

Energetic investigation of the adsorption process of CH₄, C₂H₆ and N₂ on activated carbon: Numerical and statistical physics treatment



Yosra Ben Torkia^a, Manel Ben Yahia^a, Mohamed Khalfaoui^a, Shaheen A. Al-Muhtaseb^b, Abdelmottaleb Ben Lamine^{a,*}

^a Laboratory of Quantum Physics, UR 11 ES 54, Faculty of Sciences of Monastir, Monastir 5019, Tunisia

^b Department of Chemical Engineering, Qatar University, PO Box 2713, Doha, Qatar

ARTICLE INFO

Article history:

Received 12 March 2013

Received in revised form

26 September 2013

Accepted 28 September 2013

Available online 15 October 2013

Keywords:

Interfaces

Computer modelling and simulation

Adsorption

Heterostructures

ABSTRACT

The adsorption energy distribution (AED) function of a commercial activated carbon (BDH-activated carbon) was investigated. For this purpose, the integral equation is derived by using a purely analytical statistical physics treatment. The description of the heterogeneity of the adsorbent is significantly clarified by defining the parameter $N'_m(E)$. This parameter represents the energetic density of the spatial density of the effectively occupied sites. To solve the integral equation, a numerical method was used based on an adequate algorithm. The Langmuir model was adopted as a local adsorption isotherm. This model is developed by using the grand canonical ensemble, which allows defining the physico-chemical parameters involved in the adsorption process. The AED function is estimated by a normal Gaussian function. This method is applied to the adsorption isotherms of nitrogen, methane and ethane at different temperatures. The development of the AED using a statistical physics treatment provides an explanation of the gas molecules behaviour during the adsorption process and gives new physical interpretations at microscopic levels.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Activated carbons are adsorbents of a great industrial importance. Indeed, there is a growing interest in the use of this material as an adsorbent in a variety of applications such as separation, purification and storage of gases [1]. In that context, a thorough investigation of the fine details of activated carbon surface structures is essential for the development and improvement of materials designed for specific applications. Activated carbons are known to have strongly heterogeneous surfaces. The heterogeneity stems from two sources, namely geometrical and chemical heterogeneities. The geometrical heterogeneity results from differences in the sizes and shapes of pores, as well as pits, vacancies and steps in the surface. On the other hand, the chemical heterogeneity of a surface is associated with the presence of different functional groups. The most common ways to express the heterogeneity of a solid surface are based on the adsorption energy distribution (AED) function [2].

Several studies have been focused on the characterization of the energetic heterogeneity of the surface of activated carbons.

The majority of these researches have assumed the integral equation of adsorption [3–6]

$$Q_a(P) = \int_{E_{\min}}^{E_{\max}} Q_l(E, P) \times f(E) dE \quad (1)$$

where Q_a represents the experimental adsorbed quantity measured at a temperature (T) and an equilibrium pressure (P), E is the adsorption energy, E_{\min} and E_{\max} are the minimum and maximum limits of the energy space, $f(E)dE$ is the fraction of the maximum on which the adsorption energy of the adsorbate is between E and $E + dE$ and $Q_l(E, P)$ is the local adsorption isotherm.

The application of this model was popularized by Ross and Olivier, who applied their analysis method to a large number of systems [7]. Since this earlier work, the physical model describing adsorption on a heterogeneous adsorbent has not changed but the solution methods of the integral equation to determine the energy distribution function have become progressively more sophisticated.

In view of obtaining an analytical solution of this integral equation, several researchers have made approximations of essentially the local adsorption isotherm function. Examples of these methods are the condensation approximation (CA) [8], the asymptotically correct approximation (ACA) [9], and the logarithmic symmetrical approximation (LOGA) [10]. All these methods lead to expressions for the adsorption energy distribution function $f(E)$ in terms of derivatives of the overall isotherm.

* Corresponding author. Tel.: +216 95 666 600.

E-mail addresses: yosra.bentorkia@yahoo.fr (Y. Ben Torkia), aben_lamine@yahoo.fr (A. Ben Lamine).

The second method to solve the integral equation is through numerical techniques. In principle, these methods can be used with a variety of local adsorption isotherms. The first numerical technique used in the field of adsorption science has been developed by House and Jaycock [11] and is called HILDA (heterogeneity investigated by a Loughborough distribution analysis). Recently, advanced computational methods such as the density functional theory (DFT) and the Monte Carlo simulation method (MC) had a special relevance in adsorption process [12].

The aim of this work is to determine the energy distribution function by applying the statistical physics formalism. As a first step, a derivation of the integral equation is accomplished. This development will prove that the adsorption energy distribution function is included in the expression of the derivative of the total adsorption isotherm Q_a . The second step consisted of applying a numerical method to determine adsorption energy distribution (AED). Results are based on the minimizing of the value of the average relative error (ARE). A statistical physics treatment of the Langmuir isotherm, which is taken as a local isotherm, is developed by using the grand canonical ensemble. The last step is a numerical one. The AED function, $f(E)$, is assumed to follow a normal Gaussian distribution. In this manuscript, we have applied this method to determine the energetic heterogeneity of the British Drug House (BDH)-activated carbon, which is a commercial activated carbon, towards the adsorption of nitrogen, methane and ethane at different temperatures.

2. Experimental and materials

The equilibrium data for adsorption of nitrogen, methane and ethane on BDH-activated carbon were measured over an industrially relevant range of temperatures (303.15 to 333.15 K) and a wide range of pressures (0 to 8 atm) using a volumetric adsorption apparatus. The BDH-activated carbon was received from BDH Company in England in a granular form with a particle size of 0.85–1.70 mm. Further characteristics of BDH-activated carbon were measured and estimated using an accelerated surface area and porosimetry (ASAP)-2010 apparatus and software. The BET surface area was 1220 m²/g, of which 1173 m²/g was in the micropore region. The total pore volume was 534 m³/kg, of which 479 m³/kg was in the micropore region. This calculation is based on a density functional theory (DFT) using adsorption and desorption isotherms of N₂ at 77 K and by assuming slit shaped pore geometry [32].

The gas expansion and adsorption cells are hosted in a thermostatic oven, which can be set in the temperature range of (303.15 to 493.15) K with an accuracy of ± 1 K. The pressure gauge was an analogue type with a gauge pressure range of (0 to 10) bar and an accuracy of 1%.

Applying the volumetric method, the amount adsorbed is determined from the variation of the pressure in a known volume. Then, the activated carbon used was initially regenerated by placing it in an oven at 523.15 K for 3 h. It was then placed in an evacuated desiccator (which also contains silica gel to adsorb humidity) until it reached room temperature. After that, the required sample was promptly weighed and placed in the adsorption cell. The volume of this cell, which included 78.79 g of the dried BDH-activated carbon, is 150 cm³. The adsorption runs started from a generated adsorbent at a fixed temperature and an initial pressure near zero bar. Then, the gas cylinder valve was opened to charge the expansion cells to an intermediate pressure step. The volume of the expansion cell is 150 cm³. After reaching the thermal equilibrium, the gas was allowed to expand to the sample cell where the adsorbent material was placed. The changes in pressure were monitored and recorded during this step. When

the pressure in the sample cell became constant for about 30 min, adsorption equilibrium was reached and recorded for that pressure. The amount adsorbed at that point was calculated from the difference between the total moles number present in the gas phase before and after the adsorption step. This constitutes one experimental adsorption point. Further adsorption points were determined by closing the sample cell, charging the expansion cell with the gas to a higher intermediate pressure and repeating the same procedure that was used to obtain the first adsorption point. More details for this treatment are given elsewhere [13].

3. Methodology

3.1. Developing the Langmuir adsorption isotherm from the grand canonical ensemble

The Langmuir adsorption isotherm model, derived from the kinetic or equilibrium arguments, is originally developed for gas phase adsorption. In literature, we found that this model is based on several assumptions [14], where it assumes that there is no interaction between the adsorbed molecules; and that each site of adsorbent cannot sit more than one molecule of adsorbate. In the present study, this model which will play the role of the local isotherm as established by applying grand canonical ensemble in a statistical physics approach. To treat such adsorption problem with statistical physics, some assumptions will be added [15–17]. First, it is assumed that the adsorption phenomenon is a process of transferring particles from the free state to the adsorbed state. Accordingly, the equilibrium between the adsorbed phase and the non-adsorbed phase, which is reached for each experimental measurement of the amount adsorbed, can be expressed by the following equation [16]:

$$A + S \rightleftharpoons AS \quad (2)$$

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

Second, the internal degrees of freedom of the studied molecules are neglected only the translational degrees of freedom are considered. Thus, for the treatment of the adsorption process based on the statistical physics theory, the grand canonical ensemble is used. The partition function for a single site is written in the following form [17]

$$z_{gc} = \sum_{N_i} \exp[-\beta(-\epsilon - \mu)N_i] \quad (3)$$

where $(-\epsilon)$ is the energy of adsorption of the receptor site i and is negative since an adsorption process is exothermic, μ is the chemical potential of the receptor site i , β is the Boltzmann coefficient (which is defined as $1/k_B T$, where k_B is the Boltzmann constant), and N_i is the state of occupation of receptor site i . Since it was assumed that any given receptor site can either be empty or occupied, N_i takes the value of either 0 or 1. Then, the grand canonical partition function will be

$$z_{gc} = 1 + \exp[\beta(\epsilon + \mu)] \quad (4)$$

Considering that our system is composed of N molecules of adsorbate and N_m receptor sites per unit mass of adsorbent, the grand canonical partition function describing the microscopic states of the system can be written as [17]

$$Z_{gc} = [1 + \exp[\beta(\epsilon + \mu)]]^{N_m} \quad (5)$$

The occupation number, N_0 , among N_m identical receptor sites is therefore given as follow:

$$N_0 = k_B T \frac{\partial \ln(Z_{gc})}{\partial \mu} \quad (6)$$

Then we have

$$N_0 = \frac{N_m}{1 + \exp[-\beta(\varepsilon + \mu)]} \quad (7)$$

On the other hand, by considering in a first approach that the adsorbate is an ideal gas and by considering equilibrium between the free and the adsorbed states of the gas, we have

$$\exp(\beta\mu) = \frac{P}{z_{\text{gtr}}RT} \quad (8)$$

where z_{gtr} is the partition function of translation. Then, the adsorbed quantity is written as a function of the gas pressure as

$$N_0 = \frac{N_m}{1 + \left(\frac{z_{\text{gtr}}RT}{P} \exp(-\beta\varepsilon)\right)} \quad (9)$$

If $P = z_{\text{gtr}}RT \exp(-\beta\varepsilon) \Rightarrow N_0 = N_m/2$, then we call this pressure the half-saturation pressure and it is noted down by

$$P_{1/2} = z_{\text{gtr}}RT \exp(-\beta\varepsilon) \quad (10)$$

In the case of Langmuir model the adsorbed quantity Q_a is equal to N_0 then we have

$$Q_a = \frac{N_m}{1 + (P_{1/2}/P)} \quad (11)$$

$P_{1/2}$ is related to the molar adsorption energy E by

$$P_{1/2} = P_0 \exp(-E/RT) \quad (12)$$

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

So, in the final expression of the Langmuir model, there are two parameters N_m and $P_{1/2}$. These parameters are completely defined in relation of the physico-chemical characteristics of the problem; this is due to the statistical physics treatment. While the analogue kinetic approach is noted by [30]

$$Q_a = \frac{Q_{\text{asat}} \times b \times P}{1 + bP} \quad (13)$$

with Q_{asat} is the quantity adsorbed at saturation and b is a constant.

The Langmuir equation in its linear form is given as [30]:

$$\frac{P}{Q_a} = \frac{1}{Q_{\text{asat}}b} + \frac{P}{Q_{\text{asat}}} \quad (14)$$

The product $Q_{\text{asat}} \cdot b = K_L$ is the Langmuir equilibrium constant.

Plotting the ratio of pressure (P) and the adsorbed quantity (Q_a) versus the pressure gave straight lines from which the Langmuir constants for all the studied systems were estimated.

This modeling involved K_L , which can be used to determine the mean enthalpy of adsorption, ΔH , using the Clausius–Clapeyron equation [31]

$$K_L = A \exp(-\Delta H/RT) \quad (15)$$

An estimation of the mean enthalpy ΔH could be attributed to a logarithmic slope in function of $(1/T)$ with this assumption.

3.2. A derivation of the integral equation

According to literature [7,14,19,20], the majority of studies describing the surface heterogeneity of adsorbents utilize the patchwise model. This model assumes that the adsorbent surface consists of homogeneous patches, in where the interaction energy between sites and the adsorbed molecule is E . Each of these homogenous patches obeys the local isotherm model. As mentioned before, in this study the Langmuir isotherm is taken as a local isotherm. Then, the total amount of adsorptive sites is

equal to

$$Q_a = \sum_i Q_{ai}(E_i) \quad (16)$$

where

$$Q_{ai} = \frac{N_{mi}}{1 + \left(\frac{P_0 \exp(-E_i/RT)}{P}\right)} \quad (17)$$

as Q_{ai} depends on the value of the energy of adsorption E_i , and by supposing that E_i can be varied from E_{\min} to E_{\max} , $Q_{ai}(E_i)$ can be written as following by using a Dirac distribution $\delta(E - E_i)$ [21]

$$Q_{ai}(E_i) = \int_{E_{\min}}^{E_{\max}} \frac{N_{mi}}{1 + \left(\frac{P_0 \exp(-E/RT)}{P}\right)} \delta(E - E_i) dE \quad (18)$$

The incorporation of Eq. (18) in Eq. (16) will lead to

$$Q_a = \int_{E_{\min}}^{E_{\max}} \frac{1}{1 + \left(\frac{P_0 \exp(-E/RT)}{P}\right)} dE \sum_i N_{mi} \delta(E - E_i) \quad (19)$$

Finally, we set $N'_m(E) = \sum_i N_{mi} \delta(E - E_i)$. This changes the latter discrete distribution to the following continuous distribution

$$Q_a = \int_{E_{\min}}^{E_{\max}} \frac{1}{1 + \left(\frac{P_0 \exp(-E/RT)}{P}\right)} N'_m(E) dE \quad (20)$$

with $N'_m(E)$ is an energetic distribution of the spatial density of sites $N_m(E)$.

Therefore, $\int_{E_{\min}}^{E_{\max}} dN_m$ is a definite integral that we note N_m . Here N_m is no longer variable of the energy E . It is the total spatial density of all receptor sites of the adsorbent. We can then suppose that $N'_m(E) = N_m f(E)$. We have necessarily after integration

$$\int f(E) dE = 1 \quad (21)$$

$f(E)$ represents an AED function. It is an energetic distribution of the spatial density of receptor sites in relation to energy, or more precisely, to the energy space. Thus, $f(E)dE$ is the probability to find a receptor site having an adsorption energy ranging between E and $E + dE$. Then we have,

$$Q_a = \int_{E_{\min}}^{E_{\max}} \frac{1}{1 + \left(\frac{P_0 \exp(-E/RT)}{P}\right)} N_m f(E) dE \quad (22)$$

3.3. Resolution of the integral equation by applying a numerical method

To solve the integral equation, an adequate algorithm has been developed. By using this new program, we can correlate the experimental isotherm with an integral equation from which the AED can be extracted.

This method is directly applied to the measured raw adsorption data [13]. The results are checked by comparing the calculated adsorbed quantity, Q_{acalc} , to the experimental adsorbed quantity, Q_{aexp} , at an equilibrium pressure P and a temperature T by applying the average relative error (ARE), which is given by [18]

$$\text{ARE} = \frac{100}{m} \sum_{i=1}^m \left(\frac{|Q_{\text{acalc}} - Q_{\text{aexp}}|}{Q_{\text{aexp}}} \right) \quad (23)$$

where m is the total experimental number of points for each component. Then the correct solution is obtained by minimizing the value of the ARE.

In this method, it is necessary to assume a mathematical expression for the local isotherm and an energy distribution function. In this work, the Langmuir model is used as a local isotherm. It was supposed that each patch of the surface is characterised by a half-saturation pressure value of $P_{1/2}$, which is related to the adsorption energy E as

follows

$$P_{1/2} = P_0 \exp(-E/RT) \quad (24)$$

This equation that we have established using a statistical physics treatment contains implicitly the approximation of Cerofolini [22] (or the theory of Polanyi [23]), which relates the adsorption energy to the pressure, considering it as a normal relation resulting from using the statistical physics formalism.

However the AED function cannot be derived directly without giving an approximated $f(E)$. A simple normal Gaussian function is considered to approximate the AED function

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) \quad (25)$$

E_0 represents the maximum of the Gaussian peak, and σ is the dispersion of the Gaussian distribution (which relates to the extent of heterogeneity). This latter parameter is related to the full width of the distribution at half maximum H [24].

Finally, the integral equation can be written as following

$$Q_a(P) = \int_{E_{\min}}^{E_{\max}} \frac{N_m}{1 + \left(\frac{P_0 \exp(-E/RT)}{P}\right)} \times \frac{\exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right)}{\sigma\sqrt{2\pi}} dE \quad (26)$$

Basically, the integral equation is discretized and the energy space is represented by E_i grid points. The range of pressure experimentally accessible is segmented into θ_{p_j} grid points. Also N_m , E_0 and σ are segmented into grids points: X_{N_m} , Π_{E_0} , and Ψ_{σ_h} , respectively. At the step k of the iteration process, the amount adsorbed is given by

$$Q_{a,calc}^k(P_j) = \sum_{E_{\min}}^{E_{\max}} \frac{N_{mr}}{1 + (P_0 \exp(-E_i/RT)/P_j)} \frac{\exp\left(-\frac{(E_i-E_{0l})^2}{2\sigma_h^2}\right)}{\sigma_h\sqrt{2\pi}} \Delta E \quad (27)$$

The core of the iteration process lies in the determination of the three parameters involved in this equation (N_m , E_0 and σ) corresponding to a minimum value of ARE.

A numerical optimization method is applied to determine the adsorption energy distribution of a commercial activated carbon at various temperatures. In the case of adsorption of methane the temperature range is from 303.15 to 333.15 K and for ethane and nitrogen is from 313.15 to 333.15 K.

4. Results and discussion

Figs. 1–3 show the fitted isotherm curves after modelling of the adsorption isotherms of nitrogen, methane and ethane onto BDH-activated carbon.

The corresponding AED results are illustrated in Figs. 4–6 for the adsorption of nitrogen, methane and ethane, respectively, at different temperatures. As defined previously, in Section 3.1. the adsorption energy is $(-\epsilon)$ with ϵ is a positive parameter. Then the real values of the obtained energies are all negative.

In general, it can be deduced that the adsorption process is a physisorption, since the absolute value of the adsorption energy does not exceed 25 kJ/mol. It is also clear that the AEDs present different behaviours in the case of adsorption of the three molecules, which indicate that the AED depends on both the shape and the electronic character of the adsorbed molecules.

Table 1 show the results obtained by modelling the adsorption isotherms with the integral equation using the numerical method for nitrogen, methane and ethane, respectively. The ARE values obtained are situated in the range of 0.86 to 5.21%, which is considered a very low error.

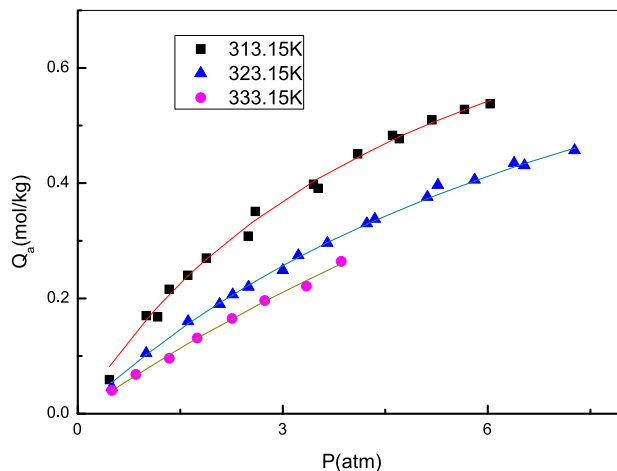


Fig. 1. Experimental (symbols) and fitted isotherms by the integral equation (lines) for the adsorption of nitrogen on BDH-activated carbon.

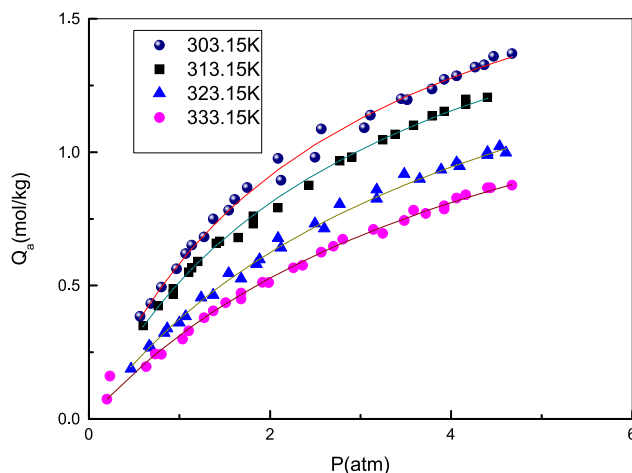


Fig. 2. Experimental (symbols) and fitted isotherms by the integral equation (lines) for the adsorption of methane on BDH-activated carbon.

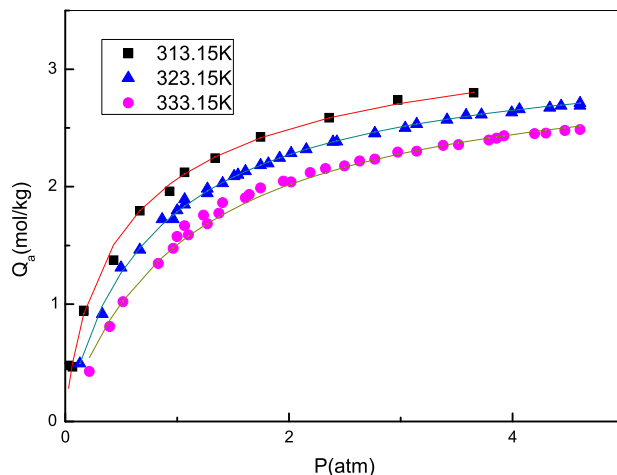


Fig. 3. Experimental (symbols) and fitted isotherms by the integral equation (lines) for the adsorption of ethane on BDH-activated carbon.

The results obtained by fitting experimental data using the simple Langmuir model and the integral equation were compared as illustrated in Tables 2 and 3. Table 2 indicates that the energy values, $-E$, and the mean enthalpy, ΔH , obtained by the simple Langmuir model are close to the mean energy values corresponding

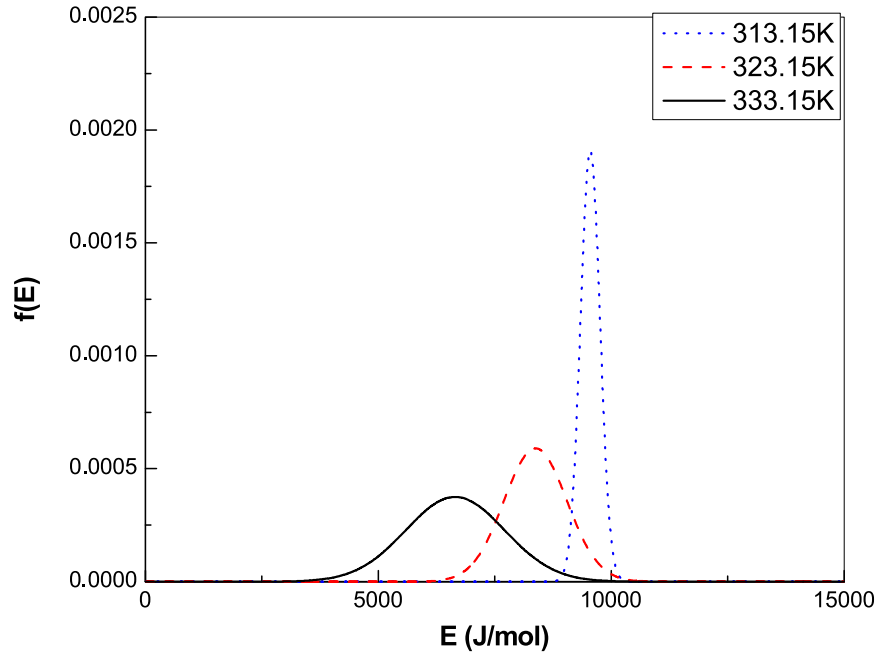


Fig. 4. Adsorption energy distribution (AED) for nitrogen.

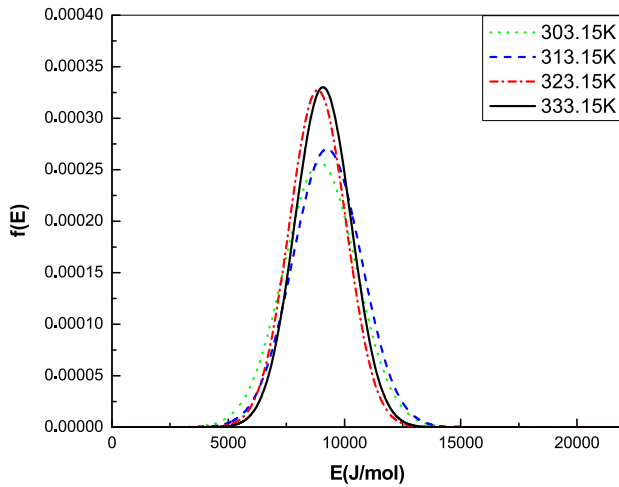


Fig. 5. Adsorption energy distribution (AED) for methane.

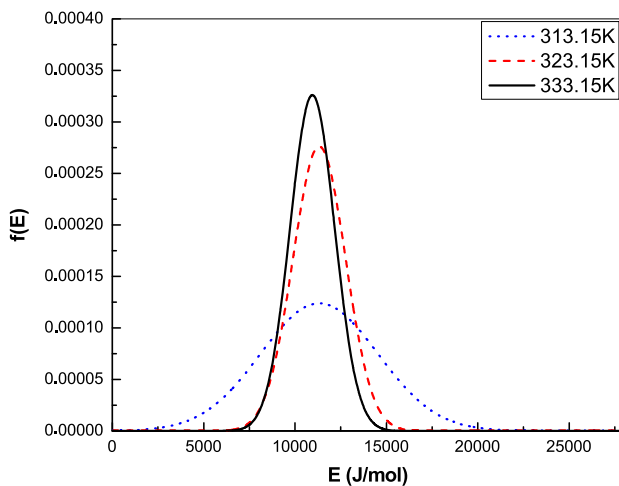


Fig. 6. Adsorption energy distribution (AED) for ethane.

Table 1

Integral adsorption isotherm parameters for nitrogen, methane and ethane.

Adsorbate	Temperature (K)	$-E_0$ (kJ/mol)	σ (kJ/mol)	H (J/mol)	N_m (mol/kg)	ARE (%)
Nitrogen	313.15	-9.55	0.19	447	1.02	5.11
	323.15	-8.37	0.67	1577	1.07	2.31
	333.15	-6.65	1.06	2496	1.60	1.91
Methane	303.15	-8.95	1.55	3650	2.35	1.77
	313.15	-9.25	1.47	3461	2.17	1.42
	323.15	-8.85	1.21	2849	2.07	2.29
	333.15	-9.07	1.20	2825	1.85	3.47
Ethane	313.15	-11.45	3.20	7535.4	3.50	5.21
	323.15	-11.32	1.43	3367.3	3.22	0.86
	333.15	-10.95	1.21	2849.3	3.15	2.58

Table 2

Comparison of the mean enthalpy (ΔH) and the mean adsorption energy ($-E$) with the maximum ($-E_0$) of the Gaussian peak.

Adsorbate	Temperature (K)	$-E$ (kJ/mol)	$-E_0$ (kJ/mol)	ΔH (kJ/mol)
Nitrogen	313.15	-9.42	-9.55	-8.28
	323.15	-8.45	-8.37	
	333.15	-6.86	-6.65	
Methane	303.15	-9.52	-8.95	-9.39
	313.15	-9.58	-9.25	
	323.15	-9.20	-8.82	
	333.15	-9.27	-9.07	
Ethane	313.15	-12.35	-11.45	-11.70
	323.15	-11.51	-11.32	
	333.15	-11.26	-10.95	

to the peaks of the Gaussian AEDs for the three gases. This indicates that the energy obtained from the Langmuir model is an average of the total adsorption energy distributions.

In the case of the parameter N_m , we confirm that we noted previously about the Eq. (20) in the theoretical treatment. Since N_m is an extensive variable, unlike E which is an intensive variable, it represents the total spatial density or the sum of all receptor

Table 3

Comparison of the N_m values obtained by the simple Langmuir model and those obtained by the integral equation.

Adsorbate	Temperature (K)	N_m (mol/kg) (Obtained by the fitting using the simple Langmuir isotherm)	N_m (mol/kg) (Obtained by the fitting using the integral equation)
Nitrogen	313.15	1.04	1.03
	323.15	1.06	1.08
	333.15	1.57	1.60
Methane	303.15	2.11	2.35
	313.15	2.04	2.17
	323.15	1.96	2.07
	333.15	1.79	1.85
Ethane	313.15	3.05	3.50
	323.15	3.12	3.22
	333.15	3.04	3.15

sites of the adsorbent $\int_{E_{\min}}^{E_{\max}} dN_m$. Table 3 indicates clearly that the N_m values obtained by the simple Langmuir model are near to those obtained by the fitting using the integral equation.

4.1. Behaviour of the AED for nitrogen molecule

It is clear from Fig. 4 that, by increasing temperature, the AED function is shifted to the lower energies. This is due to the shape of nitrogen molecule and its manner of adsorption. According to Potoff and Siepmann [25], the nitrogen molecule presents an elongated shape. In addition, and as signalled by Do et al. [26], the nitrogen molecule has two orientations in confined spaces. It can reside parallel to the surface and it can also adopt an orientation that is perpendicular to the surface. The parallel orientation has a higher energetic interaction with the surface than the vertical orientation [26]. This can be related to the values of the polarizability. Indeed, polarizability was shown to be highly correlated with both the molar volume and the cross sectional area of the molecule. A higher polarizability induces a higher interaction with the surface [29], hence greater adsorption energy. Then, Fig. 4 indicates that at lower temperatures nitrogen molecules are adsorbed parallel to the surface and the active sites are those having higher energies (Fig. 4). However, at higher temperatures, we have a greater contribution of the vertical orientation after a process of disanchorage, which is due to thermal agitation. As the vertical orientation is less energetic, the lower energies are activated (Fig. 4).

As a result, the AED is translated to the lower energies when temperature is increased. Then, a large number of weak energies are involved in the distribution and an enlargement of the peak is necessary to keep an invariant total area of the distribution since $\int f(E)dE = 1$.

4.2. Behaviour of the AED for methane molecule

It is clear in Fig. 5 that $f(E)$ has fixed distribution at different temperatures. This indicates that the variation of temperature does not affect the energy distribution of adsorption of the methane molecule. This result is due probably to the symmetrical structure of the methane molecule, which has a tetrahedral shape. Do et al. [26] has presented a model for adsorption of methane on surfaces and in confined spaces, which suggested that methane can be modelled effectively as a pseudo-sphere. This is possible because the well depth for the carbon atom is much greater than those of the four hydrogen atoms [26]. Therefore, the energy interaction is mainly contributed by the dispersion interaction of the central carbon atom. Consequently, thermal agitation can

change the orientation of the molecule. But, due to the tetrahedral symmetry, whatever the orientation is, the surface of the adsorbent will have the same types of activated sites.

4.3. Behaviour of the AED for ethane molecule

Fig. 6 presents the broadest $f(E)$ distribution at 313.15 K, which is spread over a larger interval of energies. Therefore, it can be seen that, by increasing temperature, the distribution of adsorption energies $f(E)$ is altered and extreme peak energies are noticed to disappear.

The ethane is represented as a pseudo diatomic molecule that is composed of two methyl groups [27,28]. As described in literature [27,28], three orientations of the ethane molecule with a surface can be taken into consideration. The first considers that one of the CH_3 -groups of the molecule can touch the surface, which is known as the perpendicular orientation. The second considers that both CH_3 -groups can simultaneously touch the surface, which is known as the parallel orientation. Finally, the ethane molecule can be adsorbed at an incident angle less than 45° [27]. Clearly, the adsorption energy of ethane molecules attached by both CH_3 -groups is higher than that attached by one methyl group. By increasing temperature, and by the effect of thermal agitation, the chance of adsorbing the ethane molecule by the two methyl groups decreases and that of adsorbing the ethane molecule by one methyl group increases. As a consequence, the higher energies disappeared. On the other hand, thermal agitation removes also the lower interactions of ethane molecules that are adsorbed at an incident angle less than 45° . As result, the AED at 333.15 K is the thinnest, and only the contributions of one methyl group adsorbed by the site are exhibited.

5. Conclusion

The derivation of the adsorption energy distributions (AEDs) of nitrogen, methane and ethane on BDH-activated carbon using a statistical physics treatment enables us a better understanding of the adsorption process. Indeed this treatment gives new interpretations of the adsorption process via the introduction of physicochemical parameters. The fitting of the experimental adsorption data, of each adsorbate at different temperatures, with integral equation, show an excellent correlation between experimental isotherms and calculated data. Results show that the influence of temperature on the behavior of the AED is very apparent in the case of ethane and nitrogen then methane. Indeed, we have noticed in the case of nitrogen that by increasing temperature, the AED function is shifted to the lower energies.

In the case of ethane, the extreme peak energies of the distribution are noticed to disappear. While in the case of methane the variation of temperature does not affect the energy distribution of adsorption. This is due to the structure of these adsorbates and their manner of adsorption on the surface of BDH-activated carbon.

Then, the evolution of the AEDs when varying temperature gives microscopic information about the influence of stereodynamics on gas-surface interaction, which allows us to relate the manner of the anchorage of the adsorbed molecules and the adsorption energy.

Although the present study is limited only to gas phase adsorption systems, the realized model can also be applied to liquid phase adsorption systems by using an adequate model as a local adsorption isotherm. Also it can be applied to desorption processes to deduce the energy of storage.

References

- [1] I.A.A.C. Esteves, M.S.S. Lopes, P.M.C. Nunes, J.P.B. Mota, Sep. Purif. Technol. 62 (2008) 281.
- [2] M. Jaroniec, K.P. Gadkaree, J. Choma, Colloids Surf., A 118 (1996) 203.
- [3] J. Roles, G. Guiochon, J. Chromatogr. 591 (1992) 267(212).
- [4] I. Quinones, B. Stanley, G. Guiochon, J. Chromatogr. A 849 (1999) 45.
- [5] Q. Hou, X. Lu, X. Liu, B. Hu, J. Yuan, J. Shen, J. Colloid Interface Sci. 280 (2004) 98.
- [6] K. Vasanth Kumar, M. Monteiro de Castro, M. Martinez-Escandell, M. Molina-Sabio, F. Rodriguez-Reinoso, Phys. Chem. Chem. Phys. 13 (2011) 5753.
- [7] S. Ross, J.P. Olivier, On Physical Adsorption, John Wiley and Sons, New York, 1964.
- [8] L.B. Harris, Surf. Sci. 10 (1968) 129.
- [9] G.F. Cerofolini, Thin Solid Films 23 (1974) 129.
- [10] M.M. Nederlof, W.H. Van Riemsdijk, L.K. Koopal, Environ. Sci. Technol. 26 (1992) 763.
- [11] W.A. House, M.J. Jaycock, Colloid Polym. Sci. 256 (1978) 52.
- [12] G. Calleja, B. Coto, A.M. Morales-Cas., Appl. Surf. Sci. 252 (2006) 4345.
- [13] S.A. Al-Muhtaseb, F.A. Abu Al-Rub, M. Al Zarooni, J. Chem. Eng. Data 52 (2007) 60.
- [14] Chi-Hsin Wu, Jin-Fang Shr, Chu-Fu Wu, Chien-Te Hseih, Physica E 40 (2008) 814.
- [15] L. Couture, R. Zitoun, Physique Statistique, Ellipses, 1992.
- [16] A. Ben Lamine, Y. Bouazra, Chem. Senses 22 (1997) 67.
- [17] M. Khalfaoui, S. Knani, M.A. Hachicha, A. ben Lamine, J. Colloid Interface Sci. 263 (2003) 350.
- [18] S.A. Al-Muhtaseb, Carbon 46 (2008) 1003.
- [19] E.J. Bottani, J.M.D. Tascon, Adsorption by Carbons Elsevier, 2008.
- [20] B. Charmas, R. Leboda, J. Chromatogr. A 886 (2000) 133.
- [21] P. Benoist, M. Courbage, Mathématiques pour la physique Eyrolles (1992) 1992; 134–162.
- [22] G.F. Cerofolini, Thin Solid Films 23 (1974) 129.
- [23] M. Manes, J.E. Hofer, J. Phys. Chem. 73 (1969) 584.
- [24] L.E. Cascarini de Torre, E.J. Bottani, Colloids Surf., A 116 (1996) 285.
- [25] J. Potoff, J. Siepmann, AlChE J. 47 (2001) 1676.
- [26] D.D. Do, S. Junpirom, D. Nicholson, H.D. Do, Colloids Surf., A 353 (2010) 10.
- [27] C.L. Kao, J.F. Weaver, R.J. Madix, Surf. Sci. 505 (2002) 115.
- [28] A.G. Bezus, A.V. Kiselev, A.A. Lopatkin, P.Q.G. Du, J. Colloid Interface Sci. 45 (1973) 2.
- [29] S. Giraudet, P. Pré, H. Tezel, P. Le Cloirec, Carbon 44 (2006) 1873.
- [30] I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361.
- [31] G.E.L. McKay, M. Geundi, M.M. Nassar, Water Res. 21 (1987) 1513.
- [32] P.A. Webb, C. Orr, R.W. Camp, J.P. Olivier, Y.S. Yunes, Analytical Methods in Fine Particle Technology, Micromeritics instrument corporation, GA, USA (1997) 1997; 81–90. (first ed.).