Adsorption of Organic Probes on Carbon Materials at Zero Surface Coverage

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The adsorption of several organic molecules on four carbon materials is studied by inverse gas solid chromatography at zero surface coverage. The specific retention volumes and the differential heats of adsorption (or standard enthalpies of adsorption) are used to study the influence of the porous structure and the chemical surface groups in the process. From the comparison of the differential heats of adsorption of hydrocarbons and of polar molecules one can deduce that the standard enthalpy of adsorption at zero surface coverage is not a proper criterion to distinguish between specific and nonspecific interactions when porous adsorbents are used. Values of the standard free energy of adsorption are used to determine the specific component of the adsorbate−adsorbent interaction.

1. Introduction

The adsorption of organic molecules from low to high relative pressures is an experimental tool to determine the textural characteristics of porous carbon materials. Moreover this is a process of interest because it is one way in which atmospheric pollutants can be eliminated and also because this process can be used to concentrate products of industrial interest.[1,2] Nevertheless, in the last two cases adsorption is carried out at very low gas phase concentration. The yield and selectivity of the process is determined by the nature of the adsorbate and the adsorbent. Therefore, the kind of interaction between the molecules of the gas phase and the surface of the adsorbent it is very important. The molecules can interact by London dispersion forces (nonspecific interaction), or they can be adsorbed through dipole−dipole interactions, hydrogen bonding, etc. (specific interactions). It is, therefore, of prime interest to determine the type of interaction in the adsorption processes.

From a practical point of view one should take into account that in these cases the concentration of the organic molecules in the gas phase is very low and frequently the temperature is above room temperature. In addition the molecules to be adsorbed are in flue gases, so adsorption should be carried out under dynamic conditions. To sum up, the conditions which should be used for adsorption of these organic molecules in order for the situation to be close to real are: (i) temperature above room temperature, (ii) very low gas phase concentration, and (iii) dynamic conditions. These experimental requirements are easily achieved by inverse gas solid chromatography[3−7] (IGSC).

The aim of this paper is to study the adsorption of organic molecules by several carbon materials at very low vapor concentration under dynamic conditions and at relatively high temperatures. For this purpose several chloromethane derivatives, some organic molecules with oxygen groups, and some hydrocarbons (lineal, cyclic, and branched) have been used. Four carbon materials obtained by carbonization of an organic copolymer were used as adsorbents.[8]

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2. Experimental Section

The four carbon materials used were obtained by copolymerization of furfuryl alcohol and further carbonization in N_2 flow at a very low heating rate up to 773 K. More details of the sample preparation are given elsewhere.[9]

The textural characteristics of the samples were studied by N_2 and CO_2 adsorption at 77 and 273 K, respectively. The surface areas were obtained from the BET and Dubinin−Radushkevich methods applied to these isotherms. The values of macro- (V_3) and mesopore (V_2) volumes up to ≥3.6 nm in width were obtained by mercury porosimetry. The volume of pores ≤3.6 nm in width (V_1) was determined from mercury porosimetry and He density measurements.[9]

The presence of surface oxygen complexes on the samples was shown by chemical analysis and Fourier transform infrared spectroscopy (FTIR). The carbon, nitrogen, and hydrogen contents were obtained by chemical analysis, and the oxygen content was obtained by calculating the difference. The nature of the surface complexes was studied by transmission FTIR. The spectra were recorded between 4000 and 500 cm^{-1} using a Nicolet 20 SXB spectrophotometer. The samples were pelletized with KBr.

The adsorption measurements of the organic molecules were carried out using a Carlo Erba gas chromatograph Model Fractovap 2350, equipped with a flame ionization detector. The glass column (3 mm in internal diameter) was packed with a weight of carbon ranging between 0.3 and 0.7 g. Before the adsorption measurements, the column was conditioned for 24 h at 553 K in a nitrogen flow. The adsorption experiments were carried out using nitrogen as carrier gas and at several temperatures in the range between 433 and 533 K. The following organic probes were used as adsorbates: carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloroethane (CH_2Cl_2), acetone (C_3H_6O), diethyl ether ($C_4H_{10}O$), tetrahydrofurane (C_4H_8O, THF), *n*-alkanes (C_nH_{2n+2}, from C_4 to C_7), benzene (C_6H_6), cyclohexane (C_6H_{12}), and 2,2-dimethylbutane (C_6H_{14}, 2,2-DMB). The amounts of vapors injected were in the range 0.1−3.0 μL. At least three different amounts of each probe were injected at each temperature.

Under the experimental conditions described above, the chromatographic peaks were mainly symmetrical; hence the retention times were taken at the peak maxima. For nonsymmetrical peaks the retention times were calculated from the first-

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TABLE 1: Textural Characteristics of the Samples

	S_{N2} (m^2/g)	S_{CO2} (m^2/g)	V_3[a] (cm^3/g)	V_2[b] (cm^3/g)	V_1[c] (cm^3/g)
P1	475	408	0.214	0.033	0.119
P2	24	257	0.000	0.041	0.093
P3	398	344	0.024	0.235	0.163
P4	458	468	0.241	0.000	0.105

[a] V_3 = volume of macropores. [b] V_2= volume of mesopores ≥ 3.6 nm in width. [c] V_1 = Volume of pores ≤ 3.6 nm in width.

order moment method.[10] In all cases and for each probe the retention time at each temperature was independent of the amount injected. This means that the adsorption process is produced in the region of Henry's law,[11] i.e. at the so-called zero surface coverage where adsorption is only determined by the adsorbate−adsorbent interactions. Under these conditions the equilibrium constant is the specific retention volume V_s.[12] This can be calculated using the experimental retention volume, V_R:

$$V_s = V_R/SW \tag{1}$$

where S is the surface area obtained by CO_2 adsorption, W is the weight of the adsorbent inside the column, and V_R is the retention volume obtained from

$$V_R = F_{corr}(t_R - t_0) \tag{2}$$

where F_{corr} is the flow of the carrier gas, corrected for the temperature of the experiment and the pressure drop, t_R is the retention time and t_0 is the gas holdup time.

When adsorption takes place in the Henry's law region and when the adsorbate concentration in both the vapor and the adsorbent phases is very low, the adsorbate can be assumed to behave as an ideal gas. Under these conditions the differential heat of adsorption can be identified as the standard enthalpy of adsorption $\Delta H_A°$.[13] This can be determined from the equation that relates V_s and T, which is derived from the Gibbs−Helmholtz relationship and assuming that $\Delta H_A°$ is independent of T:

$$\ln V_s = -\Delta H_A°/RT + C \tag{3}$$

The slope of the plot of ln V_s vs $1/T$ permits determination of $\Delta H_A°$ for each adsorbate.

The change of the standard free energy of adsorption $\Delta G_A°$ can be calculated from the equation

$$\Delta G_A° = -RT \ln(2.99 \times 10^8 V_S) \tag{4}$$

where V_s is expressed in meters. Eq 4 refers to the change of the standard free energy of 1 mol of adsorbate from a vapor phase at a standard pressure $P_{s,g}$ to a standard adsorbed state. To derive eq 4 several assumptions, which are reported elsewhere,[14] have to be made. Following the De Boer's approach $P_{s,g}$ is 1 atm (101 kN m^{-2}) and π, the pressure of the adsorbed state, is 0.338 mN m^{-1}.

3. Results and Discussion

Data of the textural characteristics of the samples have already been reported.[9] In spite of this, the most important data are also recorded in Table 1 in order to clarify the discussion. The samples show important differences in their macro- and mesopore structures. Moreover sample P2 has constrictions in the micropore network shown by the large difference between the surface area measured by CO_2 and N_2 ($S_{CO2} \gg S_{N2}$).[15]

The oxygen content obtained from the chemical analysis ranges from 5.8% in P2 to 11.5% in P3. The chemical analysis rendered almost a negligible nitrogen content in P3 (0.03%) and no sulfur in any of the samples. The chemical surface groups as revealed by FTIR are similar for the four samples. The spectra of P3 and P4 are shown in Figure 1, as an example. Assignment of the bands was based on previous assignments in the literature.[16−18] The chemical groups mainly consist of carboxyl carbonate structures (bands at 1620, 1440, and 1385 cm^{-1}), phenolic (bands at 3430, 1160, and 1000−1220 cm^{-1}), carbonyl (1728 cm^{-1}), and ether (bands at 1250 and 1160 cm^{-1}) (cyclic or bridged) groups.[16] These chemical groups could be responsible for the specific interactions with molecules that are capable of this kind of interactions.

Concerning the chromatographic measurements, the specific retention volumes at 473 K are collected as an example in Table 2. Sample P1 can be observed to have a molecular sieve effect for the mean molecular size between benzene (0.52 nm) and cyclohexane (0.56 nm). This behavior has also been reported[19] for the adsorption at 303 K and at high relative pressures of these molecules (up to $P/P_o = 1$). Therefore sample P1 has such a narrow distribution of micropores that it behaves similarly for adsorption in a wide range of experimental conditions, i.e. from very low relative pressure (at zero surface coverage) up to P/P_o =1, and from 303 K up to 533 K. The polar molecules have V_s values higher than cyclohexane, although in many cases their molecular sizes are larger or similar to that of cyclohexane. It is, therefore, likely that these molecules are adsorbed in part by chemical surface groups, i.e. by specific interactions. Similar behavior has been reported[19] for the adsorption of $CHCl_3$ at high relative pressures, which has also been explained as a consequence of specific interactions.

The trend of the V_s values for P4 is very similar as that observed for P1. Moreover, the same molecular sieve effect is observed in P4 for a mean molecular size between 0.52 and 0.56 nm. These data are in agreement with data previously reported.[19] P3 also has a molecular sieve effect but for a mean molecular size larger than that of P1 and P4. In this case this behavior is observed for the cyclohexane/2,2-DMB couple, i.e. between 0.56 and 0.60 nm. This is due to the fact that this sample has a wider micropore network than P1 and P4.[19] Therefore as with P1 and P4, sample P3 has a molecular sieve behavior, but for larger molecules, over a very wide range of experimental conditions: from very low to high relative pressures ($P/P_o = 1$) and between 303 and 533 K. For this sample a plot of V_s vs the mean molecular size (Figure 2) shows, with the exception of acetone and diethyl ether, a monotonic decrease of V_s as the molecular dimension increases. It is, thus, difficult to determine whether adsorption of the non hydrocarbon molecules is produced as a consequence of specific interactions (as in P1 and P4) or of the wider micropore system of this sample which allows adsorption to occur inside the micropores. It could even result from a combined mechanism in the micropores and on the chemical surface groups.

Finally for sample P2 the values of V_s are much lower than for the other samples. This can be related to several textural factors: (i) the pore constrictions in the microporosity, shown by the large difference between S_{N2} and S_{CO2}, which does not permit the adsorption of these organic molecules; (ii) The lack of macroporosity (V_3) and the almost negligible mesoporosity (V_2). Macro- and mesoporosity are known to be important factors in adsorption, as they allow the molecules to reach the micropores.

As a consequence of these factors, the molecular sieve character shown by samples P1, P3, and P4 is less apparent in

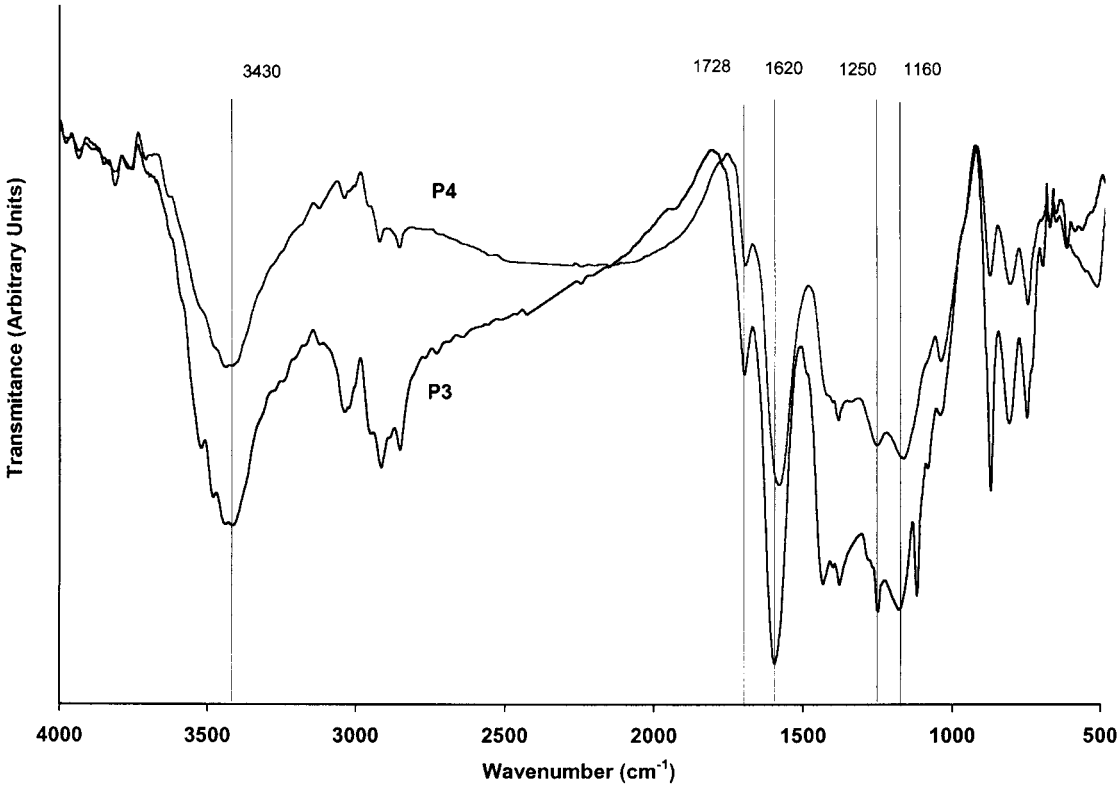

Figure 1. FTIR spectra.

TABLE 2: Specific Retention Volumes at 473 K

	V_s (cm^3/m^2)				
	P1	P2	P3	P4	mean molecular size (nm)
CCl_4	0.06 ± 0.01	0.052 ± 0.003	0.46 ± 0.02		0.64[b]
$CHCl_3$	0.77 ± 0.03	0.074 ± 0.004	1.39 ± 0.08	0.44 ± 0.02	0.59[a]
CH_2Cl_2	0.66 ± 0.03	0.112 ± 0.008	1.13 ± 0.07	0.51 ± 0.03	0.57[b]
CH_3COCH_3	1.39 ± 0.07	0.113 ± 0.005	1.03 ± 0.05	1.05 ± 0.06	0.33[b]
$CH_3CH_2OCH_2CH_3$	2.12 ± 0.09	0.094 ± 0.005	1.13 ± 0.06	1.26 ± 0.05	0.41[b]
THF	0.92 ± 0.05	0.100 ± 0.005	2.32 ± 0.09	0.52 ± 0.02	0.56[b]
C_6H_6	4.83 ± 0.09	0.131 ± 0.003	3.31 ± 0.09	3.21 ± 0.09	0.52[a]
C_6H_{12}	0.07 ± 0.01	0.054 ± 0.006	2.65 ± 0.09	0.05 ± 0.01	0.56[a]
2,2-DMB	0.05 ± 0.01	0.052 ± 0.006	0.20 ± 0.01	0.04 ± 0.01	0.60[a]

[a] From ref 19. [b] Obtained by computer modelization.

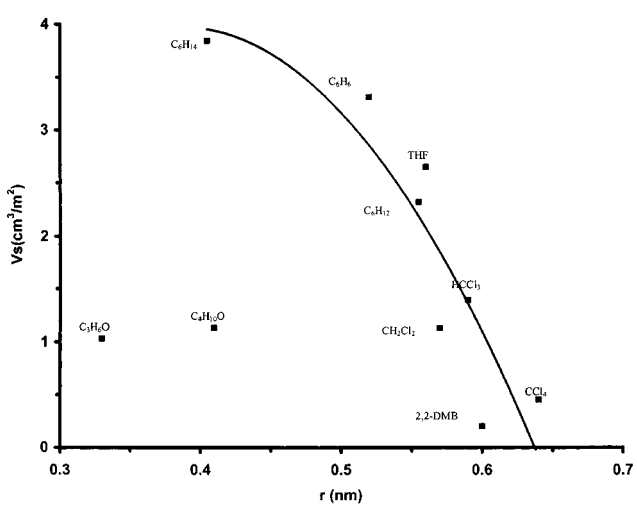

Figure 2. Variation of V_s vs the mean molecular dimension in P3.

P2, although benzene is clearly more adsorbed than cyclohexane and 2,2-DMB. It is worth noting that the behavior shown at very low vapor concentration has also been reported[19] at high relative pressures for these hydrocarbons and $CHCl_3$.

It is interesting to note that if the adsorbates $CHCl_3$, CH_2Cl_2, acetone, and diethyl ether were adsorbed nonspecifically on the four samples, their V_s should be similar to the specific retention volume of a molecule not capable of specific interactions and with the same number of carbon atoms. Therefore the V_s values of $CHCl_3$ and CH_2Cl_2 should be similar to that of CCl_4. Moreover the V_s values of acetone and diethyl ether should be similar to that of propane and pentane, respectively. The values of V_s for CCl_4 are in all cases (Table 2) lower than those of $CHCl_3$ and CH_2Cl_2. Moreover the values of V_s for propane (around 0.04 cm^3/m^2), obtained by extrapolation using the V_s data of the linear hydrocarbons, are in all cases much lower. Also, the pentane values are lower than those of diethyl ether. This supports the posibility of a combined mechanism for the adsorption of these molecules. Moreover, and also as a general rule, the molecular sieve effects found for the benzene/cyclohexane and cyclohexane/2,2-DMB couples suggest the presence of slit-shaped pores in the micropore structures of these samples.

The standard enthalpies or differential heats of adsorption were obtained using eq 3. For this purpose the slopes of the plots ln V_s vs $1/T$ were obtained. Figure 3 shows these plots for P1, as an example, and the values of $\Delta H_A°$ for all the

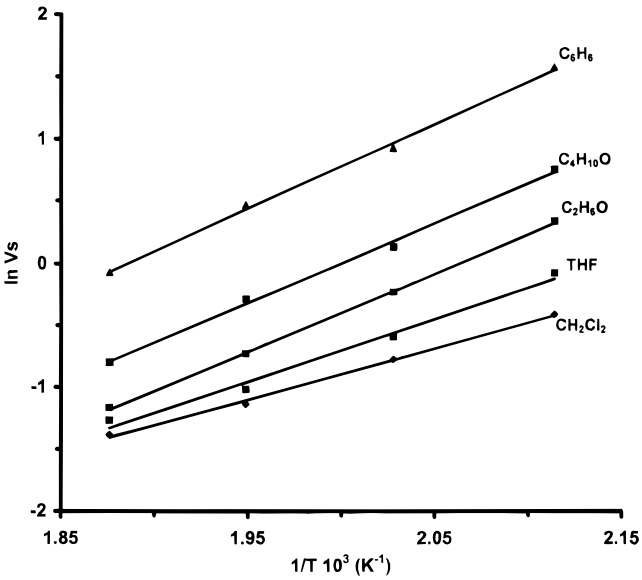

Figure 3. ln V_s vs $1/T$ for the polar molecules.

adsorbates are recorded in Table 3. At first sight the values of $\Delta H_A°$ seem to support the ideas proposed on the basis of the V_s values. Hence, the molecular sieve effect for the benzene/cyclohexane couple in P1 and P4 is shown by the dramatic decrease in $\Delta H_A°$ for cyclohexane. In P2 an important decrease in $\Delta H_A°$ is also apparent, although the V_s values (Table 2) are very small and so the adsorption is almost negligible. The molecular sieve behavior mentioned previously for the cyclohexane/2,2-DMB couple in P3 is also shown by the large difference in $\Delta H_A°$ between the two adsorbates. However the value of $\Delta H_A°$ for 2,2-DMB on P3 is clearly higher than in P1 and P4, and also the value of $\Delta H_A°$ for CCl_4 increases in comparison with the value for P1. These data support a wider microporosity for P3 than for P1 and P4, as suggested previously.

When the $\Delta H_A°$ values of the hydrocarbons are compared with their ΔH_L (liquefaction heat), it is noteworthy that for those molecules which, according to the data in Table 2, can reach the microporosity (*n*-hexane and benzene on P1 and P4 and *n*-hexane, benzene, and cyclohexane on P3), the standard enthalpy of adsorption is much higher than the liquefaction heat. Furthermore, in many cases $\Delta H_A°$ is more than 2-fold the value of ΔH_L. If it is considered that neither *n*-hexane nor cyclohexane is capable of specific interactions, these high values of $\Delta H_A°$ could be produced as a consequence of a very good fit of the molecules inside the pores,[20,21] such that the closer the size of the molecule and the pore dimension, the higher the $\Delta H_A°$. In the case of benzene it is generally accepted that high values of $\Delta H_A°$ are produced either because the adsorption occurs in slit-shaped pores with dimensions similar to the molecular size or possibly specific interactions could be taking place due to the existence of π electrons in this molecule.[11,13,14,22,23] In the case of P2 the value of $\Delta H_A°$ for benzene is close to ΔH_L, which means that the specific contribution is probably very small.

As regards the polar molecules and the P1, P3, and P4 samples, the $\Delta H_A°$ values are higher than the liquefaction heats in all cases. This means that for P1 and P4, in which the adsorption of these molecules (V_s) is not related to their molecular sizes, this is mainly controlled by specific interactions. In P3, although the interaction could probably also be specific, an apparent relationship between V_s and the molecular size has also been shown (Figure 2). Therefore, the high $\Delta H_A°$ values should be considered as having been produced as a consequence of the good fit of the molecule in the pores similar to the behavior observed for hydrocarbons. This aspect is addressed later.

What is noteworthy from the comparison of $\Delta H_A°$ values of the hydrocarbons and of the other molecules is that some of the former can be adsorbed more exothermically than polar molecules which are capable of specific interactions. To understand these data, one should bear in mind that the classification of these two types of interactions was based[24] on materials that can be considered as basically nonporous. Consequently, the $\Delta H_A°$ values for the nonspecific interactions were clearly lower than the specific ones because the former were produced on flat surfaces. However, the situation is different in the case of porous materials because adsorption can be produced on the external surface, on the chemical groups, or inside the micropores of similar size to the adsorbate. The most plausible of the three possibilities is the latter since this is thermodynamically favored. It is worth noting that the number of molecules to be adsorbed is very low (zero surface coverage); hence the probability of finding pores of similar size to the molecule is very high. However, for polar molecules the interaction produced by the dipolar moment cannot be excluded, and consequently a combined mechanism of specific + nonspecific adsorption should be considered. The data reported in Table 3 clearly indicate that it is unsafe to deduce the type of adsorbate−adsorbent interaction on the basis of the $\Delta H_A°$ values in porous materials. In other words, although there can be different reasons for the interaction, the nonspecific interactions (see for instance $\Delta H_A°$ for C_6H_{14}) are not necessarily less energetic than the specific ones, at least when adsorption is produced inside the micropores and at very low coverage.

In the case of a combined adsorption mechanism, one should determine the specific component of the surface free energy of adsorption, although this is not an easy task. Among the different approaches proposed[4,25−29] we have used the procedure described by Donnet et al.[26] This method compares the standard free energy of adsorption of the probe with that of the *n*-alkanes. For this purpose the following equation is used:

$$\Delta G_A° = K(h\nu_S)^{1/2}\alpha_S(h\nu_L)^{1/2}\alpha_L \qquad (5)$$

where K is a constant, h is Planck's constant, ν_S and ν_L are the characteristic vibration energies of the solid and the molecule, and α_S and α_L are the deformation polarizabilities. The plot of $\Delta G_A°$ vs $(h\nu_L)^{1/2}\alpha_L$ for normal hydrocarbons gives a straight line, which is used as the reference line. The points corresponding to molecules that are capable of specific interactions are located above this line. The difference between the ordinate value for each probe molecule and the corresponding value of the *n*-alkane at the same $(h\nu_L)^{1/2}\ \alpha_L$ value renders the specific component of the standard free energy of adsorption for each particular probe.

A typical plot of this method is shown in Figure 4 for P1. Plots similar to this are obtained for the other samples. Neither CCl_4 nor benzene produces specific interactions. This is understandable for CCl_4, which has no dipolar moment and can be considered as a spherical molecule. Nevertheless, this behavior is more unexpected for benzene, for which specific interactions are normally expected[11,13,14,22,23] because of the unlocalized π electrons. Since this behavior of benzene is repeated for all the samples, the adsorption of benzene is non specific in all cases and the high values of $\Delta H_A°$ (Table 3) can be explained by the fact that adsorption is produced in slit-shaped pores of a similar size as the molecule. This finding again supports the previous suggestion that $\Delta H_A°$ is not a very

TABLE 3: Standard Enthalpy of Adsorption

	$\Delta H_A°$ (kJ/mol)				
	P1	P2	P3	P4	ΔH_L (kJ/mol)
CCl_4	2.9 ± 0.5	3.6 ± 0.5	36.9 ± 0.9		31.9
$CHCl_3$	38.9 ± 0.9	17.4 ± 0.9	47.4 ± 0.8	43.1 ± 0.9	31.4
CH_2Cl_2	34.3 ± 0.9	25.4 ± 0.8	40.5 ± 0.5	44.9 ± 0.8	31.7
CH_3COCH_3	49.1 ± 0.9	33.5 ± 0.7	50.6 ± 0.8	53.5 ± 0.8	32.0
$CH_3CH_2OCH_2CH_3$	49.9 ± 0.9	42.3 ± 0.9	51.1 ± 0.9	52.6 ± 0.8	29.1
THF	44.3 ± 0.9	23.4 ± 0.9	59.5 ± 0.8	49.1 ± 0.9	29.8
C_6H_{14}	65.2 ± 0.8	42.1 ± 0.8	65.7 ± 0.7	76.9 ± 0.9	31.7
C_6H_6	53.5 ± 0.5	36.3 ± 0.9	58.8 ± 0.8	64.1 ± 0.9	34.1
C_6H_{12}	6.0 ± 0.9	8.9 ± 0.9	53.9 ± 0.7	16.1 ± 0.7	32.8
2,2-DMB	3.7 ± 0.4	3.2 ± 0.2	20.6 ± 0.5	4.2 ± 0.5	30.4

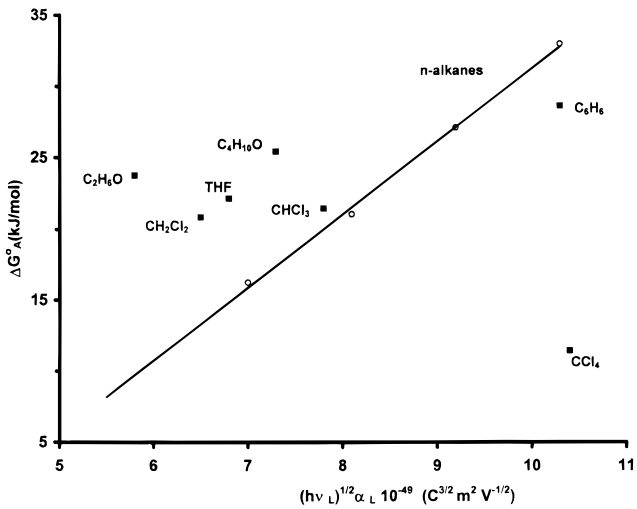

Figure 4. Variation of $\Delta G_A°$ vs $(h\nu_L)^{1/2}\ \alpha_L$.

TABLE 4: Specific Component of the Standard Free Energy

	ΔG_{sp} (kJ/mol)			
	P1	P2	P3	P4
$CHCl_3$	1.4	1.3	2.3	2.5
CH_2Cl_2	6.2	5.4	6.3	6.8
CH_3COCH_3	14.0	8.0	10.3	13.2
$CH_3CH_2OCH_2CH_3$	8.0	3.5	3.8	8.4
THF	7.2	5.0	7.9	6.8

useful criterion to establish whether an interaction is specific or nonspecific.

Values of the specific contributions obtained by the previously described method are compiled in Table 4. Very low values can be observed for $CHCl_3$, implying that although the adsorption mechanism of this molecule is considered as a combined mechanism, the porosity is much more important than the chemical surface groups (see Figure 2) because the specific contribution is never higher than 15%. On the other hand the values for acetone and diethyl ether represent more than 50% of the total value of $\Delta G_A°$ for the former and around 40% for the latter. Thus in the adsorption of these molecules the interactions with the chemical surface groups seem to be as important as the porosity of the samples, and this could explain why these two molecules do not follow the general trend shown in Figure 2. The values for the other molecules are lower than those of acetone, and in most cases they represent less than 30% of the total value. The plot of the specific component of the surface free energy vs the dipolar moment of the adsorbate molecules for sample P3 is shown in Figure 5. A similar trend is observed for all the carbons and shows a close relationship between the two parameters. Therefore, neither C_6H_6 nor CCl_4 interacts specifically with the surfaces of the samples because none of these molecules have a dipolar moment.

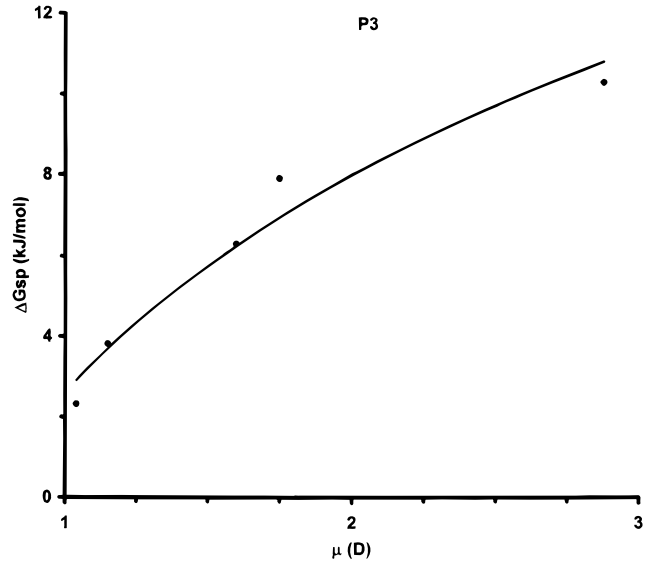

Figure 5. Specific component of the surface free energy vs the dipolar moment of the probes.

4. Conclusions

The carbon materials used in this work have a very narrow micropore distribution, which permits them to behave similarly from zero surface coverage to high surface coverage. The criterion frequently used to discriminate between specific and nonspecific interactions on the basis of the standard enthalpy of adsorption is not useful when microporous materials are used as adsorbent and when the adsorption is carried out at zero surface coverage. This is the case reported in this paper for *n*-alkanes, benzene, and cyclohexane, for which the adsorption is nonspecific although the heats of adsorption are very high. In the case of benzene, adsorption is produced in slit-shaped pores. In molecules with a dipolar moment, adsorption is produced by a combined mechanism which includes specific and nonspecific interactions.

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References and Notes

(1) Yang, R. T. *Separation by Adsorption Processes;* Butterworths: Boston, 1987.
(2) Verma, S. K. *Carbon* **1991**, *29*, 793.
(3) Carrasco-Marín, F.; Domingo-Garcia, M.; Fernández-Morales, I.; López-Garzón. F. J. *Carbon* **1991**, *29*, 629.
(4) Jagiełło, J.; Bandosz, T.; Schwarz, J. A. *Carbon* **1992**, *30*, 63.
(5) Papirer, E.; Sheng, L.; Balard, H.; Jagiełło, J. *Carbon* **1991**, *29*, 1135.
(6) Vidal, A.; Papirer, E.; Wang M. J.; Donnet, J.-B. *Chromatographia* **1987**, *23*, 121.

(7) Vukov, A. J.; Gray, D. G. *Langmuir* **1988**, *4*, 743.
(8) Moreno-Castilla, C.; Mahajan, O. P.; Walker, P. L., Jr.; Jung H.-J.; Vannice, M. A. *Carbon* **1993**, *31*, 75.
(9) Domingo-Garcia, M.; Fernández-Morales, I.; López-Garzón. F. J. *Carbon* **1993**, *31*, 75.
(10) Conder, J. R.; Young. C. L. *Physicochemical Measurements by Gas Chromatography*; Wiley: Chichester, 1979; Chapter 2.
(11) Carrasco-Marín, F.; Domingo-Garcia, M.; Fernández-Morales, I.; López-Garzón, F. J. *J. Colloid Interface Sci.* **1988**, *126*, 552.
(12) Newman. M. G. *J. Chem. Edu.* **1976**, *53*, 708.
(13) Domingo-Garcia, M.; Fernández-Morales, I.; López-Garzón, F. J.; Moreno-Castilla, C.; Prados-Ramirez, M. J. *J. Colloid Interface Sci*. **1990**, *136*, 160.
(14) López-Garzón, F. J.; Domingo-Garcia, M. *Adsorption on New and Modified Inorganic Sorbents*; Dabrowski, A., Tertykh, V. A., Eds.; Elsevier: Amsterdam, 1996; Vol. 99, Chapter 2.8.
(15) Rodríguez-Reinoso, F.; Linares-Solano, A. *Chemistry and Physics of Carbon* Thrower, P. A., Ed.; Marcel-Dekker: New York, 1989; Vol. 21, Chapter 1.
(16) Shindo, A.; Izumino, K. *Carbon* **1994**, *32*, 1233.
(17) Fanning, P. E.; Vannice, M. A. *Carbon* **1993**, *31*, 721.
(18) Zawadzki, J. *Chemistry and Physics of Carbon* Thrower, P. A., Ed.; Marcel-Dekker: New York, 1989; Vol. 21, Chapter 2.
(19) Domingo-Garcia, M.; Fernández-Morales, I.; López-Garzón, F. J.; Moreno-Castilla, C. *Langmuir* **1997**, *13*, 1218.
(20) Derouanne, E. G.; André, J. M.; Lucas, A. A. *J. Catal.* **1988**, *110*, 58.
(21) Domingo-Garcia, M.; Fernández-Morales, I.; López-Garzón. F. J.; Moreno-Castilla, C.; Pyda, M. *J. Colloids Interface Sci.* **1995**, *176*, 128.
(22) Burness, J. H.; Dillard, J. G. *Langmuir* **1991**, *7*, 1713.
(23) Cao, X. L.; Colenutt, B. A.; Sing, K. S. W. *J Chromatog.* **1991**, *555*, 183.
(24) Kiselev, A. V.; Yashin, Y. I. *Gas Adsorption Chromatography*; Plenum Press: New York, 1969; Chapter II.
(25) Saint Flour, C.; Papirer, E. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 666.
(26) Donnet, J.-B.; Park, S.-J. *Carbon* **1991**, *29*, 955.
(27) Dong, S.; Brondle, M.; Donnet, J.-B. *Chromatographia* **1989**, *28*, 469.
(28) Volkel, A. *Adsorption on New and Modified Inorganic Sorbents* Dabrowski, A., Tertykh, V. A., Eds.; Elsevier: Amsterdam, 1996; Vol. 99, Chapter 2.5.
(29) Jagiełło, J.; Bandosz, T.; Schwarz, J. A. *J. Colloids Interface Sci.* **1992**, *151*, 433.