Contribution to the Evaluation of Density of Methane Adsorbed on Activated Carbon

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The adsorption isotherms of N_2 at −196 °C, CO_2 at 0 °C, and CH_4 at 25 °C on 35 activated carbons with a wide range of micropore volumes and pore size distributions have been compared to evaluate the density of adsorbed methane. Results indicate that methane is adsorbed in the micropores of the activated carbon with a density that is a function of the carbon porosity because methane is packed more compactly in narrow than in wide micropores. An experimental procedure is proposed to evaluate the density in both types of micropores as a function of pressure. Its application to these porous carbons indicates that density of adsorbed methane increases rapidly with pressure on narrow micropores, the increase becoming slower above 1.5 MPa. The value reached at 3 MPa is 0.21 g/cm³, near that estimated as the limiting value, 0.23 g/cm³. Density in wide micropores is low, 0.09 g/cm³ at 3 MPa, but it continuously increases with pressure.

1. Introduction

Methane is a gas that can be compressed at room temperature without condensation because its critical temperature is −82.5 °C. It is usually stored in metal cylinders at around 20−25 MPa.[1] The past few years have seen an increased interest in methane as a fuel for vehicles with a driving range similar to those actually using diesel or gasoline; this methane had to be stored at a pressure much lower than the 20 MPa used for compressed methane. One way to reduce the storage pressure of methane is to use methane adsorbed on activated carbon, because methane molecules are attracted to the carbon surface by van der Waals forces and become more compactly packed than in the gas phase. The increase in methane density produced by the adsorbent permits the storage of an amount similar to that possible at 20 MPa but at a much lower pressure. A careful analysis of the literature of the past few years shows the large effort carried out to develop an activated carbon able to store at around 3.4 MPa the same amount of methane compressed at 20 MPa in the same volume.[2−5]

If one takes into account that the adsorption forces are weak on the surface of meso- and macropores of the activated carbon, in contrast with those in micropores, it is obvious that the latter range of porosity is the important one in the adsorption of methane at room temperature. In fact, the volume of large size pores, where capillary condensation takes place in the adsorption of gases and vapors at low temperature, can be ignored here since they do not increase the density of methane with respect to that of gas phase.[3−12]

The interest of the research relative to the adsorption of methane in micropores of activated carbon has been mainly focused in attempting to relate the methane uptake to the volume of micropores so that one could estimate the maximum adsorption capacity of an ideal activated carbon and thus evaluate the possibilities and limitations of activated carbon in natural gas storage.[3−5] Such studies have the additional interest of contributing to knowledge of the adsorption process at

temperatures above the critical one and of determining the density of the adsorbed phase. Thus, several authors were able to envisage, by using molecular simulation of the adsorption process of methane on a given pore shape, the effect of structure, geometry, pore size, and chemical nature of the carbon surface on the density of adsorbed methane.[13−15] Other authors have proposed methods to determine the density of methane directly from the adsorption isotherms by adjusting the experimental data to different equations.[16−20]

The objective of this work is to contribute to the experimental determination of the density of methane adsorbed at room temperature in micropores of activated carbon. To reach this objective, the adsorption data of N_2, CO_2, and CH_4 will be correlated, with both the volume of micropores and the micropore size distribution taken into account. To obtain results with a wide and valid range of application, 35 activated carbons with different natures and porosities have been selected.

2. Experimental Section

Four series of activated carbon have been prepared from the same precursor, olive stones, two of them by chemical activation and two in which additional physical (also called thermal) activation was carried out. The crushed and sieved precursor (0.1−0.5 mm particle size) was impregnated with solutions of different concentrations of phosphoric acid (series 1) or zinc chloride (series 2). The impregnated dry slurry was pressed into disks and then carbonized at 450 °C (series 1) or 500 °C (series 2). The carbonized disks were exhaustively washed to extract the chemical used for impregnation.

Some carbons of the two series were heat treated at 800 °C under an inert atmosphere to complete the carbonization process and they were then reacted in a controlled way at 750 °C (series 1) or 725 °C (series 2) with carbon dioxide to different burnoffs. This process led to series 3 (from carbons activated with phosphoric acid) and series 4 (from carbons activated with zinc chloride). The details for the preparation of all series can be found elsewhere.[21,22]

The adsorption isotherms for N_2 at −196 °C and CO_2 at 0 °C were determined in a volumetric automatic adsorption system

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TABLE 1: Characteristics of Some Selected Activated Carbons

carbon	V_{N2} (cm³/g)	V_{me} (cm³/g)	d_{He} (g/cm³)	mean pore size (nm)	V_{CO2} (cm³/g)	V_{CH4} at 3 MPa (cm³/g)	d_{CH4} (g/cm³)
1	0.31	0.01	1.62	1.15	0.30	78	0.180
2	0.40	0.02	1.64	1.13	0.34	109	0.194
3	0.69	0.31	2.18	1.47	0.35	163	0.168
4	0.66	0.16	1.96	1.34	0.43	133	0.143

(Autosorb-6 from Quantachrome) and the values of micropore volume, V_{N2} and V_{CO2}, were calculated by application of the Dubinin−Radushkevich (DR) equation.[23] The distribution of micropore size has been obtained by application of the nonlocal density functional theory (DFT) to the adsorption of N_2 at −196 °C with the software provided by Quantachrome, developed by Neimark and co-workers.[24] The volume of mesopores has been determined by subtracting the volume of micropores V_{N2} from the amount adsorbed at a relative pressure of 0.95.

The adsorption isotherms for CH_4 at 25 °C were determined experimentally in a high-pressure volumetric adsorption system (HPA100, from VTI), and the helium density of the adsorbents was determined at 25 °C in an Accupyc 1330, from Micromeritics.

3. Results and Discussion

3.1. Characterization of Pore Size. The four series of activated carbons were selected to cover a wide range of composition and microporosity. Thus, carbons of series 1 and 2 were carbonized at 450 and 500 °C, respectively, temperature which is not enough to transform the lignocellulosic precursor into carbon; on the contrary, carbons from series 3 and 4 were constituted mainly by carbon since they were treated at 800 °C.[25] The range of activation has been changed within each series, so that a wide range of micropore size distribution and pore volume could be covered. To show the variety of pore structure produced by the different activation processes, the data corresponding to four activated carbons, one from each series, are given in Table 1. The degree of activation of carbons 1 and 2 was low; consequently, the pore volume is not high and it mainly corresponds to micropores since the volume of mesopores is almost nil. On the other hand, the helium density is lower than for average activated carbons, thus showing the incomplete transformation of the lignocellulosic material into carbon at the relatively low temperature used in carbonization.[21,22]

Carbons 3 and 4 have a larger degree of activation and the volume of micropores is high even though activation has produced some micropore enlargement into mesopores. These carbons exhibit a wide micropore size distribution extending to the mesopore range, with a considerable volume. The helium density values indicate that the carbonization process is almost complete.[21,22]

The DFT pore size distribution in Figure 1 provides additional information for these four carbons. All distributions exhibit a maximum at about a pore width of 1.1 nm, and the area under the distributions corresponding to volume adsorbed follows the order for V_{N2} given in Table 1. The shape of the four curves for values of pore width below 1.1 nm is almost identical, exhibiting a shoulder peak at a pore width of 0.6 nm, which can be considered as a model-induced artifact because of the slit-shaped microporosity.[26] Essential differences are observed for wide micropores and narrow mesopores at values of pore width above 1.1 nm. Contribution of these wide micropores and especially narrow mesopores is lower in carbons 1 and 2, in contrast to carbons 3 and 4 (see also volume of mesopores in Table 1). The "mean pore size" has been calculated from the

plots of Figure 1, by calculating the area below the curves and drawing a vertical line dividing the area into halves. The data in Table 1 show that the calculated values are very near the maximum in the curves 1 and 2 but larger for the other two carbons.

The information provided by Figure 1 cannot be easily related to the methane adsorption capacity exhibited by the activated carbon. A good alternative analysis of the micropore size distribution of activated carbon can be carried out by comparing the micropore volume determined by adsorption of N_2 at −196 °C (V_{N2}) and CO_2 at 0 °C (V_{CO2}). As confirmed in previous reports,[27] V_{N2} corresponds to the total microporosity of the carbon whereas V_{CO2} corresponds to the narrow microporosity, up to 2 molecular dimensions, around 0.7 nm in this particular case. Consequently, the similarity of V_{N2} and V_{CO2} values for carbon 1 indicates that that the microporosity is narrow and homogeneous. V_{N2} is larger for carbons 3 and 4 than V_{CO2} and consequently the microporosity is wide and heterogeneous, especially in carbon 3 (larger difference); carbon 2 is somewhat intermediate, with both values relatively similar. All activated carbons lie within the range of these four carbons. Figure 2
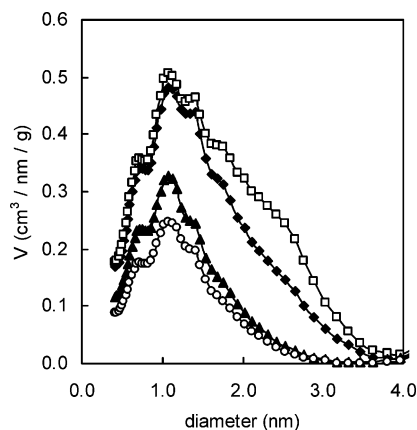

Figure 1. Micropore size distribution of some activated carbons by application of DFT to adsorption of N_2 at −196 °C (○, carbon 1; ▲, carbon 2; □, carbon 3; ◆, carbon 4).
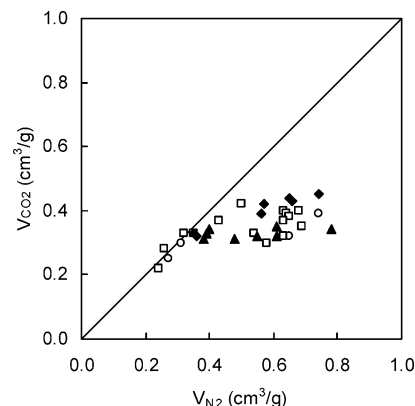

Figure 2. Comparison of the micropore volume deduced from the adsorption of N_2 at −196 °C and CO_2 at 0 °C (○, series 1; ▲, series 2; □, series 3; ◆, series 4).
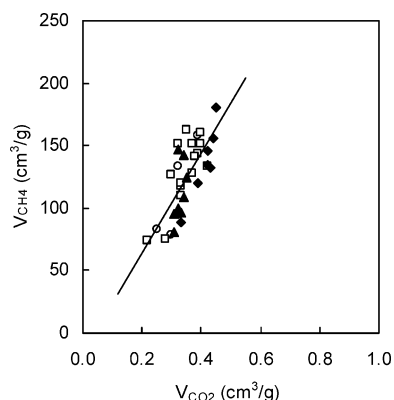
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Figure 3. Correlation between the volume of CH_4 adsorbed at 3 MPa and the micropore volume deduced from the adsorption of CO_2 at 0 °C. (○, series 1;▲, series 2;□, series 3;◆, series 4).
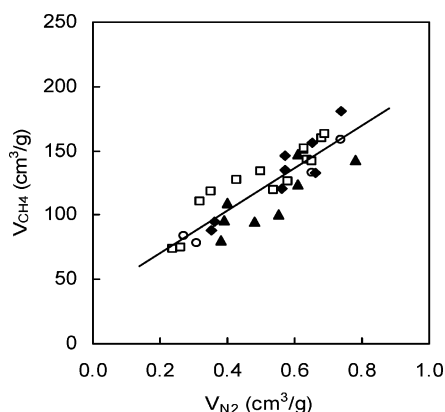

Figure 4. Correlation between the volume of CH_4 adsorbed at 3 MPa and the micropore volume deduced from the adsorption of N_2 at −196 °C. (○, series 1;▲, series 2;□, series 3;◆, series 4).

includes the values of V_{N2} and V_{CO2} for all 35 carbons, with the line corresponding to slope unity, as reference.

The information from Figure 2 can be summarized as follows: (a) When the volume of micropores is below 0.32 cm^3/g, both V_{N2} and V_{CO2} are similar, indicating a narrow microporosity. This is common for carbons with a low degree of activation, independently of the activation method used.[27] (b) When the volume of micropores is high, V_{N2} is larger than V_{CO2}. Thus, the values of V_{N2} become larger than 0.7 cm^3/g whereas V_{CO2} ranges from 0.33 to 0.44 cm^3/g. Furthermore, the differences among the values of V_{CO2} within a series are very small, with series 1 and 2 showing smaller values than series 3 and 4.

3.2. Methane Adsorption. Since the microporosity of activated carbon is critical in the adsorption of methane at room temperature, the relationship is shown in Figures 3 (for V_{CO2}) and 4 (for V_{N2}). The methane uptake was determined at 3 MPa. The best-fit straight line in Figure 3 has a low correlation coefficient, $R^2 = 0.55$, which means that carbons with the same value of V_{CO2} (for instance around 0.3 cm^3/g) adsorb very different amounts of methane, from 70 to 150 cm^3/g. On the other hand, the slope is high and consequently a large increase in methane uptake means only a small variation in V_{CO2}. The conclusion is that the volume of narrow micropores, V_{CO2}, is not a good indicator to predict the amount of methane that a carbon can adsorb at 3 MPa.

The best-fit line in Figure 4 has $R^2 = 0.80$ and the methane uptake increases linearly with V_{N2}, as suggested by other authors.[3,5,7,8,11,12] However, the intercept of the straight line is positive (at $V_{CH4} = 37$ cm^3/g). The same applies to the plot of

V_{CH4} versus surface area, the intercept corresponding then to 65 cm^3/g. This peculiarity has been described in the literature, and it is probably due to the fact that the packing of the adsorbed phase changes from one pore size to another, because if it is only a function of the micropore volume the straight line should go through the origin.[3−5,7,9,12] The tendency observed in Figure 4 indicates that the ratio V_{CH4}/V_{N2} is high when V_{N2} is small and low when V_{N2} is large. Consequently, if the density of adsorbed methane at 3 MPa is calculated as the ratio of the mass of methane adsorbed to the volume of micropores measured as V_{N2}, different values will be obtained according to the homogeneity/heterogeneity of the microporosity.[6,8,11,12] As an example, Table 1 includes the methane density so calculated, ranging from 0.14 to 0.19 g/cm^3, as an approximate function of the micropore size. Furthermore, a detailed inspection of Figure 4 reveals that carbons from series 1 and 2 are predominant below the straight line, whereas carbons for series 3 and 4 are basically above the line. As shown in Figure 2, the latter series exhibit larger volumes of narrow micropores than series 1 and 2, thus indicating the dependence of the amount of methane adsorbed at 3 MPa on the micropore size.[3−5,13,15]

3.3. Estimating Densities of Methane in Pores. Although Figure 4 may be a guide to predict the adsorption capacity of an activated carbon for methane at 3 MPa if the volume of micropores is known, the fit of the experimental points to the straight line is not excellent. This is due, partially, to the fact that the adsorption isotherms have different curvature, meaning that the pressure selected will condition the adsorbed volume. It is expected that the relationship should increase if the volume of micropores is plotted versus the maximum amount of methane adsorbed by the carbon. This value can be extrapolated from the adsorption isotherm at 25 °C simply by application of the models describing type I isotherms, for example, Langmuir or Dubinin−Radushkevich.[28]

Application of the Langmuir model to the adsorption isotherms of methane at 25 °C (plot of P/V versus P) leads to straight lines for all carbons described here, thus permitting the calculation of the Langmuir monolayer volume, V_L. This value does not have the classical meaning corresponding to the Langmuir model, but it is simply a parameter that can be associated with the maximum adsorption capacity.[3]

Values of V_L for all activated carbons have been plotted in Figure 5 as a function of the total volume of micropores. Comparison with Figure 4 indicates that the values of V_L are only slightly larger than the amount adsorbed at 3 MPa when V_{N2} is small, whereas for carbons with high values of V_{N2} (wider
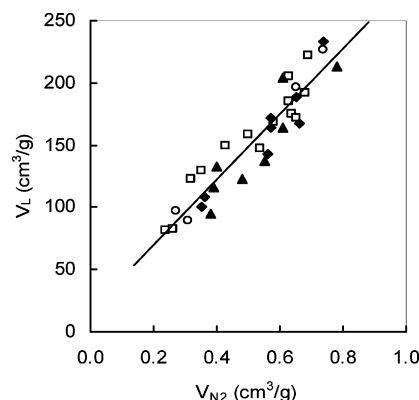

Figure 5. Correlation between the volumes of CH_4 calculated by application of the Langmuir model, V_L, and the micropore volume deduced from the adsorption of N_2 at −196 °C. (○, series 1;▲, series 2;□, series 3;◆, series 4).
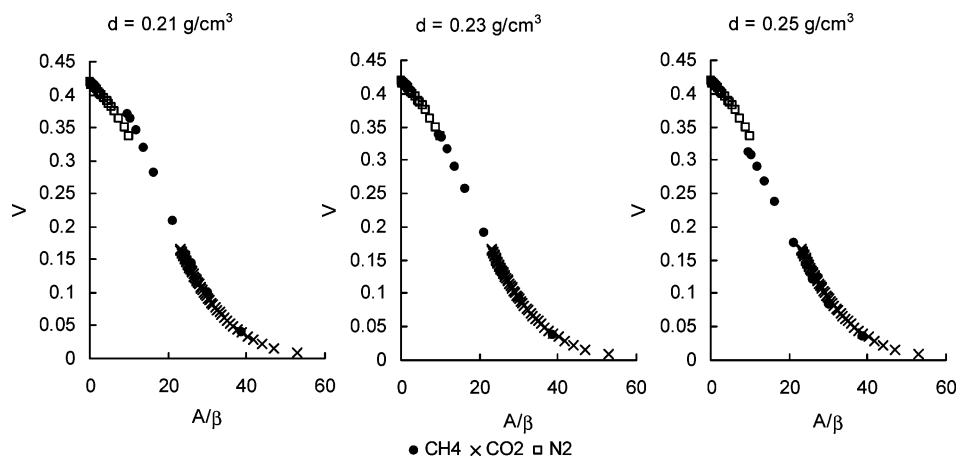
Figure 6. Characteristic curve of an activated carbon where three different values of methane density have been proposed. The best fitting is the one in the middle, $d = 0.23$ g/cm^3.

and more heterogeneous microporosity) the differences become more important. For this reason the slope in Figure 5 is larger and the intercept (17 cm^3/g) is lower than in Figure 4. This shows that even when the pressure is high the density of the adsorbate is a function of the adsorbent, but the variations are smaller than those registered at 3 MPa. Thus, if the density of the adsorbate is calculated as the ratio of the methane mass (V_L converted to mass) to the volume of micropores V_{N2}, different values are obtained for all carbons, but all of them range between 0.20 and 0.23 g/cm^3.

The Dubinin model[23] assumes the filling of micropores during the adsorption process with the adsorbate in liquid state. Consequently, application to the adsorption isotherms for gases above the critical temperature requires some modifications. The first one is the calculation of the so-called pseudo-saturation pressure, and Dubinin[23] proposed the empirical equation $P_S = (T/T_c)^2 P_c$; the second one is to express the adsorption potential in terms of fugacity instead of pressure. The thus-modified DR equation has been applied to the adsorption isotherms of methane at 25 °C; the DR plots were linear and extrapolation led to the micropore volume V_0, which is associated with the maximum capacity to adsorb methane. The values for all carbons can be plotted as a function of micropore volume (V_{N2}) as in Figure 5, but it was decided to use Dubinin's concept of characteristic curve to deduce the density of the adsorbate. The characteristic curve for each carbon has been defined by using the adsorption isotherms of N$_2$ at −196 °C and CO$_2$ at 0 °C and plotting the volume of liquid adsorbate versus the adsorption potential (density values for N$_2$ and CO$_2$ were taken as 0.808 and 1.023 g/cm^3, and β values were taken as 0.33 for N$_2$ and 0.35 for CO$_2$ and CH$_4$).[23] The experimental points for the adsorption isotherm of CH$_4$ at 25 °C have been included in the plots for all carbons, calculating the best value of density that adjusts to the characteristic curve, as shown in Figure 6 for a typical carbon in which three values of density were selected (in this case the density best fitting the plot is 0.23 g/cm^3). The density of adsorbed methane thus obtained ranged from 0.21 to 0.27 g/cm^3 for the 35 carbons.

In 24 of the 35 carbons studied, the best fitting was found when the density selected for adsorbed methane was 0.23−0.25 g/cm^3. If the carbons are analyzed by series, one can find that the most probable density for series 1 and 2 is 0.23 g/cm^3, whereas it is 0.25 g/cm^3 for carbons of series 3 and 4, with a ±0.02 g/cm^3 span that can be associated with differences in micropore size distribution. A simulation study of the adsorption of methane on microporous carbons[15] has shown that the density of the adsorbate decreases with decreasing density of carbon
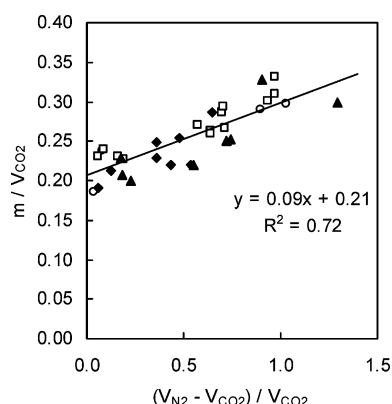

Figure 7. Graphical method to determine the density of the methane adsorbed in the micropores.

atoms in the surface of the pores. It is then probable that the differences found between the carbons of the four series are due to the fact that those of series 1 and 2 are undercarbonized, in contrast with carbons of series 3 and 4, carbonized at 800 °C, and with a lower content in superficial oxygen and hydrogen. The density of adsorbed methane in carbons of series 3 and 4 approaches the maximum value proposed by some authors,[3] 0.28 g/cm^3.

Taking into consideration the importance of the micropore size in the density of adsorbed methane, we propose now an experimental method to determine such density. The main idea of the method is to divide the microporosity into two different parts, one corresponding to narrow micropores (up to twice the molecular dimension of methane, 2σ), quantified as V_{CO2}, and a second one corresponding to wide micropores (up to 5σ), quantified as ($V_{N2} - V_{CO2}$). The mass of adsorbed methane (m) at a given pressure is then distributed into the micropores according to

$$m = d_n V_{CO2} + d_w (V_{N2} - V_{CO2}) \quad (1)$$

where d_n and d_w are the values of density in narrow and wide micropores, respectively. The equation may be also expressed as

$$m/V_{CO2} = d_n + d_w (V_{N2} - V_{CO2})/V_{CO2} \quad (2)$$

and the values of d_n and d_w can be calculated graphically.

The application of this method is shown in Figure 7 where m is the mass of methane adsorbed at 3 MPa, as deduced from the adsorption isotherm. The intercept on the ordinate and the
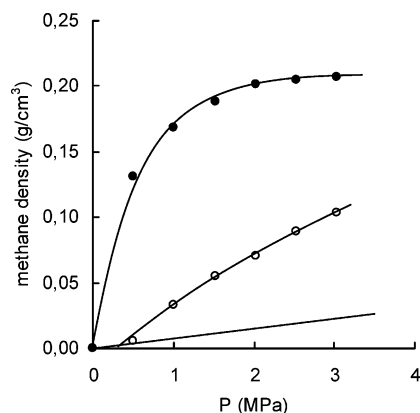
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Figure 8. Evolution of the density of the adsorbed methane with pressure:●, narrow micropores;○, wide micropores;─, compressed gas.

slope give the density in narrow micropores, 0.21 g/cm^3, and the average density in wide micropores, 0.09 g/ cm^3, respectively, at 3 MPa. These values have been deduced from the data of 35 carbons and are not specific for any given carbon. The deviation of each carbon with respect to the line in Figure 7 is very probably due to the simplification used to consider only two ranges of micropore size.

By applying the same procedure to the adsorption of methane at different pressures, plots similar to those of Figure 7 have been plotted and the values of d_n and d_w have been deduced. Figure 8 shows the evolution of density of the adsorbate with adsorption pressure and, for comparison, the density of compressed methane. Although there is a logical increase in density with adsorption pressure, d_n increases faster up to 1 MPa and slowly thereafter, whereas d_w increases continuously above 1 MPa. Simulation studies on model microporous carbons[3,15] showed that the density of adsorbed methane increases with pressure and at 3 MPa the density in pores able to accommodate two layers of molecules is 0.27 g/cm^3, somewhat higher than the value found here, 0.21 g/cm^3. Such value decreases down to 0.09 g/cm^3 when the pore size is equivalent to 6 times the molecular dimensions. In any case the density values are below the value corresponding to liquid methane at −161 °C, 0.42 g/cm^3.

By applying this method to the maximum capacity of adsorption for methane, V_L, similar values for d_n and d_w have been obtained, 0.23 and 0.21 g/cm^3, respectively. Consequently, the density at high pressures does not seem to be very different for the two types of porosity. Simulation studies[15] have shown that the density of adsorbed methane reaches values of 0.30 g/cm^3 at 10 MPa in pores equivalent to 2 and 6 molecular dimensions.

4. Conclusions

The amount of methane adsorbed at 3 MPa has been related to the volume of micropores deduced from the adsorption of N$_2$ at −196 °C (V_{N2}) and CO$_2$ at 0 °C (V_{CO2}). Results indicate that methane is adsorbed in all micropores, a linear relationship existing between the uptake and the values of V_{N2}. However, the positive intercept of the straight line is a consequence of the different density in narrow and wide micropores, higher for the former.

The density of the adsorbed methane has been calculated by a graphic method from data for 35 selected activated carbons covering a wide range of micropore size distributions. The density for methane adsorbed in narrow micropores at 25 °C reaches a value of 0.21 g/cm^3, a value near the one calculated by application of the Langmuir equation (0.20−0.23 g/cm^3) or Dubinin−Radushkevich equation (0.23−0.25 g/ cm^3). The average density of methane in wide micropores is much lower, 0.09 g/cm^3, and it increases continuously with pressure.

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