

NOTICE: this is the author's version of a work that was accepted for publication in Chemical Physics Letters. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Chemical Physics Letters, Vol. 578 (2013)DOI: [10.1016/j.cplett.2013.05.060](https://doi.org/10.1016/j.cplett.2013.05.060)

Influence of activated carbon surface oxygen functionalities on SO₂ physisorption – simulation and experiment

Sylwester Furmaniak^{1*}, Artur P. Terzyk¹, Piotr A. Gauden¹,
Piotr Kowalczyk², and Grzegorz S. Szymański¹

(1) Physicochemistry of Carbon Materials Research Group, Department of Chemistry, N. Copernicus University, Gagarin St. 7, 87-100 Toruń, Poland

(2) Nanochemistry Research Institute, Department of Chemistry, Curtin University of Technology, P.O. Box U1987, Perth, 6845 Western Australia, Australia

(*) corresponding author

Sylwester Furmaniak

Physicochemistry of Carbon Materials Research Group

Department of Chemistry

N. Copernicus University

Gagarina St. 7

87-100 Toruń

Poland

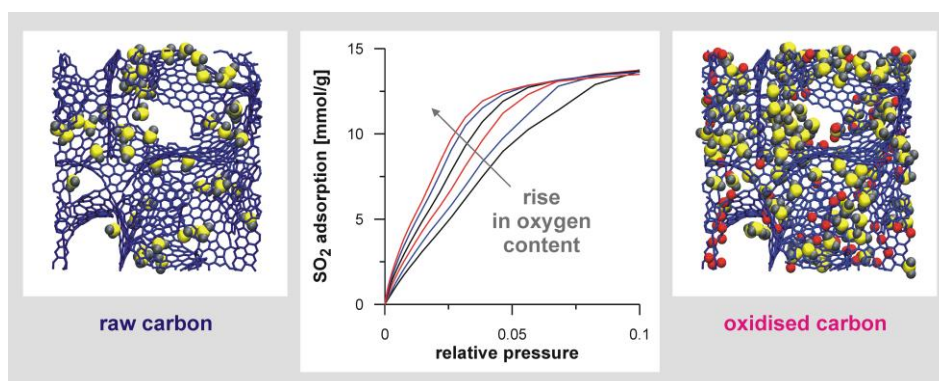
e-mail: sf@chem.umk.pl

tel. (+48) (56) 611-44-27

fax: (+48) (56) 654-24-77

url: <http://www.chem.umk.pl/~aterzyk>

Graphical Abstract



Abstract

The influence of the gradual oxidation of carbons on SO₂ physisorption was studied, by comparison of experimental and simulated SO₂ adsorption isotherms. The results confirmed a significant impact of surface groups on the SO₂ adsorption. The simulations also revealed a similar, to that observed experimentally, effect of the increase in the percentage of the smallest micropores on adsorption isotherms. The isotherms were analysed using the CMMS model. The conclusion is that this model seems to be a good and sensitive tool for studying SO₂ physisorption mechanism since a very good qualitative agreement between the experimental and simulated data was observed.

keywords

SO₂; adsorption; activated carbons; Monte Carlo simulations; surface oxygen groups

1. Introduction

Sulphur dioxide (SO_2) is one of atmospheric pollutants which contribute to acid rain. The emission of SO_2 is mainly due to the combustion of sulphur-containing fuels [1-3]. Different methods are used to reduce the emission of this gas [1]. The adsorption process, as one of these methods, has been studied very frequently due to its simplicity and low cost [4]. Thus, SO_2 adsorption on carbonaceous materials (mainly activated carbons) is still a subject of interest of different researchers [5-10].

In our previous paper [11] we studied SO_2 physisorption on a series of activated carbons obtained *via* the modification of a starting sample by a heat treatment in different atmospheres and at various temperature values. Our results revealed that the interactions between SO_2 molecules and carbon surface oxygen groups are crucial during the physisorption of this adsorbate. These observations were confirmed by the description of adsorption isotherms using the cooperative multimolecular sorption model (CMMS) proposed by Malakhov and Volkov [12]. It was shown that the equilibrium constants of CMMS equation were linearly correlated with the oxygen contents. The porosity of the considered carbons was similar, however, there were some differences between pore size distributions, BET surface areas and pore volumes. These differences may also have some influence on the obtained results. On the other hand, the porosity of the samples was characterised by low-temperature N_2 adsorption and, as was shown previously [13], the presence of surface functionalities may affect the pore size distributions calculated from adsorption isotherms, especially in the case of adsorbates having the quadrupole moment (like N_2). Thus, computer simulations seem to be the simplest way to test the influence of oxygen surface groups on SO_2 physisorption on activated carbons. Using the so-called virtual porous carbon (VPC) [14,15] makes it possible to strictly control the porosity of carbon during the introduction of surface groups. This is, due to the reasons mentioned above, practically impossible in the case of real experiments.

In this communication, Monte Carlo simulations are used to systematically study the influence of surface oxygen groups on SO_2 physisorption on activated carbons. We consider three starting VPCs generated previously [16]. Oxygen functionalities are introduced on the surface using the previously proposed virtual oxidation procedure [13]. For simplicity, only carbonyl groups are investigated (as it was shown by Jorge et al. [17] who considered water adsorption, the type of oxygen-containing group is not of critical importance, since more complex groups can effectively be represented by simpler sites). Simulated adsorption

isotherms were fitted by CMMS model. The obtained results are compared with discussed above and the previously published experimental data [11].

2. Simulation details

2.1 Simulation boxes

Three, differing in porosity, VPCs were used. They were generated following the procedure described previously [16] using simple Metropolis Monte Carlo method and one of the most sophisticated carbon force field, i.e. carbon EDIP potential proposed by Marks [18,19]. We chose the structure having density equal to 0.6, 0.8 and 1.0 g/cm³ and denoted as d0.6, d0.8 and d1.0, respectively. Basing on these VPCs, three series of carbons containing a systematically increasing number of carbonyl groups were generated using the virtual oxidation procedure [13]. The following numbers of carbonyl oxygen atoms were introduced: 34, 68, 102, 136 and 170 for the d0.6 structure, 32, 64, 96, 128 and 160 for the d0.8 structure, and 30, 60, 90, 120 and 150 for the d1.0 structure, respectively. The subsequent VPCs were denoted as dx.x_yyy, where x.x is the density of starting carbon and yyy is the number of carbonyl groups. Fig. 1 presents schematically all the considered VPCs and applied notation.

The porosity of studied VPCs was characterised by a geometrical method proposed by Bhattacharya and Gubbins (BG) [20]. The implementation of the method was described in details elsewhere [16,21]. Table S1 in Supplementary data collects the basic characteristics of the considered VPCs.

2.2 Simulations of SO₂ adsorption isotherms

SO₂ adsorption isotherms on all the generated VPCs were simulated using hyper parallel tempering Monte Carlo (HPTMC) method proposed by Yan and de Pablo [22]. The simulations were performed for ambient temperature, i.e. $T = 298$ K. For each system, 63 replicas (corresponding to the relative pressures from 1.0×10^{-6} to 1.0) were considered. The HPTMC simulations utilized 5×10^6 cycles (one cycle = 100 attempts of the change of each replica state by (i) creation, (ii) annihilation or (iii) rotation and/or displacement of a randomly chosen molecule with equal probabilities, and one attempt of a configuration swap between a pair of randomly chosen replicas) [23]. The first 1×10^6 cycles were discarded to guarantee equilibration.

For SO₂ molecules we used three-centre rigid model of Ribeiro [24]. The same force field was used successfully by others to simulate SO₂ adsorption on carbon nanotubes [25]. The energy of interactions of SO₂ molecules pair was calculated as the sum of interaction between pairs of centres:

$$U_{ff}(r, \omega_1, \omega_2) = \sum_{i=1}^3 \sum_{j=1}^3 \left[U_{LJ}^{ij}(r_{ij}) + U_{electr}^{ij}(r_{ij}) \right] \quad (1)$$

where r is the distance between the molecules, ω_1 and ω_2 determine their angular orientation, r_{ij} is the distance between the pair of centres, U_{LJ}^{ij} and U_{electr}^{ij} represent the energy of dispersive and electrostatic interactions between them, respectively. The dispersive interactions were modelled using Lennard-Jones potential [26]. Cut-offs were realized by the switching function in a quintic form [27]:

$$U_{LJ}^{ij}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \times S(r_{ij}) \quad (2)$$

where σ_{ij} and ε_{ij} are the collision diameter and the potential well depth, respectively, and S is the switching function [27]:

$$S(r_{ij}) = \begin{cases} 1 & r_{ij} \leq r_{on} \\ -6 \left(\frac{r_{ij} - r_{on}}{r_{cut} - r_{on}} \right)^5 + 15 \left(\frac{r_{ij} - r_{on}}{r_{cut} - r_{on}} \right)^4 - 10 \left(\frac{r_{ij} - r_{on}}{r_{cut} - r_{on}} \right)^3 + 1 & r_{on} < r_{ij} < r_{cut} \\ 0 & r_{ij} \geq r_{cut} \end{cases} \quad (3)$$

r_{cut} is the cut-off distance and r_{on} is the distance at which the switching function starts to apply.

The energy of electrostatic interactions was calculated using the potential proposed by Fennel and Gezelter [28]:

$$U_{electr}^{ij}(r_{ij}) = \begin{cases} \frac{q_i q_j}{4\pi\varepsilon_0} \left[\frac{\text{erfc}(\alpha r_{ij})}{r_{ij}} - \frac{\text{erfc}(\alpha r_{cut})}{r_{cut}} + \left(\frac{\text{erfc}(\alpha r_{cut})}{r_{cut}^2} + \frac{2\alpha}{\sqrt{\pi}} \times \frac{\exp(-\alpha^2 r_{cut}^2)}{r_{cut}} \right) (r_{ij} - r_{cut}) \right] & r_{ij} < r_{cut} \\ 0 & r_{ij} \geq r_{cut} \end{cases} \quad (4)$$

where q_i and q_j are the values of the charges of the centres, $\varepsilon_0 = 8.8543 \times 10^{-12}$ C²/J/m is the dielectric permittivity of free space, and $\alpha = 2.0$ 1/nm [28] is the damping factor. Eq. (4) is a simple alternative to the Ewald summation [28].

The energy of solid-fluid interactions for a molecule at a given location was also calculated as the sum interaction between the pairs of centres:

$$U_{sf} = \sum_{i=1}^{NC^*} \sum_{j=1}^3 U_{LJ}^{ij}(r_{ij}) + \sum_{i=1}^{NCO} \sum_{j=1}^2 \sum_{k=1}^3 (U_{LJ}^{ijk}(r_{ijk}) + U_{electr}^{ij}(r_{ijk})) \quad (5)$$

where NC^* is the number of non-carbonyl atoms of C and NCO is the number of carbonyl groups.

Table 1 collects all the values of parameters applied in simulations. Cross-interaction parameters were calculated using Lorentz-Berthelot mixing rules [26]. We used the same r_{cut} value (equal to 1.5 nm) for both dispersive and electrostatic interactions. We also assumed $r_{on} = 1.4$ nm. The isosteric enthalpy of adsorption (q^{st}) was calculated from the theory of fluctuations [16,26].

2.3 Description of simulated isotherms by CMMS model

For the description of simulated adsorption isotherms, we used (as previously [11]) the CMMS model [12] in the form:

$$a = \frac{a_m K_0 h}{(1 - K_{as} h)(K_0 h + w^2 (1 - K_{as} h))} \quad (6)$$

where

$$w = \frac{1}{2} \left(1 - \frac{K_1 h}{1 - K_{as} h} + \sqrt{\left(1 - \frac{K_1 h}{1 - K_{as} h} \right)^2 + \frac{4K_0 h}{1 - K_{as} h}} \right) \quad (7)$$

a and a_m are the adsorption and adsorption capacity, respectively, h is the relative pressure (i.e., the ratio of gas-phase pressure (p) to saturated vapour pressure (p_s)), K_0 is the equilibrium constant for sorption of the central unit on the primary site, K_1 is the equilibrium constant for sorption of the side unit on the primary site, and K_{as} is the equilibrium constant for sorption of the site associate.

Simulated isotherms were fitted by the CMMS model (Eqs. (6) and (7)) using the genetic algorithm proposed by Storn and Price [29] which was previously successfully applied by us for the description of different experimental data sets (see for example [30-32]). The goodness of the fit was estimated using the determination coefficient (DC) defined as:

$$DC = 1 - \frac{\sum_i (a_{theo,i} - a_{sim,i})^2}{\sum_i (a_{sim,i} - \bar{a}_{sim})^2} \quad (8)$$

where $a_{theo,i}$ and $a_{sim,i}$ are the predicted by the model and the simulated adsorption amount for i -th point, and \bar{a}_{sim} is the average value of simulated adsorption.

3. Experimental data

For the purpose of this study we use SO₂ adsorption isotherms (at 273 K) on the series of 10 carbons obtained by the heat treatment (at various temperatures and in different atmospheres) of commercial activated carbon D43/1 (CarboTech, Germany) [11]. The samples preparation, their characterisation and details of measurements were described previously [11].

4. Results and discussion

Figure 2 shows some representative experimental SO₂ adsorption isotherms on carbons having low, medium and high oxygen contents. In order to minimize the influence of differences in structural characteristics of carbons (like the surface area or the pore volume) the isotherms were normalised dividing the data by adsorption capacities (a_m) obtained from the fit by CMMS model. The rise in oxygen contents causes the change in the shape of isotherms. The isotherms become sharper, i.e. a lower pressure value is necessary to obtain a certain coverage. The differences in the shape of isotherms are reflected by the values of the constants of CMMS model (K_0 and K_1) – see Table 3 and Figure 6 in [11]. The rise in oxygen content is connected with the increase in the values of these parameters.

Figure 3 shows the histograms of pore diameters of all the considered VPCs. All the structures are strictly microporous (i.e. pore sizes do not exceed 2 nm). In the case of the raw carbons (i.e. d0.6, d0.8 and d1.0) one can see that a decrease in the percentage of wider micropores ($d_{eff} > 1$ nm) passing from the d0.6 structure to the d1.0 one. On the other hand, the virtual oxidation practically does not change the porosity of VPCs (there are observed only very small changes for the widest pores). Thus, as it was mentioned above, the applied simulation methodology makes it possible to study separately the influence of the porosity and the presence of oxygen functionalities on SO₂ adsorption.

The next figure compares simulated SO₂ adsorption isotherms and related isosteric enthalpy of adsorption for all the considered VPCs. The gradual virtual oxidation causes analogical changes in the shapes of isotherms for all the carbons. The influence of the oxygen functionalities is the most pronounced for low pressure values. The isotherms become sharper with the rise in the number of carbonyl groups. This is a consequence of the increase in the adsorption energy caused by the electrostatic interactions of SO₂ molecules with CO groups

having a dipole moment [33]. So, at the same pressure value the higher number of molecules is adsorbed in the pores of VPCs having higher oxygen contents and the lower pressure value is necessary to obtain the same coverage. Consequently, the pressure of pore filling decreases with the increase in the number of groups. The observed changes are analogous to the experimental observations – see Figure 2. Therefore, the performed simulations are an independent confirmation of a significant impact of the presence of surface oxygen groups on SO₂ physisorption. The changes in the mechanism of the process are also confirmed by the movies in the Supplementary data. They reveal the above-described regularities. The differences in the energy of SO₂ adsorption are also reflected by the regular changes of the isosteric enthalpy of adsorption. On the other hand, for the high pressure values the virtual oxidation is connected with a slight decrease in the value of adsorption capacity. This is caused mainly by the rise in the adsorbent mass caused by the introduction of oxygen atoms.

The comparison of isotherms for the raw VPCs (i.e. d0.6, d0.8 and d1.0; the lowest black curves on Figure 4) reveals also a significant influence of porosity on SO₂ adsorption. The rise in the contents of the smallest micropores ($d_{eff} < 1$ nm) causes the change in the shape of isotherms similar as the introduction of oxygen functionalities. Isotherms become sharper passing from the d0.6 structure up to the d1.0 one. This is due to a higher adsorption potential energy in smaller pores. The energetic differences are reflected by the increase in isosteric enthalpy of adsorption. Hence, not only the presence of high number of surface oxygen groups is the feature of the optimal carbon for SO₂ physisorption, but this carbon should also have a large amount of small micropores with a diameter below 1 nm, as it was also suggested in earlier reports [34,35]. The performed simulations may also suggest some caution in the interpretation of experimental data, because the influence of surface functionalities may be difficult to distinguish from the influence of changes in porosity which may be caused by an experimental procedure of introducing oxygen groups.

The details and some new insights into the adsorption mechanism can be obtained from the analysis of animations (Supplementary data) and the solid-fluid potential energy profiles (for selected systems) shown in Figures 5 and S1-S3 in Supplementary data. One can observe that the introduction of surface oxygen groups causes two important effects. Some molecules are adsorbed at the vicinity of groups however, the appearance of functionalities also rises the potential energy at the curved fragments of the structure. Since electrostatic interactions are long ranged one can observe the densification of SO₂ molecules even at places where the groups are absent.

Table S2 in Supplementary data collects the values of the best-fit parameters obtained from the fitting of the simulated isotherms by the CMMS model (Eqs. (6) and (7)). The quality of data description is satisfactory as evidenced by the high values of the determination coefficient. The differences in the shape of isotherms are mainly reflected by the changes in the values of parameters connected with adsorption on primary sites (i.e. K_0 and K_I). On the other hand, the values of association constant (K_{as}) are close to zero for all the simulated isotherms. This is connected with their shape and the presence of the final plateau for the high pressure values. The observed decrease in adsorption capacity caused by a gradual oxidation is reflected by the decrease in the values of a_m parameter. Figure 5 presents the correlations between the oxygen contents and the parameters K_0 and K_I for experimental data (a) and for simulated isotherms (b-d). One can observe that both values are linearly correlated with the oxygen contents. These regularities confirm the above-described influence of oxygen groups on the mechanism of SO_2 physisorption *via* the increase in the energy of adsorption. The behaviour of both experimental and simulated data is similar, but there are also some differences. In the case of the best-fit parameters obtained from experimental isotherms the K_0 values are higher than the K_I ones. A reverse situation occurs for the simulated data. However, comparing the data for d0.6, d0.8 and d1.0 series one can see the reduction in differences between both values with increasing in the percentage of the smallest micropores. In the case of the most oxidised structures of d1.0 series the constants K_0 and K_I have similar values. This regularity may suggest that a further reduction in pore sizes may reverse the relation between the values of both constants (i.e. K_0 become higher than K_I). Despite the fact that experimentally investigated carbons contain not only narrow micropores but also wider pores (see Figure 4 in [11]), the ratio of K_0 and K_I constants is different than in the case of the considered strictly microporous VPCs. The possible explanation of this can be the limitations in the experimental procedure of isotherms measurements. The isotherms were measured only for the range of $p/p_s \leq 0.33$ [11]. In this range, mainly the adsorption in the smallest pores contributes to the total adsorption value. So, lack of the data for a high-pressure range may affect the obtained results.

5. Conclusions

We have studied the influence of the gradual oxidation of carbons on SO_2 physisorption. The comparison of the experimental and simulated data of SO_2 adsorption has confirmed the significant impact of surface functionalities on the mechanism of the adsorption

process. The main reason is the increase in the adsorption energy due to electrostatic interactions of SO₂ molecules with carbonyl groups having dipole moment. The results of simulations have also revealed the important role of carbon porosity. The increase in the percentage of the smallest pores ($d_{eff} < 1$ nm) has caused the similar changes in the shape of isotherms as the introduction of carbonyl groups. So, the optimal carbon for SO₂ physisorption should not only contain a high number of oxygen functionalities but also have the high contents of the smallest micropores. The results of the performed simulations may also suggest some caution in the interpretation of experimental data, because the influence of surface functionalities may be difficult to distinguish from the influence of changes in porosity caused by an experimental oxidation procedure.

The fit of isotherms by the CMMS model has led to the conclusion that this model is a useful and sensitive tool in the study of the SO₂ adsorption mechanism. The differences in the constants of the model (K_0 and K_1) have reflected the systematic changes in the shape of isotherms. The values of these constants (obtained from the simulated data) have been linearly correlated with the oxygen contents. The analogous correlation has been observed for the experimental data. This fact is an independent confirmation of the performed simulations validity.

Acknowledgments

The authors acknowledge the use of the computer cluster at Poznań Supercomputing and Networking Centre (Poznań, Poland) and the Information and Communication Technology Centre of the Nicolaus Copernicus University (Toruń, Poland).

Appendix A. Supplementary data

Animations of SO₂ adsorption process on raw VPCs and the selected oxidised ones obtained from d0.6 (movie_1), d0.8 (movie_2) and d1.0 (movie_3) structures. The view after dividing simulation boxes into two equal parts. Supplementary data associated with this article can be found in the online version.

References

- [1] R.K. Srivastava, Controlling SO₂ Emissions, Nova Science Publishers Inc., New York, 2003.
- [2] R.K. Srivastava, W. Jozewicz, C. Singer, Environ. Prog. 20 (2001) 219.

- [3] F. Kazanc, R. Khatami, P.M. Crnkovic, Y.A. Levendis, *Energy Fuels* 2011, 25, 2850.
- [4] B.E. Alver, M. Sakizci, E. Yörükoğullari, *Adsorpt. Sci. Technol.* 29 (2011) 413.
- [5] N. Karatepe, İ. Orbak, R. Yavuz, A. Özyuğuran, *Fuel* 87 (2008) 3207.
- [6] E. Atanes, A. Nieto-Márquez, A. Cambra, M.C. Ruiz-Pérez, F. Fernández-Martínez, *Chem. Eng. J.* 211-212 (2012) 60.
- [7] U. Narkiewicz, A. Pietrasz, I. Pelech, W. Arabczyk, *Pol. J. Chem. Technol.* 14 (2012) 41.
- [8] J.A. Arcibar-Orozco, J.R. Rangel-Mendez, T.J. Bandosz, *J. Hazard. Mater.* 246-247 (2013) 300.
- [9] Y. Guo, Y. Li, T. Zhu, M. Ye, X. Wang, *Adsorption* doi 10.1007/s10450-013-9539-y.
- [10] F. Sun, J. Gao, Y. Zhu, G. Chen, S. Wu, Y. Qin, *Adsorption* doi 10.1007/s10450-013-9504-9.
- [11] S. Furmaniak, A.P. Terzyk, G.S. Szymański, P.A. Gauden, M. Motak, P. Kowalczyk, G. Rychlicki, *Langmuir* 22 (2006) 6887.
- [12] A.O. Malakhov, V. V. Volkov, *Polym. Sci. Ser. A* 42 (2000) 1120.
- [13] S. Furmaniak, A.P. Terzyk, P.A. Gauden, P.J.F. Harris, P. Kowalczyk, *J. Phys.: Condens. Matter* 21 (2009) 315005.
- [14] M.J. Biggs, A. Buts, *Mol. Simul.* 32 (2006) 579.
- [15] A.P. Terzyk, S. Furmaniak, P.A. Gauden, P.J.F. Harris, P. Kowalczyk, in: J.M.D. Tascón (Ed.), *Novel Carbon Adsorbents*, Elsevier, 2012, p. 61.
- [16] S. Furmaniak, *Comput. Methods Sci. Technol.* 19 (2013) 47.
- [17] M. Jorge, Ch. Schumacher, N.A. Seaton, *Langmuir* 18 (2002) 9296.
- [18] N.A. Marks, *Phys. Rev. B* 63 (2000) 035401.
- [19] N. Marks, *J. Phys.: Condens. Matter* 14 (2002) 2901.
- [20] S. Bhattacharya, K.E. Gubbins, *Langmuir* 22 (2006) 7726.
- [21] S. Furmaniak, A.P. Terzyk, P.A. Gauden, N.A. Marks, R.C. Powles, P. Kowalczyk, *J. Colloid. Interface Sci.* 360 (2011) 211.
- [22] Q. Yan, J.J. de Pablo, *J. Chem. Phys.* 111 (1999) 9509.
- [23] M. Wiśniewski, S. Furmaniak, P. Kowalczyk, K.M. Werengowska, G. Rychlicki, *Chem. Phys. Lett.* 538 (2012) 93.
- [24] M.C.C. Ribeiro, *J. Phys. Chem. B* 110 (2006) 8789.
- [25] W. Wang, X. Peng, D. Cao, *Environ. Sci. Technol.* 45 (2011) 4832.
- [26] D. Frenkel, B. Smit, *Understanding Molecular Simulation*, Academic Press, San Diego, 1996.

- [27] K.F. Lau, H.E. Alper, T.S. Thacher, T.R. Stouch, *J. Phys. Chem.* 98 (1994) 8785.
- [28] C.J. Fennel, D. Gezelter, *J. Chem. Phys.* 124 (2006) 234104.
- [29] R. Storn, K. Price, *J. Glob. Optim.* 11 (1997) 341.
- [30] S. Furmaniak, A.P. Terzyk, R. Gołembiewski, P.A. Gauden, *Chem. Phys. Lett.* 499 (2010) 141.
- [31] S. Furmaniak, A.P. Terzyk, P.A. Gauden, *Drying Technol.* 29 (2011) 984.
- [32] S. Furmaniak, *Transp. Porous Media* 92 (2012) 21.
- [33] Z.-M. Wang, K. Kaneko, *J. Phys. Chem. B* 102 (1998) 2863.
- [34] E. Raymundo-Piñero, D. Cazorla-Amorós, C. Salinas-Martinez de Lecea, A. Linares-Solano, *Carbon* 38 (2000) 335.
- [35] A. Bagreev, S. Bashkova, T.J. Bandosz, *Langmuir* 18 (2002) 1257.

Table 1

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

Object	Geometric parameters	Centre	σ [nm]	ϵ/k_B [K]	q/e	Reference
SO ₂	$l_{S=O} = 0.14321$ nm $\varphi_{O=S=O} = 119.5^\circ$	S	0.3585	154.4	+ 0.470	[24]
		O	0.2993	62.3	- 0.235	
VPC	$l_{C=O} = 0.1233$ nm	C ^a	0.3400	28.0	-	[17]
		C ^b	0.3400	28.0	+ 0.500	
		O	0.2960	105.8	- 0.500	

^a non-carbonyl group atom of C

^b carbonyl group C atom

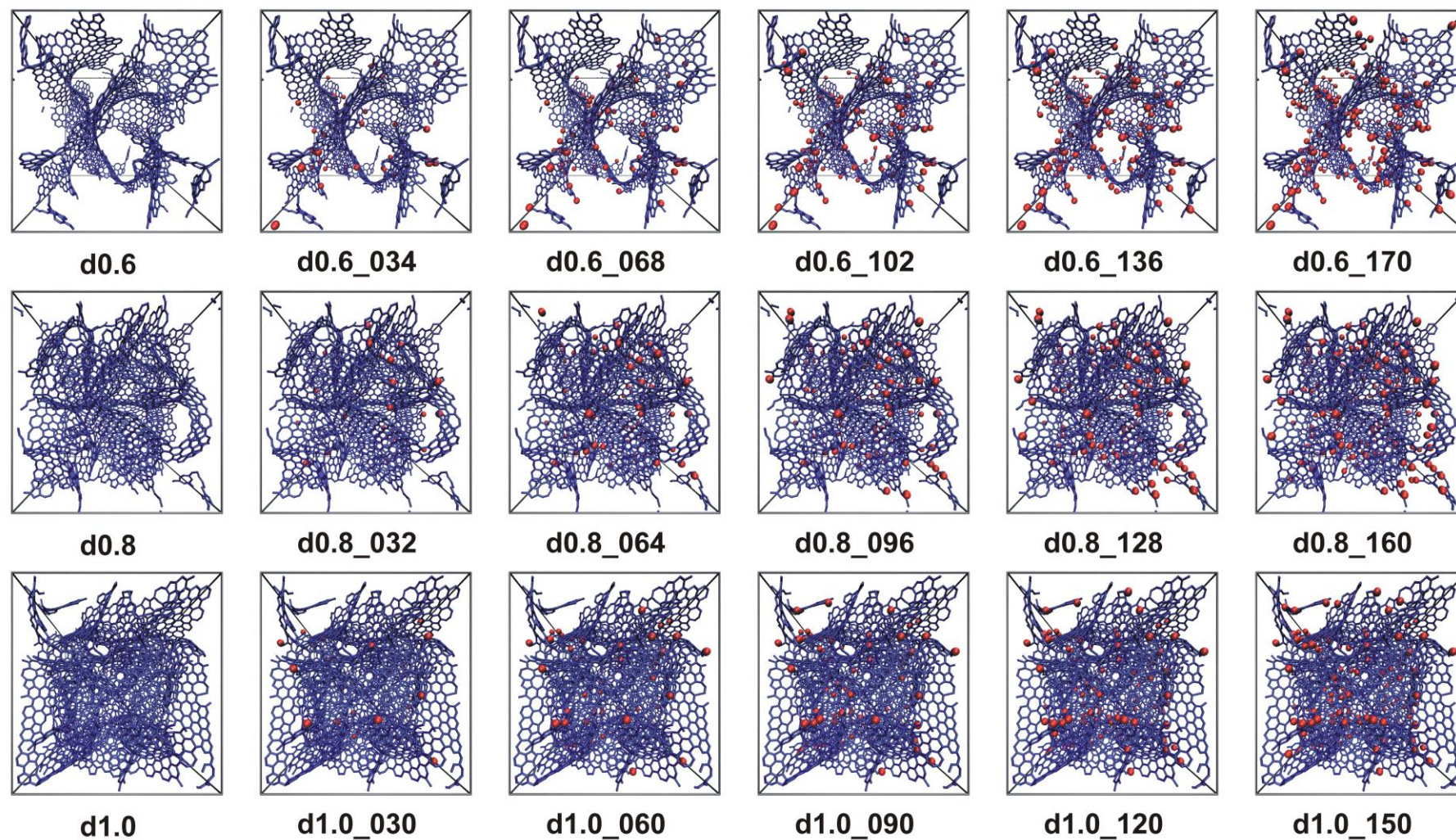


Figure 1 The schematic representation of considered series of oxidised VPCs (oxygen atoms are marked as the red balls; the frames reflect the size of the simulation box).

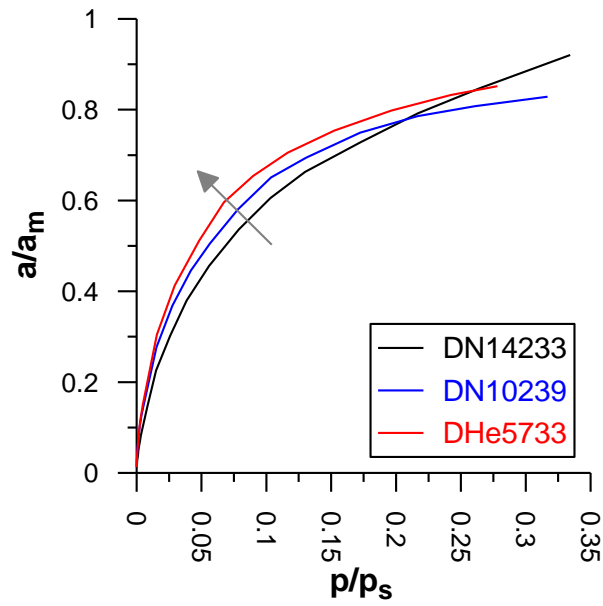


Figure 2 The experimental SO_2 adsorption isotherms ($T = 273 \text{ K}$) on carbons DN14233, DN10239) and DHe5733 having low (0.32 %), medium (1.74 %) and high (4.67 %) oxygen contents, respectively. Adsorption amount is normalised by the adsorption capacities values (a_m) in CMMS model (Eqs. (6) and (7)) taken from [11]. The arrow shows the direction of changes connected with the rise in the oxygen contents.

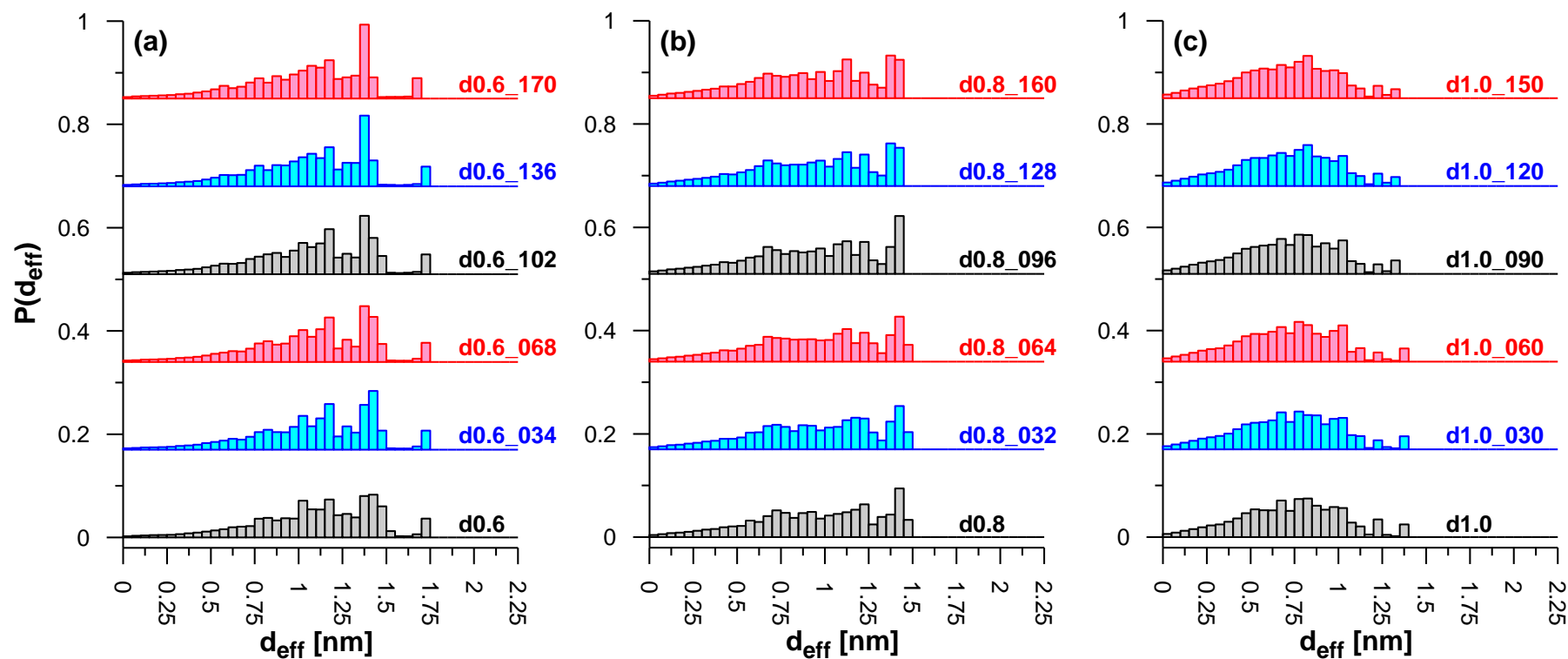


Figure 3 The histograms of pore diameters for the series of oxidised VPCs based on the d0.6 (a), d0.8 (b) and d1.0 (c) structures. The subsequent histograms are shifted by 0.17 from the previous ones.

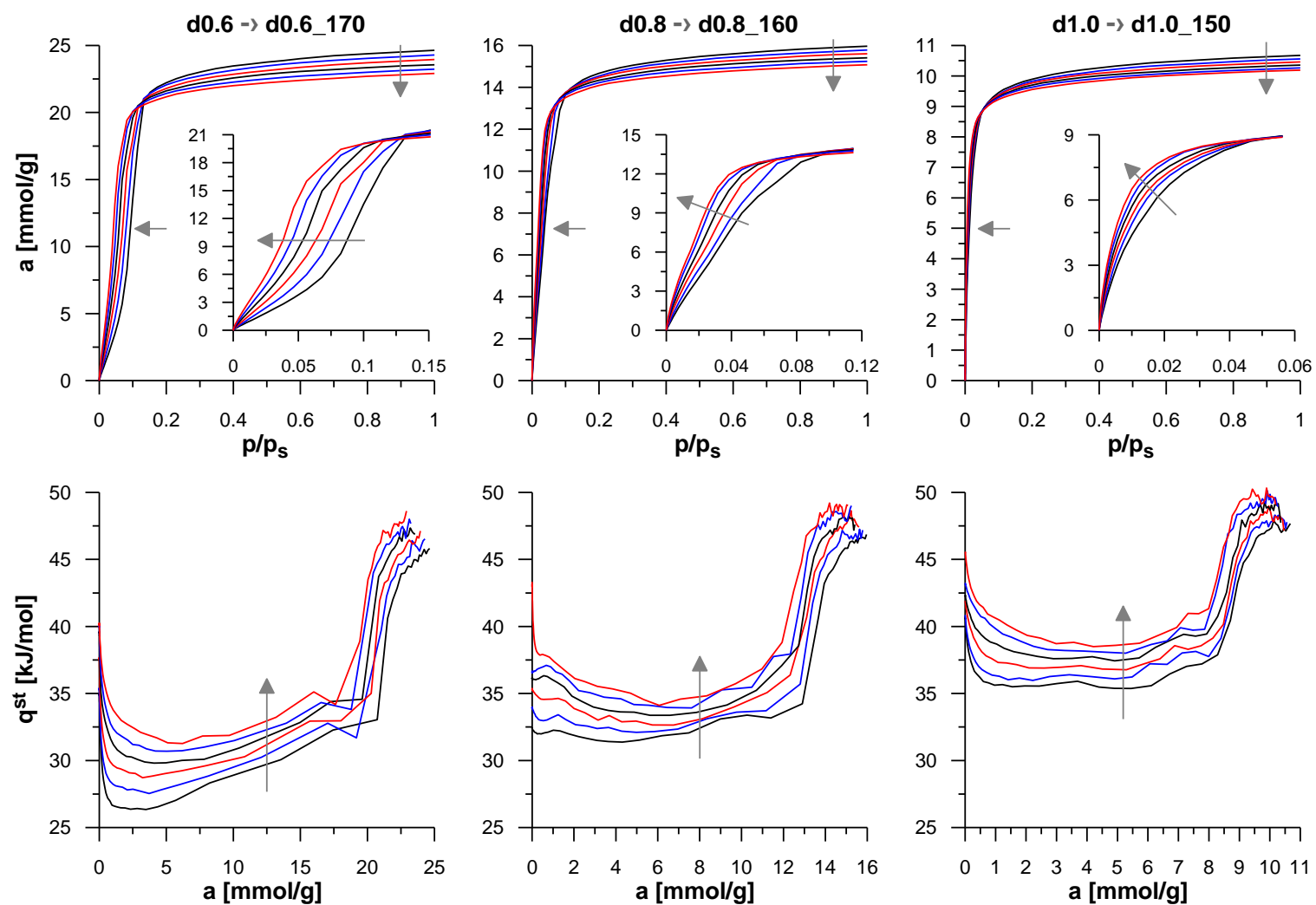


Figure 4 The comparison of SO₂ adsorption isotherms ($T = 298$ K) and related isosteric enthalpy of adsorption for all the considered VPCs. The arrows show the direction of changes connected with the rise in the number of carbonyl groups.

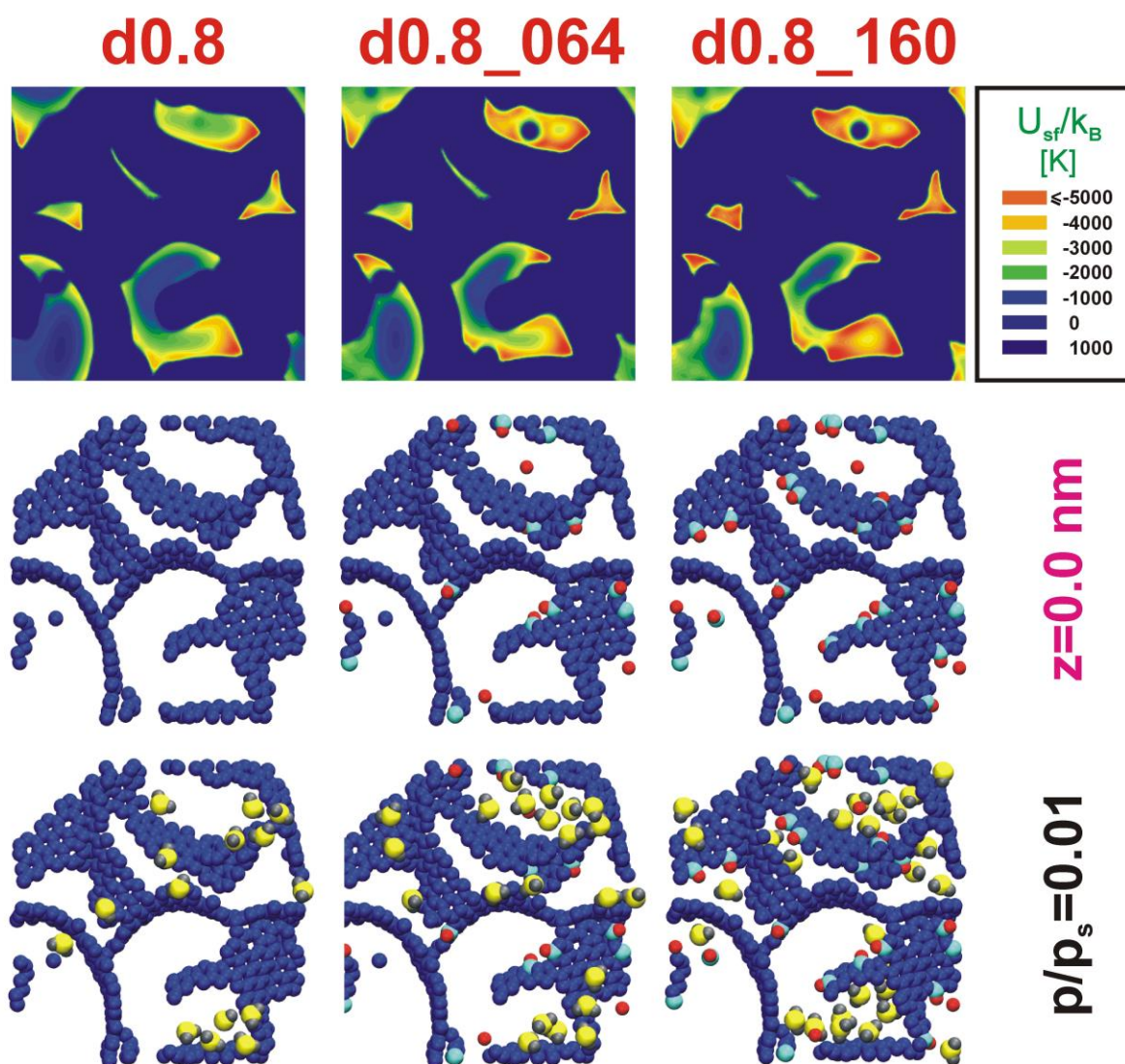


Figure 5 The comparison of solid-fluid interaction energy (see Figures S1-S3 in Supplementary data) inside the d0.8, d0.8_064 and d0.8_160 boxes for the plane $z = 0$. In addition, the slices of the adsorbent structure (having a thickness of 0.5 nm) surrounding the considered planes and the equilibrium snapshots of SO_2 equilibrium configurations (for $p/p_s = 0.01$) planes are shown.

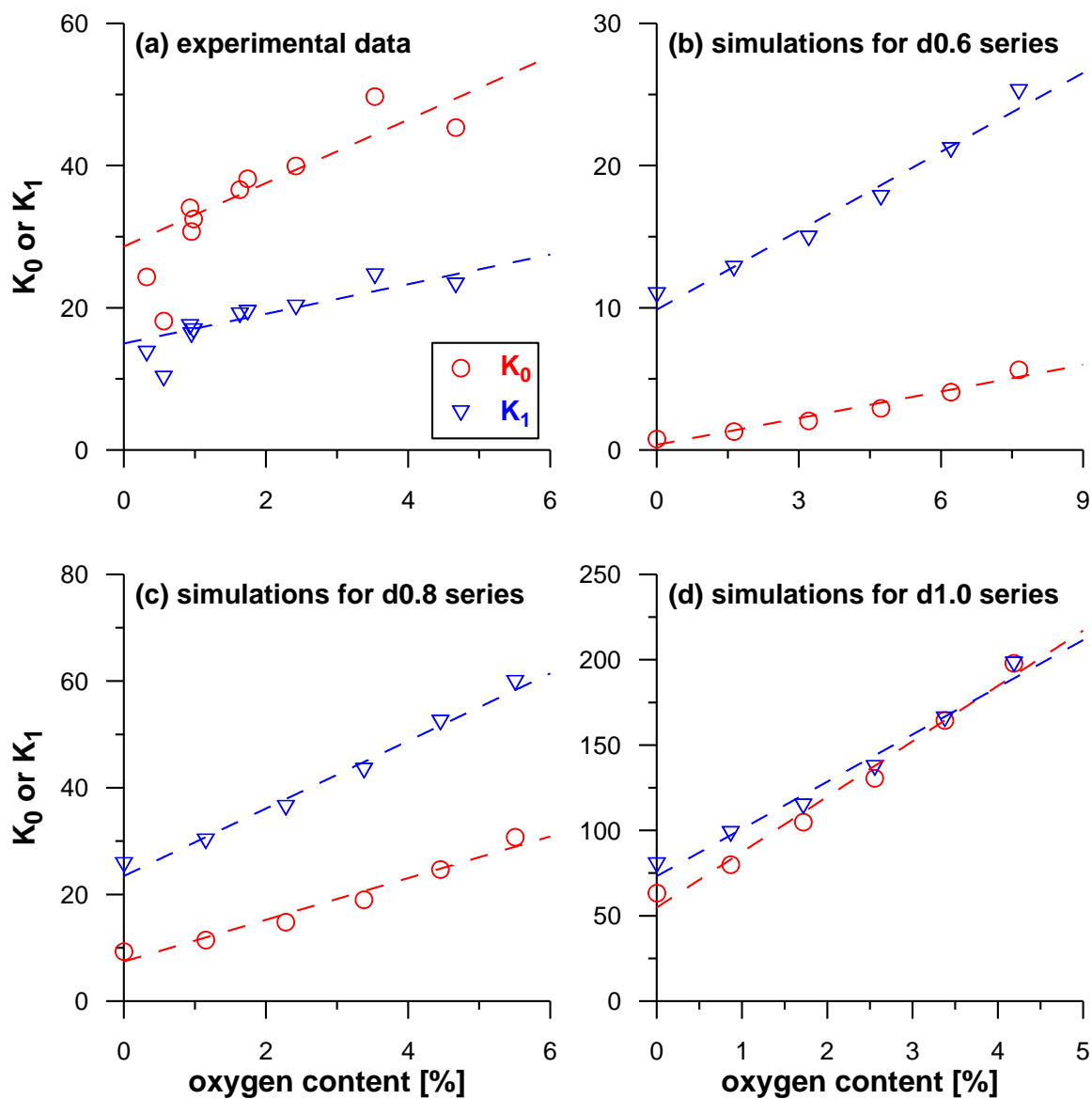


Figure 5 The correlation between the parameters of CMMS model (K_0 and K_1) for experimental isotherms (a; data taken from [11]) and simulated isotherms (b-d; table S2 in Supplementary data). The dashed lines were drawn to guide the eye.