

Article

## Adsorption of Carbon Dioxide on Activated Carbon

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**Abstract:** The adsorption of CO<sub>2</sub> on a raw activated carbon A and three modified activated carbon samples B, C, and D at temperatures ranging from 303 to 333 K and the thermodynamics of adsorption have been investigated using a vacuum adsorption apparatus in order to obtain more information about the effect of CO<sub>2</sub> on removal of organic sulfur-containing compounds in industrial gases. The active ingredients impregnated in the carbon samples show significant influence on the adsorption for CO<sub>2</sub> and its volumes adsorbed on modified carbon samples B, C, and D are all larger than that on the raw carbon sample A. On the other hand, the physical parameters such as surface area, pore volume, and micropore volume of carbon samples show no influence on the adsorbed amount of CO<sub>2</sub>. The Dubinin-Radushkevich (D-R) equation was the best model for fitting the adsorption data on carbon samples A and B, while the Freundlich equation was the best fit for the adsorption on carbon samples C and D. The isosteric heats of adsorption on carbon samples A, B, C, and D derived from the adsorption isotherms using the Clapeyron equation decreased slightly increasing surface loading. The heat of adsorption lay between 10.5 and 28.4 kJ/mol, with the carbon sample D having the highest value at all surface coverages that were studied. The observed entropy change associated with the adsorption for the carbon samples A, B, and C (above the surface coverage of 7 ml/g) was lower than the theoretical value for mobile adsorption. However, it was higher than the theoretical value for mobile adsorption but lower than the theoretical value for localized adsorption for carbon sample D.

**Key words:** carbon dioxide; adsorption; heat of adsorption; activated carbon

### 1. Introduction

Activated carbon was a highly microporous material with a large surface area and has been employed as one of the main adsorbents for desulfurization. The method of removing CS<sub>2</sub> by using activated carbon at normal temperature was considered to be economical and appropriate [1]. However, CO<sub>2</sub> and water vapor that existed in the industrial gases led easily to lower selectivity and sulfur capacity of activated carbon. In recent years, modified activated carbon was considered to be a potential adsorbent due to its

better selectivity [2–4]. The effect of water vapor on the removal of organic sulfur-containing compounds by activated carbon modified with organic amine was investigated [2] and water vapor was found to have a negative effect on the removal of CS<sub>2</sub>. The adsorption kinetics of CS<sub>2</sub> from damp gas on activated carbon were also studied in a fixed-bed and by using the thermogravimetric technique, respectively [5,6], and their results revealed that both Bangham and Elovich equations could be used to describe the adsorption kinetic behavior of CS<sub>2</sub> but Bangham equation was more favorable.

In the previous studies, the adsorption proper-

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ties of  $\text{CS}_2$  on a raw and three modified activated carbon samples were investigated by the gravimetric method and a FT-IR that was equipped with a vacuum adsorption system [7,8]. In this study, the  $\text{CO}_2$  adsorption isotherms, at different temperatures on the above-mentioned four carbon samples, were measured gravimetrically using the vacuum adsorption system and the adsorption data fitted to different isotherm equations. The isosteric heat of adsorption was derived from isotherm equations. The thermodynamic analysis of the adsorption was also given. The adsorption properties of  $\text{CO}_2$  on the four activated carbon samples with the aim of obtaining more information about the effect of  $\text{CO}_2$  on removal of organic sulfur-containing compounds in industrial gases was also studied. This would be important for the further development of the adsorbents.

## 2. Experimental

### 2.1. Materials

Four carbon samples A, B, C, and D were used in this study. Sample A was a commercially activated carbon, ZL-30, which was obtained as a raw material from the Xinhua Chemical Plant in China. The three modified carbon samples B, C, and D were prepared by raw materials that were impregnated with different solutions. The saturated carbon samples were kept humid for 24 h at room temperature. Sample B that was impregnated with 4% KOH solution was heated at 373–393 K for 2–3 h and then dried in a vacuum oven at 353–373 K for 3 h. Sample C was impregnated with a mixture of ethylenediamine and ethanol (the volume ratio of ethylenediamine and ethanol was 2:1) and then dried at 343–363 K for 3 h. Sample D was impregnated with a mixture of 4% KOH, ethylenediamine, and ethanol (the volume ratio of ethylenediamine and ethanol was 2:1) and then dried at 343–363 K for 3 h. The physical properties of the four carbon samples were given in the related reference [8].

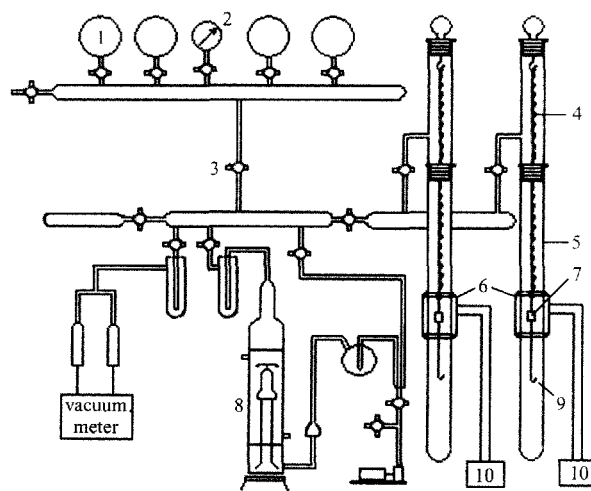
The pure carbon dioxide gas (purity > 99.99%) was purchased from Beijing Haipu Beifen Gas Industry Corporation. All the chemicals used were of A.R. grade.

### 2.2. Apparatus and reaction conditions

Adsorption experiments of  $\text{CO}_2$  gas were carried out in a glass vacuum system as shown in Figure 1.

The small quartz basket in the adsorption column was packed with 40 to 60 mesh carbon samples. The vacuum before adsorption was at the range of  $10^{-3}$ – $10^{-4}$  Pa. About 200 mg of the samples was heated to a given temperature and held at this temperature for 45 minutes to reach thermodynamic equilibrium at a certain pressure of  $\text{CO}_2$ . The weight of the sample was then recorded and the amount adsorbed was calculated. The adsorption was usually carried out under a pressure of 0–40000 Pa.

The adsorption kinetics on four carbon samples was measured at three or four temperatures: 303 K, 313 K, 323 K, or 333 K, respectively.



**Figure 1. The vacuum system for the adsorption of carbon dioxide**

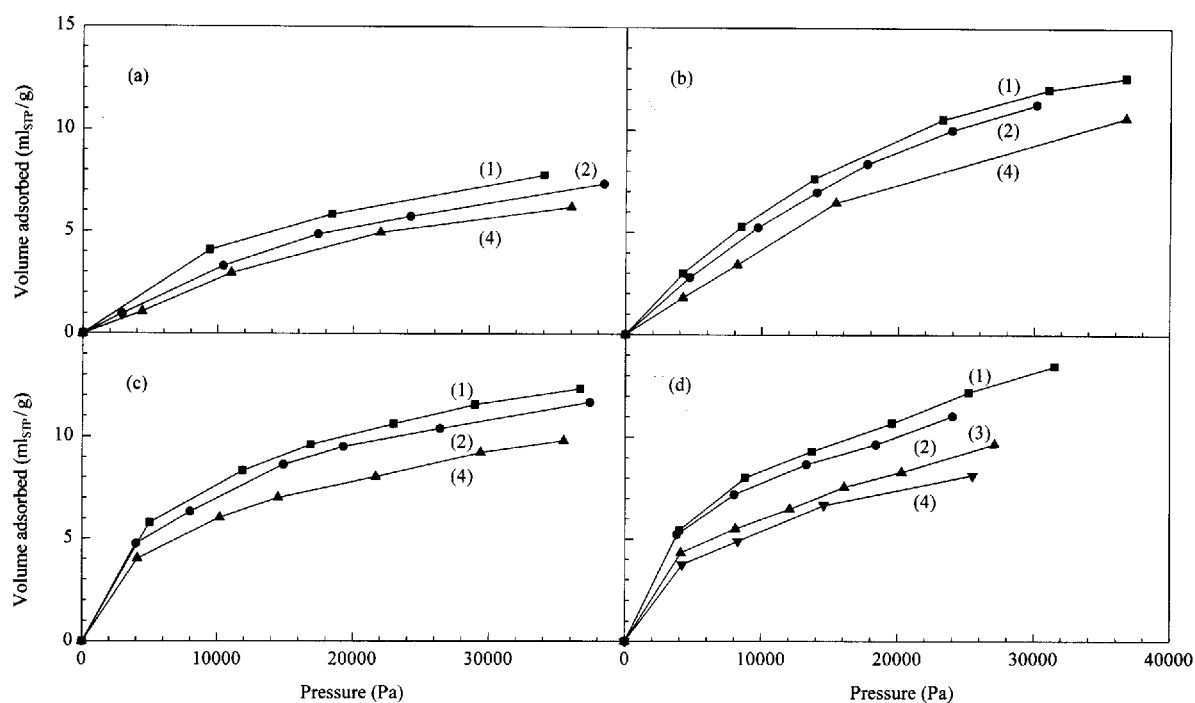
1—Gas sample flask, 2—Pressure gauge, 3—Glass cock, 4—Quartz spring balance, 5—Adsorbing column, 6—Heating furnace, 7—Quartz basket, 8—Vacuum pump, 9—Mark point, 10—Temperature controller

## 3. Results and discussion

### 3.1. Adsorption isotherms

The adsorption isotherms of carbon dioxide at different temperatures on the four activated carbon samples are shown in Figure 2.

The adsorption data were fitted to standard isotherm models, Langmuir [9], Freundlich [10], Dubinin-Radushkevich (D-R) [11–16], and Temkin [17] by linear regression, respectively. The best fitting isotherm models along with the regression coefficients and the relative error for isotherm fits are given in Table 1. The Dubinin-Radushkevich model was found to give the best fit for the adsorption of carbon dioxide



**Figure 2. Adsorption isotherms of carbon dioxide at different temperatures on the four activated carbon samples**

(a) sample A, (b) sample B, (c) sample C, (d) sample D; (1) 303 K, (2) 313 K, (3) 323 K, (4) 333 K

on carbon samples A and B at 303, 313, and 333 K. The Freundlich model was found to give the best fit for the adsorption of carbon dioxide on carbon sample C at 303, 313, and 333 K and carbon sample D at 303, 313, 323, and 333 K, respectively. The D-R equation is in the form of:

$$\ln V = \ln V_0 - D[\ln(P_0/P)]^2 \quad (1)$$

where,  $V_0$  is D-R micropore capacity,  $P_0$  is adsorbate saturation vapor pressure, and  $D$  is D-R model constant. The Freundlich equation takes the form of:

$$V = KP^{1/n} \quad (2)$$

where,  $K$  and  $n$  are Freundlich model constants. The estimated values of the parameters of the best fitting isotherm models are presented in Table 2.

**Table 1. Regression coefficient and average relative error for the best fitting isotherm model**

Activated carbon	Temperature (K)	Best fitting model	Regression coefficient	Average relative error* (%)
A	303	D-R	0.9996	0.87
	313		0.9993	2.24
	333		0.9998	0.68
B	303	D-R	0.9990	2.10
	313		0.9990	2.02
	333		0.9978	3.60
C	303	Freundlich	0.9978	1.38
	313		0.9963	2.30
	333		0.9988	1.17
D	303	Freundlich	0.9981	1.36
	313		0.9988	1.08
	323		0.9970	1.75
	333		0.9968	2.05

\*Average relative error =  $(100/N) \sum_{j=1}^N \text{abs}(V_{\text{cal.}} - V_{\text{exp.}})_j / V_{\text{exp.}}$ , where  $N$  = number of data points.

**Table 2. Constants of the best fitting isotherm models for the adsorption of carbon dioxide on the four activated carbon samples**

Activated carbon	<i>T</i> /K	Best fitting model	Constants of the best fitting isotherm models	
			D	<i>V</i> <sub>0</sub> (ml <sub>STP</sub> /g)
A	303	D-R	0.1421	9.096
	313		0.1710	8.292
	333		0.2015	7.830
B	303	D-R	0.1600	14.769
	313		0.1754	14.288
	333		0.1956	12.761
C	303	Freundlich	K	<i>n</i>
	313		0.2256	2.61
	333		0.1585	2.43
D	303	Freundlich	K	<i>n</i>
	313		0.1419	2.47
	323		0.1571	2.33
	333		0.1995	2.52

### 3.2. Isothermic heat of adsorption

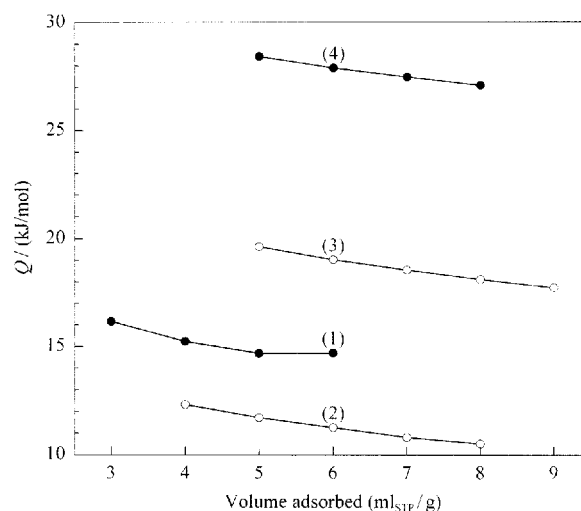
The isothermic heat of the adsorption of carbon dioxide, *Q*, at a given specific surface loading *V<sub>x</sub>* was calculated from the adsorption isotherms at different temperatures using the Clapeyron equation:

$$Q = RT^2 \left[ \frac{\partial \ln P}{\partial T} \right]_{V_x} = -R \left[ \frac{\partial \ln P}{\partial (1/T)} \right]_{V_x} \quad (3)$$

Where, *R* is the gas constant, *T* is temperature, and *P* is pressure. The best fitting isotherm models listed in Table 2 were used to calculate *Q* in this study.

The isothermic heat of adsorption for the four carbon samples at different surface loadings is plotted in Figure 3. The value of adsorption heat on carbon sample A decreased slightly from 16.2 to 14.7 kJ/mol and the surface coverage increased from 3 to 6 ml/g. The isothermic heat of adsorption on carbon sample B decreased from 12.3 to 10.5 kJ/mol and the surface coverage increased from 4 to 8 ml/g. The isothermic heat of adsorption on carbon sample C also shows a small decrease from 19.6 to 17.7 kJ/mol and an increase in the surface coverage from 5 to 9 ml/g. On increased loading, there was a small decrease in the heat of adsorption on carbon sample D and the value of *Q* was about 28 kJ/mol. When compared with the

carbon samples A, B, and C, the value of the heat of adsorption on carbon sample D was the highest at all surface coverage. It was suggested that carbon dioxide was adsorbed more strongly on carbon sample D than on carbon samples A, B, and C. The observed small decrease in the heat of adsorption with increase of surface coverage suggests weak repulsive interactions between adsorbed carbon dioxide molecules.



**Figure 3. Isothermic heat of adsorption as a function of surface loading.**  
(1) sample A, (2) sample B, (3) sample C, (4) sample D

### 3.3. Gibbs energy and entropy of adsorption

The thermodynamic data for the adsorption at surface coverage of 6 ml/g are presented in Table 3. The values of free energy and entropy changes due to adsorption were estimated from the adsorption data using the following expressions [18]:

$$\Delta G = RT \ln P_s / P \quad (4)$$

$$\Delta G = \Delta H - T \Delta S \quad (5)$$

$$S_a = S_g + \Delta S \quad (6)$$

where,  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are the standard free energy, enthalpy (isothermic heat of adsorption under isothermal conditions), and entropy changes in the adsorption process, respectively.  $S_g$  is the entropy of the adsorbate at standard pressure  $P_s$  (101.325 kPa).  $S_a$  is the entropy of the adsorbed phase, and  $P$  is the equilibrium pressure of the adsorbate. The values of  $S_g$  for the carbon dioxide gases are taken from the data given elsewhere [19, 20].

**Table 3. Thermodynamic data for the adsorption on carbon samples A, B, C, and D at the surface coverage of 6 ml<sub>STP</sub>/g**

Activated carbon	Temperature (K)	$\Delta G$ /(kJ/mol)	$-\Delta S$ /(J/(mol·K))	$S_g^*$ /(J/(mol·K))	$S_a$ /(J/(mol·K))
A	303	4.29	62.7	214.3	151.6
	313	3.58	58.4	215.5	157.1
	333	3.18	53.7	217.8	164.1
B	303	5.98	56.9	214.3	157.4
	313	5.79	54.5	215.5	161.0
	333	5.44	50.1	217.8	167.7
C	303	7.46	87.4	214.3	126.9
	313	7.03	83.2	215.5	132.3
	333	6.29	76.0	217.8	141.8
D	303	7.66	117.4	214.3	96.9
	313	7.69	113.7	215.5	101.8
	323	6.40	106.2	216.7	110.5
	333	5.83	101.3	217.8	116.5

\*The values are taken from references [19, 20];  $S_g$ —entropy of the adsorbate at standard pressure.

The thermodynamic data calculated reveal that the values of  $\Delta G$  and  $-\Delta S$  decreased with increasing surface coverage on the four carbon samples. In all cases,  $\Delta G$  and  $-\Delta S$  decreased with the increase of temperature. The entropy of the adsorbed phase for the four carbon samples,  $S_a$  (and hence the mobility), increased as carbon dioxide loadings increased and also increased with increasing adsorption temperature.

Figure 4 shows a comparison at 303 K between the observed entropy change ( $-\Delta S_m$ ) associated with the adsorption (after correcting for the contributions of entropy change in the vapor phase and in the adsorbed phase) at different surface loadings and the theoretical entropy change ( $S_{t3D} - S_{t2D}$ ). The value of ( $-\Delta S_m$ ) can be obtained from  $\Delta S$  using the relation [21]:

$$\Delta S_m = \Delta S + R \ln \frac{A^+}{A} \quad (7)$$

where,  $A^+$  is the standard molecular area ( $4.08 T \times 10^{-16} \text{ cm}^2$ ) and  $A$  is the molecular area of the adsorbate estimated using the relation suggested by Emmett and Brunauer [22].

The theoretical entropy change for the mobile film model [21] in the adsorption can be calculated from the following relation:

$$\Delta S_t = S_{t3D} - S_{t2D} \quad (8)$$

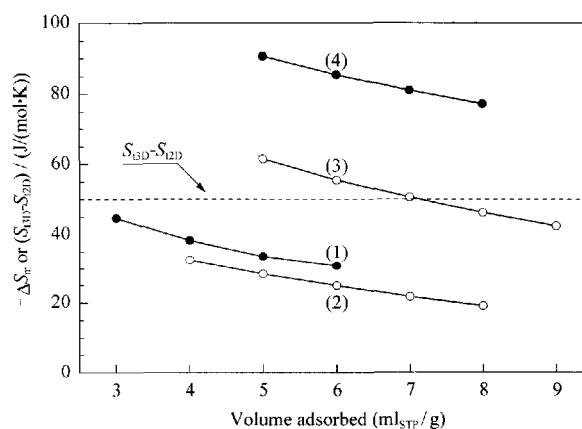
where  $S_{t3D}$  and  $S_{t2D}$  are the translational entropies for the three-dimensional and two-dimensional adsor-

bate vapors, respectively.  $S_{t3D}$  and  $S_{t2D}$  can be estimated from the following expressions [21] [23]:

$$S_{t3D} = R \ln(M^{1.5} T^{2.5}) - 9.61 \quad (9)$$

$$S_{t2D} = 0.667 S_{t3D} + 2.76 \ln T - 12.71 \quad (10)$$

The theoretical entropy changes for the mobile and localized adsorption models were expected to be equal to ( $S_{t3D} - S_{t2D}$ ) and  $S_{t3D}$ , respectively. The observed entropy change ( $-\Delta S_m$ ) and the theoretical entropy change for mobile adsorption ( $\Delta S_t = S_{t3D} - S_{t2D}$ ) at different adsorbate loadings are plotted in Figure 4.



**Figure 4. Comparison of the observed entropy change ( $-\Delta S_m$ ) at different adsorbate loadings with the theoretical entropy change for mobile adsorption ( $S_{t3D} - S_{t2D}$ ) in the adsorption of carbon dioxide on the four carbon samples at 303 K**

(1) sample A, (2) sample B, (3) sample C, (4) sample D

The results in Figure 4 show that the observed entropy change ( $-\Delta S_m$ ) for the four carbon samples decreased slightly with increasing surface loadings in all cases. For the adsorption on carbon samples A and B, the entropy change ( $\Delta S_m$ ) was lower than that for the mobile adsorption ( $S_{t3D}-S_{t2D}$ ) in the entire range of adsorbate loading studied. For the adsorption on carbon sample C, the entropy change crossed the theoretical value for the mobile adsorption above the adsorbate loading of 7 ml/g. For the adsorption on carbon sample D, the entropy change was higher than that for the mobile adsorption ( $S_{t3D}-S_{t2D}$ ) in the entire range of adsorbate loading that was studied.

### 3.4. Comparison of adsorption properties

A comparison of the adsorption data in temperatures ranging from 303 to 333 K on four carbon samples as shown in Figure 3 reveal that the volume adsorbed on the modified carbon samples B, C, and D, which were impregnated with KOH, ethylenediamine, and the mixture of KOH and ethylenediamine, respectively, were generally larger than that on the raw carbon sample A. The probable reason could be because of the attractive interactions between the impregnated ingredients and adsorbed carbon dioxide molecules. The volume adsorbed on the four carbon samples decreased with increasing temperature in all cases. However, the volume adsorbed does not exhibit any relationship with the physical properties of the four carbon samples [8] such as BET surface area, pore volume, or micropore volume. The volume adsorbed of carbon dioxide was much lower than that of carbon disulfide on the same carbon samples [7].

The D-R equation was found to give the best fit for the adsorption of carbon dioxide on carbon samples A and B. The Freundlich equation was found to be the best model for the adsorption of carbon dioxide on carbon samples C and D. A comparison of the heat of adsorption on four carbon samples as in Figure 3 reveals the following order:

Sample B < Sample A < Sample C < Sample D.

The heat of adsorption on carbon samples A, B, C, and D are about 15, 12, 19, and 28 kJ/mol, respectively, and the value of carbon sample D was the highest in all surface coverage studied. It is unexpected that the heat of adsorption on carbon sample B was the lowest due to the small change of volume adsorbed with temperature.

The thermodynamic data for the adsorption reveals that the mobility for the four carbon samples

A, B, C, and D increased as the surface loading increases. This implies that in the initial stages of adsorption it was the sites of highest adsorption potential which were occupied first. These adsorption sites might be in the narrowest of the microporosity. As the adsorption process continues, the adsorption sites changed to pores of lower adsorption potential and more and more adsorbed carbon dioxide molecules were mobile on the surface of activated carbons. The entropy change ( $-\Delta S_m$ ) due to the adsorption on the four carbon samples decreased with the increase of surface loadings and the values of ( $\Delta S_m$ ) for the carbon samples A, B, and C were lower than the theoretical value for the mobile adsorption ( $S_{t3D}-S_{t2D}$ ) in the entire range of adsorbate loading studied except for the carbon sample C at low surface coverage (below 7 ml<sub>STP</sub>/g). In the case of carbon sample D, the entropy change ( $-\Delta S_m$ ) was higher than the theoretical value for the mobile adsorption ( $S_{t3D}-S_{t2D}$ ) but much lower than the theoretical value for the localized adsorption ( $S_{t3D}$ ).

### 4. Conclusions

The results show that the adsorption of carbon dioxide on the four carbon samples does not follow the same adsorption isotherm equation. The D-R equation was found to fit well the adsorption data on carbon samples A and B. The Freundlich equation was found to give the best fit for the adsorption on carbon samples C and D. It was also found that the active ingredients impregnated in the carbon samples had significant influence on the adsorption of carbon dioxide and the volumes adsorbed on the modified carbon samples B, C, and D were all larger than that on the raw carbon sample A. However, the physical properties, surface area, pore volume, and micropore volume of carbon samples showed no influence on the amount adsorbed. The isosteric heat of adsorption ( $Q$ ) derived from their equilibrium lay between 10.5 and 28.4 kJ/mol at surface coverage studied and the value of  $Q$  for carbon sample D was the highest. The value of the heat of adsorption indicated that the adsorption might be physical adsorption. In all cases, the heat of adsorption decreased slightly as the surface loading increased.

Analysis of the thermodynamic data showed that the mobility for the adsorption increased as the surface loading increased in all cases. The entropy change ( $-\Delta S_m$ ) for the carbon samples A, B, and C (above

the surface coverage of 7 ml/g) was lower than the theoretical value for the mobile adsorption. However, the value of  $-\Delta S_m$  for carbon sample D was higher than the theoretical value for the mobile adsorption but lower than the theoretical value for the localized adsorption.

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