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Adsorption Energy and Pore-Size Distributions of Activated Carbons Calculated Using Hill's Model

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ABSTRACT: An integral equation derived using a statistical physics treatment by considering the adsorption energy distribution (AED) was used to model the adsorption of ethylene and ethane on resorcinol–formaldehyde-based activated carbon xerogels. Hill's model was taken as a local adsorption isotherm. This model was based on a grand canonical ensemble. Then a relationship between the energetic and the structural heterogeneities is used to determine the pore-size distribution (PSD) function. The AED and PSD obtained illustrate the greater affinity of activated carbon for adsorption of ethylene compared to ethane. In addition, this method was applied to determine the PSD of the British Drug House (BDH) activated carbon. The behaviour of the obtained PSDs at different temperatures was examined and related to the adsorption capacity of BDH activated carbon towards ethane, methane and nitrogen.

1. INTRODUCTION

Separation and purification of gas mixtures by adsorption has become a major process in many chemical and petrochemical industries (Yang 1987; Sitprasert *et al*. 2011). Physical adsorption offers a very promising solution for lowering the storage pressure of compressed gas fuels such as natural gas, which is considered as an appropriate alternative fuel due to its wide availability, low price and low harmful gas emission.

The choice of an adsorbent plays a central role in both process design (for achieving efficient output) and economics (cost). Microporous solids, such as activated carbons, are reported to show promise for separation processes and natural gas storage, because they have a strong heterogeneous surface and a large microporous volume (Sircar *et al*. 1996). The activation processes in the carbon matrix makes its surface microporous and creates a very high surface area with an intricate network of small pores. Therefore, there are two approaches to describe the heterogeneity of activated carbons. One approach uses an adsorption energy distribution (AED) concept, whereas the other uses a pore-size distribution (PSD) to describe its structural heterogeneity. The AED has been studied by many authors (Dormant and Adamson 1977; Morrison and Ross 1977; House *et al*. 1982; Jaroniec 1983; Jaroniec and Madey 1988; Tikhonov and Arsenin 1997; Rudzinski *et al*. 2000) by applying different methods. The most widely used method is the condensation approximation approach (Tikhonov and Arsenin 1997; Rudzinski *et al*. 2000). The AED can also be derived by applying advanced numerical algorithms (Dabrowski *et al*. 2003), which are based on the local adsorption isotherm. Some of these isotherm equations are based on theories of adsorption mechanism, whereas others are purely empirical, or semi-empirical, such as the Langmuir model, Freundlich model and other models (Diu *et al*. 1989;

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Vasanth Kumar *et al*. 2010, 2011). A detailed search of the literature indicated that the description of an adsorption isotherm by these models is not sufficient for rigorous engineering design of the adsorption process.

By contrast, many studies were carried out to understand the relationship between the microstructure of activated carbons and their adsorption capacity (Prinz and Littke 2005). Establishing new adsorption theories to determine the PSD, with clear physical insight and theoretical basis, as well as less computational time, continues to be a huge challenge. Advanced computational methods such as density functional theory (DFT; Ravikovitch *et al*. 1998; Ravikovitch and Neimark 2000) or Monte Carlo simulation (Gusev *et al*. 1997; He and Seaton 2005) have been applied by several authors, based on their application to the textural characterization of porous media in relation to adsorption data of several molecules. The first method is based on a mean field approximation of fluid–fluid attraction, but applying this model may produce inaccurate results for fluids confined within very small pores. The second method models actual molecular microscopic configurations of the confined fluid using realistic intermolecular interaction potentials.

The aim of this study was to describe the heterogeneity of the copper-based resorcinol–formaldehyde activated carbon xerogel (Cu-based activated carbon xerogel). This adsorbent was synthesized by Al-Muhtaseb (2008) by applying the sol–gel synthesis method and using a homogeneous, copper-based, catalyst solution. The adsorption of ethylene and ethane on this xerogel at 333.15 K was investigated by determining the AED. For this purpose, we have developed a methodology that helps to determine the integral equation using a statistical physics approach. The Hill's isotherm, which was obtained by applying the grand canonical ensemble in a statistical physics approach (Couture and Zitoun 1992; Ben Lamine and Bouazra 1997; Khalfaoui *et al*. 2003), was used as a local isotherm. The advantage of applying this model is that it gives a physical meaning to the parameters involved in the model as well as new interpretations for the adsorption of gases at the molecular level. In the second step, a PSD function was derived by applying a relationship between the adsorption energy and the pore width. We have adopted the slit-shaped pore model because it not only represents a physically plausible pore shape, but is also the simplest pore model that can fit the experimental data for adsorption on carbon surfaces (Sweatman and Quirke 2001). The PSD function was incorporated into the integral equation with the objective to fit experimental isotherms and to determine the corresponding PSD. It is important to stress the fact that this method is not intended to mimic the real porous structure of activated carbon, but is rather an idealization intended to reproduce, with a maximum degree of accuracy, the performance of this adsorbent. The AED and PSD were obtained by applying advanced numerical algorithms (numerical method). This numerical method also provides the fitting of the experimental isotherm, in addition to the AED and PSD. Moreover, this method is economical when considering the time spent on calculations, with outcomes consistent with the results obtained at the molecular level, thereby making it a suitable option for industrial applications.

In the second part of this work, we have characterized the commercial adsorbent, that is, British Drug House (BDH) activated carbon. The behaviour of the obtained PSD of BDH activated carbon was investigated and interpreted with regard to its adsorption of ethane, methane and nitrogen.

2. MATERIALS

In the first part of this work, as mentioned earlier, we are interested in determining the AED and PSD of Cu-based activated carbon xerogel for the adsorption of ethylene and ethane at 333.15 K.

The adsorbent was synthesized by applying the sol–gel synthesis method using a homogeneous, copper-based, catalyst solution (Al-Muhtaseb 2008). The resorcinol–formaldehyde xerogel was then carbonated and activated to produce a copper-based resorcinol–formaldehyde activated carbon xerogel. This activated carbon xerogel was characterized by its very small particle size and very small density.

In the second part, the PSDs of BDH activated carbon were determined with regard to its adsorption of ethane, methane and nitrogen at different temperatures (Al-Muhtaseb *et al*. 2007). This activated carbon is a commercial adsorbent.

3. DETERMINATION OF AED USING A STATISTICAL PHYSICS TREATMENT

In order to describe adsorption on energetically heterogeneous surfaces, the Langmuir model is usually used as the local adsorption isotherm model (Vasanth Kumar *et al*. 2010). However, this model only expresses a simple and particular adsorption process in which a receptor site interacts with only one (but whole) adsorbate molecule. In order to describe the general case, that is, for a process in which many molecules are adsorbed on one receptor site or one molecule can be anchored to many receptor sites, the AED was proposed using the Hill's model as local isotherm. This model was established by applying the grand canonical ensemble in a statistical physics approach (Couture and Zitoun 1992). To treat such an adsorption problem with a statistical physics approach, the following assumptions are made (Couture and Zitoun 1992; Ben Lamine and Bouazra 1997):

- During this phase, we consider that a variable number of molecules N are adsorbed onto N_m receptor sites per mass unit of adsorbent as it is imposed by the grand canonical ensemble.
- In our treatment, the starting point is the grand canonical partition function describing the microscopic states of the studied adsorption system, because the adsorbed quantity is variable and it corresponds to a thermodynamically open system.
- A receptor site is supposed to be empty or occupied with adsorption energy $-\varepsilon$ and a chemical potential μ. For this reason, we define the state of occupation N_i and it is assumed that any given receptor site can be either empty or occupied, and consequently N_i takes the value of either 0 or 1.

The grand canonical partition function in this case, for only one site, has the following form (Ben Lamine and Bouazra 1997; Khalfaoui *et al*. 2003):

$$z_{gc} = 1 + \exp\left[\beta(\varepsilon + \mu)\right] \tag{1}$$

where β is the Boltzmann factor, and for N_m identical and independent receptor sites, the total grand canonical partition function describing the microscopic states of the system is as follows (Ben Lamine and Bouazra 1997; Khalfaoui *et al*. 2003):

$$Z_{gc} = \left\{1 + \exp\left[\beta(\varepsilon + \mu\right]\right\}^{N_m} \tag{2}$$

The mean occupation number for N_m identical receptor sites is therefore given as follows:

$$N_0 = K_B T \frac{\partial \mathrm{In}(z_{gc})}{\partial \mu} \tag{3}$$

From equation (3), the following is obtained:

$$N_0 = \frac{N_m}{1+\exp\left[-\beta(\varepsilon+\mu)\right]} \tag{4}$$

The chemical potential is related to the gas pressure by the following relationship (Ben Lamine and Bouazra 1997; Khalfaoui *et al*. 2003):

$$\exp(\beta\mu) = \frac{P}{z_{gtr}RT} \tag{5}$$

As a result, the adsorbed quantity is written as a function of the gas pressure as follows:

$$Q_a = nN_0 = \frac{nN_m}{1+(P_{1/2}/p)^n} = \frac{Q_{asat}}{1+(P_{1/2}/p)^n} \tag{6}$$

where N_m is the density of the effectively occupied sites per mass unit of adsorbent and not necessarily all the existing ones; Q_{asat} is the quantity adsorbed at saturation and n is the fraction (or number) of adsorbed molecule(s) per site. Furthermore, n is a stoichiometric coefficient involved in the adsorption reaction.

$$nA + S \rightleftharpoons A_nS \tag{7}$$

where A represents the adsorbate molecule and S is the receptor site.

$P_{1/2}$ is the pressure at half-saturation, which is related to the adsorption energy E by

$$P_{1/2} = P_0 \exp(-E/RT) \tag{8}$$

where P_0 is the saturated vapour pressure, R is the universal gas constant and T is the absolute temperature.

In this method, we suppose that E can vary from E_{min} to E_{max}. Then, the total amount of adsorbed molecules is equal to

$$Q_a = \sum_i Q_{ai}(E_i) \tag{9}$$

where Q_{ai} is the partially adsorbed quantity on the i^{th} adsorptive site which is given by

$$Q_{ai} = \frac{n_i N_{mi}}{1+\left[\frac{P_0 \exp(-E_i/RT)}{P}\right]^{n_i}} \tag{10}$$

As Q_{ai} depends on the value of energy of adsorption E_i, $Q_{ai}(E_i)$ can be written as follows using a Dirac distribution $\delta(E - E_i)$ and its integral property (Benoist and Courbage 1992; Ben Torkia *et al*. 2014a):

$$Q_a = \int_{E_{min}}^{E_{max}} \sum_i \frac{n_i N_{mi}}{1+\left[\frac{P_0 \exp(-E_i/RT)}{P}\right]^{n_i}} \delta(E-E_i)dE \tag{11}$$

Assuming in a first approach that all n_i's are identical to n, in which case it can be considered a mean value of all different n_i's

$$Q_a = \int_{E_{min}}^{E_{max}} \frac{n}{1+\left[\frac{P_0 \exp(-E/RT)}{P}\right]^n} dE \sum_i N_{mi}\delta(E-E_i) \tag{12}$$

Finally, we set $$N'_m(E) = \sum_i N_{mi}\delta(E-E_i) \tag{13}$$

with $N_m'(E)$ being the energetic density of the spatial density of sites $N_m(E)$. We can then say that the adsorption on a heterogeneous adsorbent is described by $N_m'(E) = N_m f(E)$,
where f(E) represents an AED function.

Then we have

$$Q_a = \int_{E_{min}}^{E_{max}} \frac{n}{1+\left[\frac{P_0 \exp(-E/RT)}{P}\right]^n} N_m f(E)\, dE \tag{14}$$

where Q_a represents the experimentally adsorbed quantity measured at the temperature T and the equilibrium pressure P; E is the adsorption energy; and E_{min} and E_{max}, respectively, are the lower and higher limits of the energy band in the energy space.

An algorithm has been developed to obtain the energy distribution function from an adsorption isotherm. This method has two outcomes. The first is the fitting of experimental isotherm with an integral model. The second is the calculation of the AED.

A priori, the function f(E) can be any complicated shape. However, in the first approach it can be approximated by a simple normal Gaussian function. It is characterized by the two parameters, namely, E_0 and σ

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right] \tag{15}$$

This function presents a maximum for $E = E_0$ and σ is the dispersion of the Gaussian distribution, which is also called the *heterogeneity parameter*.

It is clear that the integration of equation (15) is equal to unity

$$\int_{E_{min}}^{E_{max}} f(E)\, dE = 1 \tag{16}$$

By incorporating equation (16) into equation (14) we obtain

$$Q_a = \int_{E_{min}}^{E_{max}} \frac{nN_m}{1+\left[\frac{P_0 \exp(-E/RT)}{P}\right]^n} \frac{\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right]}{\sigma\sqrt{2\pi}} dE \tag{17}$$

The AEDs are obtained by applying a numerical integration method. This method allowed us to determine the four parameters in equation (17), namely, n, N_m, E_0 and σ. Our objective is to obtain the correct values of these four parameters. This result is based on the values of the average relative error (ARE), which is given as follows (Al-Muhtaseb *et al*. 2007):

$$ARE = \frac{100}{m}\sum_{i=1}^{m}\left(\frac{\left|Q_{acalc} - Q_{aexp}\right|}{Q_{aexp}}\right)_i \tag{18}$$

where Q_{acalc} and Q_{aexp} are the calculated and experimental adsorbed quantity, respectively, at an equilibrium pressure P, and m is the total number of points for each component. The summation is extended over all the experimental points of the isotherm.

4. DETERMINATION OF THE PSD

To determine the PSD, we must first relate the adsorption energy to the pore width. This relation can be obtained using the Kelvin equation (Russell and Levan 1994)

$$In\left(\frac{P}{P_0}\right) = \frac{-2\gamma V_m}{rRT} \tag{19}$$

where P is the pressure, P_0 is the saturated vapour pressure, γ is the surface tension, V_m is the molar volume, T is the temperature, R is the universal gas constant and r is the radius of the pore.

The Kelvin equation gives the change in saturated vapour pressure due to the liquid/vapour interface radius whenever a capillary condensation occurs, and therefore a direct relationship between pressure and pore radius is established.

In the literature we find that this equation is applied in the case of mesoporous materials. However, in the case of microporous carbons, the Kelvin equation should be replaced by another relationship that relates pressure and pore radius. This is achieved by other relationships deduced by applying Polanyi equation (Manes and Hofer 1969) and Lennard-Jones potential (Katsumi *et al*. 1992). Therefore, many complex equations were developed from the sum of the Lennard-Jones interaction between the atoms in the solid and a single molecule in the gas phase (Everett and Powl 1976). Using these equations, we can relate the adsorption energy to the pore size (Chen and Yang 1996).

In this work, we have initially adopted the Kelvin equation to identify the relationship between the adsorption energy and the pore size.

The implication of using this relation is perhaps a deficiency in accurately predicting the microporous zone; however, this imprecision is negligible because the number of adsorbate molecules could still define a meniscus of condensation.

By contrast, the approximation of Cerofolini relates the adsorption energy to the pressure by the following equation (Cerofolini 1974; Vasanth Kumar *et al*. 2010):

$$In\left(\frac{P}{P_0}\right) = -\frac{E}{RT} \tag{20}$$

By applying the equality of equations (19) and (20), the following equation is obtained:

$$\frac{E}{RT} = \frac{2\gamma V_m}{rRT} \tag{21}$$

Whence

$$E = \frac{constant}{r} \tag{22}$$

where constant = $2\gamma V_m/RT$.

In order to apply the numerical method for the determination of the PSD from experimental isotherms, we adopt, in the first step, the previous relationship between the energy and pore size by stating that

$$E = \frac{k}{w} \tag{23}$$

where w is pore width and k is the characteristic constant for a defined adsorbate/adsorbent pair.

By differentiating equation (23), we obtain

$$dE = -\frac{k}{w^2}dw \tag{24}$$

Finally, the integral equation is given as follows:

$$Q_a(p) = \int_{w_{min}}^{w_{max}} \frac{nN_m}{1+\left[\frac{P_0 \exp(-k/wRT)}{P}\right]^n} \frac{k}{w^2\sigma\sqrt{2\pi}} \exp\left[-\frac{\left(\frac{1}{w}-\frac{1}{w_0}\right)^2}{2\sigma^2}k^2\right] dw \tag{25}$$

$$Q_a(p) = \int_{w_{min}}^{w_{max}} \frac{nN_m}{1+\left[\frac{P_0 \exp(-k/wRT)}{P}\right]^n} g(w)\,dw \tag{26}$$

Using the PSD function, g(w) can be written as follows:

$$g(w) = \frac{k}{w^2\sigma\sqrt{2\pi}} \exp\left[-\frac{\left(\frac{1}{w}-\frac{1}{w_o}\right)^2}{2\sigma^2}k^2\right] \tag{27}$$

We can suppose that

$$n\,N_m g(w) = Q_{asat}\,g(w) = Q'_{asat}(w) \tag{28}$$

Then

$$Q'_{asat}(w)\,dw = dQ_{asat}(w) \tag{29}$$

Thus, the integral equation can be written as follows:

$$Q_a(p) = \int_{w_{min}}^{w_{max}} \frac{1}{1+\left[\frac{P_0 \exp(-k/wRT)}{P}\right]^n} Q'_{asat}(w)dw \tag{30}$$

$Q'_{asat}(w)$ is the density of the adsorption capacity in the pores that have a width between w and w + dw.

$$\int_{E_{min}}^{E_{max}} d\,Q_{asat}(w) = Q_{total} \tag{31}$$

where Q_{total} is the total adsorbed quantity at saturation or the total adsorption capacity.

To determine the corresponding parameters {n, N_m (Q_{asat} dw = nN_m), k, w_0 and σ} from each experimental isotherm and the PSDs, we have developed an adequate algorithm. A numerical integration method is then used to solve equation (25) and to extract the corresponding parameters. This method is directly applied to the measured raw adsorption data. The results are checked by comparing the calculated adsorbed quantity, Q_{acalc}, and the experimental adsorbed quantity, Q_{aexp}, at an equilibrium pressure P by applying the ARE [equation (18)].

5. RESULTS AND DISCUSSION

5.1. AED of Cu-Based Activated Carbon Xerogel for Adsorption of Ethane and Ethylene

Figure 1 shows the experimental and the fitted isotherms. We notice that the numerical method gives good results for the fitting of adsorption isotherms. The fitting parameters in equation (17) and the corresponding ARE values are illustrated in Table 1.

The ARE values obtained are 11.32% for ethane and 3.24% for ethylene (Table 1), which are considered very low. Table 1 indicates that ethane or ethylene molecules are never adsorbed in a parallel configuration relative to the surface of adsorbent, because n is always superior to 1, meaning that one receptor site is occupied by more than one molecule. Indeed the values of n may be greater or less than unity and the molecule has several ways to be anchored onto the receptor sites. If $n < 1$, the molecule is adsorbed in a parallel configuration relative to the surface; and if $n \geq 1$, the molecule is adsorbed in a vertical (or not parallel) configuration relative to the surface.

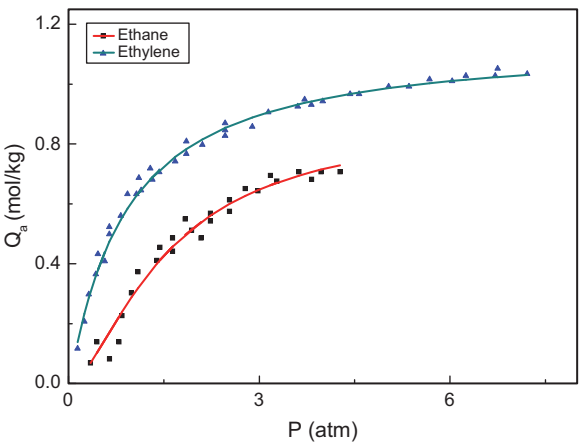

Figure 1. Comparison of experimental isotherms (symbols) with correlated equations (lines) in the case of adsorption of ethylene and ethane on Cu-based activated carbon xerogel at 333.15 K.

TABLE 1. Fitting Parameters Obtained by the AED Method for the Adsorption of Ethane and Ethylene on Cu-Based Activated Carbon Xerogel at 333.15 K

	E_0 (kJ/mol)	σ (kJ/mol)	N_m (mol/kg)	n	ARE (%)
Ethane	10.22 (±1.15)	1.02 (±0.11)	0.45 (±0.05)	1.85 (±0.20)	11.32
Ethylene	12.12 (±0.39)	1.57 (±0.05)	0.95 (±0.03)	1.18 (±0.03)	3.24

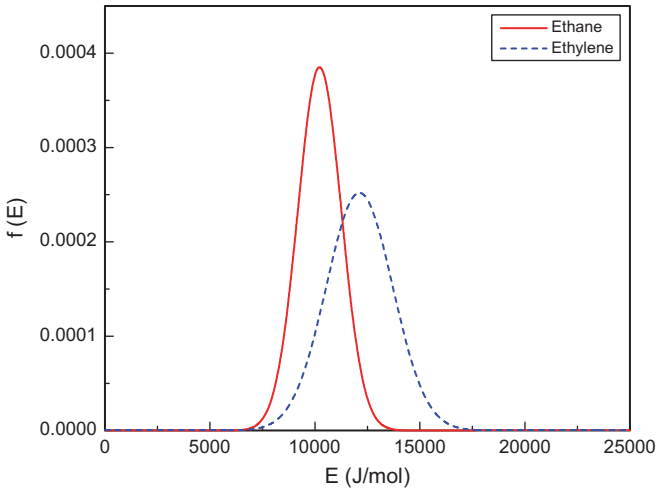

Figure 2. AEDs obtained in the case of adsorption of ethane and ethylene on Cu-based activated carbon xerogel at 333.15 K.

In the case of ethane, n seems to be significantly higher than 1 and in the case of ethylene n is close to 1; however, because the value of n for these two molecules exceeds 1, these molecules cannot be adsorbed parallel to the surface.

By contrast, the value of the density of effectively occupied sites (N_m) obtained in the case of ethane is only half of that obtained in the case of ethylene. From this, it can be deduced that the sites of this adsorbent are more saturated in the case of adsorption of ethylene.

Figure 2 shows the comparison of the AED for the two molecules. It can be seen that ethylene has the highest energies of adsorption on the xerogel. We deduce strong interactions between molecules of ethylene and the surface of the Cu-based activated carbon xerogel as compared with ethane. This is due to the interactions between the double bond of ethylene molecules and copper.

5.2. AED of BDH Activated Carbon

Table 2 presents the values of the fitting parameters in equation (17) and the corresponding ARE in the case of adsorption of ethane, methane and nitrogen on BDH activated carbon at different temperatures. A complete description of the statistical interpretation of the AEDs of ethane, methane and nitrogen at different temperatures is given elsewhere (Ben Torkia *et al*. 2014a).

5.3. PSDs of the Activated Carbons

To determine the PSD, an experimental isotherm of nitrogen adsorption at 77 K is routinely used. However, studies have further shown that for the same porous adsorbent, different gas probes may give different PSDs (Lastoskie *et al*. 1993; Heuchel *et al*. 1999). For example, there is an obvious difference between the PSDs obtained from nitrogen at a low temperature (77 K) and the adsorption of carbon dioxide at 293 K (Scaife *et al*. 2000; Vasanth Kumar *et al*. 2010b). As explained in various studies, at this temperature the carbon dioxide can easily access micropores (<7 Å), which would present a diffusion resistance for nitrogen at 77 K despite the fact that the critical molecular dimensions of both gases are similar (Konstantakou *et al*. 2007).

In this work, the experimental adsorption data of ethylene and ethane on Cu-based activated carbon xerogel at 333.15 K in the first step, and that of methane, ethane and nitrogen on BDH activated carbon at different temperatures on the second step were applied as an input to determine PSDs from the integral equation (25). The obtained PSDs for the samples using the different probe

TABLE 2. Fitting Parameters Obtained by the AED Method for the Adsorption of Ethane, Methane and Nitrogen on BDH Activated Carbon at Different Temperatures

	Temperature (K)	E_0 (kJ/mol)	σ (kJ/mol)	Nm (mol/kg)	n	ARE (%)
Ethane	313.15	10.00 (±0.48)	2.10 (±0.10)	5.95 (±0.28)	0.69 (±0.03)	4.87
	323.15	11.44 (±0.09)	1.92 (±0.01)	2.95 (±0.02)	1.07 (±0.01)	0.84
	333.15	11.60 (±0.13)	1.82 (±0.02)	2.05 (±0.02)	1.37 (±0.01)	1.20
Methane	303.15	8.92	1.87	2.28	1.03	1.76
	313.15	(±0.15)	(±0.03)	(±0.04)	(±0.01)	1.30
	323.15	8.78	1.85	2.40	0.98	2.13
	333.15	(±0.11)	(±0.02)	(±0.03)	(±0.01)	3.47
		8.67	1.90	2.02	1.06	
		(±0.18)	(±0.04)	(±0.04)	(±0.02)	
		8.52	1.92	2.02	1.01	
		(±0.29)	(±0.06)	(±0.07)	(±0.03)	
Nitrogen	313.15	10.82	1.95	0.50	1.57	3.27
	323.15	(±0.35)	(±0.06)	(±0.01)	(±0.05)	1.65
	333.15	9.05	1.95	0.77	1..21	2.48
		(±0.14)	(±0.03)	(±0.01)	(±0.02)	
		7.88	1.90	1.03	1.06	
		(±0.19)	(±0.09)	(±0.02)	(±0.02)	

molecules represent the range of the pore sizes detected by these gases and not necessarily all the real ones. Although it does not represent the entire structural range of activated carbons, it indeed reflects some relationships between the detected pore sizes and the characteristics of the molecule (e.g. geometrical and energetic characteristics).

5.3.1. PSD of Cu-Based Activated Carbon Xerogel

Figure 3 shows the PSD of Cu-based activated carbon xerogel for the adsorption of ethylene and ethane at 333.13 K. The fitting parameters in equation (25) and the corresponding ARE values are illustrated in Table 3. The pore sizes are in the range of 8–23.4 Å for ethylene and 16.8–32.4 Å for ethane (Figure 3). These results are close to those obtained by Al-Muhtaseb (2008), who used the DFT method. In that study, the pore sizes of Cu-based activated carbon are in the range of 15–30 Å Thus, it be confirmed that the statistical physics treatment applied by considering the PSD approach can describe the adsorption on heterogeneous activated carbons.

Figure 4 also shows the density of the adsorption capacity for the adsorption of ethylene and ethane at 333.15 K. It can be deduced that the ethylene molecule has the maximal density in the smaller pores compared with ethane. This is expected because of the strong interactions between ethylene and the adsorbent in smaller pores. Thus, it can be deduced that adsorption in smaller pores induces greater adsorption of ethylene, which is supported by the Q_{asat} value (Table 3; the value of Q_{asat} in the case of ethylene is greater than that obtained in the case of ethane). As a result, the Cu-based activated carbon xerogel has a higher capacity for the ethylene molecule as compared with the ethane molecule, which explains the greater affinity of this adsorbent to ethylene than ethane.

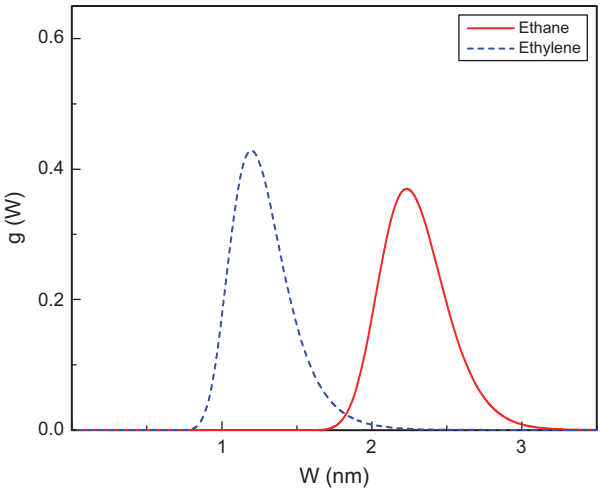

Figure 3. PSD obtained in the case of adsorption of ethane and ethylene on Cu-based activated carbon xerogel at 333.15 K.

TABLE 3. Fitting Parameters Obtained by the PSD Method for the Adsorption of Ethane and Ethylene on Cu-Based Activated Carbon Xerogel at 333.15 K

	w_0 (Å)	σ (kJ/mol)	k (kJÅ/mol)	N_m (mol/kg)	n	Q_{asat} (mol/kg)	ARE (%)
Ethane	22.72 (±2.55)	0.96 (±0.10)	114.90 (±12.91)	0.48 (±0.05)	1.77 (±0.19)	0.84 (±0.09)	11.24
Ethylene	12.54 (±0.47)	1.82 (±0.06)	73.60 (±2.73)	1.11 (±0.04)	1.08 (±0.04)	1.19 (±0.04)	3.71

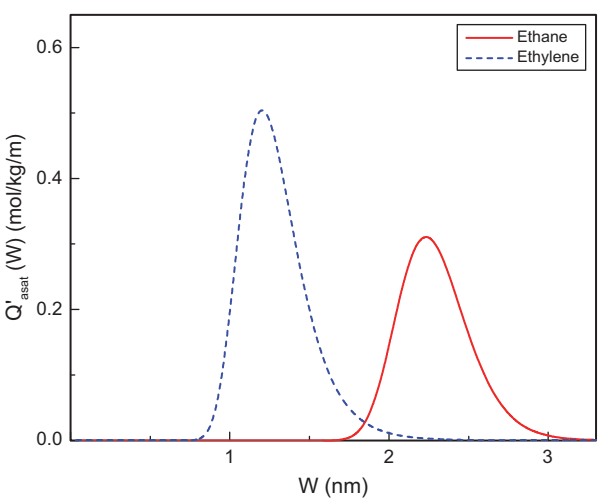

Figure 4. Comparison of the density of the adsorption capacity obtained for ethylene and ethane on Cu-based activated carbon xerogel at 333.15 K.

5.3.2. PSD of BDH Activated Carbon

The determined PSDs for the adsorption of three components (nitrogen, methane and ethane) on BDH activated carbon are depicted in Figure 5, and all the adjusted parameters in the integral equation are given in Tables 4–6.

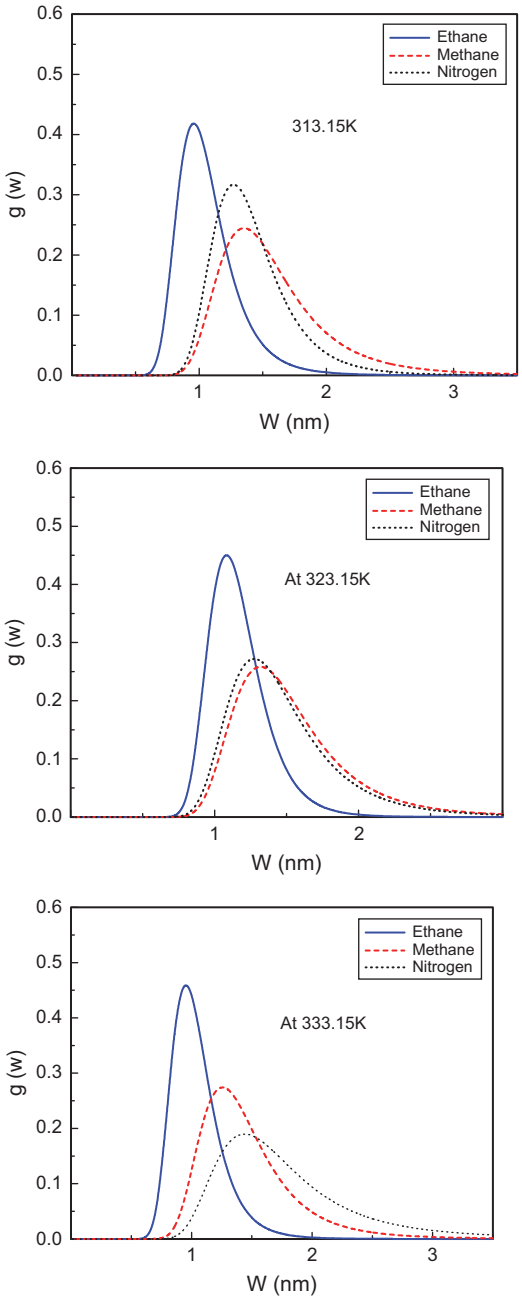

Figure 5. Comparison of the PSD obtained for the adsorption of ethane, methane and nitrogen on BDH activated carbon at different temperatures.

TABLE 4. Fitting Parameters Obtained by the PSD Method for the Adsorption of Ethane on BDH Activated Carbon at Different Values of Temperature

Temperature (K)	w_0 (Å)	σ (kJ/mol)	k (kJÅ/mol)	N_m (mol/kg)	n	ARE (%)
313.15	10.24 (±0.49)	2.05 (±0.20)	53.20 (±2.56)	6.05 (±0.29)	0.70 (±0.03)	4.83
323.15	11.36 (±0.09)	1.85 (±0.01)	64.80 (±0.53)	3.05 (±0.02)	1.05 (±0.01)	0.82
333.15	10.06 (±0.11)	2.13 (±0.02)	59.60 (±0.65)	1.94 (±0.02)	1.48 (±0.01)	1.10

TABLE 5. Fitting Parameters Obtained by the PSD Method for the Adsorption of Methane on BDH Activated Carbon at Different Values of Temperature

Temperature (K)	w_0 (Å)	σ (kJ/mol)	k (kJÅ/mol)	N_m (mol/kg)	n	ARE (%)
303.15	13.32 (±0.23)	1.97 (±0.03)	59.20 (±1.04)	2.28 (±0.04)	1.04 (±0.01)	1.76
313.15	14.84 (±0.18)	2.04 (±0.02)	63.40 (±0.81)	2.51 (±0.03)	0.98 (±0.01)	1.28
323.15	14.40 (±0.30)	2.03 (±0.04)	62.90 (±1.33)	1.94 (±0.04)	1.09 (±0.02)	2.13
333.15	13.72 (±0.47)	1.95 (±0.06)	58.00 (±1.99)	2.06 (±0.07)	1.01 (±0.03)	3.44

TABLE 6. Fitting Parameters Obtained by the PSD Method for the Adsorption of Nitrogen on BDH Activated Carbon at Different Values of Temperature

Temperature (K)	w_0 (Å)	σ (kJ/mol)	k (kJÅ/mol)	N_m (mol/kg)	n	ARE (%)
313.15	13.52 (±0.42)	2.14 (±0.06)	73.90 (±2.32)	0.45 (±0.01)	1.70 (±0.05)	3.15
323.15	13.90 (±0.22)	2.08 (±0.03)	63.20 (±1.04)	0.75 (±0.01)	1.24 (±0.02)	1.65
333.15	16.40 (±0.35)	2.12 (±0.04)	60.00 (±1.03)	1.18 (±0.02)	1.06 (±0.02)	2.17

The comparisons between the experimental data and the model correlations are given in Figure 6. It can be observed from Figure 6 that a very good fit of the model to the experimental data is obtained for the three gases at different temperatures.

The ARE values given in Tables 4–6 also show satisfactory correlations between experimental data and the theoretical model. In this study, the ARE values are in the interval [0.82, 4.83%] (Tables 4–6), which is considered a very low error. These results indicate that our model can successfully represent the adsorption behaviour of real systems.

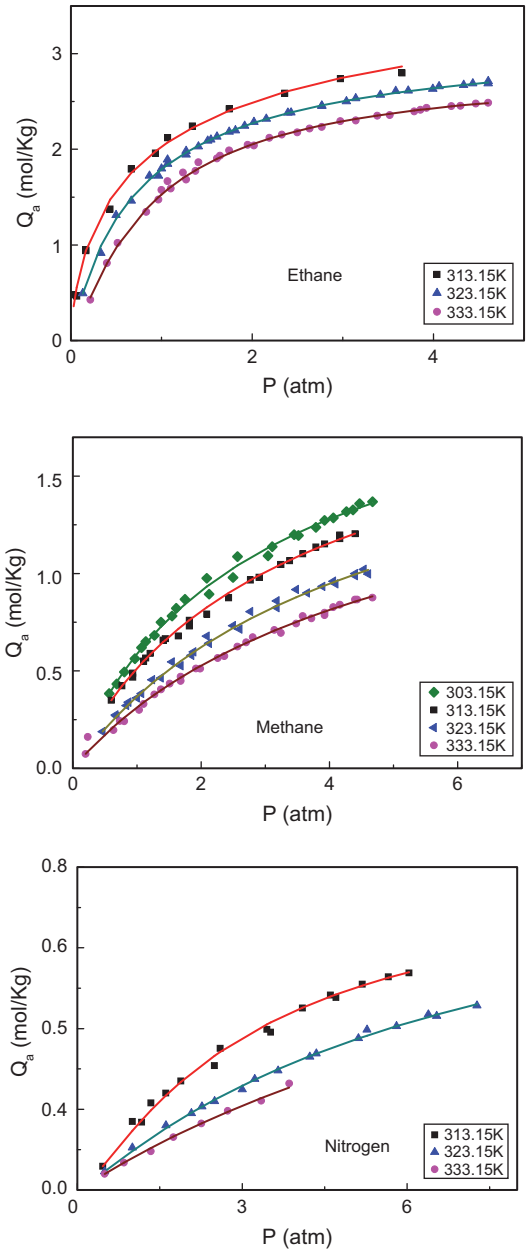

Figure 6. Comparison of experimental adsorption data (symbols) with model fitting (lines) for adsorption of the three gases on BDH activated carbon.

Figure 5 shows the comparison between the PSDs obtained for the three components. As shown in Figure 5, all the PSDs indicate that the BDH activated carbon has a large portion of microporous structure. The maximum of the peak is at around 9.5–10.8 Å for ethane, around 12.2–13.5 Å for methane and around 12.6–14.3 Å for nitrogen. At the three temperatures studied, it is clear that ethane molecules detect the smallest pores on the adsorbent. Compared with ethane

and methane molecules, nitrogen is smaller. However, in our case, although the nitrogen molecule is the smallest, the smallest pore sizes were not detected by this molecule.

Indeed, the AEDs and the interpretation discussed by Ben Torkia *et al*. (2014b) show that ethane molecules have the highest density of receptor sites and the highest energies followed by methane and then nitrogen, indicating the strong interactions between molecules of ethane and the surface of the activated carbon as compared with molecules of methane and nitrogen.

By contrast, in the present work, the PSDs show that ethane molecules detect the smallest pore sizes at the three temperatures studied, despite nitrogen being the smallest molecule. This fact could be explained by the gradient of the chemical potential. However, there are two possible gradients of this chemical potential, which are as follows:

- The first one is related to the diffusion process, which is governed by the Fick equation (Couture and Zitoun 1992)

$$J = -D\,\mathrm{grad}(c) \tag{32}$$

where J is the flux density, D is the diffusion coefficient, c is the concentration in the gaseous state, which is proportional to the chemical potential (Couture and Zitoun 1992)

$$\mu = kT\log\left(\frac{c}{c_s}\right) \tag{33}$$

where k_B is the Boltzmann constant, T is the temperature and c_s is the solubility concentration.

According to equation (33), grad(c) is related to the chemical potential. Then the transfer of molecules, which is due to the variation of the concentration, is in favour of an easy transfer of nitrogen in the micropores due to a high diffusion coefficient D of N_2.

- The second gradient of the chemical potential is due to the adsorption process, which is governed by the potential difference between the free state (or the gaseous state) and the adsorbed state. This potential difference (or gradient of potential) is proportional to the adsorption energy and is in favour of adsorption of ethane molecules in the micropores because the adsorption energy of ethane molecules is the highest compared with methane and nitrogen molecules.

In the case of adsorption of ethane, methane and nitrogen on BDH activated carbon, it is obvious that the factor 'adsorption energy' is the most important in relation to the potential difference. As a consequence, despite its smaller size, nitrogen molecules are not enough attracted in micropores as compared with the ethane molecules.

Tables 4–6 present the values obtained for the parameter N_m in the case of adsorption of ethane, methane and nitrogen. By comparing these values, it can be seen that nitrogen presents the minimum values, indicating that the corresponding density of occupied sites is the lowest.

By contrast, it can be deduced from Figure 7 that by varying the temperature, the PSDs in the case of methane and ethane maintain their shape without remarkable variations. Whereas in the case of nitrogen, the PSD becomes larger upon increasing the temperature. This result is mainly related to the physical properties of adsorbates. Indeed, ethane can be considered as a linear molecule model and it is characterized by its non-polar nature. In addition, the methane molecule has no dipole moment, and it can be modelled as a single-site sphere. Therefore, when there is a variation in temperature, both ethane and methane molecules are able to penetrate into the same pores and their PSDs maintain the same shapes.

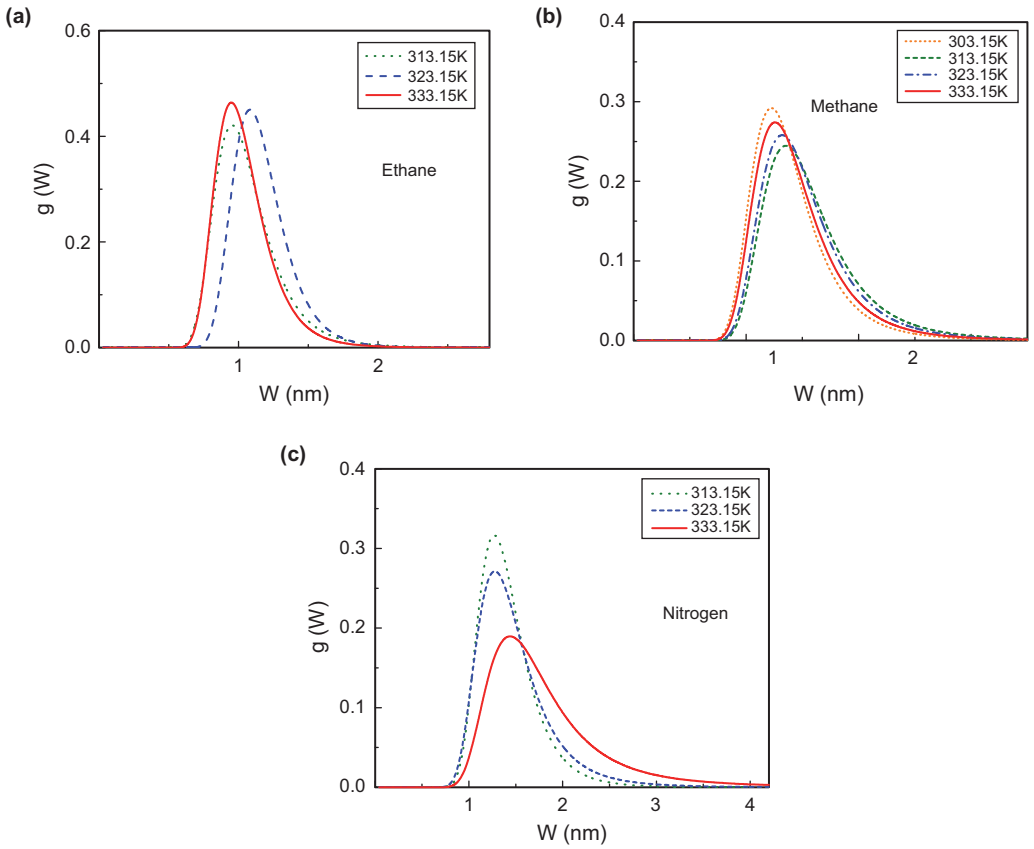

Figure 7. PSD obtained for the adsorption of (a) ethane, (b) methane and (c) nitrogen on BDH activated carbon.

In the case of adsorption of nitrogen molecules, the PSDs obtained at different temperatures behave differently to the PSDs obtained for the adsorption of methane and ethane molecules. This can be related to the quadrupole moment of nitrogen molecule (Sakurovs *et al*. 2012), and in particular to its manner of adsorption. Table 6 indicates that the value of n decreases with increasing temperature. At 313.15 K, n = 1.7, which indicates that there is a great percentage of nitrogen molecules adsorbed with an average of two molecules per site. However, at 333.15 K, n = 1.06, suggesting that the nitrogen molecule is adsorbed with an average of one molecule per site. This can be explained by the fact that when temperature increases, thermal agitation minimizes the cohesion between adsorbed nitrogen molecules. It breaks the bimolecular molecule adsorption assembly, and the adsorption phenomenon transforms from two molecules per site to one molecule per site. Obviously, the interaction energy of two separated molecules with the adsorbent surface (at high temperature) is weaker than the energy of interaction of two linked molecules (at low temperature; Table 2). Therefore, at high temperatures the weaker energies increase (in the case of nitrogen: Table 2), and it can be seen how the pore size increases (Table 6) as the energy of adsorption decreases.

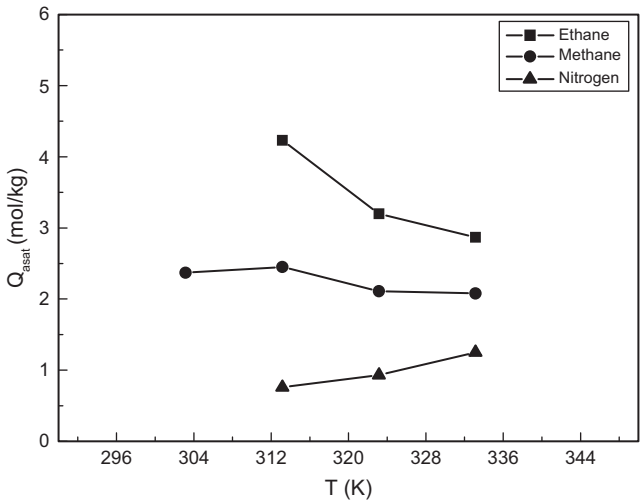

Figure 8. Variation of the total quantity adsorbed at saturation at various temperatures for the three gases on BDH activated carbon at different temperatures.

From Figure 8 it can be seen that the total adsorbed quantity at saturation for ethane is always higher than that of methane, which in turn is higher than that of nitrogen. This behaviour can be related to the results depicted in Figure 9, which shows the density of the adsorption capacity of the three gases at a given temperature. As it is deduced previously, ethane molecules have the maximal adsorption in the smaller pores compared with methane and nitrogen. At the three temperatures, the pore width for ethane is usually around 6–20 Å (Figure 9).

It should be accepted without doubt that for relatively smaller pores, the pore-filling process is more rapid, whereas it is slower for larger pores. In addition, for larger pore sizes, the interaction between the adsorbate and the adsorbent is weaker, which leads to a reduction in adsorption. As a result, the BDH activated carbon has a higher capacity for ethane molecule as compared with methane and nitrogen molecules. By contrast, it can be noticed that at the same range of pore sizes, methane has the higher adsorption density as compared with nitrogen, suggesting that the BDH activated carbon has a higher capacity for methane as compared with nitrogen.

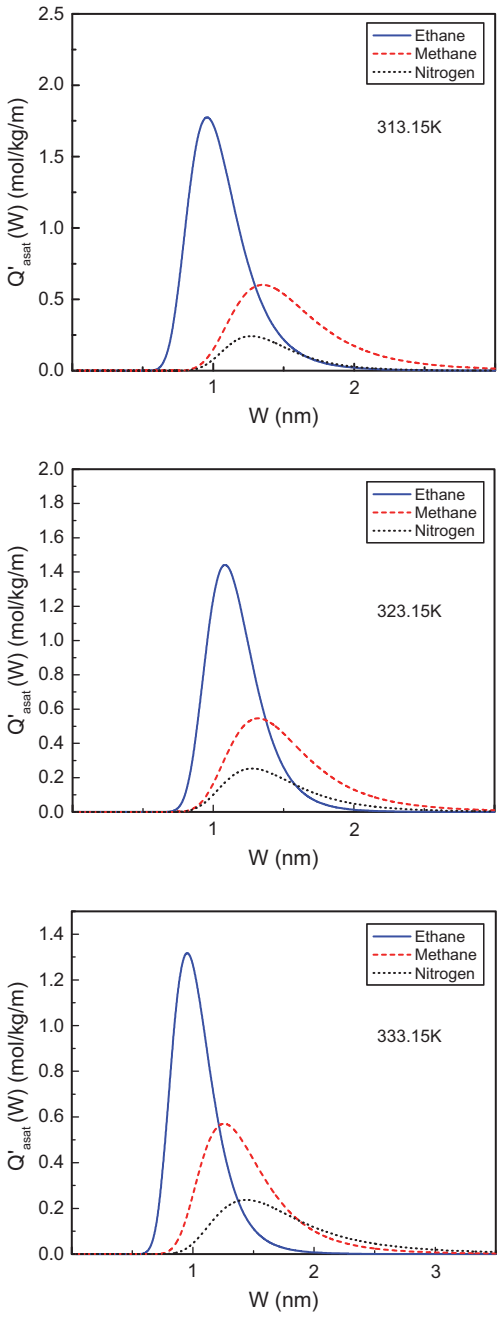

Figure 9. Comparison of the density of the adsorption capacity obtained for the three gases at different temperatures.

6. CONCLUSIONS

The integral equation was developed using a statistical physics treatment and by incorporation of the AED function, which was related to the PSD function. Both distribution functions could describe the adsorption equilibrium of different gases on activated carbons. The AED and PSD of Cu-based activated carbon xerogel were obtained at 333.15 K. Such an adsorbent has a greater affinity towards ethylene than ethane, which is an area of immense commercial interest, as it is a key step in selective separations for petrochemical industries. The adsorption of ethane, methane and nitrogen on BDH activated carbon was also studied in this paper by determining the PSD corresponding to each experimental isotherm. The adsorption data of pure components under different temperatures can be fitted well. Reasonable PSDs are obtained through the adsorption data of pure components. It can be concluded that different gases explore different ranges of pore sizes.

The PSD is a proper characterization of the adsorbent, and therefore it should neither depend on the probe molecule used nor on the temperature. In the presented case, it can be noted that PSD is not invariable. Although imprecision does not exceed few percentages in the temperature ranges used with the same probe, it is notable if the probe is changed. By comparing our results with other methods, we can notice that the PSD of resorcinol–formaldehyde-based activated carbon xerogel, obtained in the case of adsorption of ethane, is close to the PSD obtained using the DFT method. Thus, it can be concluded that ethane molecules can be used to characterize this type of adsorbent. This seems to be a satisfactory result as ethane is a good probe and could better penetrate into micropores for energetic considerations. However, the PSD determined on the actual BDH activated carbon represents, to our knowledge, the first determined PSD of this type of adsorbent, and therefore no comparisons could be performed with other studies in the literature.

In conclusion, additional information about PSD was obtained by analyzing the adsorption of ethane, methane and nitrogen at different temperatures, which is important for the characterization of materials considered for their application in energy-storage systems and industrial separation processes. Indeed, this method can be extended to the adsorption equilibrium of mixtures. At present, this attempt is still in progress.

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