

# Determination of the Micropore Texture of Some Glassy Carbons Using Molecular Probes<sup>†</sup>

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The micropore systems of three glassy carbons prepared using different recipes in the polymerization and carbonization of furfuryl alcohol have been studied by adsorption kinetic measurements and the adsorption–desorption isotherms of five adsorptives, with different molecular geometries, sizes, and polarity. The analysis of the adsorption isotherms has been carried out by comparing the results obtained when Dubinin–Radushkevich, the binomial Dubinin equation, and Dubinin Ashtakhov approximations are applied.

## Introduction

When adsorbent materials are going to be used in the adsorption of specific molecular compounds, they should at first have a suitable porosity with micropore dimensions of the order of the molecular size of the adsorbate.

Although activated carbons usually exhibit polymodal distribution of pores, the diameters of which vary from molecular dimensions to several hundred nanometers, the production of carbonaceous adsorbents with the desired porosity and micropore size distribution should be possible using the appropriate starting material, as well as an adequate method of preparation and activation process. This is why organic polymers turn out to be good raw materials, as they give rise to carbonaceous adsorbents with molecular sieve character and good retention capacity.

In the present paper we investigate the microporous texture of three glassy carbons prepared using different recipes in the polymerization of furfuryl alcohol and evaluate their potential applicability in the adsorption and separation of different organic molecules.

Among the numerous methods available to study the micropore system of an adsorbent, the one that probably gives the most detailed information is the adsorption of different adsorptives which vary, not only in the minimum critical size and conformation of their molecules but also in some of their chemical physical properties such as saturation vapor pressure at the adsorption temperature and dipole moment. In our study we have used three nonpolar molecular probes, benzene, *n*-hexane, and 2,2-dimethylbutane (2,2-DMB), and two polar molecules, methyl iodide and chloroform. We have chosen methyl iodide as one of the polar molecules because the elimination of this compound from a gaseous flow has been a subject of great interest for a long time, as in the form of <sup>131</sup>I is produced in the nuclear fission process that survives in the atmosphere. One of the aims of this work, therefore, is to study the possible application of these carbons in the selective elimination of methyl iodide.

Kinetic measurements for adsorption of benzene and methyl iodide on all the adsorbents have been carried out.

The adsorption–desorption isotherms of all these adsorbates on the three carbons have been analyzed by the application of several semiempirical models whose results have been compared and discussed.

## Experimental Section

The preparation of the samples has already been reported.<sup>1</sup> It basically consists of the polymerization and slow carbonization of furfuryl alcohol adding a pore former and/or a dispersing agent in different proportion for each carbon, following the recipes which are given in Table 1.

The adsorption–desorption isotherms of benzene, *n*-hexane, 2,2-DMB, methyl iodide, and chloroform were determined at 303 K in a conventional gravimetric system. Some of the physical properties of these adsorptives are compiled in Table 2. Two hours of adsorption time was allowed for each isotherm point. For the adsorption of benzene, methyl iodide and chloroform the isotherms were repeated allowing 12 h of adsorption time for each point, and for benzene the last point at  $P/P_0 = 0.9$  was left for 5 days. Previous to the adsorption runs the samples were outgassed during 12 h at 383 K to a residual pressure of  $10^{-6}$  Torr.

Kinetic measurements were also obtained in the same experimental system and they were carried out measuring the amount adsorbed against time at a relative pressure of 0.6 and 303 K.

## Results and Discussion

The glassy carbons used were previously characterized by mercury porosimetry up to 4000 kg/cm<sup>2</sup> and by N<sub>2</sub> and CO<sub>2</sub> adsorption at 77 and 273 K, respectively. In order to obtain the apparent surface areas, the BET equation was applied to the N<sub>2</sub> adsorption isotherm and the Dubinin–Radushkevich equation to the CO<sub>2</sub> adsorption isotherm. It is well documented<sup>5</sup> that in the case of microporous carbons the adsorption of N<sub>2</sub> at 77 K can present some disadvantages due to activated diffusion into the micropores, and in these cases it has been recommended<sup>5</sup> to use the CO<sub>2</sub> adsorption at 273 K to complete the adsorption data. The characteristics of the samples were given in a previous paper<sup>1</sup> and are summarized here in Table 3. Important differences in the pore size distribution in the region of meso, V<sub>2</sub>, and macropores, V<sub>3</sub>, were found depending on the preparation

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**Table 1. Recipes for Preparation of Samples**

sample	FA (cm <sup>3</sup> )	PEG (cm <sup>3</sup> )	TX-100 (cm <sup>3</sup> )	PTSA (cm <sup>3</sup> )
P1	60	30		10.2
P2	40	30	30	8.6
P3	40		40	6.8

<sup>a</sup> Key: FA, furfuryl alcohol (carbon yielding binder); PEG, polyethylene alcohol (pore former and dispersant); TX-100, Triton X-100 (dispersing agent); PTSA, *p*-toluenesulfonic acid (catalytic agent for the polymerization of furfuryl alcohol).

recipes. Moreover,  $S_{N_2} \ll S_{CO_2}$ , which indicates that the microporosity is very narrow or there are constrictions in the entry of the micropores.<sup>5</sup>

**Adsorption of the Nonpolar Molecular Probes.** The kinetic adsorption curves for benzene on the three carbons are shown in Figure 1a and the values of the adsorption rates ( $R_L$ ), calculated from the slope of the linear region in the plot of the volume adsorbed ( $V$ ) at a time ( $t$ ) versus the square root of this time ( $t^{1/2}$ ) are given in Table 4. Diffusion parameters were obtained under unsteady state conditions, for small values of  $t$  at the beginning of the adsorption process<sup>6,7</sup> applying eq 1

$$(V - V_0)/(V_e - V_0) = 6/\pi^{1/2}(Dt/r_0^2)^{1/2} \quad (1)$$

where  $V_0$  is the volume at the initial time and  $V_e$  the volume when the equilibrium is attained. The diffusion parameters ( $D^{1/2}/r_0$ ) are given in Table 4. The errors of all magnitudes were obtained from the standard deviation of the linear regression. These data indicate considerable differences for the adsorption process of benzene on each carbon, particularly on sample P2 for which  $R_L$  and  $D^{1/2}/r_0$  values appear to be more than 10 times lower than for P1 and more than 20 times lower than for P3. One can, therefore, assume important differences in the porous system of the three carbon samples due to the different preparation recipes. Actually, from data given in Table 3 we can observe that carbon P2 has no macroporosity at all, whereas P1 presents a large one. It is known that macroporosity is very important for the transport and quick penetration of the adsorbate to the micropore system. However, the kinetic parameters are lower for carbon P1 than for carbon P3, although the latter shows a less extensive macroporosity. This fact, together with data in Table 4 and the restricted  $N_2$  adsorption at 77 K for carbon P2 due to pore constrictions, suggests that there are also important differences in their micropore system.

The adsorption isotherms of the nonpolar hydrocarbons used as molecular probes are depicted in Figures 2 and 3 and they can be assigned to BDDT type I, which corresponds to a predominantly microporous adsorbent; nevertheless, differences in their shape and in the desorption process are found indicating a variety in the pore characteristics.

Isotherms of benzene on the three samples studied are depicted in Figure 2. For carbons P1 and P3 the isotherms obtained with adsorption times of 2 h were coincident to those obtained after 12 h. Therefore only the isotherms obtained with long adsorption times are depicted in Figure 2. For carbon P2, however, quite different isotherms are derived from each case and these have both been depicted in this figure. The first sight of their shape suggests that while sample P1 appears to have a predominant adsorption

on micropores with little participation on the external surface, samples P2 and P3 exhibit an upward deviation in the region of high relative pressure which is normally interpreted either as capillary condensation in supermicropores and small mesopores or adsorption on the external surface of the adsorbent. These two effects follow a different adsorption mechanism to that of adsorption on micropores and often produce a hysteresis loop at high relative pressures when the desorption process is carried out. Desorption isotherms, represented in Figure 2, show a very small deviation from the adsorption branch for samples P1 and P3 which extend to the lowest relative pressure region. The value of these deviations in volume of adsorbate is less than 0.01 cm<sup>3</sup>/g. Nevertheless, a very pronounced hysteresis loop, in the complete range of relative pressures studied, is found for the two isotherms of carbon P2. Bailey et al.<sup>8</sup> and McEnaney<sup>9</sup> have suggested that low-pressure hysteresis is produced by the irreversible intercalation of the adsorbate molecules in pores to which they are not normally accessible. This intercalation can be due to the swelling of the particles that accompanies adsorption and distorts or even fractures the structure, opening up cavities which were previously inaccessible to adsorbate molecules. According to McEnaney a "memory" effect in the carbon network would lead to trapping of some adsorbate molecules during the desorption run. Nonetheless, the degree to which a solid expands during adsorption depends on the overall rigidity of the sample; for samples with high rigidity the swelling is of minor importance and the major cause of the low pressure hysteresis will be the activated passage of molecules through pre-existing constrictions into wider cavities.<sup>10,11</sup> Glassy carbons are known to be rigid materials. Therefore of the several hypotheses mentioned above we consider that activated passage of molecules through pre-existing constrictions into wider cavities appears to be the most appropriate for our samples. This interpretation is consistent with the restricted adsorption of  $N_2$  at 77 K found which yields a  $S_{N_2}$  value much lower than  $S_{CO_2}$ , as mentioned before.

The adsorption isotherms for the other nonpolar molecular probes, *n*-hexane and 2,2-DMB (obtained only with equilibrium times of 2 h), are depicted in Figure 3. *n*-Hexane gives the same kind of isotherms as those obtained for benzene on every carbon but, when the minimum critical size of the molecular probe increases from *n*-hexane to 2,2-DMB, drastic molecular sieve behavior appears for the adsorption of the last adsorbate on P1 and P2 carbons. The adsorption isotherms of 2,2-DMB on P1 and P2 do not appear in Figure 3 because no adsorption at all was detected for these two glassy carbons.

**Adsorption of the Polar Adsorptives.** The kinetic adsorption curves obtained for methyl iodide are shown in Figure 1b. The adsorption rate and diffusion parameter of this adsorbate on the three glassy carbons (Table 4) are much higher than those of benzene, and this occurrence is more marked for samples P1 and P2 than for P3.

On the other hand, adsorption-desorption isotherms of both methyl iodide and chloroform (Figure 4) show a behavior comparable to that of benzene. Nevertheless, for methyl iodide on sample P2 at relative pressures less than 0.4 the deviation between the adsorption and desorption branches becomes much smaller than that for benzene, with the hysteresis loop being similar to that

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**Table 2. Physical Properties of the Adsorptives**

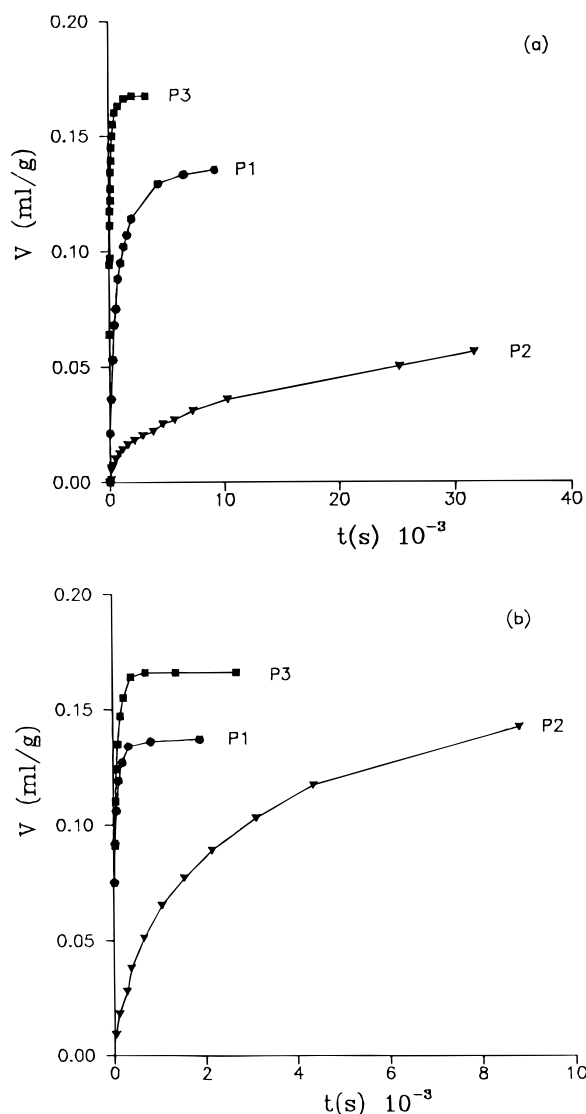
sample	dimension (nm) <sup>a</sup>			$\beta^d$	$P_0$ (303 K) <sup>e</sup> (mbar)	$\mu$ (D)	$\rho$ (303 K) (g/cm <sup>3</sup> )
benzene	0.37(t)	0.67(w)	0.74(l) <sup>b</sup>	1	156		0.868
<i>n</i> -hexane	0.40(t)	0.49(w)	1.03(l) <sup>b</sup>	1.22	265		0.650
2,2-DMB	0.59(t)	0.60(w)	0.77(l) <sup>b</sup>	1.51	520		0.638
methyl iodide	0.38(t)	0.42(w)	0.56(h) <sup>c</sup>	0.76	620	1.62	2.255
chloroform	0.55(t)	0.63(w)	0.43(h) <sup>c</sup>	0.88	338	1.04	1.483

<sup>a</sup> t = thickness; w = width; h = height; l = length. <sup>b</sup> From ref 2. <sup>c</sup> Calculated from molecular model. <sup>d</sup> From ref 3. <sup>e</sup> From ref 4.

**Table 3. Surface Area and Textural Characteristics of the Glassy Carbons**

sample	$S_{N_2}$ (m <sup>2</sup> /g)	$S_{CO_2}$ (m <sup>2</sup> /g)	$V_2^a$ (cm <sup>3</sup> /g)	$V_3^b$ (cm <sup>3</sup> /g)
P1	475	408	0.033	0.214
P2	24	257	0.041	0.000
P3	398	344	0.235	0.024

<sup>a</sup>  $V_2$  volume of pores with diameters between 50 and 3.6 nm. <sup>b</sup>  $V_3$  volume of pores with diameters larger than 50 nm.



**Figure 1.** (a) Adsorption kinetic curves of benzene on glassy carbons P1, P2, and P3. (b) Adsorption kinetic curves of methyl iodide on glassy carbons P1, P2, and P3, at a relative pressure of 0.6 and 303 K.

expected for capillary condensation on supermicropores or mesopores. This result, together with the kinetic parameters, indicates that methyl iodide passes more easily through the pore constrictions than benzene does, in spite of their minimum critical dimensions being very similar.

With respect to chloroform, which has a minimum critical dimension between that of *n*-hexane and 2,2-DMB, the adsorption process on the three samples is comparable to that of benzene and completely different to that of 2,2-DMB. Thus, the above mentioned molecular sieve effect shown by carbons P1 and P2 only appears between chloroform and 2,2-DMB.

**Dubinin–Radushkevich Plots.** It has been widely observed that for adsorption of gases on activated carbons particularly with molecular sieve properties, the Dubinin–Radushkevich equation (2) is very often followed over a large range of relative pressures and temperatures.<sup>11–15</sup> From the isotherms already discussed we know that at least carbons P1 and P2 show molecular sieve behavior; thus to start with, this model has been chosen for the quantitative analysis of the different isotherms.

$$V = V_0 \exp[-B(T/\beta)^2 \log^2(P_0/P)] \quad (2)$$

$V$  is the volume of the adsorbate condensed in the micropores at temperature  $T$  and relative pressure  $P/P_0$ ,  $V_0$  is the total volume of the micropores,  $\beta$  is the “similarity coefficient”, and  $B$  is the so-called structural constant.

In Figure 5, the characteristic curves obtained for the different vapors on each carbon sample are depicted. The data correspond to the adsorption isotherms obtained after 12 h of equilibrium time for benzene, methyl iodide, and chloroform and after 2 h of equilibrium time for *n*-hexane and 2,2-DMB. From this figure one can see the differences in the microporous systems of the three carbons much more clearly. The micropore volume,  $V_0$ , accessible to each molecular probe on every carbon has been calculated from the more extended linear region of the curves where equilibrium has been attained and where the DR equation fits with a correlation coefficient of the order of  $r^2 = 0.99$ . This value, together with the adsorption volume at  $P/P_0 = 0.9$ ,  $V_s$ , is given in Table 5. The errors of the magnitudes were obtained as before.

For carbon P1 the plots in Figure 5a seem to indicate that the adsorption of benzene, *n*-hexane, methyl iodide, and chloroform takes place on the same type of micropores, although the downward deviations from linearity observed for benzene, *n*-hexane, and chloroform at low relative pressures can indicate that in this region the equilibrium is not attained for the adsorption of these molecules. This type of deviation is often explained in terms of restricted diffusion into the narrowest pores or because the molecular sieve effect can lead to difficulties in adsorption at low relative pressure.<sup>16,17</sup> It should be noticed that for *n*-hexane this deviation extends to much higher values of relative pressure than for chloroform, although the minimum critical size of the latter is somewhat greater. This could be due to the great length of *n*-hexane, which

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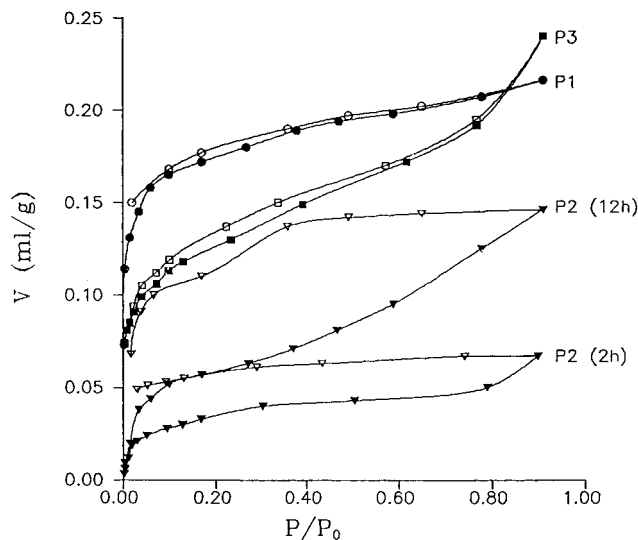
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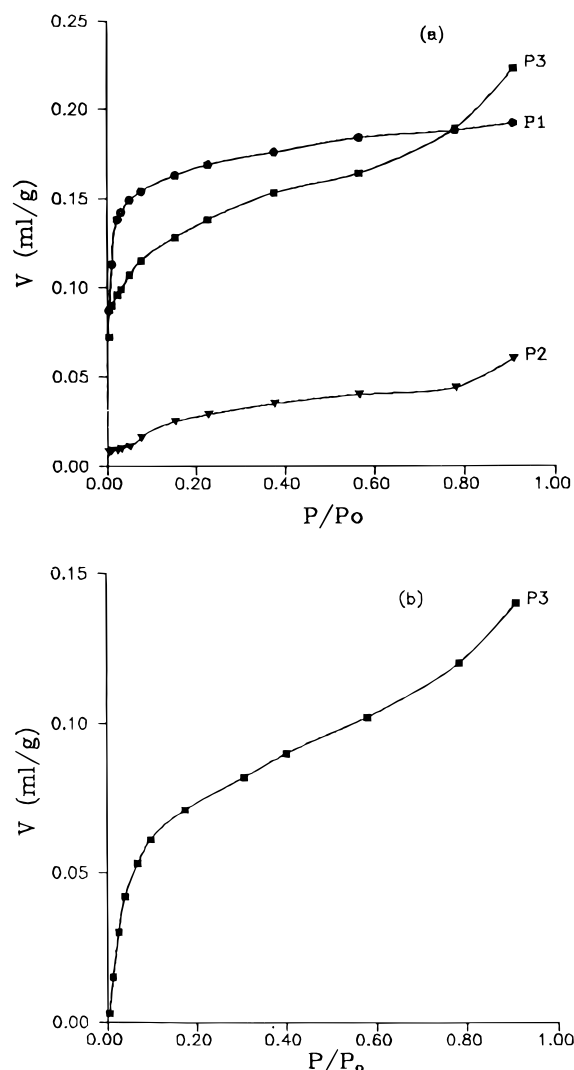
**Table 4.** Apparent Rate of Adsorption,  $R_L$ , and Diffusion Parameters,  $D^{1/2}/r_0$ , for the Adsorption of Methyl Iodide and Benzene

	$R_L$ (cm <sup>3</sup> g <sup>-1</sup> min <sup>-1/2</sup> )			$D^{1/2}/r_0$ (min <sup>-1/2</sup> )		
	P1	P2	P3	P1	P2	P3
benzene	0.023 ± 0.008	0.002 ± 0.001	0.043 ± 0.006	0.178 ± 0.002	0.020 ± 0.001	0.419 ± 0.020
methyl iodide	0.049 ± 0.006	0.015 ± 0.001	0.068 ± 0.008	0.572 ± 0.020	0.097 ± 0.001	0.580 ± 0.020

**Figure 2.** Adsorption (close symbols) desorption (open symbols) isotherms of benzene on glassy carbons P1, P2, and P3. P2 (2 h) is the isotherm with an equilibrium time of 2 h for each data point, P2 (12 h) is the isotherm with 12 h of equilibrium time.

could be causing packing restrictions in the micropores.<sup>17</sup> However, in the case of methyl iodide the downward deviation does not appear but, on the contrary, at very low relative pressures an upward linear deviation appears, suggesting that this molecule has good accessibility into the narrowest pores.

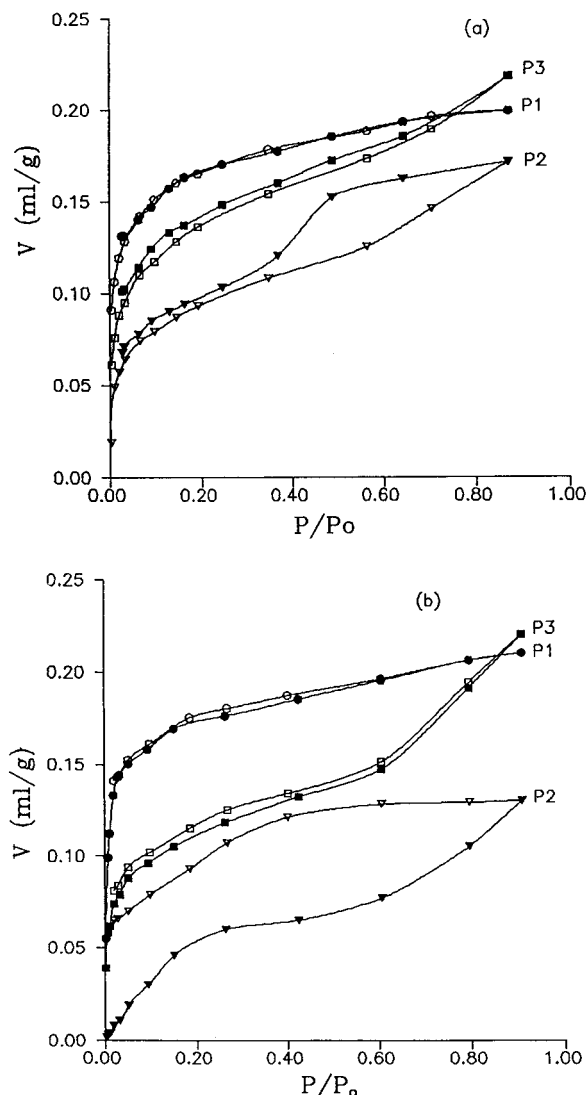
For carbon P2 the DR characteristic curves of the four adsorbates are depicted in Figure 5b. On this adsorbent the curves of benzene, methyl iodide, and chloroform corresponding to isotherms with the same adsorption time are not at all coincident. As indicated by the kinetic adsorption measurements, benzene and methyl iodide present very low diffusion parameters on this carbon (Table 4), although for the latter this is almost five times higher than for the former. Actually, the volume of benzene adsorbed at a relative pressure of  $P/P_0 = 0.9$ ,  $V_s$ , increased from 0.07 cm<sup>3</sup>/g after 2 h of adsorption time to 0.14 cm<sup>3</sup>/g after 12 h and to 0.17 after 5 days. For methyl iodide the same volume of 0.17 cm<sup>3</sup>/g was attained after 2 or 12 h. This fact could explain the very different slopes for the corresponding characteristic curves. So, although adsorption on carbon P2 appears to be kinetically restrictive for the three adsorbates, the restriction is much smaller for methyl iodide than for benzene with chloroform having the highest restriction. As already suggested this restriction seems to be due to some kind of constriction at the entrance of the pores, so the fact that methyl iodide is adsorbed better than benzene in the complete range of relative pressures, even when their minimum critical dimensions are almost the same, might be explained in terms of the probability that a specific molecule passes through the constriction. In this respect, it is clear that the methyl iodide molecule is geometrically more able to pass the constriction than the benzene molecule because, of the three dimensions given in Table 2, the former has two smaller than 0.43 nm while benzene has two larger than 0.66 nm. This means that when methyl iodide approaches the entrance of the pore, it has a greater chance of fitting inside it.

**Figure 3.** (a) Adsorption isotherms of *n*-hexane on the three glassy carbons. (b) Adsorption isotherm of 2,2-DMB on P3.

Another factor to be considered is the high dipole moment of methyl iodide which can produce specific interactions with the oxygen functional groups on the carbon surface which accumulate with the dispersion forces leading to a considerable increase of the adsorption energy in the initial region of the adsorption process, i.e., at very low relative pressure. The contribution of this specific interaction decreases following micropore filling of the adsorbent.<sup>18,19</sup> Chloroform is the less easily adsorbed of the three adsorbates as its critical dimension of 0.43 nm is the greatest. The fact that chloroform, which is also a polar molecule, has a similar behavior to that of benzene, indicates that the main parameter controlling access through the pore constrictions is the shape and dimensions of the molecule. With respect to *n*-hexane, the adsorption of this molecule is lower than for benzene due to either an insufficient equilibrium time or its higher critical dimension. The molecular sieve effect between

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**Figure 4.** (a) Adsorption (close symbols) desorption (open symbols) isotherms of methyl iodide. (b) Adsorption (open symbols) desorption (close symbols) of chloroform.

benzene and 2,2-DMB found for these two carbons P1 and P2 (see Table 5) confirms the network of these to be made up by slit-shaped micropores.

As pointed out earlier, the micropore system of carbon P3 also seemed to have important differences with respect to those of carbons P1 and P2, which becomes more obvious when analyzing the characteristic curves of the adsorbates given also in Figure 5c; the most important difference for this carbon is the significant adsorption capacity of 2,2-DMB. Nevertheless, on comparison of the curves obtained for the different hydrocarbons, strong restrictions appear for the adsorption of 2,2-DMB and the slope of the linear region of its curve is much steeper than that of the other curves. Apart from this, the curves of benzene and methyl iodide are coincident as well as those of *n*-hexane and chloroform; the adsorption of *n*-hexane seems to suffer some restrictions at low relative pressures while for chloroform only a linear region that extends over a wide range of relative pressures,  $P/P_0$ , from  $10^{-3}$  to  $1.5 \times 10^{-1}$  is found; moreover, at very low relative pressures an upward deviation appears not only for the characteristic curve of methyl iodide but also for that of benzene. On the other hand, on studying the  $V_s$  values given in Table 5, it is evident that a certain molecular sieve behavior between 2,2-DMB and the rest of the adsorbates is also shown by carbon P3. The adsorption of this molecular probe probably takes place in the region of supermi-

cro pores and small mesopores, as also suggested by the steep slope of its characteristic curve.

The characteristic curves of adsorption of the adsorbates on the three carbons show an upward deviation from the linearity near the saturation pressures which can be attributed to the filling of supermicropores by a cooperative mechanism which involves little if any enhancement of the adsorption energy.<sup>20</sup>

Characteristic energies of adsorption,  $E_0$ , can be calculated from the slopes of the linear regions of the characteristic curves using the relation with the structural constant,  $B$ ,  $E_0 = 0.01915/B^{1/2}$ , and from these energies the corresponding average micropore widths,  $L_0$ , are obtained applying the expression proposed by McEnaney et al.<sup>21</sup>

$$L_0 = 4.699 \exp(-0.0666E_0) \quad (3)$$

As an example, data for benzene, methyl iodide, and 2,2-DMB are listed in Table 6 along with the range of validity for relative pressures in which these parameters have been obtained. As mentioned above data for carbon P2 are doubtful because, with the exception of methyl iodide, equilibrium does not seem to have been attained.

The parameters in this table do not correspond to especially narrow microporous systems. The average micropore width,  $L_0$ , calculated for carbon P1 with benzene is quite coincident with that calculated with methyl iodide; however, for carbon P3 a more significant difference of this parameter is found with each adsorbate. The very low characteristic adsorption energy,  $E_0$ , of 6.1 kJ/mol corresponding to 2,2-DMB on this carbon is typical of adsorption on supermicropores or even small mesopores as we have pointed out before.

In cases such as the adsorption of methyl iodide on carbons P1 and P3 or benzene on P3 where the characteristic curve presents an upward linear deviation in the region of low relative pressures, Dubinin<sup>22</sup> considered that this kind of characteristic curve results from the superposition of two extreme ranges of microporosity and can be well approximated by a binomial equation, known as the Dubinin–Isotova equation

$$V = V_{01} \exp[-B_1(T/\beta)^2 \log^2(P_0/P)] + V_{02} \exp[-B_2(T/\beta)^2 \log^2(P_0/P)] \quad (4)$$

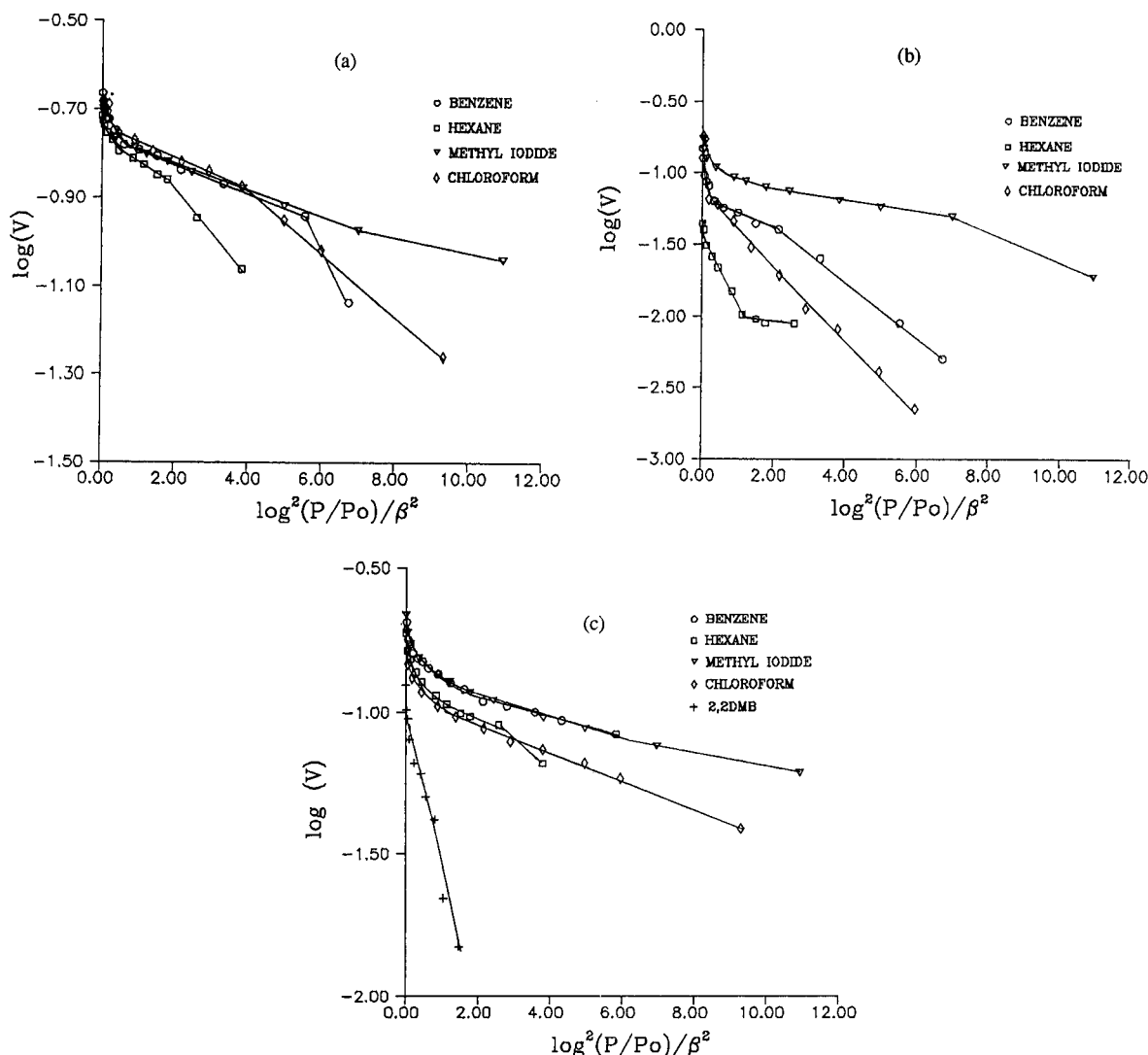
By extrapolation of the first region at low relative pressures to the origin and subtracting it from the total characteristic curve, a second plot with a much steeper slope than the original one was obtained. Figure 6 shows, as an example, the resulting curves for the adsorption of methyl iodide on P3 after applying eq 4. According to Stoeckli et al.,<sup>23</sup> one can assume that the linear region at very low relative pressures corresponds to the primary micropore filling process, while the linear part of the second plot reflects the beginning of the secondary micropore filling process, i.e., the adsorption on the walls of relatively large micropores, so the volume,  $V_{02}$ , obtained from the initial section of this second plot provides information on the monolayer capacity of the largest micropores walls; a value of adsorption energy,  $E_{02}$ , has also been worked out from this section. The upward deviation from linearity of the second plot near the saturation pressures might be attributed to the filling of these wider micropores by the

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**Figure 5.** Dubinin–Radushkevich plots of benzene, *n*-hexane, 2,2-DMB, methyl iodide, and chloroform on (a) P1, (b) P2, and (c) P3.

**Table 5.** Micropore Volume,  $V_0$ , Obtained by DR Equation and Volume Adsorbed at  $P/P_0 = 0.9$ ,  $V_s$

	P1		P2		P3	
	$V_0$ (cm <sup>3</sup> /g)	$V_s$ (cm <sup>3</sup> /g)	$V_0$ (cm <sup>3</sup> /g)	$V_s$ (cm <sup>3</sup> /g)	$V_0$ (cm <sup>3</sup> /g)	$V_s$ (cm <sup>3</sup> /g)
benzene	$0.173 \pm 0.003$	0.21	$0.068 \pm 0.002$	0.14	$0.156 \pm 0.003$	0.23
<i>n</i> -hexane	$0.169 \pm 0.001$	0.19	$0.030 \pm 0.001$	0.06	$0.113 \pm 0.001$	0.22
2,2-DMB					$0.092 \pm 0.003$	0.13
methyl iodide	$0.176 \pm 0.002$	0.20	$0.093 \pm 0.001$	0.17	$0.144 \pm 0.003$	0.23
chloroform	$0.177 \pm 0.003$	0.21	$0.072 \pm 0.006$	0.13	$0.113 \pm 0.003$	0.22

**Table 6.** Characteristic Adsorption Energy,  $E_0$ , and the Corresponding Pore Width,  $L_0$

		benzene	methyl iodide	2,2-DMB
P1	$E_0$ (kJ/mol)	$20.9 \pm 0.7$	$21.7 \pm 0.7$	
	$L_0$ (nm)	$1.17 \pm 0.05$	$1.10 \pm 0.05$	
	range of validity for $P/P_0$	$4.5 \times 10^{-3}$ to $1.7 \times 10^{-1}$	$1.3 \times 10^{-2}$ to $3.5 \times 10^{-1}$	
P2	$E_0$ (kJ/mol)	$11.0 \pm 0.3$	$18.9 \pm 0.4$	
	$L_0$ (nm)	$2.20 \pm 0.04$	$1.30 \pm 0.03$	
	range of validity for $P/P_0$	$3.4 \times 10^{-2}$ to $2.6 \times 10^{-1}$	$9.8 \times 10^{-3}$ to $10^{-1}$	
P3	$E_0$ (kJ/mol)	$17.1 \pm 0.5$	$19.8 \pm 0.6$	$6.1 \pm 0.3$
	$L_0$ (nm)	$1.50 \pm 0.05$	$1.26 \pm 0.05$	
	range of validity for $P/P_0$	$2.7 \times 10^{-2}$ to $1.6 \times 10^{-1}$	$3.0 \times 10^{-2}$ to $3.5 \times 10^{-1}$	$4.0 \times 10^{-2}$ to $3.0 \times 10^{-1}$

already mentioned cooperative mechanism. Table 7 contains the new adsorption parameters of methyl iodide on P1 and P3 and benzene on P3 by applying eq 4.

It is interesting to compare the data in Tables 5, 6, and 7. Thus, as mentioned above, from the values of  $E_0$  and  $L_0$  obtained by adsorption of benzene and methyl iodide on P1 (Table 6) using eq 2, this carbon cannot be presumed to have especially narrow micropores. However, when

these two parameters are worked out from the first linear region of the characteristic curve of methyl iodide using eq 4 (Table 7), it appears that more than 70% of the total adsorption volume,  $V_s$ , on this carbon takes place on micropores with an average dimension  $L_{01}$ , of 0.74 nm; nevertheless, this last value is still not small enough to explain the drastic molecular sieve behavior found for 2,2-DMB or the restricted diffusion of benzene at very low

**Table 7. Parameters Obtained from the Dubinin and Isotova Equation (4)**

adsorbate	$V_{01}$ (cm <sup>3</sup> /g)	$E_{01}$ (kJ/mol)	$L_{01}$ (nm)	range of validity for $P/P_0$	$V_{02}$ (cm <sup>3</sup> /g)	$E_{02}$ (kJ/mol)	range of validity for $P/P_0$
P1 methyl iodide	$0.146 \pm 0.003$	$27.7 \pm 1.3$	$0.74 \pm 0.06$	$3.0 \times 10^{-3}$ to $3.0 \times 10^{-2}$	$0.040 \pm 0.003$	$7.7 \pm 0.2$	$3.0 \times 10^{-2}$ to $5.0 \times 10^{-1}$
P3 benzene	$0.128 \pm 0.001$	$21.4 \pm 0.3$	$1.10 \pm 0.02$	$3.0 \times 10^{-3}$ to $3.0 \times 10^{-2}$	$0.049 \pm 0.004$	$5.0 \pm 0.1$	$3.0 \times 10^{-2}$ to $6.0 \times 10^{-1}$
methyl iodide	$0.120 \pm 0.002$	$23.2 \pm 0.6$	$1.01 \pm 0.04$	$3.0 \times 10^{-3}$ to $3.5 \times 10^{-2}$	$0.047 \pm 0.004$	$6.4 \pm 0.1$	$4.0 \times 10^{-2}$ to $5.0 \times 10^{-1}$

**Table 8. Application of Dubinin–Astakhov Equation**

adsorbent	adsorbate	$n$	$V_0$ (cm <sup>3</sup> /g)	$E_0$ (kJ/mol)	$L_0$ (nm)	range of validity for $P/P_0$
P1	benzene	0.92	$0.215 \pm 0.001$	$22.5 \pm 0.5$	1.04	$3.0 \times 10^{-3}$ to $7.0 \times 10^{-1}$
	methyl iodide	1.10	$0.201 \pm 0.001$	$23.2 \pm 0.2$	0.99	$3.0 \times 10^{-3}$ to $8.7 \times 10^{-1}$
P3	benzene	0.73	$0.219 \pm 0.001$	$14.8 \pm 0.2$	1.75	$3.0 \times 10^{-3}$ to $7.0 \times 10^{-1}$
	methyl iodide	0.77	$0.223 \pm 0.001$	$18.3 \pm 0.2$	1.40	$3.0 \times 10^{-3}$ to $7.0 \times 10^{-1}$
	2,2-DMB	0.78	$0.143 \pm 0.001$	$4.0 \pm 0.2$		$4.0 \times 10^{-2}$ to $8.0 \times 10^{-1}$

values of  $P/P_0$ , which could be explained by some kind of constriction at the entrance of the micropores system. It should be pointed out that eq 4 is not applicable to the adsorption of benzene on P1 because of the negative deviation at low relative pressures.

The  $V_{01}$  and  $E_{01}$  values obtained for benzene and methyl iodide on carbon P3 are quite close and indicate that 56% of the total adsorption volume on this carbon takes place on micropores of about 1 nm or less.

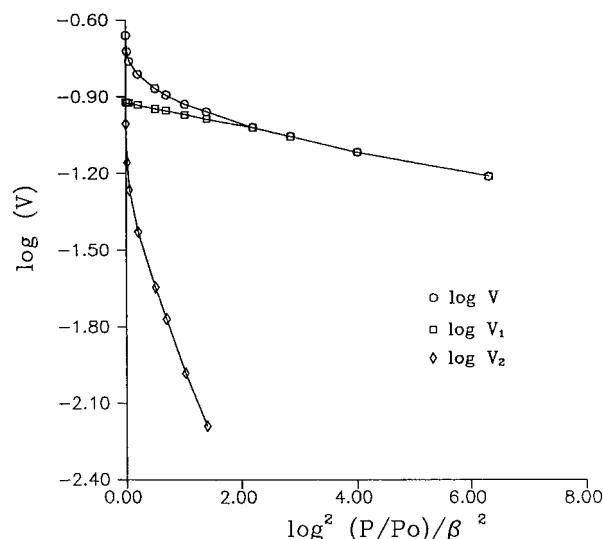
Values of adsorption energy,  $E_{02}$ , calculated from the second plot of the two carbons are very low, between 5 and 8 kJ/mol, as expected for a secondary micropore filling mechanism.

**Dubinin Astakhov Equation.** In order to know the extent of the heterogeneity in the microporous system of carbons P1 and P3, we have applied the more general equation of micropore filling theory given by Dubinin and Astakhov<sup>24,25</sup>

$$V = V_0 \exp[-A/\beta E_0]^n \quad (5)$$

where  $A = RT \ln(P/P_0)$  and  $n$  is the exponent that makes the representation of  $\log V$  against  $\log^2(P/P_0)$  linear, reflecting the width of the energy distribution itself related to the pore size distribution.

This equation has been applied to isotherms of benzene and methyl iodide on carbon P1 and P3 and 2,2-DMB on P3 in the complete range of relative pressures studied using the iterative method explained elsewhere<sup>11,24</sup> to determine the exponents  $n$  and the adsorption parameters which are shown in Table 8. In all cases the correlation coefficients in the linear region are always better than 0.99. The very low values of the exponent  $n$  suggest highly heterogeneous micropore systems; however, for carbon P1 the average micropore dimensions,  $L_0$ , calculated for both adsorbates, are quite small and even smaller than those obtained by applying the DR equation in a more restricted range of relative pressures (Table 6). So the low  $n$  values for this carbon could be due to two extreme kinds of micropores, the majority with a width of approximately 0.74 nm or less and a small fraction in the range of supermicropores which causes the parameter  $n$  to decrease; nonetheless, the complete molecular sieve effect between chloroform and 2,2-DMB shown by this carbon (Table 5) seems to indicate that the constrictions or narrowness at the entrance of the micropores also affects this second fraction of wider pores. For carbon P3 the situation is somewhat different, with the fraction of widest pores being more extensive than for carbon P1 without constrictions at their entrance which is clear from the amount of 2,2-DMB adsorbed with a very low adsorption

**Figure 6.** The two terms of the Dubinin–Isotova equation for adsorption of methyl iodide on glassy carbon P3.

energy,  $E_0$ , meaning that this adsorbate is almost exclusively retained in these wider pores.

## Conclusions

First, carbons P1 and P2 show a complete molecular sieve behavior between the adsorption of chloroform, with a critical dimension of around, 0.43 nm, and 2,2-DMB, with a critical dimension of around 0.59 nm. Nevertheless, when the isotherms of benzene or methyl iodide are analyzed by the application of the DR and DA models, these carbons are found to have a wide micropore size distribution with average micropore sizes that do not justify this behavior. From this fact together with the adsorption kinetic measurements of benzene and methyl iodide on the three glassy carbons, it could be concluded that constrictions or some kind of narrowness at the entrance of the micropores must be the cause of the observed molecular sieve behavior. A close knowledge of the reason of this effect and the kind of pore system that produces it can be attained by studying the adsorption of different molecular probes which differ not only in their minimum critical dimension but also in other characteristics such as molecular geometry or dipole moment.

Finally, it should be pointed out that these glassy carbons appear to be good at the selective adsorption of methyl iodide compared to other hydrocarbons of similar molecular dimensions and physical properties, which could be of great interest for their technical application.

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