OH_060_CB_020	563.0	27.59	2.067	0.9992
S20_116	678.9	22.98	1.900	0.9985	S35_OH_096	552.2	25.11	2.025	0.9993	S35_CX_020_OH_040_CB_040	573.6	27.63	1.997	0.9989
S20_174	684.2	25.05	2.042	0.9987	S35_OH_120	550.8	25.97	2.128	0.9991	S35_CX_020_OH_020_CB_060	570.2	28.15	2.038	0.9992
S20_232	692.3	26.95	2.183	0.9988	S35_CB_024	547.9	22.84	1.827	0.9993	S35_CX_020_OH_000_CB_080	570.1	28.01	2.037	0.9991
S20_290	695.0	28.89	2.387	0.9987	S35_CB_048	550.1	23.77	1.890	0.9994	S35_CX_000_OH_090_CB_030	554.5	26.09	2.124	0.9992
S35_000	544.9	21.87	1.719	0.9994	S35_CB_072	553.1	24.68	1.986	0.9994	S35_CX_000_OH_060_CB_060	556.1	26.30	2.151	0.9992
S35_072	556.4	24.22	1.939	0.9991	S35_CB_096	558.8	25.61	2.080	0.9992	S35_CX_000_OH_030_CB_090	557.7	26.36	2.152	0.9991
S35_144	565.0	26.57	2.099	0.9993	S35_CB_120	560.1	26.58	2.179	0.9991					
S35_216	575.0	28.76	2.269	0.9994										
S35_288	581.5	31.19	2.429	0.9995										
S35_360	593.5	33.17	2.525	0.9995										

The second analysed series (series 2) of simulation boxes is based on the structure S35 and contains three groups of VPCs with different carbon surface functionalities occurring in real carbons (i.e. carboxyls, hydroxyls and carbonyls); these groups are located exactly at the same places, and their amount decreases. Since among the considered functionalities the carboxylic group is the largest one, the maximum number of introduced carboxyls determines the maximum number of other groups. The first stage of simulation box creation is exactly the same as described above (i.e. introduction of the largest possible number of carboxyls). To do this, the two-bonded carbon atoms (potential sites for bonding) in the structure are detected, and next (in a random way) a carboxylic group is attached (the group is located in a way excluding overlaps). The direction of a bond between a carbon atom in the structure and a carbon atom in the carboxylic groups is determined by the secant of an angle C–C–C (the middle C denotes an atom where the group is bonding; the remaining atoms are those in the structure and bonded with this carbon). In the same series the structures containing surface hydroxyl groups (with random angular orientation) and carbonyls (attached to the same two-bonded carbon atoms) were generated (the characteristics of groups are given in table 2). The maximal possible number of carboxylic groups in the structure S35 is close to 120. Using the procedure of random deletion of groups (20% as described above) three series of VPCs (5 structures in each group) were obtained containing all three types of surface oxygen functionalities (the number of groups decreases, and they are located at exactly the same places). The reference structure for this series is S35 (named S35_000). For the structures of the second series containing carboxylic, hydroxylic and carbonyl groups the following notation was applied: ‘S35_CX_ddd’, ‘S35_OH_ddd’ and ‘S35_CB_ddd’, where ‘ddd’ denotes the number of oxygen groups in a structure.

The third generated series (series 3) of structures is also based on VPC S35. In the boxes of this series mixtures of different groups are present. It was assumed that all structures contain the same number of oxygen atoms (therefore have similar percentage content of oxygen) i.e. 120. We start from the structures of second series with the maximal number (120) of the three analysed types of groups introduced. The program for creation of structures remains (at random positions) random types of groups (but in assumed amount). The following notation is applied: ‘S35_CX_ddd_OH_ddd_CB_ddd’, where ‘ddd’, ‘ddd’ and ‘ddd’ denote the number of carboxylic, phenolic or carbonyl groups, respectively.

Figure 1 shows a schematic representation of the procedure of creation of all the studied structures. Pore size distributions (PSD) of all VPCs were calculated by the geometric method proposed by Bhattacharya and Gubbins [16] using the procedure described in detail previously [1].

2.2. Molecular interactions

The CO₂ molecule was modelled using the three centre model of TraPPE type [12]. Each centre located on the atom of a molecule is the Lennard-Jones centre and possesses the point

charge. The energy of interaction of a pair of molecules, with the centres separated by a distance r , can be written as (this energy is also a function of angular orientation):

$$U(r) = \sum_{i=1}^3 \sum_{j=1}^3 U_{\text{LJ}}^{ij}(r_{ij}) + U_{\text{electr}}(r) \quad (1)$$

where $U_{\text{LJ}}^{ij}(r_{ij})$ is the energy of dispersion interactions between a pair of centres i and j (in the interacting molecules) located at the distance r_{ij} , and calculated from the truncated LJ potential:

$$U_{\text{LJ}}^{ij}(r_{ij}) = \begin{cases} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & r_{ij} < r_{\text{cut},ij} \\ 0 & r_{ij} \geq r_{\text{cut},ij} \end{cases} \quad (2)$$

where σ_{ij} and ε_{ij} are the collision diameter and the depth of the potential well for interactions between the centres of the type i and j . The second term in equation (1) ($U_{\text{electr}}(r)$) describes electrostatic interactions of a pair of molecules, described by:

$$U_{\text{electr}}(r) = \begin{cases} \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^3 \sum_{j=1}^3 \frac{q_i q_j}{r_{ij}} & r < r_{\text{cut},C} \\ 0 & r \geq r_{\text{cut},C} \end{cases} \quad (3)$$

where q_i and q_j are the values of the charges of the centres, and ε_0 ($8.8543 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$) is the dielectric permittivity of free space. One can observe that, as previously, we use the cut-offs for electrostatic interactions, but this is used for whole molecules [17], i.e. if the centres of mass of two molecules are located at a distance smaller than $r_{\text{cut},C}$ the sum of interactions between all pairs of charges occurring in both molecules is calculated, otherwise the electrostatic interactions are neglected. In this study this distance ($r_{\text{cut},C}$) is assumed as equal to 1.5 nm. At this distance the energy of interactions of a pair of molecules is negligibly small (the energy of electrostatic interactions for the studied molecules (having quadrupole moments) decreases proportionally to the fifth power of the distance [18]).

The energy of interactions between adsorbed molecules and the structure of the adsorbent is given by:

$$U_{\text{st}} = \sum_{i=1}^3 \left\{ \sum_{j=1}^{ND} U_{\text{LJ}}^{ij}(r_{ij}) + \frac{1}{4\pi\varepsilon_0} \sum_{j=1}^{NC} \frac{q_i q_j}{r_{ij}} \right\} \quad (4)$$

where ND and NC denote the number of LJ centres and the number of point charges in the structure of an adsorbent, respectively. For all LJ-type interactions the cut-off is assumed as equal to $r_{\text{cut},ij} = 5\sigma_{ij}$. Table 3 collects all the values of the applied interaction parameters (we used the Lorentz–Berthelot mixing rules).

2.3. Simulations

Carbon dioxide adsorption isotherms were simulated for 298 K in the range of pressures ca. 1 Pa up to ca. 5.5 MPa ($p_s = 6.4121 \text{ MPa}$ [19]). All simulation boxes have the same sizes (analogous to the sizes of structures) i.e. $4.6 \text{ nm} \times 4.6 \text{ nm} \times$

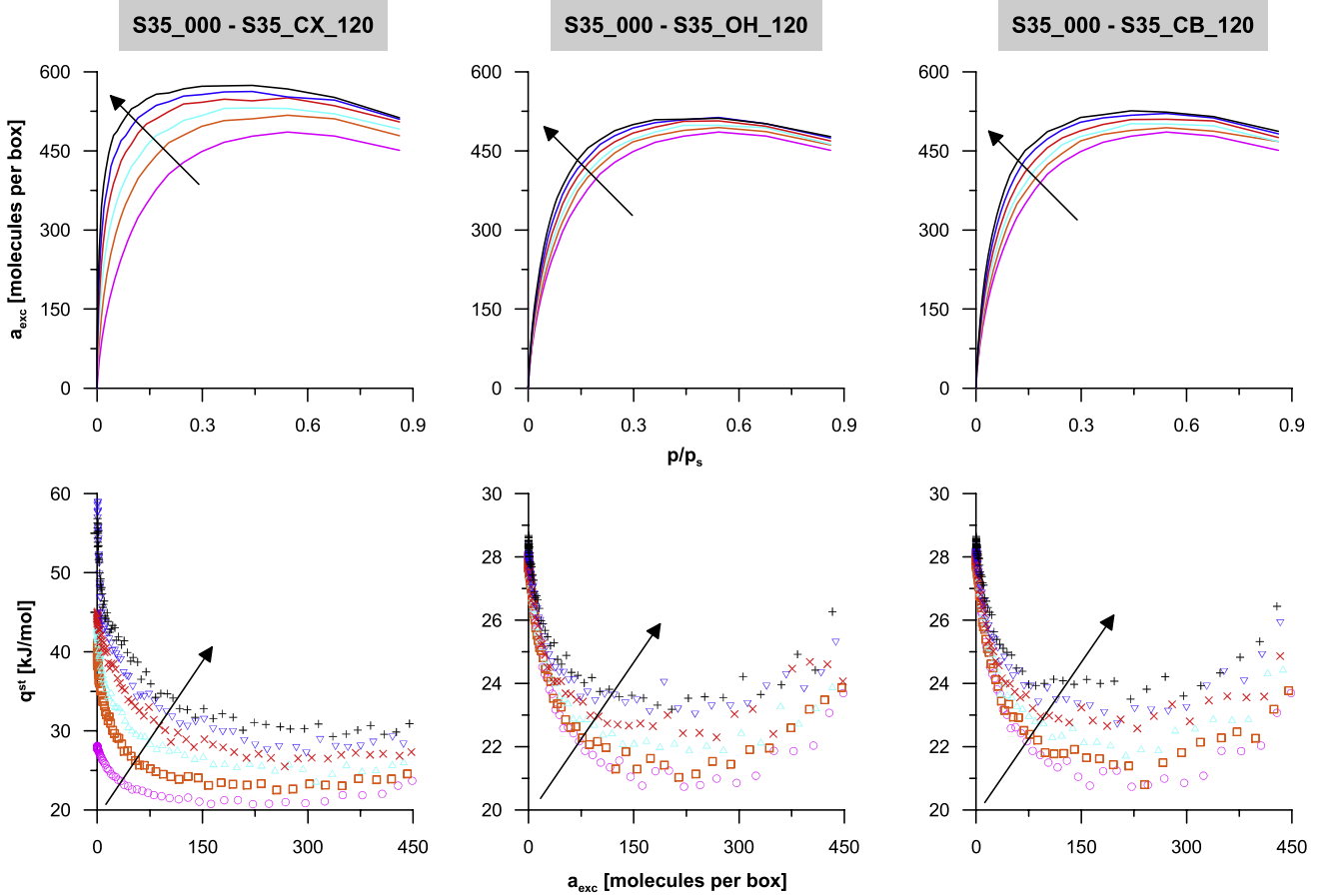


Figure 3. The comparison of adsorption isotherms (and isosteric enthalpy) simulated for the second series (containing different groups but located at the same places, from the left carboxyls, hydroxyls and carbonyls). Arrows show the direction of changes from the structure without groups up to the structure with the maximum number of groups.

4.6 nm (we applied periodic boundary conditions in all three directions). A typical GCMC method was applied [20]. The probability of attempts of changing of a state of a system by creation, annihilation, 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 25×10^6 iterations were performed during the equilibration, and the next 25×10^6 were 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). The enthalpy of the adsorption values were calculated from the theory of fluctuations.

2.4. 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:

$$a = a_0 \exp \left[- \left(\frac{RT \ln \frac{p_s}{p}}{\beta E_0} \right)^n \right] \quad (5)$$

where 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_0 is the characteristic energy of adsorption, β is the affinity

coefficient (assumed as equal to 0.35 [21]), n is a parameter related to heterogeneity, and R is the gas constant.

Simulated excess isotherms were described in the range of increasing adsorption i.e. up to $p/p_s < 0.5$. Genetic algorithms were applied for fitting equation (5) to experimental data [2–4, 22, 23]. The goodness of the fit was estimated using the values of the determination coefficients:

$$DC = \frac{\sum_{i=1}^{NP} (a_{\text{theo},i} - a_{\text{sim},i})^2}{\sum_{i=1}^{NP} (a_{\text{sim},i} - \bar{a}_{\text{sim}})^2} \quad (6)$$

where $a_{\text{theo},i}$ and $a_{\text{sim},i}$ are the theoretical values and values obtained from simulations, respectively, of adsorption for the i th point on the isotherm, \bar{a}_{sim} is the average value of the latter, and NP is the number of points on the adsorption isotherm.

3. Results and discussion

Figures S1 and S2 (supplementary data available at stacks.iop.org/JPhysCM/22/085003/mmedia) show the geometric PSD curves for the studied structures. One can observe that the introduction of surface groups practically does not change the geometric PSD. The only exception is for the case of structures containing surface carboxylic groups (being the

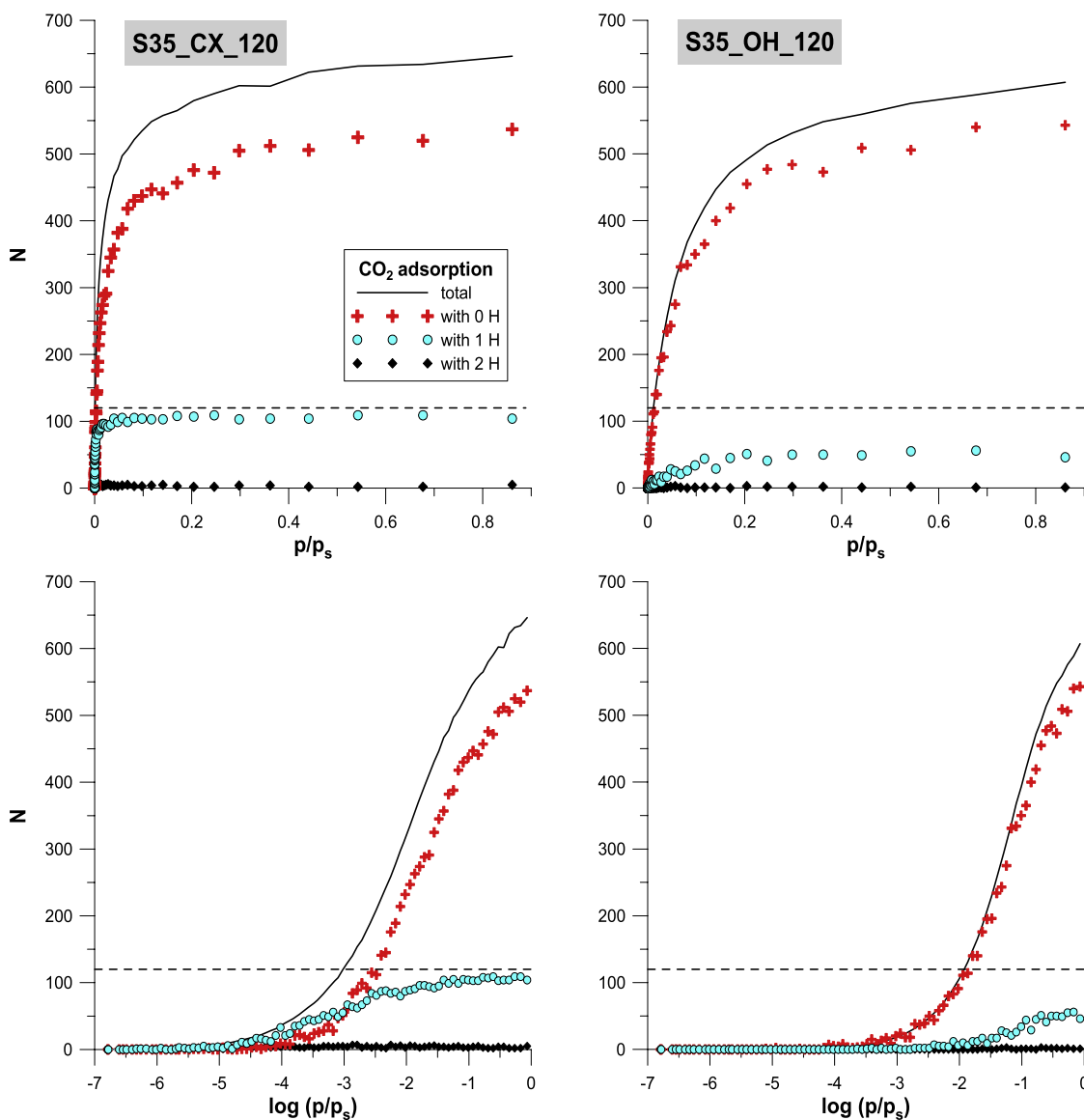


Figure 4. Adsorption isotherms (number of molecules in a simulation box (N) from the final configuration) for the systems shown in the movie (available at stacks.iop.org/JPhysCM/22/085003/mmedia), divided into molecules interacting with two, one or zero surface groups. Dashed horizontal lines show the number of surface groups in the structures.

largest ones), where we observe a shift toward smaller pore diameters (by ca. 0.2 nm) with a rise in the number of surface groups in a structure. Figure 2 shows the results of simulations for the first series. One can observe a rise in adsorption as well as in the value of the isosteric enthalpy of adsorption with a rise in the number of surface carbonyls. A detailed analysis of the number of groups interacting with carbon dioxide leads to the conclusion that for this case there is a competition between adsorption in small pores (where the potential energy of interaction is high) and adsorption in larger pores with surface groups, where the latter leads to a rise in the energy of adsorption by the appearance of electrostatic interactions. Figure 3 shows the differences in CO₂ adsorption mechanisms if different groups (located at the same places) in the structure are present. As one can observe, for surface hydroxyls a similar situation is seen as for carbonyls, however for carboxylic groups the influence on adsorption isotherms is the largest,

and differences in adsorption enthalpy values are observed from the start of the adsorption process. This is caused by the large energy of interaction between those groups and adsorbed CO₂ molecules, leading to saturation of almost all the groups at low coverages. The movie in the supplementary data (available at stacks.iop.org/JPhysCM/22/085003/mmedia) shows the animations of adsorption on structures S35 with carboxylic and hydroxylic groups on the surface (second series, maximum number of both group types in structures). We use different colours to mark molecules interacting only with the carbon structure, with one and two hydrogen atoms of the functional groups (it was assumed that the interaction with a surface group occurs if the distance between one of the oxygen atoms of the CO₂ molecule and the hydrogen atom of a group is not larger than 0.24 nm). One can see that for the case of a structure containing carboxylic functionalities (S35_CX_120) the number of carbon dioxide

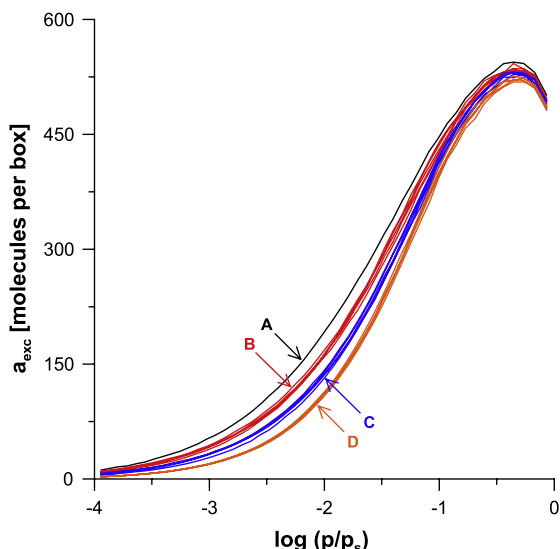


Figure 5. The comparison of adsorption isotherms simulated for the series containing different groups in different ratios but with a constant (120) number of oxygen atoms in each box: **A:** S35_CX_060_OH_000_CB_000; **B:** S35_CX_040_OH_040_CB_000, S35_CX_040_OH_030_CB_010, S35_CX_040_OH_020_CB_020, S35_CX_040_OH_010_CB_030, S35_CX_040_OH_000_CB_040; **C:** S35_CX_020_OH_080_CB_000, S35_CX_020_OH_060_CB_020, S35_CX_020_OH_040_CB_040, S35_CX_020_OH_020_CB_060, S35_CX_020_OH_000_CB_080; **D:** S35_CX_000_OH_090_CB_030, S35_CX_000_OH_060_CB_060, S35_CX_000_OH_030_CB_090, S35_OH_120, S35_CB_120.

molecules interacting with surface groups is larger than for the structure containing hydroxyls (S35_OH_120). Figure 4 shows adsorption isotherms for the systems from the movie (available at stacks.iop.org/JPhysCM/22/085003/mmedia), divided into molecules interacting with two, one or zero surface groups. It can be observed that the number of CO₂ molecules interacting with surface groups is larger for carbon containing

carboxylic groups on the surface. The above-mentioned differences in mechanisms of adsorption (i.e. the appearance of those interactions from the start of the adsorption process) are manifested by the Langmuirian shape of the isotherm responsible for interaction with one surface carboxylic group (figure 4). Moreover, it can also be seen that one CO₂ molecule can interact simultaneously with two groups located in the structure at small distances. The interaction occurs between negatively charged oxygen atoms of the adsorbate and hydrogen atoms of the carboxylic groups. Interactions with carboxylic functionalities lead to a rise in the enthalpy of adsorption, which, in the case of the structure with a maximum number of carboxylic groups, is twice as large as the value observed for the initial unoxidized carbon. Note, that experimental calorimetric data of carbon dioxide adsorption on a series of ‘hard’ carbons, published by Rychlicki [24], also showed a rise in adsorption enthalpy after carbon oxidation (a further rise was observed after introduction of metal cations on carbon surface). Moreover, the values of measured adsorption enthalpy (30–45 kJ mol⁻¹) are in a similar range to those obtained from our simulations. Since carboxylic groups are observed in almost all ‘commercial’ activated carbons, the application of CO₂ for determination of the parameters of porous structure is, for this case, questionable. This is also true for the case of carbons containing a mixture of different surface groups. The results from figure 5 show that, in this case, simulated isotherms can be divided into four groups, depending on the contents of carboxylic groups. One can see that with a rise in the number of carboxyls in the structure adsorption increases.

The application of the DA model (equation (5)) to a description of simulated data leads to relatively good values of the determination coefficients collected in table 4. For the majority of cases the maximum adsorption value increases linearly with the number of surface oxygen functionalities, but no more than by about 10% (the two exceptions are the structures S12 from the first series—where we observe

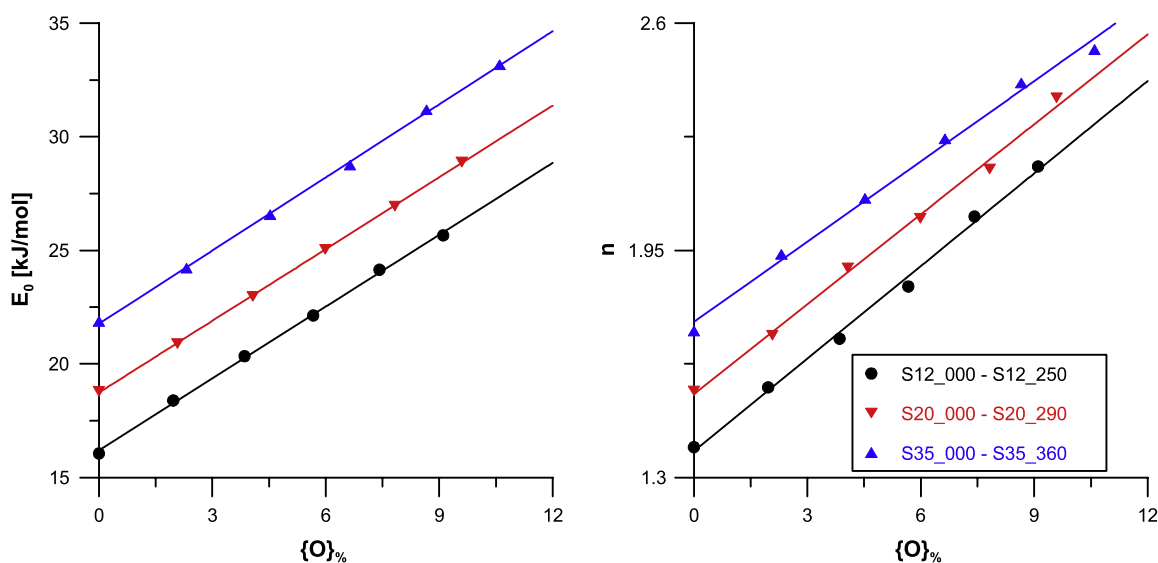


Figure 6. Correlations between the values of the best fit parameters of the DA adsorption isotherm equation obtained from a description of the simulated isotherm for the first series, and the contents of oxygen in the structures.

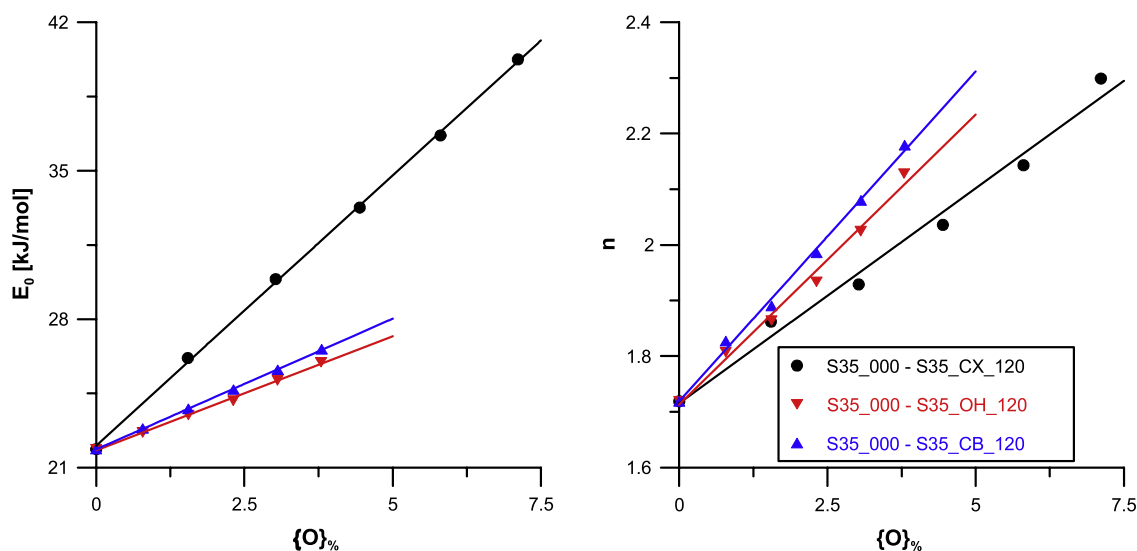


Figure 7. The same as in figure 4, but for isotherms simulated for the second series.

a decrease by ca. 3%, and S35_OH from series 2 where the increase is between 0.8 and 1.6%). Therefore it is reasonable to conclude that the introduction of surface functionalities changes the maximum adsorption of the DA equation by a small amount. On the other hand, the characteristic energy of adsorption (E_0), as well as the heterogeneity parameter of the DA model (n) are linearly correlated with oxygen contents (figures 6 and 7) and/or concentration of surface carboxylic groups (figure 8) in the carbon structure. The obtained lines are almost parallel for different structures if the number of one type of groups changes (figure 5). However, from figure 6 one can observe that if the same structure (but possessing different groups) is considered the largest slope is observed for carboxyls, whereas for carbonyls and hydroxyls similar changes in E_0 with percentage contents of oxygen are recorded. Since the diameters of carbon micropores (x) are usually calculated by simple inverse-type relations between x and E_0 , and the latter is obtained from fitting of experimental data by the DA model, one can conclude that large differences in pore diameters calculated in this way will be observed. In fact pore diameters are almost the same for a given structure (figures S1 and S2—supplementary data available at stacks.iop.org/JPhysCM/22/085003/mmedia) irrespective of oxygen contents.

4. Conclusions

Systematic studies on the influence of carbon surface functionalities on the parameters of the DA model lead to the conclusion that the presence of surface carboxylic groups to the largest extent affect those parameters. For carbon models with different pore size distributions, as well as containing three types of the most frequently occurring surface groups (and their mixtures), we observe the remarkable influence of oxygen on the characteristic energy of adsorption and the heterogeneity parameter of the DA model, while the maximum adsorption is affected to a smaller degree. Since the largest

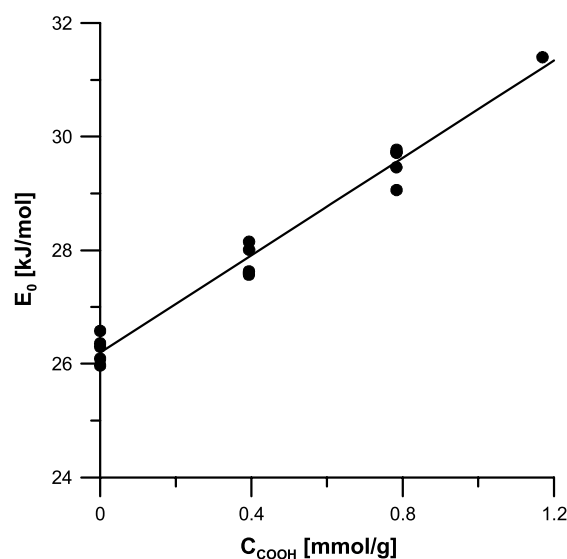


Figure 8. Correlation between the characteristic energies of adsorption (obtained from the description of the data for the third series) and the concentration of surface carboxylic groups.

influence is observed for surface carboxylic groups (being the most frequently observed in commercial carbons) the results of porosity parameters calculated based on fitting of the DA model to experimental CO_2 adsorption data are questionable.

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