

Thermodynamics of the CMMS Approach and Carbon Surface Chemistry in SO₂ Adsorption

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In this study, we develop the equation describing the enthalpy of adsorption corresponding to the cooperative multimolecular sorption approach proposed by Malakhov and Volkov. For different shapes of adsorption isotherms plotted from this model (and analyzed by Rutherford and Coons), we generated the corresponding enthalpy of adsorption curves. We also discuss other enthalpy plot shapes predicted by the CMMS. The new relations are verified for simultaneous description of SO₂ adsorption data, and enthalpy of sorption, measured on graphitized carbon black and on activated carbon. Finally, we apply the CMMS model to description of adsorption data of SO₂ measured on the series of modified activated carbons. The porosity of adsorbents was characterized via description of low-temperature N₂ isotherms applying the method of Nguyen and Do. Oxygen content in carbons was measured applying the elemental analysis. From the results of the correlations between the parameters of the CMMS and elemental analysis data, it is concluded that the interaction between SO₂ molecules and carbon surface oxygen groups is crucial during adsorption of this adsorbate. Our results explain and summarize up the conclusions concerning the effect of carbon surface nitrogen functionalities on SO₂ sorption mechanism presented by other authors. Finally, we conclude that the CMMS approach can be successfully applied to the description of this process.

1. Introduction

The problem of SO₂ adsorption on carbons is widely studied in the literature particularly in view of flue gas desulfurization. There are, however, some contradictory results and observations considering the influence carbon surface modifications (especially those leading to creation of nitrogen containing functionalities) on SO₂ adsorption capacity. One of the most important problems of the theoretical description of adsorption of polar molecules (among them SO₂) on carbons is the lack of theoretical models being able to describe the adsorption isotherms and related adsorption enthalpy data. Therefore, some new models are still proposed to take into account the possibility of association of adsorbed molecules.

Here a very important and interesting attempt was made by Malakhov and Volkov,¹ who proposed in 2000 the new equation of cooperative multimolecular sorption (called the CMMS). They assumed that the adsorption process follows the scenario of cooperative filling of channels (interrelated nanovoids) of the adsorbent, and this process is combined with the growth of associates of sorbed molecules within the sorbent bulk. The final adsorption equation, which can be reduced to the Henry's, Langmuir, Ising, and/or BET models, can be written as^{1–4}

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

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

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

where K_1 is the equilibrium constant for sorption of the side unit on the primary site.

The properties of the CMMS were extensively studied by Malakhov and Volkov themselves.¹ Moreover, its applicability to the description of experimental data was well documented. It should be pointed out that the original CMMS theory was proposed to explain the uptake of alcohols in a high free volume polymer.¹ This theory has been subsequently applied to water–carbon systems,^{2–4} and it was also employed to characterize the various types of observed equilibrium isotherms. It was shown that CMMS theory can account for type I, II, III, and V and hybrid equilibrium isotherms (II/III and II/V) which fall between these types.³ On the other hand, this theory suffers from the inability to characterize type IV isotherms. Therefore, Rutherford⁴ modified the original model proposed by Malakhov and Volkov¹ and the dual (hybrid) equation was developed (i.e., the sum of two CMMS ones) where the result of simplification is a composite isotherm with contributions from the Ising equation (representing the first mode of water adsorption) and the Langmuir equation

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(representing the second mode). Moreover, the theoretical dependence of the Fickian diffusivity and the linear driving force rate constants upon relative pressure was studied applying the different shapes of the mentioned above adsorption isotherm equation. Additionally, the parameters derived from fitting of equilibrium data were shown to be correlated with the primary adsorption sites density.²

On the other hand, it is interesting to derive the enthalpy of adsorption formula related to the CMMS theory and to verify the applicability of this model to simultaneous description of experimental adsorption and adsorption enthalpy data. This is the major subject of our study. We also show that CMMS can be successfully applied as the useful tool for the investigation of the role of carbon surface chemical composition playing during SO₂ adsorption.

2. Enthalpy of Adsorption Related to the CMMS Model

Development of Equations and Simulations of the Properties. Developing the formula describing the enthalpy of adsorption, we assumed the following well-known temperature dependence of the parameters of the model:

$$K_0 = K_0^0 \exp\left(\frac{q_0}{RT}\right) \quad (2a)$$

$$K_{as} = K_{as}^0 \exp\left(\frac{q_{as}}{RT}\right) \quad (2b)$$

$$K_1 = K_1^0 \exp\left(\frac{q_1}{RT}\right) \quad (2c)$$

where q_i are the average enthalpy values connected with the constant K_i and K_i^0 are the entropic factors being slightly dependent on the temperature.

During derivation also very applicable are the following relations:

$$dw(h,T) = \left(\frac{\partial w}{\partial h}\right)_T dh + \left(\frac{\partial w}{\partial T}\right)_h dT \quad (3a)$$

$$\frac{dw}{dT} = \left(\frac{\partial w}{\partial h}\right)_T \frac{dh}{dT} + \left(\frac{\partial w}{\partial T}\right)_h \quad (3b)$$

The double-sided multiplication of eq 1 by the denominator, the differentiation with respect to the temperature, and the application of the following notation

$$B_1 = 2\left(\frac{\partial w}{\partial h}\right)_T \quad (4a)$$

$$B_2 = \frac{2RT^2}{h} \left(\frac{\partial w}{\partial T}\right)_h \quad (4b)$$

together with the Clausius–Clapeyron formula, and with eqs 3a and 3b, lead to

$$q^{st} - L = RT^2 \left(\frac{\partial \ln h}{\partial T}\right)_a = \frac{q_0 a_m K_0 + q_{as} a K_{as} (K_0 h + w^2 (1 - K_{as} h)) + a(1 - K_{as} h)(-q_0 K_0 + w B_2 (1 - K_{as} h) + q_{as} w^2 K_{as})}{a_m K_0 + a K_{as} (K_0 h + w^2 (1 - K_{as} h)) + a(1 - K_{as} h)(-K_0 - w B_1 (1 - K_{as} h) + w^2 K_{as})} \quad (5)$$

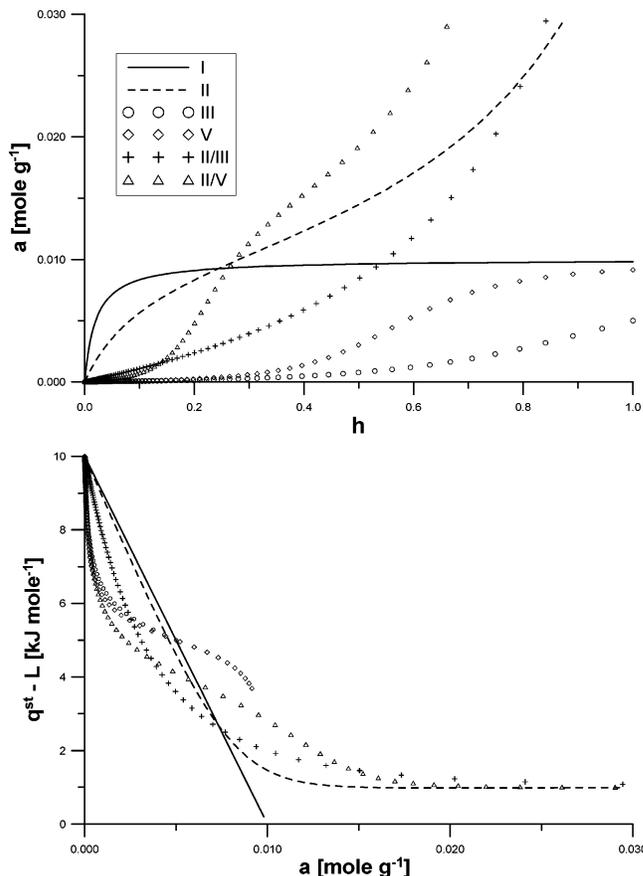


Figure 1. Shapes of adsorption isotherms generated by Rutherford and Coons³ from CMMS model (eq 1) and related adsorption enthalpy plots (eqs 5 and 6). The values of the appropriate parameters are taken from Table 1.

where

$$B_1 = -\frac{1}{(1 - K_{as} h)^2} \left(K_1 + \frac{K_1 \left(1 - \frac{K_1 h}{1 - K_{as} h}\right) - 2K_0}{\sqrt{\left(1 - \frac{K_1 h}{1 - K_{as} h}\right)^2 + \frac{4K_0 h}{1 - K_{as} h}}} \right) \quad (6a)$$

$$B_2 = \frac{1}{(1 - K_{as} h)^2} \left(K_1 (q_1 + (q_{as} - q_1) K_{as} h) + \frac{K_1 \left(1 - \frac{K_1 h}{1 - K_{as} h}\right) (q_1 + (q_{as} - q_1) K_{as} h) - 2K_0 (q_0 + (q_{as} - q_0) K_{as} h)}{\sqrt{\left(1 - \frac{K_1 h}{1 - K_{as} h}\right)^2 + \frac{4K_0 h}{1 - K_{as} h}}} \right) \quad (6b)$$

It can be pointed out that the procedure leading to eq 5 is similar to that applied by us recently.⁵

As it was described above, Rutherford and Coons³ showed recently that the CMMS model (eq 1) can generate the isotherm

Table 1. Values of the Parameters Applied for the Calculation of Adsorption Isotherms from the CMMS Model Shown in Figure 1 (*Based on the Results Published by Rutherford and Coons³)

type of isotherm*	a_m [mol g ⁻¹]	K_0^*	K_1^*	K_{as}^*	q_0 [kJ mol ⁻¹]	q_1 [kJ mol ⁻¹]	q_{as} [kJ mol ⁻¹]
I	0.01	50	50	0	10	5	
II	0.01	10	10	0.77	10	5	1
III	0.01	0.05	1	0	10	5	
V	0.01	0.057	1.71	0	10	5	
II/III	0.01	1	1	0.88	10	5	1
II/V	0.01	0.27	3.5	1	10	5	1

of types I, II, III, and V (and intermediate) from the BET classification. Figure 1 shows the recalculated results of those authors, together with the corresponding enthalpy of adsorption plots (eqs 5 and 6). We applied the parameters collected in Table 1. It can be noticed that for the first type of BET isotherm the CMMS model generates the linearly decreasing enthalpy plot (Figure 1). This is caused by the assumed equality between both of the constants (Table 1). For other types of isotherms, progressively decreasing hyperbolic-like plots are observed. On the other hand, Figure 2 shows other possible shapes of the

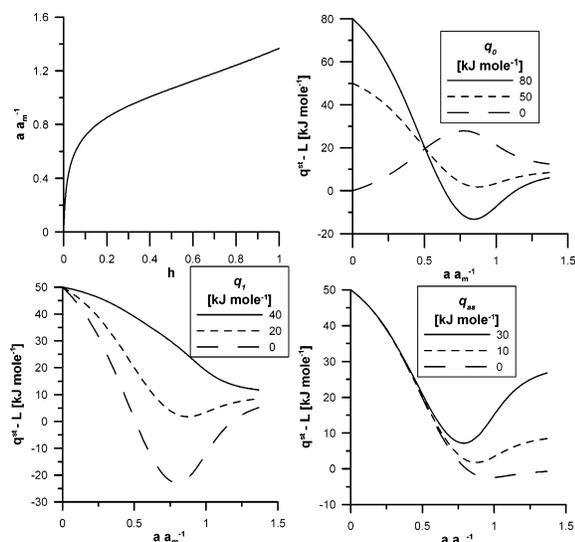


Figure 2. Influence of the parameters (q_0 , q_1 , and q_{as} , respectively) on the shapes of adsorption enthalpy plots generated from the CMMS model ($K_0 = 60$, $K_1 = 30$, $K_{as} = 0.3$, $q_0 = 50$ kJ mol⁻¹, $q_1 = 20$ kJ mol⁻¹, and $q_{as} = 10$ kJ mol⁻¹). Note that all enthalpy plots are generated for the same adsorption isotherm.

adsorption enthalpy plots generated from eqs 5 and 6. It can be noticed that for the same adsorption isotherm shown in this figure, due to the combination of the parameters, there are possible different nonmonotonic plots of the enthalpy very similar to those measured experimentally and reported in the literature.⁶ Summing up, this makes the CMMS model very promising for further studies.

Validity of CMMS: Description of the SO₂ Adsorption Isotherms and Related Enthalpy Data. The validity of the CMMS model was checked for three sets of data reported previously. Applying the genetic algorithm of Storn and Price,^{7–9} we fitted the data of SO₂ adsorption measured on graphitized carbon black at 273 K by Beebe and Dell¹⁰ and the data of the

same adsorbate measured on Norit A carbon (323 and 373 K) and reported by Murphy et al.¹¹ As it can be observed from Figure 3, the fit of the CMMS model to experimental data is

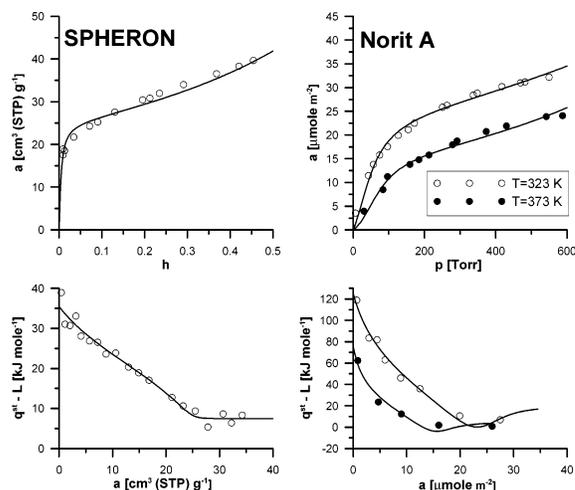


Figure 3. Applicability of the CMMS model (eq 1) and related enthalpy formula (eqs 5 and 6) (lines) for description of SO₂ adsorption and adsorption enthalpy data (points) measured on graphitized carbon black SPHERON 6 (273 K)¹⁰ and on activated carbon Norit A (323 and 373 K).¹¹ The best-fit parameters – SPHERON: $a_m = 24.97$ cm³ (STP) g⁻¹; $K_0 = 137.2$; $K_1 = 209.2$; $K_{as} = 0.8115$; $q_0 = 35.45$ kJ mole⁻¹; $q_1 = 21.35$ kJ mol⁻¹; $q_{as} = 7.461$ kJ mol⁻¹; DC_{isotherm} = 0.9819; DC_{enthalpy} = 0.9747; Norit A (323 K): $a_m = 24.26$ μmol m⁻²; $K_0/p_s = 0.007485$ Torr⁻¹; $K_1/p_s = 0.01843$ Torr⁻¹; $K_{as}/p_s = 0.0005264$ Torr⁻¹; $q_0 = 125.2$ kJ mol⁻¹; $q_1 = 36.22$ kJ mol⁻¹; $q_{as} = 20.47$ kJ mol⁻¹; DC_{isotherm} = 0.9881; DC_{enthalpy} = 0.9866; Norit A (373 K): $a_m = 15.41$ μmol m⁻²; $K_0/p_s = 0.003786$ Torr⁻¹; $K_1/p_s = 0.01315$ Torr⁻¹; $K_{as}/p_s = 0.0006930$ Torr⁻¹; $q_0 = 75.90$ kJ mol⁻¹; $q_1 = 17.10$ kJ mol⁻¹; $q_{as} = 4.977$ kJ mol⁻¹; DC_{isotherm} = 0.9825; DC_{enthalpy} = 0.9660.

satisfactory. Summing up, we can conclude, that the CMMS adsorption isotherm equation postulates very realistic model of adsorption of associating molecules.

3. Description of SO₂ Adsorption on Carbons

Experimental. Carbon samples with different surface chemistry were obtained from the de-ashed commercial activated carbon D43/1 (CarboTech, Essen, Germany) by heat treatment at various temperatures in ammonia, hydrogen, or helium (DN, DH, and DHe series, respectively). The detailed conditions of chemical modification are given in Table 2. The samples were stored in air. The porous structure of carbon samples was elucidated from low-temperature nitrogen adsorption data. The adsorption measurements were conducted volumetrically with an automatic ASAP 2010 sorption apparatus (Micromeritics, Atlanta, USA) at 77 K. Before the experiment, the samples were heated at 498 K under vacuum to constant pressure (10⁻³ Torr) and then outgassed at room temperature up to the pressure of

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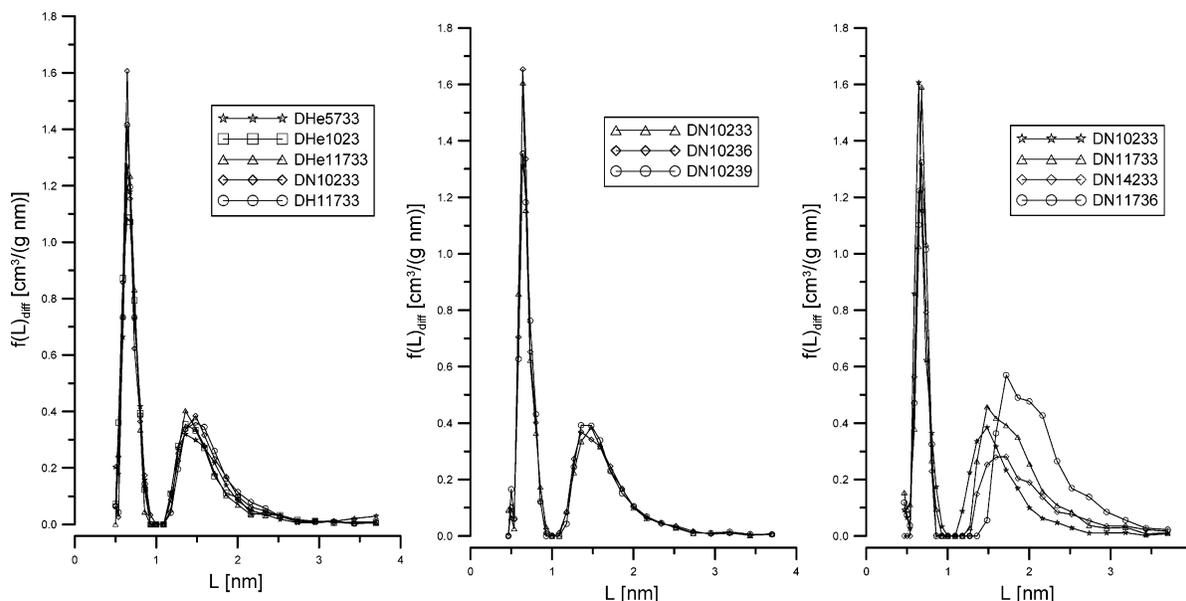


Figure 4. Differential pore size distributions obtained on the basis of the ND method.

Table 2. Conditions and Agent of the Carbon D43/1 Modifications

carbon	applied procedures
D	D43/1 de-ashed with concentrated HCl and HF solutions (298 K)
DHe5733	D heated in He (20 dm ³ /h, 573 K, 3 h), cooled in He (25 dm ³ /h)
DHe1023	D heated in He (20 dm ³ /h, 1023 K, 3 h), cooled in He (25 dm ³ /h)
DHe11733	D heated in He (20 dm ³ /h, 1173 K, 3 h), cooled in He (25 dm ³ /h)
DH11733	D heated in H ₂ (20 dm ³ /h, 1173 K, 3 h), cooled in He (25 dm ³ /h)
DN10233	D heated in NH ₃ (20 dm ³ /h, 1023 K, 3 h), cooled in He (25 dm ³ /h)
DN10236	D heated in NH ₃ (20 dm ³ /h, 1023 K, 6 h), cooled in He (25 dm ³ /h)
DN10239	D heated in NH ₃ (20 dm ³ /h, 1023 K, 9 h), cooled in He (25 dm ³ /h)
DN11733	D heated in NH ₃ (20 dm ³ /h, 1173 K, 3 h), cooled in He (25 dm ³ /h)
DN11736	D heated in NH ₃ (20 dm ³ /h, 1173 K, 6 h), cooled in He (25 dm ³ /h)
DN14233	D heated in NH ₃ (20 dm ³ /h, 1423 K, 3 h), cooled in He (25 dm ³ /h)

10⁻⁶ Torr. Elemental composition was determined using a vario El III CHN analyser (Elementar Analysensysteme GmbH, Hanau, Germany). Sulfur dioxide adsorption under static conditions was carried out at 273 K up to $p/p_s = 0.33$, using conventional volumetric equipment. The irreversible adsorption of SO₂ at 273 K was determined by evacuation at 273 K of the sample with previously adsorbed SO₂ up to constant pressure (10⁻³ Torr) and subsequent readsorption of SO₂. Prior to the adsorption measurements, the samples were outgassed at 423 K up to constant pressure (10⁻³ Torr).

Carbon Porosity. Pore size distributions (PSDs) of studied adsorbents were determined applying the method proposed by Nguyen and Do¹²⁻¹⁵ and the ASA code developed by us^{14,15} recently. Figure 4 shows the plots of obtained differential PSDs. Nearly all of the studied carbons reveal the same porosity. There are observed two peaks corresponding to pores having the diameters around 0.7 and 1.5 nm, respectively. The plots show that for only two of the carbon samples (DN1173 and DN11736) applied modification procedures lead to the changes in porosity and the second PSD peak is shifted toward larger pore diameters. This causes the increase (by about 25%) in the value of the BET apparent surface area. Therefore, it is reasonable to assume that the differences in surface chemical composition of studied carbons are mainly responsible for observed differences in SO₂ adsorption, especially at low relative pressures, as it is reported below.

SO₂ Adsorption. Activated carbons are often used for flue gas desulfurization because of their ability to adsorb SO₂, especially when they demonstrate well developed microporosity and “proper” surface chemistry, i.e., a surface with basic properties.¹⁶⁻²¹ The basic properties of carbons are mainly ascribed to the presence of surface basic oxides^{16,18,19,22} as well as to the electron donor–acceptor interactions involving delocalized π electrons of carbon platelets.²³ Another way to obtain basic carbons is the incorporation of nitrogen into a carbon matrix.^{17,19,21,24-30}

It was shown that the presence of certain nitrogen groups on the carbon surface enhances its adsorption ability to SO₂

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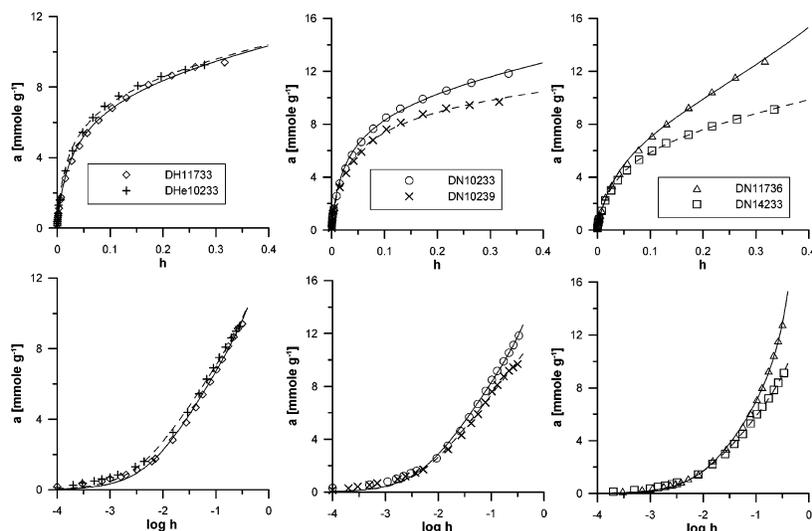


Figure 5. Graphical representation of the results of the fitting of SO_2 experimental adsorption data (points) by CMMS model (eq 1, lines) for six arbitrarily chosen samples (the best-fit parameters and the values of the determination coefficient are shown in Table 3).

Table 3. The Results of the Fitting of SO_2 Adsorption Data by CMMS Model. DC Is the Value of the Determination Coefficient

carbon	a_m [mmol g^{-1}]	K_0	K_1	K_{as}	DC
DH11733	10.86	32.51	16.71	0.3296	0.9978
DHe11733	10.85	39.97	20.04	0.1368	0.9973
DHe10233	10.30	49.72	24.43	0.3590	0.9978
DHe5733	10.30	45.36	23.15	0.2134	0.9979
DN10233	12.90	36.63	18.95	0.3499	0.9974
DN10236	12.36	30.74	16.15	0.2894	0.9963
DN10239	11.69	38.16	19.31	0.1692	0.9963
DN11733	10.01	34.08	17.29	0.9619	0.9970
DN11736	12.32	18.15	10.03	0.8807	0.9990
DN14233	9.901	24.36	13.55	0.4513	0.9988

too.^{21,22,24,25,28–30} In some cases, when the adsorption of dry SO_2 was conducted at room temperature in the presence of oxygen, some positive correlations were found between nitrogen content and SO_2 adsorption capacity^{28,29} or adsorption energy calculated from the Dubinin–Rhadushkevich adsorption isotherm equation, respectively.²¹ However, for dry SO_2 adsorption and in the absence of oxygen, any such relationship was reported. Thus, the objective of this work was to obtain some additional information about the role of surface oxygen and nitrogen species in the process of adsorption of pure SO_2 , especially at low relative pressures.

Our results show that there is no irreversible adsorption of SO_2 at 273 K. All of the investigated carbons demonstrate considerable adsorption capacity toward SO_2 (Figure 5). Among them, the most effective sorbents for SO_2 are the samples heated in ammonia. However, there is no correlation between sorption capacity and nitrogen content. The highest sorption capacity at $p/p_s = 0.33$ demonstrates the sample treated in ammonia for 6 h at 1173 K (DN11736) which possesses the best developed porosity. Annealing, at higher temperatures (DN14233) or for longer time (DN10239) diminishes the adsorption capacity toward SO_2 .

Besides the experimental data of SO_2 adsorption on studied carbons (six arbitrarily chosen systems are shown), Figure 5 shows also the results of the fitting by eq 1. As above we applied the genetic algorithm of Storn and Price.^{7–9} As one can notice from this figure and from Table 3 (where the data for all studied systems are included), the CMMS model describes the data very well. What is more interesting, we observe the correlations between oxygen content and the values of the constants K_0 and K_1 (Figure 6). Similar tendencies were also observed for the

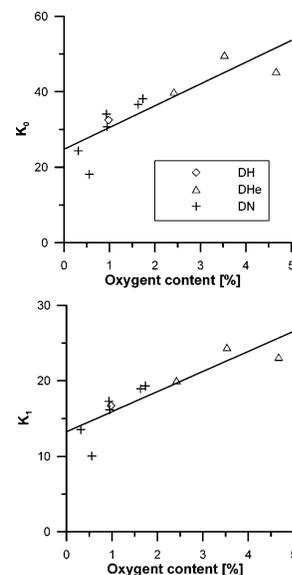


Figure 6. Correlations between the constants of eq 1 and the content of oxygen in studied carbons as determined from elemental analysis.

cited data of Beebe and Dell¹⁰ (the data of Murphy et al.¹¹ concerns only two samples, see the Supporting Information). In this case, an excellent fit to the experimental data is observed as is the correlation between oxygen content and the values of the constants K_0 and K_1 . However, for the latter constant the tendencies are not so obvious due the fact that the heat treated Spheron samples contain very close and small amounts of oxygen in comparison to the untreated sample. This correlation can be explained based on the data from Figure 7 and the detailed analysis of the features of eq 1. One can observe that the rise in K_0 (Figure 7) leads to the increase in adsorption at low pressures (at larger pressures the denominator in eq 1 decreases the adsorption value), and the rise in the value of K_1 leads to an increase in adsorption in the whole relative pressure limit (see eq 1). The correlation between the values of the both constants and the oxygen content on surfaces of studied carbons leads to the conclusion that at low relative pressures (low surface coverage) polar SO_2 molecules adsorb mainly via the interactions with surface oxygen groups. This is in agreement with previous investigations about SO_2 adsorption

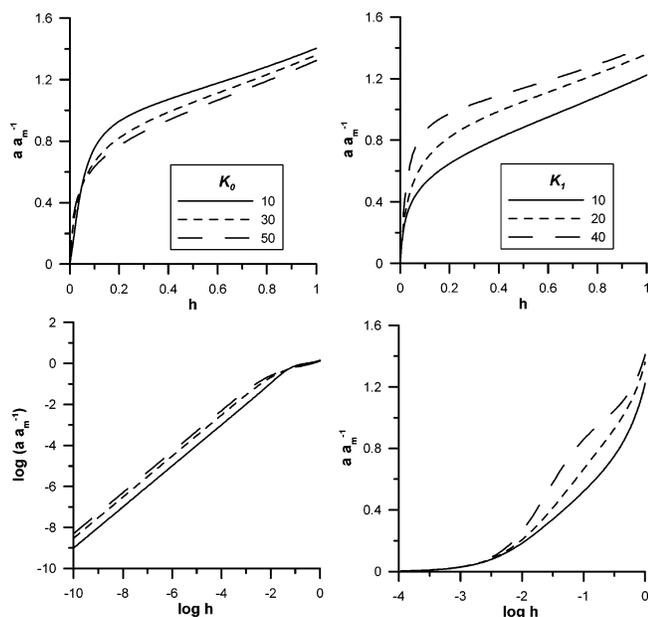


Figure 7. Influence of the constants K_0 ($K_1 = 20$; $K_{as} = 0.3$) and K_1 ($K_0 = 30$; $K_{as} = 0.3$) of the CMMS equation on the plots of adsorption isotherms generated from eq 1.

on different carbon materials.^{10,11,31–35} It was observed that adsorption of pure SO_2 increased with the oxygen content.^{10,11,31–35} Wang and Kaneko, using adsorption calorimetry, established a high value of adsorption energy of SO_2 on activated carbon fibers and activated carbons at low surface coverage.^{32,33} On the basis of additional potential calculations, they attributed the observed high adsorption energy to the electrostatic interactions of the SO_2 dipole with the local surface field at the surface functional group, although the interaction was not so strong to give rise to an irreversible adsorption of SO_2 .^{32,33} Note that since the authors dealing with SO_2 adsorption usually use some popular models to the description of adsorption data, we also tried to apply probably two of the most popular adsorption isotherm equations (Toth and BET) for the description of the data shown in Figure 5. The results are shown in the Supporting Information (Figures 1S and 3S). One can observe that sometimes the tendencies similar to those shown in Figure 6 are observed (see Figures 2S and 4S), but fitting to the straight line is poor (i.e., not as good as that observed for the CMMS model parameters). This is due to the physical assumptions of the CMMS approach and the reality of the adsorption mechanism of polar molecules assumed in this model.

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In conclusion, carbon modification procedures, as applied in this study, change SO_2 adsorption not by the incorporated surface nitrogen-containing functionalities but rather by the changes in the content of surface oxygen groups. According to XPS results, ammonia treated carbons contain several nitrogen and oxygen functional groups. The incorporated nitrogen exists in the form of pyridine, pyrrolic, “quaternary nitrogen”, pyridine-*N*-oxide, and pyridone structures,^{22,24–26,28,29} whereas oxygen forms hydroxyl and carbonyl groups as well as ether structures.^{24–26,28,29} These oxygen structures may result from the presence of oxygen in the raw material as well as from oxygen chemisorption during storage under air.^{24–26,28,29} The incorporated nitrogen species during NH_3 treatment facilitate the dissociative chemisorption of O_2 as the superoxide ions and enhance the surface oxidation of aqueous H_2SO_3 to H_2SO_4 .^{27,29}

It was proven that the observed high SO_2 adsorption ability of the nitrated carbon materials during adsorption of SO_2 in the presence of oxygen and water results at least partially from oxidative adsorption of SO_2 .^{22,25,28,29} In the presence of water, the formed SO_3 is converted into H_2SO_4 which is accumulated in pores on basic sites.^{22,25,28,29}

Thus, the lack of an evident relationship between the nitrogen content and adsorption capacity during SO_2 adsorption in the absence of oxygen and water even for carbon sorbents with similar porosity as in our case results from the absence of oxidative adsorption.

4. Conclusions

We present the development of the enthalpy of adsorption formula related to the cooperative multimolecular sorption model. Successful simultaneous fitting the experimental SO_2 adsorption and enthalpy data measured for different systems, and at different temperatures, leads to the conclusion that the CMMS is very promising tool in the studying of the process of sorption of SO_2 molecules on different carbon materials. For the well characterized series of modified carbons, we show the applicability of the CMMS equation to the description of SO_2 sorption data. The correlations obtained between the content of surface oxygen and the constants of the CMMS equation leads to the mechanism of SO_2 sorption on carbons and the role of surface nitrogen functionalities playing in this mechanism. Our results show that the lack of evident relationship between the nitrogen content and adsorption capacity during SO_2 adsorption in the absence of oxygen and water (even for carbon sorbents with similar porosity as in our case) results from the absence of oxidative adsorption.

Supporting Information Available: 1. Fitting of the data by Toth adsorption isotherm equation. 2. Fitting of the data by BET adsorption isotherm equation. 3. Fitting the data of Beebe and Dell. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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