Thermodynamics of the CMMS Approach and Carbon Surface Chemistry in SO\textsubscript{2} 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 SO\textsubscript{2} 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 SO\textsubscript{2} measured on the series of modified activated carbons. The porosity of adsorbents was characterized via description of low-temperature N\textsubscript{2} 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 SO\textsubscript{2} 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 SO\textsubscript{2} 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 SO\textsubscript{2} adsorption on carbons is widely studied in the literature particularly in view of flue gas desulfurization. There are, however, some contradictory results and observations concerning the influence carbon surface modifications (especially those leading to creation of nitrogen containing functionalities) on SO\textsubscript{2} adsorption capacity. One of the most important problems of the theoretical description of adsorption of polar molecules (among them SO\textsubscript{2}) 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,† 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

\[ a = \frac{a_m}{(1 - K_{ah})(K_h + w^2(1 - K_{ah}))} \]

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 \( (p_0) \)), \( K_h \) 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

\[ w = 2 \left( \frac{1 - K_{ah}}{1 - K_{ah}} + \sqrt{\left( \frac{K_{ah}}{1 - K_{ah}} \right)^2 + \frac{4K_h}{1 - K_{ah}}} \right)^{-1} \]

where \( K_1 \) is the equilibrium constant for sorption of the side unit on the primary side.

The properties of the CMMS were extensively studied by Malakhov and Volkov themselves.† 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.† This theory has been subsequently applied to water—carbon systems,§— 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 IV/V) which fall between these types.\footnote{On the other hand, this theory suffers from the inability to characterize type IV isotherms. Therefore, Rutherford\textsuperscript{4} modified the original model proposed by Malakhov and Volkov and the dual (hybrid) equation was developed (i.e., the sum of two CMMC 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} 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 IV/V) which fall between these types.\footnote{On the other hand, this theory suffers from the inability to characterize type IV isotherms. Therefore, Rutherford\textsuperscript{4} modified the original model proposed by Malakhov and Volkov and the dual (hybrid) equation was developed (i.e., the sum of two CMMC 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} The properties of the CMMS were extensively studied by Malakhov and Volkov themselves.† 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.† This theory has been subsequently applied to water—carbon systems,§— 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 IV/V) which fall between these types.\footnote{On the other hand, this theory suffers from the inability to characterize type IV isotherms. Therefore, Rutherford\textsuperscript{4} modified the original model proposed by Malakhov and Volkov and the dual (hybrid) equation was developed (i.e., the sum of two CMMC 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} 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 IV/V) which fall between these types.\footnote{On the other hand, this theory suffers from the inability to characterize type IV isotherms. Therefore, Rutherford\textsuperscript{4} modified the original model proposed by Malakhov and Volkov and the dual (hybrid) equation was developed (i.e., the sum of two CMMC 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}
(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 SO\(_2\) 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:

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

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

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

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

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

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

\[
q'' - L = RT^2 \frac{\partial \ln h}{\partial T} = q_aK_0^0 + q_{as}aK_{as}(K_0h + w^2(1 - K_{as}h)) + a(1 - K_{as}h)(-q_0K_0 + wB_2(1 - K_{as}h) + q_{as}w^2K_{as})\quad (5)
\]

\[
K_0^0 + aK_{as}(K_0h + w^2(1 - K_{as}h)) + a(1 - K_{as}h)(-K_0 - wB_2(1 - K_{as}h) + w^2K_{as})\quad (6a)
\]

\[
K_{as}^0 \exp \left( \frac{q_{as}}{RT} \right) \quad (6b)
\]

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 Coons\(^3\) showed recently that the CMMS model (eq 1) can generate the isotherm

\[
B_1 = \frac{1}{(1 - K_{as}h)^2} \left[ K_1 \left( 1 - \frac{K_0h}{1 - K_{as}h} \right) - 2K_0 \right] \sqrt{\left( 1 - \frac{K_0h}{1 - K_{as}h} \right)^2 + 4K_0^2h^2} \quad (6a)
\]

\[
B_2 = \frac{1}{(1 - K_{as}h)^2} \left[ K_1(q_1 + (q_{as} - q_1)K_{as}h) + \frac{K_1}{1 - K_{as}h} \left( q_1 + (q_{as} - q_1)K_{as}h \right) \right] \quad (6b)
\]

we fitted the data of SO$_2$ adsorption measured on graphitized Summing up, this makes the CMMS model very promising for those measured experimentally and reported in the literature.6 different nonmonotonic plots of the enthalpy very similar to due to the combination of the parameters, there are possible noticed that for the same adsorption isotherm shown in this figure, adsorption enthalpy plots generated from eqs 5 and 6. It can be

Figure 2. Influence of the parameters ($q_0$, $q_1$, and $q_m$, 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 $q_m = 10$ kJ mol$^{-1}$). Note that all enthalpy plots are generated for the same adsorption isotherm.

different types of isotherms, progressively decreasing hyperbolic-like plots are observed. On the other hand, Figure 2 shows other possible shapes 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 satisfactory. Summing up, we can conclude, that the CMMS adsorption isotherm equation postulates very realistic model of adsorption of associating molecules.

3. Description of SO$_2$ 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

Table 1. Values of the Parameters Applied for the Calculation of Adsorption Isotherms from the CMMS Model Shown in Figure 1

<table>
<thead>
<tr>
<th>type of isotherm*</th>
<th>$a_m$ [mol g$^{-1}$]</th>
<th>$K_0^*$</th>
<th>$K_1^*$</th>
<th>$K_{as}^*$</th>
<th>$q_0$ [kJ mol$^{-1}$]</th>
<th>$q_1$ [kJ mol$^{-1}$]</th>
<th>$q_m$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.01</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>0.01</td>
<td>10</td>
<td>10</td>
<td>0.77</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>0.01</td>
<td>0.05</td>
<td>1</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>V</td>
<td>0.01</td>
<td>0.057</td>
<td>1.71</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>II/III</td>
<td>0.01</td>
<td>1</td>
<td>1</td>
<td>0.88</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>II/V</td>
<td>0.01</td>
<td>0.27</td>
<td>3.5</td>
<td>1</td>
<td>10</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

conditions was carried out at 273 K up to constant pressure (3 Torr). Elemental composition was determined using a vario El III CHN analyser (Elementar Analyensysteme GmbH, Hanau, Germany). Sulfur dioxide adsorption under static conditions and the second PSD peak is shifted toward larger pore diameters. Therefore, it is reasonable to assume that for only two of the carbon samples (DN1173 and DN11736) nearly all of the studied carbons reveal the same porosity. Thus, it was shown that the presence of certain nitrogen groups on the surface of carbons is the incorporation of nitrogen into a carbon matrix,17,19,21,24 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 surface enhances its adsorption ability to SO₂.

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 oxides16,18,19,22 as well as to the electron donor–acceptor interactions involving delocalized π electrons of carbon platelets.23

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

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

<table>
<thead>
<tr>
<th>carbon</th>
<th>applied procedures</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>D43/1 de-ashed with concentrated HCl and HF solutions (298 K)</td>
</tr>
<tr>
<td>DHe5733</td>
<td>D heated in He (20 dm³/h, 573 K, 3 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DHe1023</td>
<td>D heated in He (20 dm³/h, 1023 K, 3 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DHe11733</td>
<td>D heated in He (20 dm³/h, 1173 K, 3 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DN10233</td>
<td>D heated in NH₃ (20 dm³/h, 1023 K, 3 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DN10236</td>
<td>D heated in NH₃ (20 dm³/h, 1023 K, 6 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DN10239</td>
<td>D heated in NH₃ (20 dm³/h, 1023 K, 9 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DN11733</td>
<td>D heated in NH₃ (20 dm³/h, 1173 K, 3 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DN11736</td>
<td>D heated in NH₃ (20 dm³/h, 1173 K, 6 h), cooled in He (25 dm³/h)</td>
</tr>
<tr>
<td>DN14233</td>
<td>D heated in NH₃ (20 dm³/h, 1423 K, 3 h), cooled in He (25 dm³/h)</td>
</tr>
</tbody>
</table>

Figure 4. Differential pore size distributions obtained on the basis of the ND method.
In some cases, when the adsorption of dry SO₂ was conducted at room temperature in the presence of oxygen, some positive correlations were found between nitrogen content and SO₂ adsorption capacity or adsorption energy calculated from the Dubinin–Rhadushkevich adsorption isotherm equation, respectively. However, for dry SO₂ 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 SO₂, especially at low relative pressures.

Our results show that there is no irreversible adsorption of SO₂ at 273 K. All of the investigated carbons demonstrate considerable adsorption capacity toward SO₂ (Figure 5). Among them, the most effective sorbents for SO₂ 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 SO₂.

Besides the experimental data of SO₂ 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. 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
cited data of Beebe and Dell[10] (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 SO₂ molecules adsorb mainly via the interactions with surface oxygen groups. This is in agreement with previous investigations about SO₂ adsorption.
high value of adsorption energy of SO\textsubscript{2} on activated carbon fibers. Wang and Kaneko, using adsorption calorimetry, established a formula related to the cooperative multimolecular sorption model. For the well characterized group, although the interaction was not so strong to give rise to an irreversible adsorption of SO\textsubscript{2},\textsuperscript{32,33} On the basis of additional potential calculations, they attributed the observed high adsorption energy to the electrostatic interactions of the SO\textsubscript{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\textsubscript{2}.\textsuperscript{32,33} Note that since the authors dealing with SO\textsubscript{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.

In conclusion, carbon modification procedures, as applied in this study, change SO\textsubscript{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.\textsuperscript{22,24–26,28,29} Whereas oxygen forms hydroxyl and carbonyl groups as well as ether structures.\textsuperscript{24–26,28,29} These oxygen structures may result from the presence of oxygen during the raw material as well as from oxygen chemisorption during storage under air.\textsuperscript{24–26,28,29} The incorporated nitrogen species during NH\textsubscript{3} treatment facilitate the dissociative chemisorption of O\textsubscript{2} as the superoxide ions and enhance the surface oxidation of aqueous H\textsubscript{2}SO\textsubscript{3} to H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{27,29}

It was proven that the observed high SO\textsubscript{2} adsorption ability of the nitrated carbon materials during adsorption of SO\textsubscript{2} in the presence of oxygen and water results at least partially from oxidative adsorption of SO\textsubscript{2}.\textsuperscript{22,25,28,29} In the presence of water, the formed SO\textsubscript{3} is converted into H\textsubscript{2}SO\textsubscript{4} which is accumulated in pores on basic sites.\textsuperscript{22,25,28,29}

Thus, the lack of an evident relationship between the nitrogen content and adsorption capacity during SO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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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