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Determination of the Porous Structure of Activated Carbons Using the IAE Concept. Influence of the Local Adsorption Model

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Abstract. In this paper we study a method for the determination of the micropore volume distribution function of activated carbons. This method is based on the Integral Adsorption Equation concept (IAE). The micropore volume distribution function is assumed to be a Gaussian of which the parameters are unknown. These parameters are determined using adsorption isotherms of carbon dioxide on a given activated carbon (F30/470 CHEMVIRON CARBON) at 278, 288, 298, 303, 308, 318 and 328 K and for pressures up to 100 kPa. Several local adsorption models are used (Langmuir, Volmer, Fowler-Guggenheim, Hill-de Boer). The influence of the choice of the local model on the pore volume distribution function is discussed. The physical validity of this function and the performances of the different models are presented. It appears that the effect of the temperature on the adsorption isotherms is difficult to model over a wide range of relative pressure. The Hill-de Boer and the Langmuir local models are the most efficient (average errors respectively equal to 3.53% and 2.80% in the studied range of temperature and pressure). They provide the most meaningful parameters for the pore volume distribution function.

Keywords: activated carbons, characterization, isotherms, integral adsorption equation

Introduction

The concept of Integral Adsorption Equation (IAE) has been widely used since its introduction by Ross and Olivier (1964). It aims at extending the domain of validity of adsorption models primarily developed for homogeneous adsorbents in order to apply them to heterogeneous ones. Given a local model which expresses the adsorbed mass m_{local} as a function of temperature T and pressure P on an energetically homogeneous surface, it is possible to calculate the corresponding adsorbed mass m on a heterogeneous surface by

$$m(T, P) = \int_{\varepsilon i}^{\varepsilon f} m_{\text{local}}(T, P, \varepsilon) F(\varepsilon)\, d\varepsilon \qquad (1)$$

where ε is the adsorption energy and $F(\varepsilon)$ is the energy distribution function for a given adsorbate-adsorbent system.

Such a procedure has first been applied to well known adsorption local models and for simple mathematical expressions of $F(\varepsilon)$. The analytical form of $F(\varepsilon)$ is assumed a priori. The parameters of the energy distribution function are determined by minimization of the discrepancies between experimental and calculated isotherms, Eq. (1) being solved by analytical or numerical way depending on the mathematical expressions chosen for $F(\varepsilon)$ and m_{local}. It is sometimes possible to determine analytically $F(\varepsilon)$ without assumption on its analytical expression using a given form for $m(T, P)$ and a simple local model. For example, the Freundlich, Dubinin-Radushkevich and Temkin empirical overall isotherm equations can be related to the Langmuir local model using respectively a decreasing exponential, a Gaussian and a constant energy distribution function. Extensive works have been conducted on the numerical determination of $F(\varepsilon)$ without any assumption neither on the mathematical form of $F(\varepsilon)$, nor on $m(T, P)$. Among the most well known, let us quote the HILDA and regulation methods. A good review of the existing studies devoted to adsorption on heterogeneous surfaces is given by Ross and Olivier (1964), Jaroniec and Madey (1988), and Rudzinski and Everett (1992).

Some authors have tried to correlate the energy distribution function $F(\varepsilon)$ which is a characteristic of the binary system adsorbate-adsorbent to the pore volume distribution function $F_V(H)$, H being the pore diameter (Bojan et al., 1992; Matranga et al., 1992; Cracknell et al., 1993; Jagiello and Schwarz, 1993). This correlation can be easily established for activated carbons. Indeed, it is commonly assumed that activated carbons exhibit an energetically homogeneous surface. The adsorption potential energy of a pore surface—adsorbate molecule system can be described by a classical Lennard-Jones function. Besides, the pores are considered to be slit-shaped. Their apparent heterogeneity on the energetic point of view is linked to their heterogeneous geometric structure. The integral adsorption equation concept coupled to an efficient modelling of the correlation between $F(\varepsilon)$ and $F_V(H)$ allow the determination of the pore volume distribution function of such solids from adsorption experimental data. The main advantage of such a function compared to the energy distribution function is that it can be considered as a characteristic of the adsorbent itself. The availability of such $F_V(H)$ functions is very interesting. Indeed, the adsorptive properties of activated carbons are widely governed by their porous structure which is not the case for other sorbents like silica gels for which the adsorptive properties are mainly due to their surface heterogeneity. Different approaches have been used for the determination of the pore volume distribution function of activated carbons. Some authors (Huber et al., 1978; Dubinin, 1985; Jaroniec and Pietrowska, 1986) have extended the basic Dubinin-Radushkevich equation considering it as a local model in Eq. (1). They have introduced a pore volume distribution function of the characteristic energy which has a physical meaning similar to the adsorption energy. The characteristic energy has been related to the pore size of activated carbons (Dubinin and Plavnik, 1968) so that it is possible to replace the pore volume distribution function of this characteristic energy by the corresponding pore volume distribution of the pore size. This procedure is rather simple. It allows the determination of a pore volume distribution function which should be independent on the adsorbate so that it should be possible to simulate adsorption isotherms of a given adsorbate on a given carbon using the pore volume distribution function of this adsorbent predetermined from adsorption data relevant to another adsorbate.

For the past five years, extensive researches have been performed on the determination of the pore volume distribution function of activated carbons using the Density Functional Theory to describe the adsorption process in a pore (Lastoskie et al., 1994; Olivier et al., 1994). Such a treatment is one of the more rigorous. It requires experimental adsorption data for simple molecules such as argon or nitrogen. Unfortunately, it does not allow the simulation of adsorption data relevant to other adsorbates using the predetermined pore volume distribution.

A third approach consists in using classical models such as the Langmuir, Volmer, Fowler-Guggenheim and Hill-de Boer models as local theory in Eq. (1) (Brauer et al., 1993; Jagiello and Schwarz, 1993; Heuchel et al., 1994; Jagiello et al., 1994). The pore volume distribution function is assumed to have a given analytical form and a classical correlation is used between $F(\varepsilon)$ and $F_V(H)$. In a previous paper (Frère et al., 1996), we have presented such a method. The pore volume distribution function had been considered to be a double Gaussian. The Hill-de Boer equation had been used as local model. A classical development leading to the relation between $F(\varepsilon)$ and $F_V(H)$ had also been presented in that paper. We had shown that using such a technique, it was possible to calculate adsorption isotherms for several adsorbates on the same adsorbent once the pore volume distribution function of this adsorbent and the adsorption energy of the different adsorbates on a graphite surface had been determined. Our calculations had been extended to the prediction of adsorption heats. We had shown that such an approach was realistic within given temperature and pressure ranges and for simple molecular structures of the adsorbates.

It is clear that the physical validity of this procedure is connected to the choice made for the local model and for the analytical form of the pore volume distribution function. The correlation which relates $F_V(H)$ to $F(\varepsilon)$ is also very important. In our previous paper, we had shown that it was difficult to model adsorption isotherms in a wide range of temperature. As the temperature appears mainly in the expression of the local model, we propose to study the effect of the choice of this local model on the performances of the overall procedure. In this paper, we will not pay attention to the validity of the analytical form of $F_V(H)$. We will not try to model adsorption isotherms for different adsorbates. Our only purpose will be to show the influence of the local model on the pore volume distribution function and to point out the model which leads to the best description of the temperature effect. The analytical form of $F_V(H)$ is taken to be a Gaussian so that the parameters to be determined are the average pore diameter, the standard deviation and the total micropore volume. We consider the Langmuir, Volmer, Fowler-Guggenheim and Hill-de Boer models. We use experimental adsorption isotherms of carbon dioxide on activated carbon (F30/470 CHEMVIRON CARBON) at temperatures of 278, 288, 298, 303, 308, 318, 328 K and for pressures up to 100 kPa (Berlier and Frère, 1996).

Theory

Considering a given adsorbate-adsorbent system, we compute, using the integral adsorption formulation, the adsorbed mass m at a given temperature T and pressure P by solving the integral:

$$m(T, P) = \int_0^\infty M\Gamma(T, P, H)F_A(H)\,dH \qquad (2)$$

where H is the pore diameter, $F_A(H)$ is the surface distribution function, M is the molar mass of the adsorbate, and $\Gamma(T, P, H)$ is the surface concentration.

We have now to choose mathematical expressions to describe $F_A(H)$ and $\Gamma(T, P, H)$. Considering the slit-like pores of activated carbons, the surface distribution function $F_A(H)$ is calculated from the pore volume distribution $F_V(H)$ by

$$F_A(H) = \frac{x(H)F_V(H)}{H} \qquad (3)$$

where

- $x(H)$ expresses the steric effect. It can take values in the segment [1, 2]. $x(H) = 1$ if the pore is so narrow that only one layer of molecules can be adsorbed between the walls, $x(H) = 2$ for large pores: one layer of adsorbed molecules may occupy each of the two surfaces of the pore.
- $x(H)$ has intermediate values when steric effect prevents the complete filling of each surface.
- $x(H)$ can be calculated as a function of H for a given adsorbate molecule size. In this way, $F_A(H)$ is relative to the surface effectively available to the adsorbate molecules;

$F_V(H)$ is assumed to be Gaussian:

$$F_V(H) = \frac{V_p}{\sqrt{2}\sigma_H}\exp\left(-\frac{(H - m_H)^2}{2\sigma_H^2}\right) \qquad (4)$$

where m_H is the average pore diameter, σ_H is the standard deviation, and V_p is the total micropore volume.

$\Gamma(T, P, H)$ is calculated using classical local models for homogeneous surfaces (Langmuir, 1916; Fowler and Guggenheim, 1939; Hill, 1960; Lyklema, 1991, 1994). In this paper we consider four such models: the Langmuir model (noted L), the Volmer model (noted V), the Fowler-Guggenheim model (noted FG) and the Hill-de Boer model (noted HdB). We present hereafter the expressions of $\Gamma(T, P, H)$ for the FG and HdB models. We also explain how it is possible to obtain such expressions for the L and V models from the ones corresponding respectively to the FG and HdB models.

The FG isotherm equation is

$$P = K_0^{\mathrm{FG}}\exp\left(\frac{U_0}{RT}\right)\frac{\Gamma b}{1 - \Gamma b}\exp\left(-c\Gamma b\frac{\omega}{RT}\right) \qquad (5)$$

and

$$K_0^{\mathrm{FG}} = \frac{RT(2\pi MRT)^{3/2}}{N_0^4 h^3}\frac{z_{g,\mathrm{rot}}z_{g,i}}{z_{s,\mathrm{rot}}z_{s,i}}\frac{1}{z_{s,\mathrm{vibr}}} \qquad (6)$$

with

$$\frac{1}{z_{s,\mathrm{vibr}}} = \prod_{j=x,y,z}\frac{1 - \exp\left(-\frac{N_0 h f_j}{RT}\right)}{\exp\left(-\frac{N_0 h f_j}{2RT}\right)} \qquad (7)$$

In these equations:

U_0	is the adsorption energy (J mol^{-1});
R	is the ideal gas constant ($R = 8.314$ J mol^{-1} K^{-1});
b	is the molar surface of the adsorbate (m^2 mol^{-1});
c	is the number of nearest-neighbor adsorption sites in the surface lattice;
ω	is the interaction energy between adsorbed molecules on adjacent sites (J mol^{-1}); it is taken positive;
N_0	is the Avogadro's number ($N_0 = 6.022 \times 10^{23}$ mol^{-1});
h	is the Planck's constant ($h = 6.626 \times 10^{-34}$ J s);
$z_{g,\mathrm{rot}}$	is the rotational contribution to the partition function of a molecule in the gas phase;
$z_{g,i}$	is the partition function contribution for internal degrees of freedom of a molecule in the gas phase;
$z_{s,\mathrm{rot}}$	is the rotational contribution to the partition function of a molecule in the adsorbed phase;

$z_{s,i}$	is the partition function contribution for internal degrees of freedom of a molecule in the adsorbed phase;
$z_{s,\text{vibr}}$	is the vibrational contribution to the partition function of a molecule in the adsorbed phase;
f_j	is the vibration frequency of the adsorbed molecules along the j-axis (s^{-1}),
$j = x, y, z$	are the three spatial directions. The x and y-axes are parallel to the adsorption surface, the z-axis is perpendicular to the adsorption surface.

When we take $\omega = 0$, Eq. (5) leads to the Langmuir isotherm equation.

The HdB isotherm equation is:

$$P = K_0^{\text{HdB}} \exp\left(\frac{U_0}{RT}\right) \frac{\Gamma}{1-\Gamma b} \exp\left(\frac{\Gamma b}{1-\Gamma b}\right) \times \exp\left(-\frac{2a\Gamma}{RT}\right) \tag{8}$$

and

$$K_0^{\text{HdB}} = \frac{RT(2\pi MRT)^{1/2}}{N_0 h} \frac{z_{g,\text{rot}} z_{g,i}}{z_{s,\text{rot}} z_{s,i}} \frac{1}{z_{s,\text{vibr}}} \tag{9}$$

with

$$\frac{1}{z_{s,\text{vibr}}} = \frac{1 - \exp\left(-\frac{N_0 h f_j}{RT}\right)}{\exp\left(-\frac{N_0 h f_j}{2RT}\right)} \tag{10}$$

where $j = z$.

In Eqs. (8), (9) and (10), the only new parameter is a. It takes into account the interaction energy between the mobile adsorbed molecules. It has more or less the same physical meaning as $c\omega$ in Eq. (5).

Taking $a = 0$ in Eq. (8) leads to the Volmer isotherm equation.

In Eqs. (5) to (10) the parameters are a, b, c, ω, U_0, f_j for $j = x, y$ and z.

The parameters a and b are calculated respectively from the energetic and geometric van der Waals parameters (Ross and Olivier, 1964, Frère et al., 1996) available in literature (Lange, 1967).

Given we want the two models to give the same contribution of the interactions between adsorbed molecules, we lay down:

$$T_{c_{2D}}^{\text{HdB}} = T_{c_{2D}}^{\text{FG}} \tag{11}$$

where $T_{c_{2D}}^{\text{HdB}}$ and $T_{c_{2D}}^{\text{FGB}}$ are respectively the two-dimension critical temperatures calculated from the HdB and FG models.

Given these critical temperatures can be expressed as functions of the different parameters a, b and c, ω:

$$T_{c_{2D}}^{\text{HdB}} = \frac{2(a/b)}{6.75R} \tag{12}$$

$$T_{c_{2D}}^{\text{FG}} = \frac{c\omega}{4R} \tag{13}$$

Using Eq. (11) with Eqs. (12) and (13), and taking $c = 6$, it is then possible to express ω as a function of a and b:

$$\omega = 0.1975\left(\frac{a}{b}\right) \tag{14}$$

f_j and U_0 are functions of the pore diameter H. The computation of these functions requires the knowledge of the potential energy function U_{pot} of an adsorbate molecule in a pore. The full description of the procedure leading from U_{pot} to $f_j(H)$ and $U_0(H)$ is given in Frère et al. (1996). Such a computation appeals for two new parameters: σ_{ms} is the geometric Lennard-Jones parameter for the adsorbate molecule-surface system and U_e is the energetic parameter corresponding to the well depth of U_{pot} when H tends to infinity. The procedure described in order to obtain f_j is only valid for its z component (vibration perpendicularly to the adsorption surface). In this paper, we assume that $f_x = f_y = f_z$ as commonly proposed (Ross and Olivier, 1964). The parameter σ_{ms} is the average of σ_{mm} and σ_{ss} respectively the geometric L.-J. parameters for the adsorbate and for the adsorption surface. The first one is available in Hirschfelder et al. (1964). The second one is also known for a graphite surface: $\sigma_{\text{ss}} = 3.4$ Å. As to U_e, it is unknown.

The four models studied in this paper are characterized by some common assumptions. Other ones differ from one model to another. The common assumptions express that:

- the gas is ideal;
- the adsorption on a pore surface is monolayer;
- the adsorbed molecules are randomly distributed on the surface;

Table 1. Parameters of the different models.

	a (J m^2 mol^{-2})	b (m^2 mol^{-1})	c	ω (J mol^{-1})	σ_{ms} (Å)	M (kg mol^{-1})
CO_2	421995712	98948	6	842.3	3.943	0.044098

- the vibrations of the adsorbed molecules are considered to be harmonic;
- there is no change in the rotational and internal behaviors of the adsorbate molecules when passing from the gas phase to the adsorbed phase so that in Eqs. (6) and (9):

$$\frac{z_{g,\mathrm{rot}} z_{g,i}}{z_{s,\mathrm{rot}} z_{s,i}} = 1 \tag{15}$$

The particular assumptions of the L model are:

- the molecules are fixed on the surface and can thus vibrate along the x, y and z-axes;
- there is no interaction between the adsorbed molecules.

The particular assumptions of the V model are:

- the molecules are mobile on the surface and can thus vibrate only along the z-axis.
- there is no interaction between the adsorbed molecules.

The particular assumptions of the FG model are:

- the molecules are fixed on the surface and can thus vibrate along the x, y and z-axes;
- interactions between adsorbed molecules are taken into account.

For the HdB model:

- the molecules are mobile on the surface and can thus vibrate only along the z-axis;
- interactions between adsorbed molecules are taken into account.

For a given adsorbate-adsorbent system, it is possible to calculate the adsorbed mass m at given T and P using Eq. (2). In this equation $F_A(H)$ is calculated thanks to Eqs. (3) and (4) in which m_H, σ_H and V_p are unknown parameters (characteristics of the pore volume distribution function). $\Gamma(T, P, H)$ is calculated by Eqs. (5), (6) and (7) if we consider the FG (L) local model or by Eqs. (8), (9) and (10) for the HdB (V) local model. In Eqs. (5) to (10), the parameters a, b, c, ω can be determined easily. Their values are listed in Table 1.

Equations (5) to (10) make also appear U_0 and f_j which are functions of H. Their calculation involved two other parameters σ_{ms} and U_e. The first one is known (Bojan et al., 1992; Matranga et al., 1992; Cracknell et al., 1993) and is also given in Table 1; the other one (U_e) must be determined. It is then possible to determine the four unknown parameters m_H, σ_H, V_p and U_e from experimental adsorption isotherms. Such a procedure will allow us to compare the values obtained for these parameters when using the L, V, FG and HdB models and to show the predictive performances of the overall procedure when taking such different expressions for the local adsorption model. Similar studies have already been conducted, but in most of them, the authors have considered an energy distribution function instead of a pore volume distribution function, their choice being justified by the sorbent they use (Jaroniec et al., 1976; House, 1978; Brauer et al., 1982; Sircar, 1984). Jagiello (Jagiello and Schwarz, 1993; Jagiello et al., 1994) has followed a procedure similar to ours. Neverthelsss, he has considered that the K_0 parameter could not be calculated and had to be determined by optimization. In this paper, K_0 parameters are calculated using Eqs. (6), (7), (9) and (10). These equations results from statistical thermodynamic developments. Their use implies some assumptions which can not be a priori justified. It is very difficult to state which one of the procedures is the most correct. Thus, the originality of this paper is to study the equivalence of the classical local models once used in the Integral Adsorption Equation with calculated K_0 and considering a pore volume distribution function.

Experimental

This study requires the confrontation between experimental and calculated adsorbed mass in a wide range of temperature. Given some restrictive assumptions of the procedure, the experimental data must be measured within a given range of conditions:

- the molecular structure of the adsorbate must remain as simple as possible;
- the assumptions on the gas ideality and on monolayer behavior of the adsorbed phase are valid at low relative pressure.

That is the reason why we use carbon dioxide adsorption isotherms at seven temperatures: 278, 288, 298, 303, 308, 318 and 328 K. The maximum pressure is, in all cases, 100 kPa.

The measurement of these adsorption isotherms has been performed with a thermobalance coupled to a calorimeter (TG-DSC 111 SETARAM). Such an apparatus allows the simultaneous determination of the mass change and heat flow during the adsorption process. The experimental procedure and the results are described elsewhere (Berlier and Frère, 1996). In this work, we do not use the calorimetric results.

The experimental error is about 0.05 kPa on the pressure and 0.1 K on the temperature. As to the adsorbed mass, different kinds of errors must be taken into account. The measurement accuracy on the mass of the adsorbent sample and on the mass uptake during adsorption is generally good (error <0.5%). However, the buoyancy effect causes systematic errors in the mass measurement with typical values of 0 to 1%. These errors are within the same range as the deviation between experimental values when repeating the same experiment with different samples of the same adsorbent.

We use as sorbent an activated carbon provided by CHEMVIRON CARBON. Its main structural properties are given in Table 2. These characteristics have been determined from nitrogen adsorption isotherm at 77 K using the classical t-plot and the DA procedures.

Results and Discussion

Using the seven carbon dioxide adsorption isotherms we determine the four unknown parameters of our procedure that is to say the average pore diameter m_H, the standard deviation σ_H of the pore volume distribution function, the total micropore volume V_p and the adsorption energy U_e. These parameters are determined for the L, V, FG and HdB models by minimization of the following objective function:

$$OF = \frac{1}{N}\sum_{k=1}^{N}\frac{|m_{k,\text{exp}} - m_{k,\text{calc}}|}{m_{k,\text{exp}}} \tag{16}$$

where N is the total number of experimental data, $m_{k,\text{exp}}$ is the experimental mass; $m_{k,\text{calc}}$ is the corresponding calculated mass.

Table 2. Main structural characteristics of activated carbon F30/470 CHEMVIRON CARBON ($V_{p,t}$: total micropore volume obtained by the t-method, $V_{p,DA}$: total micropore volume obtained by the Dubinin-Astakhov method, A_{mpores}: specific surface area of the micropores obtained by the t-method).

	$V_{p,t}$ ($\text{m}^3\ \text{kg}^{-1}$)	$V_{p,DA}$ ($\text{m}^3\ \text{kg}^{-1}$)	A_{mpores} ($\text{m}^2\ \text{kg}^{-1}$)
F30/470	3.861×10^{-4}	3.826×10^{-4}	993.5×10^3

Table 3 gives the determined parameters for the L, V, FG and HdB models. The different models lead to quite different pore volume distribution functions. These functions are presented in Fig. 1. The Volmer model gives unrealistic results. The pore volume distribution function is very narrow ($\sigma_H = 0.058$ Å) and the average pore diameter is very low ($m_H = 7.169$ Å). Such results are not compatible with the adsorptive properties of our activated carbon which is able to adsorb big molecules. Besides, the total micropore volume is high compared to the usual values (see Table 2). Considering the average pore diameter and the standard deviation, the L and FG models give more or less the same results ($m_H \approx 8.600$ Å, $\sigma_H \approx 0.160$ Å which are realistic results). The only differences are in the total micropore volume and in the adsorption energy. The FG model gives a weak value for V_P ($V_P = 2.800 \times 10^{-4}$ $\text{m}^3\ \text{kg}^{-1}$). The L model seems to compensate the absence of interactions between adsorbed molecules by increasing the micropore volume and the adsorption

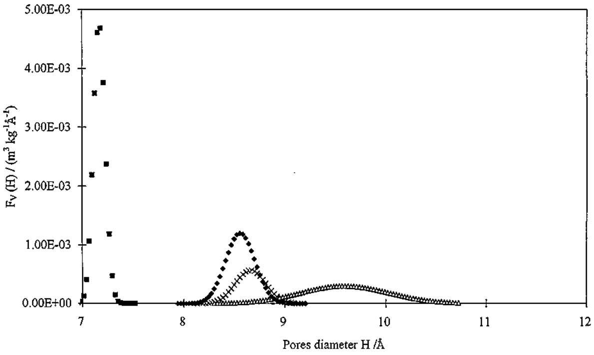

Figure 1. Micropore volume distribution functions of activated carbon (type F30/470 CHEMVIRON CARBON) (♦: L model, ■: V model, ×: FG model, Δ: HdB model).

Table 3. Parameters of the pore volume distribution functions obtained by the different models.

Parameters	L model	V model	FG model	HdB model
m_H (Å)	8.561	7.169	8.636	9.734
σ_H (Å)	0.144	0.058	0.181	0.512
V_p ($m^3\ kg^{-1}$)	4.314×10^{-4}	6.924×10^{-4}	2.800×10^{-4}	3.636×10^{-4}
U_e ($J\ mol^{-1}$)	13524.9	14595.8	12774.1	12075.6

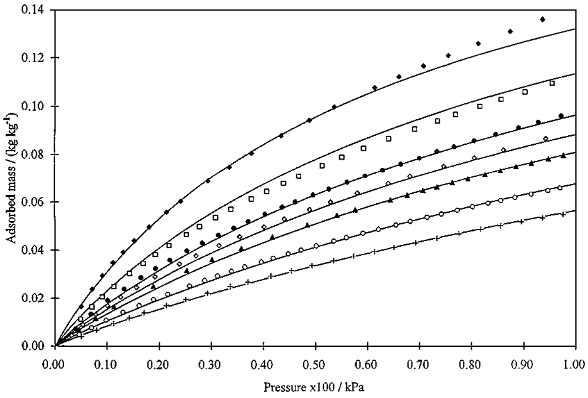

Figure 2. Adsorption isotherms of carbon dioxide on activated carbon (type F30/470 CHEMVIRON CARBON) (—: calculated from the L model at 278, 288, 298, 303, 308, 318, 328 K, ♦: experimental 278 K, □: experimental 288 K, ●: experimental 298 K, ◊: experimental 303 K, ▲: experimental 308 K, ○: experimental 318 K, +: experimental 328 K).

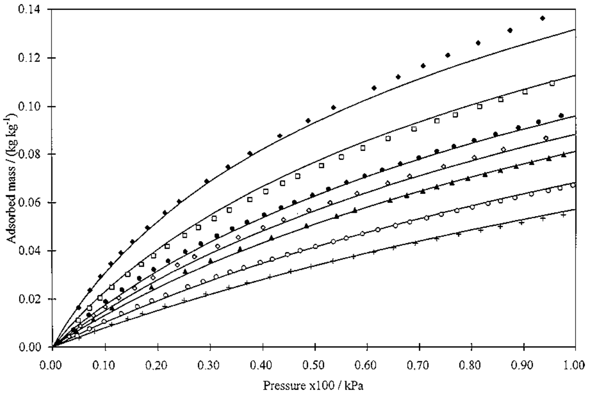

Figure 3. Adsorption isotherms of carbon dioxide on activated carbon (type F30/470 CHEMVIRON CARBON) (—: calculated from the V model at 278, 288, 298, 303, 308, 318, 328 K, ♦: experimental 278 K, □: experimental 288 K, ●: experimental 298 K, ◊: experimental 303 K, ▲: experimental 308 K, ○: experimental 318 K, +: experimental 328 K).

energy ($V_P = 4.314 \times 10^{-4}$ $m^3\ kg^{-1}$, $U_e = 13524.9$ $J\ mol^{-1}$). The HdB exhibits completely different results. The function is located in a range of higher H values and is wider than the ones provided by the other models ($m_H = 9.734$ Å, $\sigma_H = 0.512$ Å). The total micropore volume is physically correct ($V_P = 3.636 \times 10^{-4}$ $m^3\ kg^{-1}$).

The comparison between the calculated and experimental isotherms is presented in Figs. 2, 3, 4 and 5 respectively for the L, V, FG and HdB models. The average deviations between experimental and calculated masses are respectively 2.80, 3.00, 3.57 and 3.53%. The V model seems to give very good results except at the lowest temperature for which the highest relative pressure is reached. However, as already stated, the pore volume distribution function provided by this model is not realistic. Once applied to simulate adsorption of bigger molecules such as butane, this function would lead to quasi-zero adsorbed masses, which is not experimentally the case. The HdB model leads to poorer simulation results (3.53%) but the physical significance of the pore volume distribution function is better. This model seems to give a good representation of the shape of the isotherms but only the intermediate temperatures isotherms are perfectly fitted (average

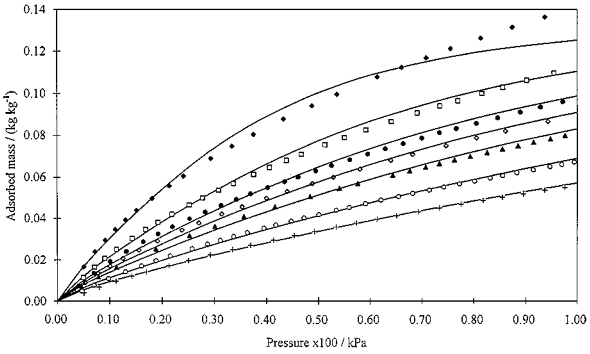

Figure 4. Adsorption isotherms of carbon dioxide on activated carbon (type F30/470 CHEMVIRON CARBON) (—: calculated from the FG model at 278, 288, 298, 303, 308, 318, 328 K, ♦: experimental 278 K, □: experimental 288 K, ●: experimental 298 K, ◊: experimental 303 K, ▲: experimental 308 K, ○: experimental 318 K, +: experimental 328 K).

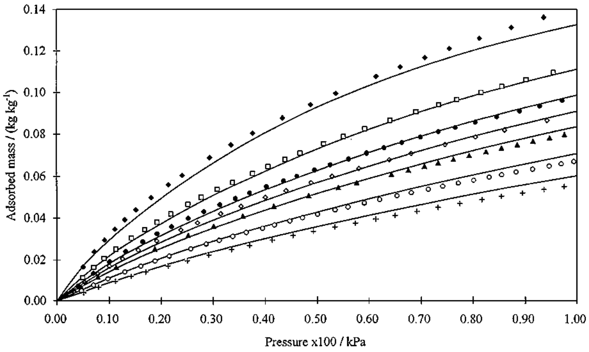

Figure 5. Adsorption isotherms of carbon dioxide on activated carbon (type F30/470 CHEMVIRON CARBON) (—: calculated from the HdB model at 278, 288, 298, 303, 308, 318, 328 K, ◆: experimental 278 K, □: experimental 288 K, ●: experimental 298 K, ◊: experimental 303 K, ▲: experimental 308 K, ○: experimental 318 K, +: experimental 328 K).

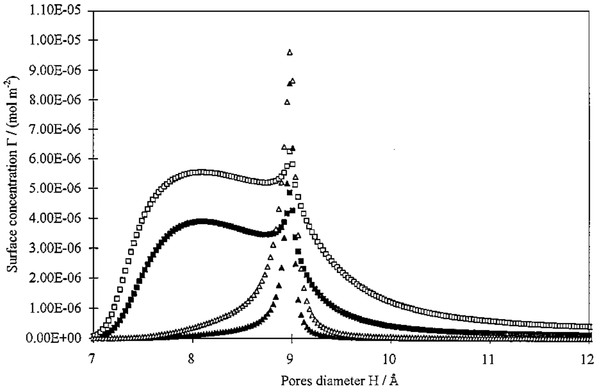

Figure 6. Surface concentration as a function of H for the L and V models (▲: calculated from the L model at $T = 328$ K and $P = 17$ kPa, △: calculated from the L model at $T = 328$ K and $P = 50$ kPa, ■: calculated from the V model at $T = 328$ K and $P = 17$ kPa, □: calculated from the V model at $T = 328$ K and $P = 50$ kPa).

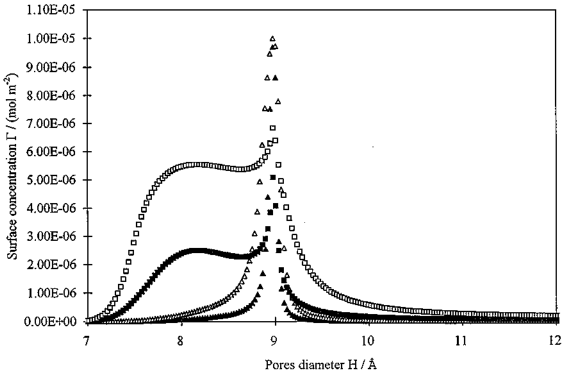

Figure 7. Surface concentration as a function of H for the FG and HdB models (▲: calculated from the FG model at $T = 328$ K and $P = 17$ kPa, △: calculated from the FG model at $T = 328$ K and $P = 50$ kPa, ■: calculated from the HdB model at $T = 328$ K and $P = 17$ kPa, □: calculated from the HdB model at $T = 328$ K and $P = 50$ kPa).

deviation ≈2.80% at 303 K). The lower temperatures isotherms are undervalued by the model (average deviation at 278 K ≈ 5.20%). However, the high temperatures isotherms are overvalued (average deviation at 328 K ≈ 6.2%). The L model gives both good simulation results (2.8%) and physically acceptable parameters. On the other hand, the FG model does not allow a good representation of the experimental results (3.57%) and gives a rather low value of the pore volume. Its main failing is that it gives bad isotherms shapes. Indeed, for a given isotherm, given the pressure range, the adsorbed mass is either overestimated or underestimated. These deviations tend to grow in importance at low temperature.

Such differences in the pore volume distribution functions and in the performances of the overall procedure show the difficulty to obtain reliable information about the microporous structure of activated carbons. These differences in the pore volume distribution functions may be explained by the fact that the models lead to different behaviors of the adsorbed phase. Figures 6 and 7 show the evolution of Γ as a function of H for a given temperature ($T = 328$ K), for two different pressures ($P = 17$ kPa and $P = 50$ kPa). For clarity, Fig. 6 presents the curves for the L and V models. Figure 7 is devoted to the FG and HdB models. Such curves are in fact intermediate results in the calculation of adsorption isotherms. Such Γ curves are completely independent of $F_V(H)$. We see that whatever the pressure and the model Γ is equal to zero for very narrow micropores (repulsive micropores). Considering the V model, Γ increases rapidly for increasing H. It reaches a kind of plateau with a first maximum at $H = 8.160$ Å which corresponds to the maximum of the adsorption energy $|U_0(H)|$. A second maximum appears at $H = 8.980$ Å. It corresponds to the minimum value of the vibrational frequency of the adsorbed molecules perpendicularly to the surface. For upper values of H, the decrease of Γ is less rapid than the initial increase.

Considering the L model, the Γ curves have a completely different behavior. The only maximum appears for $H = 8.980$ Å. This maximum is characterized by very high values of $\Gamma(\Gamma \approx 10^{-5}$ mol m^{-2} for both the high pressure and low pressure curves) which is higher than the maximum Γ value obtained with the V model.

The initial increase of Γ is slower than the one observed for the V model. On the other hand, the decrease of Γ for $H > 8.980$ Å is rather sharp. When passing from the low pressure to the high pressure, the curve has a tendency to broaden. For both the V and L models, the shape of the local isotherm (Γ as a function of P for a given H) is strongly dependent on H.

When we compare Fig. 6 with Fig. 7, we see that the behaviors of the L and V models are similar, respectively to the ones of the FG and HdB models. The high pressure curves are more or less the same for the V and HdB models. On the other hand, the low pressure curve of the V model exhibits higher Γ values compared to the corresponding HdB curve. This could seem surprising as the Volmer model does not take into account the interactions between adsorbed molecules. Such interactions enhance the adsorption phenomenon. However, the U_e parameter is higher in the case of the Volmer model ($U_e = 14595.8$ J mol^{-1} instead of 12075.6 J mol^{-1} for the HdB model). We know that high U_e values lead to important initial slopes of the isotherms especially in pores of molecular dimensions ($H = 7.5$ to 8.5 Å). As a consequence, the effect of H on the local isotherms will be different for the V and HdB models in this region.

The comparison between the L and FG models (Figs. 6 and 7) does not show important quantitative differences neither for the high pressure curve nor for the low pressure one. In fact, a mathematical study of Eq. (5) would show that within certain limits there is no effect of $c\omega$ and U_e on Γ at its maximum. Besides, in the vicinity of this maximum, Γ seems to be nearly independent on the pressure ($H \approx 8.980$ Å, $\Gamma \approx 10^{-5}$ mol m^{-2} whatever the pressure). In fact, the local isotherm has a tendency to show a sharp increase at very low pressures with a plateau for higher P values. That is the reason why there is no difference in the behaviors of the L and FG models. Differences could occur for lower value of $H (H < 8.98$ Å) because in this area the adsorption energy U_e and the interaction between adsorbed molecules seem to play a more important role. Nevertheless, once again, the fact that $c\omega = 0$ for the L model leads to a higher value of U_e for this model ($U_e = 13524.9$ J mol^{-1}; for the FG model, $U_e = 12774.1$ J mol^{-1}). It results from it that no significant differences appear. It seems that the effect of H on the local isotherm is rather similar when comparing the L and FG models.

The shape of the pore volume distribution function is strongly dependent on the shape of the Γ curves. Indeed, the pore volume distribution function must be such as that the integration over H of $\Gamma \frac{x(H) F_V(H)}{H}$ fits the experimental isotherms in the studied ranges of temperature and pressure. In order to obtain correct values of m, using the FG or L local models in Eq. (2), it is clear that the pore volume distribution function must be located in the range of H for which Γ is significantly high that is to say between 8.5 and 9.5 Å. Equation (9) shows that, given these low values of H, the pore volume does not have to be high to give a sufficient adsorption surface. These qualitative considerations allow to explain the shape of $F_V(H)$ for the FG model ($m_H = 8.636$ Å, $\sigma_H = 0.181$ Å and $V_P = 2.800 \times 10^{-4}$ m^3 kg^{-1}). We see that the pore volume distribution is not centred at $H = 8.980$ Å which would lead to bad isotherm shapes. That is the reason why m_H is located for H slightly lower than $H = 8.980$ Å with a small standard deviation. Given there is almost no differences between the Γ curves provided by L and FG models, it is clear that the two pore volume distribution functions should be similar. It is the case for the average pore diameter and for the standard deviation. On the other hand, the L model provides a more important pore volume. This is mainly due to the fact that both m_H and σ_H provided by the L model have weaker values than those provided by the FG model. It corresponds smaller Γ values in the case of the L model. Besides, for such low values of H, only one layer of molecules can enter the pores, leading to a greater pore volume. Anyway it must be noticed that the L model leads to a better simulation of the experimental data. Indeed, the effect of the temperature is well represented. On the contrary, the FG model gives bad isotherms shapes. This effect cannot be discussed from the Γ curves in Figs. 6 and 7 as we only compared two different pressures setting a constant temperature. Anyway, when we examine Eq. (5), we see that the quantities U_0 and $c\omega$ appear in terms depending on the temperature ($U_0/(RT)$, $(c\omega\Gamma b)/RT$). As U_e (parameter in the calculation of U_0) and $c\omega$ differ when passing from the L model to the FG model, it is not surprising to find differences in the dependence of Γ with the temperature. Besides, given U_0 is a function of H, this explains why m_H and σ_H are slightly different for the L and FG models although the examined Γ curves in Figs. 6 and 7 look exactly the same. Given the broader domain of H in which Γ has significant values, the pore volume distribution function provided by the HdB model exhibits a higher standard deviation ($\sigma_H = 0.512$ Å). The kind of plateau located between the two maxima ($H = 8.160$ Å and $H = 8.980$ Å) in which Γ reaches important values tends to move the pore volume distribution function in a higher H values area (compared to the V and FG models) ($m_H = 9.734$ Å). It results from this high average pore diameter that the total pore volume required to develop a sufficient adsorption surface is greater than the one obtained by the FG model. Such a reasoning is not valid for the V model. Indeed, although the V and HdB Γ curves have similar qualitative behaviors, we have shown that the V model had a tendency to give local isotherms characterized by high initial slopes which is not the case experimentally. The only way to escape from this situation is to locate the pore volume distribution function in the low pore diameter range for which the evolution of Γ with pressure P is smoother. In this H values area, Γ is so weak that the pore volume is very important.

Conclusion

It appears from this study that the use of the Integral Adsorption Equation procedure for the determination of the micropore volume distribution function of heterogeneous sorbents must be carried on with care. Indeed the link between the fundamental notion of pore volume distribution function and the macroscopic adsorption data is not obvious. Its mathematical expression requires numerous assumptions. In this paper we have tried to emphasize the importance of the local model.

When considering only the deviations between experimental and calculated data the V and L models seem more interesting. Nevertheless, we have shown that minimum discrepancies between experiment and theory was not a good criterion. Indeed, the dependence of Γ on P and T is very complex. The adsorption energy (U_e) and the interaction between adsorbed molecules ($c\omega$, a) play an important role in this dependence. Besides the local isotherms $\Gamma = f(T, P)$ are function of H which leads to completely different pore volume distribution functions for the different models. Such a complexity appeals for a critical analysis of the parameters obtained from the mathematical optimization procedure. It appears from this analysis that the Langmuir model leads to quite interesting results. The physical significance of the pore volume distribution is obvious and the only discrepancies between experiment and theory occur at higher relative pressure where the multilayer adsorption in mesopores becomes important.

The FG model is poor. Anyway we must not forget that we have set the value of the interaction parameter $c\omega$. An interesting solution should be to consider the FG model with lower value of $c\omega$. In the same order of idea we have to keep in mind that we have fixed the analytical form of $F_V(H)$. Given the influence of H on the local isotherm, the choice of this function indirectly influences our comments about the validity of the local model.

Anyway it is surprising that the L and FG models (assuming a localised adsorption) give good results at such high temperatures. Indeed, when considering the 'mobile adsorption' models (V and HdB), the provided results are less satisfactory.

The HdB model gives physically correct parameters but poor simulation results. The conclusions are opposite for the V model. As for the FG model, the HdB model with a weaker value for a (a should be considered as a floating parameter) could be a good compromise. The same reasoning as to the influence of $F_V(H)$ may be repeated.

Given the high density of the adsorbed phase, the use of more sophisticated equation of state could also lead to interesting results. It appears from this first study that our procedure should be tested in a wider range of experimental conditions using several adsorbates and allowing a more flexible analytical form of the pore volume distribution function. More sophisticated equations of state should be tested and the parameters relative to interactions between adsorbed molecules should no longer be calculated from the corresponding three-dimension parameters.

These proposals are obliged ways for the validation of the use of the IAE concept for porous solids characterization.

Nomenclature

a	Energetic parameter of the two-dimension van der Waals equation of state	J m^2 mol^{-2}
A_{mpores}	Surface developed by the micropores; determined by the t-method	m^2 kg^{-1}
b	Geometric parameter of the two-dimension van der Waals equation of state, adsorbate molar surface	m^2 mol^{-1}
c	Number of nearest-neighbor adsorption	—

	sites in the surface lattice	
f_j	Vibrational frequency of the adsorbed molecules along the j-axis	s^{-1}
F	Adsorption energy distribution function	mol J^{-1}
F_A	Surface distribution function	m^2 kg^{-1} $Å^{-1}$ or m^2 kg^{-1} m^{-1}
F_v	Pore volume distribution function	m^3 kg^{-1} $Å^{-1}$ or m^3 kg^{-1} m^{-1}
h	Planck's constant: $h = 6.626 \times 10^{-34}$ J s	
H	Pore diameter	Å or m
$j = x, y, z$	Spatial directions, the x and y-axes are parallel to the adsorption surface, the z-axis is perpendicular to the adsorption surface	—
K_0^{FG}	Pre-exponential factor for the Fowler-Guggenheim model	kPa
K_0^{HdB}	Pre-exponential factor for the Hill-de Boer model	kN mol^{-1}
m	Adsorbed mass	kg kg^{-1}
m_H	Average pore diameter	Å or m
$m_{k,\mathrm{calc}}$	kth calculated adsorbed mass	kg kg^{-1}
$m_{k,\mathrm{exp}}$	kth experimental adsorbed mass	kg kg^{-1}
m_{local}	Local adsorbed mass	kg kg^{-1}
M	Molar mass of the adsorbate	kg mol^{-1}
N	Number of experimental data	—
N_0	Avogadro's number: $N_0 = 6.022 \times 10^{23}$ mol^{-1}	
P	Pressure	kPa
R	Ideal gas constant: $R = 8.314$ J mol^{-1} K^{-1}	—
T	Temperature	K

$T_{c_{2\mathrm{D}}}^{\mathrm{HdB}}$	Two-dimension critical temperature according to the HdB model	K
$T_{c_{2\mathrm{D}}}^{\mathrm{FG}}$	Two-dimension critical temperature according to the FG model	K
U_0	Adsorption energy, minimum value of U_{pot} for a given H	J mol^{-1}
U_e	Minimum value of U_{pot} when H tends to ∞	J mol^{-1}
U_{pot}	Potential energy function of an adsorbate molecule located in a pore	J mol^{-1}
V_p	Total micropore volume	m^3 kg^{-1}
$V_{p,\mathrm{DA}}$	Total micropore volume determined by the D-A method	m^3 kg^{-1}
$V_{p,t}$	Total micropore volume determined from the t-method	m^3 kg^{-1}
x	Weighing factor for the surface filling	—
$z_{g,i}$	Partition function contribution for internal degrees of freedom of a molecule in the gas phase	—
$z_{g,\mathrm{rot}}$	Rotational contribution to the partition function of a molecule in the gas phase	—
$z_{s,i}$	Partition function contribution for internal degrees of freedom of a molecule in the adsorbed phase	—
$z_{s,\mathrm{rot}}$	Rotational contribution to the partition function of a molecule in the adsorbed phase	—
$z_{s,\mathrm{vibr}}$	Vibrational contribution to the partition function of a molecule in the adsorbed phase	—
ε	Adsorption energy on an homogeneous surface	J mol^{-1}

Γ	Surface concentration	mol m^{-2}
σ_{mm}	Geometric Lennard-Jones parameter for the adsorbate molecule	Å or m
σ_{ms}	Geometric Lennard-Jones parameter for the adsorbed molecule-surface system	Å or m
σ_{ss}	Geometric Lennard-Jones parameter for the adsorption surface ($\sigma_{\mathrm{mm}} = 3.400$ Å for graphite)	Å
σ_H	Standard deviation of the pore volume distribution function	Å or m
ω	Interaction energy between adsorbed molecules on adjacent sites (taken positive)	J mol^{-1}.

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