

Study of Hydrogen Sulfide Adsorption on Activated Carbons Using Inverse Gas Chromatography at Infinite Dilution

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Adsorption of hydrogen sulfide on fifteen samples of activated carbons (unmodified and catalytic with introduced basic nitrogen groups) was studied using inverse gas chromatography (IGC) at infinite dilution. Porous structure of carbons was evaluated using sorption of nitrogen. From the retention volume measured in IGC experiments, heats of adsorption, free energy of adsorption, entropy, and Henry's constants were calculated. The results showed the dependence of these quantities on pore sizes of the adsorbents. The strong dependence of the isosteric heat of adsorption on the temperature of measurement and, following this, unusually high heat capacity suggest the strong effect of specific interactions and catalytic influence of carbon surface even unmodified. The calculated Henry's constants are in agreement with the literature data. The adsorption on carbons with incorporated basic nitrogen groups is characterized by stronger adsorbent–adsorbate interactions than on unmodified carbons.

Introduction

Activated carbons are widely used adsorbents to remove contaminants from air and water. The effectiveness of their performance is governed by such characteristics as large surface area, high pore volume, small pore sizes and the catalytic effects of their surfaces.¹ To evaluate the behavior of carbon as an adsorbent of specific contaminants, usually the adsorption isotherms are measured from zero to the saturation pressure. The measurement of isotherms is a relatively easy task when nontoxic and nonhazardous substances are taken into consideration. When toxic species are studied, the measurement of isotherms is not feasible due to the health and environmental hazards. This directs the attention of the researchers toward new molecular simulation techniques and toward methods which can help estimate the sorption capacity of carbons for toxic substances and which are not hazardous to humans.

One of the methods that can be used to evaluate the performance of carbon/toxic substance system is inverse gas chromatography (IGC). IGC is a variation of a classical chromatographic method. The term “inverse” indicates that the stationary phase, not solute, is under investigation.^{2–7} Based on the retention time of the solute studied, such thermodynamic quantities as the free energy of adsorption, enthalpy of adsorption, and entropy can be calculated. From them, Henry's constants can be predicted.^{2–5}

Inverse gas chromatography experiments can be performed at two extreme conditions: at finite concentration and at infinite dilution.^{2–7} In the latter method, the small amounts of the solutes are injected and it is assumed that the adsorption is governed by the Henry's law. The lateral interactions are negligible owing to the extremely low concentration of the adsorbate. This assumption leads to the calculation of the Henry's constant, which is important for the prediction of adsorption isotherms.

The objective of this paper is to describe the adsorption of hydrogen sulfide on activated carbon using the inverse gas chromatography method. From the experiment, the thermodynamic functions along with Henry's constants, K_H , are calculated. They may be used to predict the adsorption process. Changes in the heat of adsorption with temperature are discussed. Differences in the thermodynamic behavior of unmodified and catalytic carbons are pointed out.

Experimental Section

Materials. Activated carbons of different origins were chosen for this study. They are as follows: RB3 – peat based, pellet shaped carbon (2 × 1 mm) supplied by Norit America, Inc.; S208c – coconut shell based, granular carbon supplied by Waterlink Barnebey Sutcliffe; wood based BAX 1500 (pellets), WVA-900 (granules), WVA-1100 (granules), and experimental UMC supplied by Westvaco corporation. Carbons are referred to as N, S, W1, W2, W3, and W4, respectively. To broaden the spectrum of materials, the S and N carbons were oxidized with nitric acid and ammonium persulfate.⁸ The carbons after oxidation are referred to as N1 and N2 and S1 and S2. Digits “1” and “2” refer to nitric acid and ammonium persulfate oxidations, respectively.

Another series of samples was prepared by treatment of the W1 and N samples with urea at elevated temperatures.⁹ The samples after this treatment have suffix “u” followed by the temperature of heating in centigrade. W1 carbons after modification with urea are considered as catalytic materials for H₂S oxidation. In addition to carbons modified in our laboratory, two catalytic carbons designed for H₂S removal were studied. They are: Centaur, manufactured by Calgon Carbon, and ROZ3 manufactured by Norit. We refer to them as C and R, respectively.

Before further experimentation, the carbons were extensively washed with H₂O to constant pH in a Soxhlet apparatus to remove water soluble species.

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Methods

Inverse Gas Chromatography. The chromatographic experiments were performed with an SRI gas chromatograph equipped with a flame ionization detector. The injector temperature was 473 K. The stainless steel columns (20 cm long, 2.17 mm in diameter) were filled with carbon particles of size ranging from 0.2 to 0.4 mm. Helium was used as a carrier gas with a flow rate 30–120 cm³/min and methane as a nonretained species. The pressure drop on the column was between 250 and 700 Torr depending upon the sample. The samples were conditioned at 473 K in the chromatographic column under helium gas flow for 12 h prior to the measurement. Injection volume was in the range 0.1 to 1.0 mL of 5% mixture of H₂S in nitrogen. The range of experimental temperatures was 313–473 K (20 K step). For each temperature at least five injections with different volumes of H₂S were done. Under these conditions, all chromatographic peaks were symmetrical and retention times did not depend on amount injected, indicating that the Henry's law region was attained. Retention volumes were corrected for the gas compressibility using James–Martin factor.³ The precision of the measurement of retention times was 5%. The temperature of the column was stabilized with accuracy at ± 0.1 K.

Nitrogen Adsorption. Nitrogen adsorption isotherms were measured using an ASAP 2010 analyzer (Micromeritics) at -196 °C. Before the experiment the samples were degassed at 120 °C to constant vacuum 10^{-5} Torr. The isotherms were used to calculate the specific surface area, S_{N_2} , micropore volume, V_{mic} , and total pore volume, V_t . All of the parameters were determined using density functional theory, DFT.^{10–11} From the isotherms, the characteristic energy of adsorption was calculated using the Dubinin–Radushkevich equation.¹² It was used to calculate the average pore width, L_{mic} , following the approach of Stoeckli et al.¹³

Calculation of Basic Thermodynamic Quantities from IGC Experiments

The basic quantity determined from IGC experimentation is the net retention volume, V_N . It is calculated from the retention time using the flow rate of the carrier gas and compressibility correction factor.^{2–4} Another useful quantity is the specific retention volume, V_s , obtained from the following expression

$$V_s = \frac{V_N}{Sm} \quad (1)$$

where S is the specific surface area of adsorbent and m is its mass. The quantities V_N and V_s are directly related to the Henry's constant, K_H .^{3,4}

$$V_N = K_H RT Sm \quad (2)$$

$$V_s = K_H RT \quad (3)$$

where R and T are the gas constant and the temperature in Kelvin.

The isosteric heat of adsorption Q_{st} at zero surface coverage can be found from the measurements of V_s at various temperatures using the expression

$$Q_{st} = R \frac{\partial \ln(V_s/T)}{\partial(1/T)} \quad (4)$$

The standard enthalpy of adsorption $\Delta H^\circ = -Q_{st}$.

TABLE 1: Structural and Energetic Parameters Calculated from Sorption of Nitrogen

sample	S_{N_2} [m ² /g]	V_{mic} [cm ³ /g]	V_t [cm ³ /g]	E_{N_2} [kJ/mol]	E_o [kJ/mol]	L_{mic} [nm]
W1	1400	0.56	1.21	5.05	15.88	2.26
W2	1025	0.36	1.24	5.13	16.13	2.17
W3	1100	0.41	1.18	5.31	16.70	1.99
W4	1790	0.79	1.03	5.64	17.74	1.71
S	1030	0.39	0.41	7.33	23.05	0.92
S1	972	0.37	0.40	7.28	22.89	0.93
S2	876	0.32	0.36	7.51	23.62	0.87
N	787	0.3	0.37	7.10	22.33	0.99
N1	782	0.31	0.39	6.93	21.79	1.04
N2	800	0.33	0.38	7.01	22.04	1.01
N-u750	790	0.31	0.37	7.10	22.33	0.99
N-u950	790	0.31	0.37	6.90	21.79	1.05
W1-u450	1145	0.47	0.90	5.44	17.11	1.88
W1-u950	1024	0.37	0.71	6.24	19.62	1.34
C	632	0.24	0.29	7.26	22.83	0.94
R	798	0.26	0.37	7.33	23.05	0.92

The standard free energy of adsorption, ΔG° , can be calculated from specific retention volume

$$\Delta G^\circ = -RT \ln \frac{V_s P}{\Pi_o} \quad (5)$$

where ΔG° is the change of a standard free energy of adsorption of one mole of solute from a standard gas phase state defined by the pressure P of the solute to a standard state defined by the spreading pressure Π_o of the adsorbed film (two-dimensional fluid). For the adsorbate behaving as an ideal gas in the mobile phase, standard state is defined by a partial pressure of 1 atm (1.013×10^5 Pa). For the calculation of Π_o the approach of Kembal–Rideal¹⁴ or DeBoer¹⁵ can be used. In the latter, which we follow in this study, $\Pi_o = 3.38 \times 10^{-4}$ N/m. Substituting values P and Π_o into eq 5

$$\Delta G^\circ = -RT \ln(2.99 \cdot 10^8 V_s) \quad (6)$$

Once ΔH° and ΔG° are known, the standard entropy of adsorption, ΔS° , is derived from the Gibbs expression

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (7)$$

The differential change in the heat capacity of adsorbate is calculated from the heat of adsorption

$$\Delta C_{v,s} = - \frac{\partial Q_{st}}{\partial T} \quad (8)$$

$\Delta C_{v,s}$ is related only to the changes in the heat capacity of adsorbate if there is not apparent dependence of the heat on the temperature of measurement.

Results and Discussion

The nitrogen adsorption isotherms along with pore size distributions for the carbons studied were presented elsewhere.^{8,9} Here, in Table 1 we report the surface areas, S_{N_2} , and pore volumes (micropores, V_{mic} , and total, V_t) calculated using the density functional theory.^{10,11} The results show that carbons differ in their pore structure. The differences in the pore sizes are also revealed in the values of the characteristic adsorption energies of nitrogen, E_{N_2} , and standard vapor (benzene), E_o , calculated from the Dubinin–Radushkevich (DR) equation.¹² The adsorption energy is the smallest for Westvaco carbons and the largest for the S series, indicating the presence of larger pores in the former materials. In Table 1 we also report an

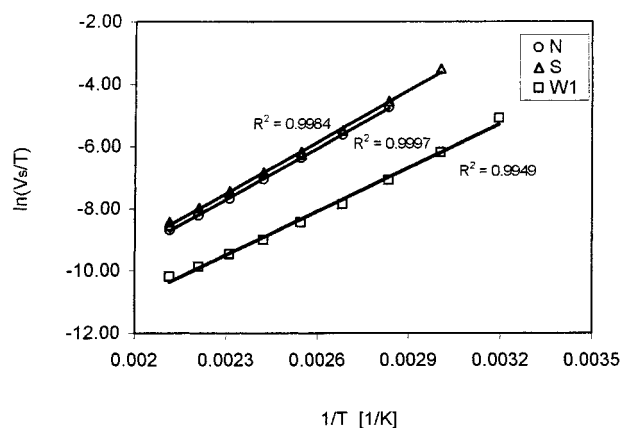


Figure 1. Linear relationship of $\ln(V_s/T)$ vs $1/T$ for N, S, and W1 carbons.

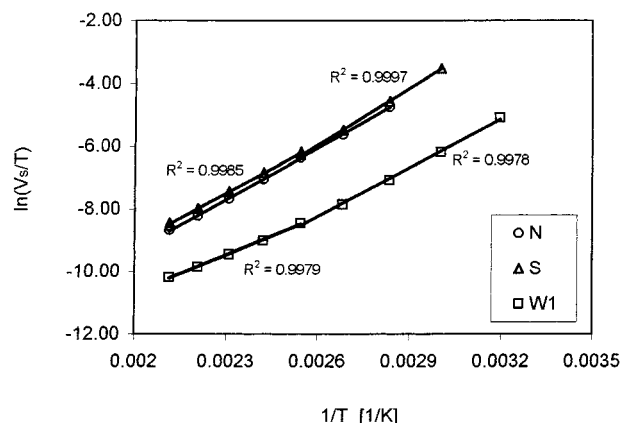


Figure 2. Changes in the slope of $\ln(V_s/T)$ vs $1/T$ for N, S, and W1 carbons.

average micropore width (for slit-shape pores) calculated using the approach proposed by Stoeckli et al.¹³ As expected, on the basis of the results of density functional theory and the values of characteristic energy of adsorption, the smallest pores are present in the S series of carbons. Modification of carbons with urea slightly decreases pore sizes in the case of wood-based carbon. The detailed description of these materials was presented elsewhere.⁹

The isosteric heats of adsorption were calculated using eq 4. The examples of the dependence of $\ln(V_s/T)$ on $1/T$ are presented in Figure 1. Although the correlation coefficient in the case of noncatalytic carbons is equal to or better than 0.99 for a whole temperature range, a close look at the slope indicates the presence of the two perfectly linear regions (Figure 2). A similar phenomenon was noticed by Martin-Hopkins et al.¹⁶ and Gilpin et al.¹⁷ for adsorption of hydrocarbons on chemically modified porous carbons, and by Domingo-Garcia et al. for adsorption of formaldehyde and other organic species.¹⁸ The explanation in the former case was based on the existence of two types of interactions: those with native carbon surface and those with chemically immobilized aryl-siloxane ligands.^{16,17} The authors suggested three ranges for the dependence of V_s on the temperature. According to them, at high temperature only minimum adsorption energy can be calculated. In the intermediate temperature range the energy calculated represents the sum of the minimum energy of adsorption and energy resulting from carbon heterogeneity. In the low-temperature range the deviations from linearity are considered as the most significant. Domingo-Garcia and co-workers¹⁸ discussed various options of non linearity of the plot used to calculate the heat of adsorption.

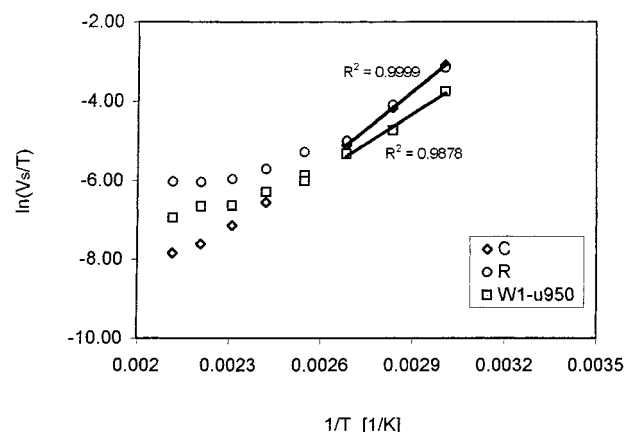
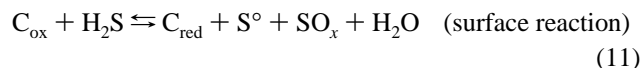
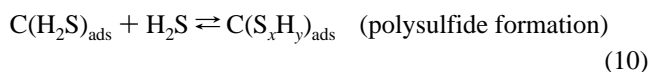
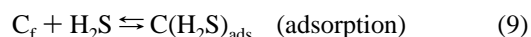


Figure 3. $\ln(V_s/T)$ vs $1/T$ for catalytic C, R, and Wu-950 carbons.

They investigated the catalytic effect of the carbon surface, changes in the adsorbed state of the molecules, and textural properties of the materials. After detailed analysis of the thermodynamic data they concluded that two distinctive slopes of the dependence of $\ln V_s$ on $1/T$ were the results of adsorption in smaller pores at lower temperatures and in larger pores at higher temperatures.¹⁸ In the case of our catalytic carbons a good linear correlation is noticed only for temperatures lower than 353 K (Figure 3). Lack of correlation at higher temperatures suggests that the catalytic effect of the carbon surface starts to play a significant role in the adsorption process of hydrogen sulfide.⁹ The measured retention times are much shorter than they would be if the lower temperature range was followed. Although only one symmetrical peak was observed in all cases, the possibility of chemical transformation cannot be excluded because very small amounts of solutes were injected. As reported by Lee and Reucroft, the interactions of hydrogen sulfide with activated carbons are much stronger than the interactions of carbon tetrachloride and acetone with carbon surface.¹⁹ Supportive of the occurrence of the catalytic effect is the fact that the deviation from linearity is more pronounced for catalytic carbons than for noncatalytic carbons, despite their similar pore sizes.

Because small amounts of solutes were injected, it is likely that the whole injected volume was converted into new species which have weaker interaction with the carbon surface (decrease in the retention time). Our previous study suggests that the following reactions take place on the carbon surface when hydrogen sulfide is adsorbed.



Here, C_f is a free active site on the carbon surface, C_{ox} is a surface oxygen group, and C_{red} represents the product of the reduction of that group.

The products of the reactions 9 to 11 are not expected to interact more weakly than hydrogen sulfide with the activated carbon surface. This suggests that another surface process, not considered previously, occurs. Taking into account shorter retention times measured at higher temperatures, it is likely that molecular dissociation of hydrogen sulfide takes place resulting in the presence of HS^\bullet radicals.²⁰ Those species may interact more weakly than H_2S with activated carbon.



To further investigate the discrepancy from linearity, the heats of adsorption were calculated from eq 4 using the slope between each two points. Figure 4 shows the dependence of the isosteric heats calculated in this way on the temperature of measurement. We have chosen only S, N, and W1 carbons as the representatives of each noncatalytic series. The analysis of the trend indicates a decrease in the heat with an increasing temperature of measurement, which is consistent with the findings of Domingo-Garcia and co-workers¹⁸ and Gilpin et al.¹⁷ This decrease is about 15 kJ/mol for the S and N series and 20 kJ/mol for the Westvaco series where larger pores are present. On the slope, three well-defined ranges are noticed. The first rapid decrease is at $T < 300$ K. It is followed by a relatively constant heat to 425 K and then another rapid decrease is noticed. A decrease in the heat of adsorption with temperature is expected due to the changes in the heat capacity, $C_{V,S}$, of the adsorbed phase.^{2,3} Kiselev and co-workers² reported about 10–15% decrease with 100 degree increase in temperature in the heat measured in IGC experiments for various adsorbates on carbon blacks. It is noteworthy that in our case the differential change in the heat capacity calculated using eq 8 shows unusually high values (Figure 5). For the range of temperatures used in the experiments, the average heat capacities of hydrogen sulfide in the gas and liquid phase are expected to be in the range of 27.3 J/(mol K) and 37.9 J/(mol K), respectively.²¹

To evaluate a possible decrease in the heat of adsorption with increasing temperature as the effect of surface energy heterogeneity, an approach proposed by Jagiello et al. was used.⁷ Assuming that energies in pores are distributed in the range from 20 to 40 kJ/mol (H_2S heat of adsorption on carbon black was reported to be 20.9 kJ/mol²²), a decrease in the heat for our measurement temperatures owing to surface energy heterogeneity is expected to be about 1 kJ/mol. If it happens that the real energy range is much broader due to the existence of specific interactions, a decrease in the heat with increasing temperature of measurement should be more pronounced. On the basis of this finding and the above discussion, it is likely that the strong temperature dependence observed even for non catalytic carbons is a result of the contribution of specific interactions/catalytic effect on the adsorption process with an increasing temperature. When Q_{st} is calculated from the slope of the dependence of retention volume on temperature in a whole temperature range, the average effective value of the heat is obtained. When the heat is calculated from two subsequent measurements, the temperature dependence is revealed.

The values of Q_{st} calculated for the temperature range smaller than 373 K (smaller than 353 K for catalytic carbons) are collected in Table 2. In all cases the heats are close to or slightly higher than the doubled value of the heat obtained on the flat carbon surface (20.9 kJ/mol).²² This indicates that the adsorption occurs in very small pores, which is in fact expected from IGC experiments. The highest heats are obtained for catalytic carbons. Since their pores sizes are equal to or larger than those for the S and N series, the effect of enhancement in the isosteric heat is likely caused by the adsorption of hydrogen sulfide molecules on the basic nitrogen centers located in small pores.⁹ The heats of adsorption obtained for the N and S series of noncatalytic carbons are higher than for the W series. This happens due to the enhancement in the adsorption potential due to the existence of small pores in the former materials (Table 1).

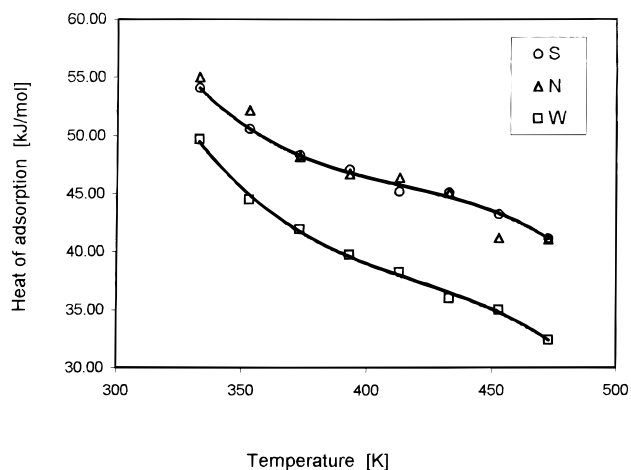


Figure 4. Dependence of isosteric heat of H_2S adsorption on the temperature of measurement for N, S, and W1 carbons.

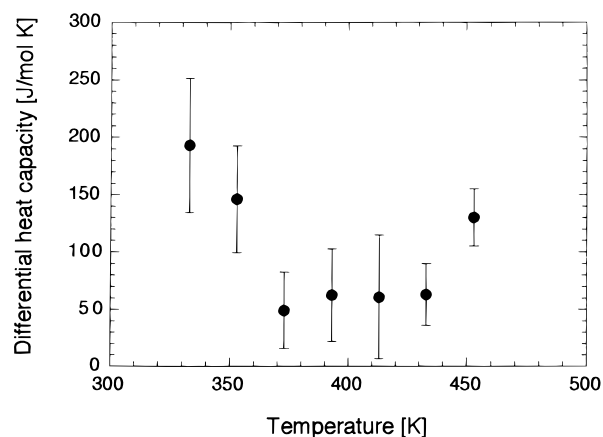


Figure 5. Changes in the heat capacity for N, S, and W1 carbons.

TABLE 2: Thermodynamic Quantities and Henry's Constants Calculated Using the Free Energy of Adsorption

sample	Q_{st} [kJ/mol]	$-\Delta S$ [J/(mol K)]	$-\Delta G$ (293 K) [kJ/mol]	K_H (293 K) [mol/(m ² Pa)]
W1	39.0	43.1	26.37	$0.69 \cdot 10^{-7}$
W2	40.4	39.9	28.71	$1.81 \cdot 10^{-7}$
W3	40.5	46.4	26.90	$0.86 \cdot 10^{-7}$
W4	42.6	35.6	32.17	$7.51 \cdot 10^{-7}$
S	46.7	52.5	31.32	$5.30 \cdot 10^{-7}$
S1	46.5	45.2	33.26	$1.17 \cdot 10^{-6}$
S2	46.6	48.1	32.51	$8.63 \cdot 10^{-7}$
N	45.6	45.7	32.21	$7.64 \cdot 10^{-7}$
N1	47.4	43.4	34.68	$2.11 \cdot 10^{-6}$
N2	46.2	47.1	32.40	$8.26 \cdot 10^{-7}$
N-u750	49.3	46.4	35.70	$3.21 \cdot 10^{-6}$
N-u950	45.2	35.2	34.89	$2.29 \cdot 10^{-6}$
W1-u450	47.2	59.6	29.74	$2.77 \cdot 10^{-7}$
W1-u950	50.0	52.9	34.50	$1.96 \cdot 10^{-6}$
C	54.5	68.1	34.55	$1.99 \cdot 10^{-6}$
R	47.6	43.6	34.83	$2.23 \cdot 10^{-6}$

Drago and co-workers²³ studying adsorption equilibria of various molecules at supercritical temperatures found the dependence of the heat of adsorption on the square root of van der Waals a constant for an adsorptive. In their approach it is assumed that adsorption isotherm consists of several equilibrium processes corresponding to adsorption into a distinct pore size regime. In each regime (usually three were found for various sorbents^{23–26}) a Langmuir isotherm is fitted and an equilibrium constant K is calculated. Using the relationship between the heat of adsorption and $a^{1/2}$ established by Drago et al.,²³ the expected heat of H_2S adsorption on activated carbon in the range of small, medium, and large pores is expected to be about 35, 27, and

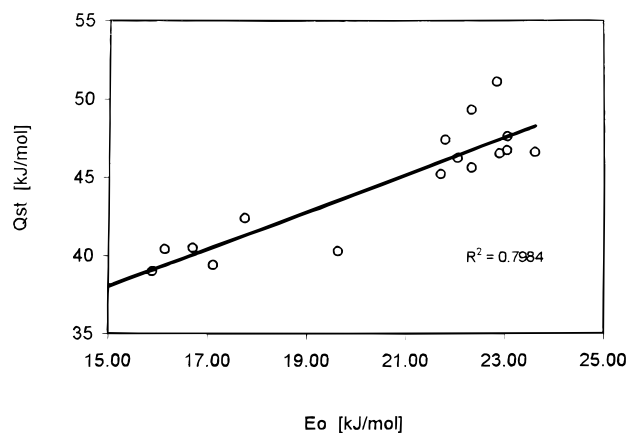


Figure 6. Dependence of isosteric heat of H_2S adsorption on characteristic energy of standard vapor adsorption.

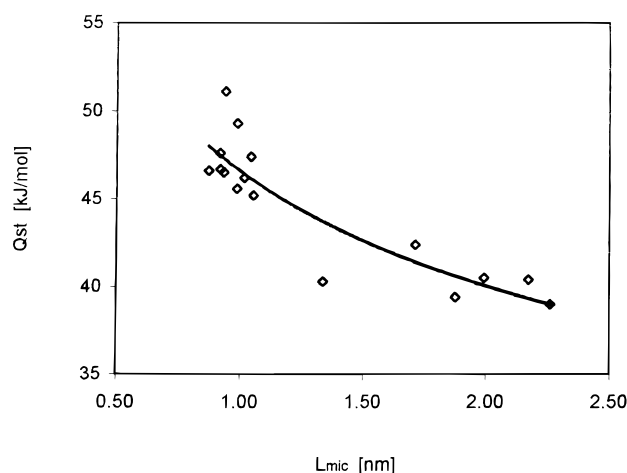


Figure 7. Dependence of isosteric heat of adsorption on the average width of micropores.

21 kJ/mol, respectively. It is worth mentioning that the heat of adsorption for the large pore region is almost the same as that obtained by Doleva and Kiselev on nonporous carbon black.²² This result is expected because adsorption in large pores should be energetically similar to the adsorption on a flat carbon surface.²⁷ The difference between the heat reported in this paper and the heat evaluated using the data obtained by Drago and co-workers (about 15 kJ/mol) is associated with the fundamental difference in the approaches used. However, the heat evaluated based on the value of van der Waals parameters refers to the adsorption in small pores and heterogeneity in their sizes within the region 1 of adsorption (following the notations in ref 23) must exist. The obvious existence of the distribution in the pore sizes indicates that the heat calculated following the approach of Drago and co-workers is the average heat in this region, and one can expect a significant increase in its value for the pores similar in size to the hydrogen sulfide molecule.²⁷ In the IGC methods, when the measurement is done at infinite dilution, only the smallest pores are expected to contribute to the adsorption process, resulting in heat that can be considered as a heat at “zero surface coverage”. This heat must be higher than the heat evaluated using the approach of Drago and co-workers.²³

The dependence of Q_{st} upon the characteristic energy of adsorption is presented in Figure 6. The magnitude of these two parameters depends on the pore sizes of the carbons studied, therefore the linear relationship is expected.⁸ Figure 7 shows the relationship between the isosteric heat of adsorption and

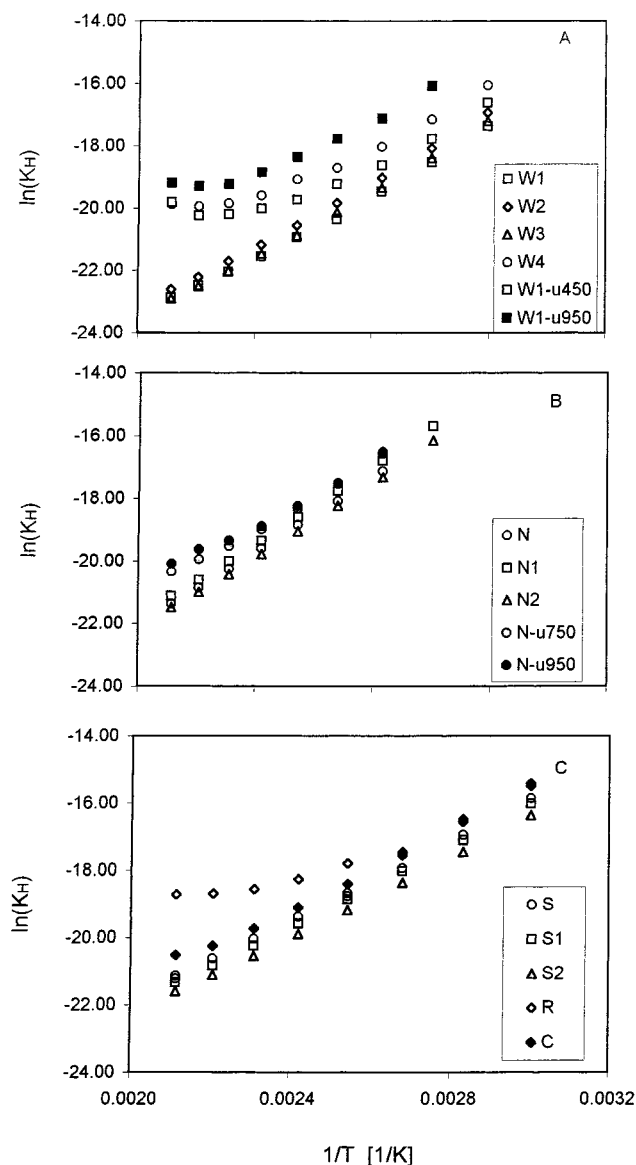


Figure 8. Dependence of $\ln K_{\text{H}}$ on the temperature of measurement.

average micropore sizes, L_{mic} , calculated using the approach of Stoeckli et al.¹³ In this case we expect the isosteric heat to have its maximum for pores equal in their size to the hydrogen sulfide molecule (~ 4.2 Å) and then the heat should decrease as a result on a decrease in the adsorption potential.²⁷ The limiting value of the heat is expected to be around 20–25 kJ/mol, as determined experimentally by Doleva et al. for nonporous carbon blacks.²² Although the pores in our carbons cover only a narrow range of sizes, fitting of the experimental points using the power equation follows the expected trend.

The values of the free energy of adsorption, entropy, and predicted Henry's constants at 293 K calculated using the isosteric heats of adsorption, and entropy are collected in Table 2. The variations in ΔG for the carbons studied follow the differences in the heat of adsorption related to the average pore sizes of the adsorbents. The Henry's constants are bigger for microporous coconut shell and peat-based carbons (S and N series) than for wood-based materials. It is noteworthy that the values of K_{H} are much higher for the catalytic carbons, indicating stronger interactions of hydrogen sulfide with the carbon surface. It is in agreement with the data of Drago and co-workers²³ who found that with decreasing size of the pores occupied by adsorbed molecules the equilibrium constants increased.

TABLE 3: Review of the Published Data on H₂S Adsorption

method	sample	conditions	K_H (calc) [mol/m ² Pa]	$-\Delta H$ [kJ/mol]	E_{H_2S} [kJ/mol]	investigators/ref
IGC	carbon black	$T = 373\text{--}453\text{ K}$		20.6		Doleva et al. ²²
	carbon "Saran"			25.6		
	carbon "S"					
adsorption	$S = 1000\text{ m}^2/\text{g}$	$P_{H_2S} = 1.4\text{--}67\text{ kPa}$ $T = 293\text{--}313\text{ K}$		33.6		Boki and Tanada ²⁹
	AC		4.8×10^{-10}	22.5	11.5	
	$S = 460\text{ m}^2/\text{g}$		5.7×10^{-10} 7.2×10^{-10}	31.4 51.0	11.0 10.8	
adsorption	AC (wood)	$P_{H_2S} = 1.1\text{--}16\text{ kPa}$ $T = 293\text{ K}$				Lee and Reucroft ¹⁹
	$S = 783\text{ m}^2/\text{g}$		9.1×10^{-10}		12.2	
	$S = 1075\text{ m}^2/\text{g}$		3.4×10^{-10}		11.3	
adsorption	$S = 1807\text{ m}^2/\text{g}$	$P_{H_2S} = 1.3\text{--}13\text{ kPa}$ $T = 318\text{ K}$ $T = 328\text{ K}$ $T = 338\text{ K}$ $T = 345\text{ K}$	1.5×10^{-10}		8.9	Iwasawa and Ogasawara ³⁰
	polynaphtho-quinone		6.0×10^{-11}	30.0		
	$S = 73\text{ m}^2/\text{g}$		4.1×10^{-11} 2.9×10^{-11} 2.3×10^{-11}			
kinetic of H ₂ S oxidation	AC	$P_{H_2S} = 0.4\text{--}2\text{ kPa}$ $T = 398\text{ K}$ $T = 448\text{ K}$ $T = 473\text{ K}$	6.2×10^{-9}	16.0		Ghosh and Tolleffson ³¹
	$S = 487\text{ m}^2/\text{g}$		4.9×10^{-9} 2.7×10^{-9}			
kinetic of H ₂ S oxidation	AC	$P_{H_2S} = 2\text{--}8\text{ kPa}$ $T = 398\text{ K}$ $T = 448\text{ K}$ $T = 473\text{ K}$	3.9×10^{-9}	23.8		Dalai and Tolleffson ³²
	$S = 487\text{ m}^2/\text{g}$		2.2×10^{-9} 1.1×10^{-9}			

The calculated theoretical change in the translation entropy of hydrogen sulfide due to the loss of one degree of freedom (at 293 K) is expected to be 42.8 J/mol K.²⁸ The changes in entropy collected in Table 2 are very close to the theoretical value and they suggest that hydrogen sulfide at our temperature range behaves as an ideal two-dimensional gas. The observed slightly larger entropy change for catalytic carbons can be the result of the stronger adsorption on basic nitrogen centers.

Table 3 collects the review of the data published in the literature describing the adsorption of hydrogen sulfide on activated carbons and carbons blacks. We collected there the basic characteristics of carbons studied, conditions of the experiment, heats of adsorption, and the characteristic energy of H₂S adsorption along with K_H evaluated from the published experimental data. The evaluated Henry's constants have a similar order of magnitude to the K_H calculated from the heat and entropy of adsorption (Table 2). It is worth mentioning that we do not expect the perfect agreement since in the majority of the published data the pressure range is far away from the Henry's region and from our experimental conditions. The heats of adsorption and the characteristic energies of adsorption calculated from our experiments (E_{H_2S} is between 7.7 and 12 kJ/mol) also agree with the data summarized in Table 3.^{19,29}

Henry's constants were also calculated from the specific retention volume using eq 3. The obtained values for two temperatures are collected in Table 4. Like the data in Table 3, the values of Henry's constants for catalytic carbons are 1 order of magnitude greater than those for other carbons. Following the trends in the isosteric heats of adsorption the plot of $\ln K_H$ on $1/T$ shows bigger deviations from linearity for Westvaco and catalytic carbons than for the S and N series (Figure 8). With increasing temperature of measurement the value of K_H decrease. A similar trend was described by Drago et al.^{23–26}

Conclusions

The data reported in this paper describe the adsorption of hydrogen sulfide on noncatalytic and catalytic carbons at a very low surface coverage where adsorption is governed by Henry's law. The heat of adsorption and free energy of adsorption show the dependence on the sizes of pores. In the case of catalytic

TABLE 4: Specific Retention Volumes and Henry's Constants Calculated Using Eq 3

sample	$V_S(353\text{ K})$ [mol/m ²]	$K_H(353\text{ K})$ [mol/(m ² Pa)]	$V_S(473\text{ K})$ [mol/m ²]	$K_H(473\text{ K})$ [mol/(m ² Pa)]
W1	1.03×10^{-5}	3.52×10^{-9}	4.67×10^{-7}	1.17×10^{-10}
W2	1.61×10^{-5}	5.49×10^{-9}	6.02×10^{-7}	1.53×10^{-10}
W3	1.17×10^{-5}	4.00×10^{-9}	4.44×10^{-7}	1.13×10^{-10}
W4	4.33×10^{-5}	1.48×10^{-8}	9.21×10^{-7}	2.34×10^{-9}
S	1.28×10^{-4}	4.35×10^{-8}	2.36×10^{-6}	6.69×10^{-10}
S1	1.09×10^{-4}	3.73×10^{-8}	2.11×10^{-6}	5.38×10^{-10}
S2	7.71×10^{-4}	2.63×10^{-8}	1.64×10^{-6}	4.17×10^{-10}
N	1.06×10^{-4}	3.61×10^{-8}	2.07×10^{-6}	5.27×10^{-10}
N1	1.49×10^{-4}	5.07×10^{-8}	2.67×10^{-6}	6.79×10^{-10}
N2	8.75×10^{-4}	2.99×10^{-8}	1.84×10^{-6}	4.69×10^{-10}
N-u750	1.90×10^{-4}	6.49×10^{-8}	1.28×10^{-5}	3.27×10^{-9}
N-u950	1.93×10^{-4}	6.58×10^{-8}	7.70×10^{-6}	1.96×10^{-9}
W1-u450	2.40×10^{-5}	8.18×10^{-8}	1.57×10^{-4}	6.04×10^{-8}
W1-u950	1.06×10^{-4}	3.63×10^{-8}	1.85×10^{-5}	4.64×10^{-9}
C	1.89×10^{-4}	6.45×10^{-8}	4.82×10^{-6}	1.23×10^{-9}
R	2.03×10^{-4}	6.97×10^{-8}	2.99×10^{-5}	7.47×10^{-9}

carbons, the high heat and free energy of adsorption indicate the strong interactions of hydrogen sulfide molecule with nitrogen-containing adsorption centers. The detailed analysis of the isosteric heats reveals their dependence on the temperature of measurement. Even for noncatalytic carbons, with an increasing temperature, the heats gradually decrease. This may be the result of the presence of specific interactions along with the catalytic effect of the carbon surface. The observed two slopes on the dependence of V_S on $1/T$ are also likely the results of the above-mentioned processes other than nonspecific physical adsorption. The calculated Henry's constants are greater for the catalytic carbons than for the noncatalytic adsorbents owing to the enhanced interactions of H₂S with basic adsorption centers.

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