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Determination of the Micropore Volume Distribution Function of Activated Carbons by Gas Adsorption

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Abstract. A new method for the determination of the micropore volume distribution function of activated carbons is presented. It is based on the treatment of pure gas adsorption isotherms by a theoretical model derived from the Hill-de Boer theory. Adsorption data (isotherms and heat curves) for carbon dioxide, ethane and ethylene on activated carbon (F30/470 CHEMVIRON CARBON) have been provided by a thermobalance coupled to a calorimeter (TG-DSC 111 SETARAM) at different temperatures (233, 273, 303 and 323 K) for pressures up to 100 kPa. Adsorption isotherms of carbon dioxide and ethane at 303 and 323 K have been used for the determination of the micropore volume distribution function of the activated carbon of interest. The knowledge of its structure has then allowed the simulation of adsorption isotherms and heats for the same adsorbates at the same temperatures as those experimentally studied. Similar calculations have been conducted for ethylene. Whatever the adsorbate (carbon dioxide and ethane used for the determination of the micropore volume distribution function or ethylene), the mean deviation between experimental and calculated isotherms does not exceed 4% at quasicritical and supercritical temperatures (303 and 323 K). In the same temperature conditions, discrepancies between calculation and experiment reach about 10% for adsorption heats. For both isotherms and heats, large discrepancies appear at low temperature (233 and 273 K). This method allows the determination of the micropore volume distribution function of activated carbons. The validity of the results is insured using several isotherms of several adsorbates and taking into account the calorimetric effect of the phenomenon. That is the reason why this method can also be seen as a new possible model for pure gas adsorption data prediction. This paper also presents a brief summary of the state of the art in this field.

Keywords: activated carbons, characterization of structure, equilibrium, heat of adsorption, theory

Introduction

The availability of adsorption data is of prime importance in the design of industrial processes. Depending on the applications, these data may cover a wide range of temperature and pressure conditions and concern the calorimetric and massic aspects as well as the thermodynamic and kinetic ones. Such data are often obtained by experimental means coupled to theoretical models. These models allow the interpolation of adsorption data within the limits of conditions in which the experimental data have been obtained. Some of them allow light extrapolations outside these limits. Others are able to predict gas mixtures adsorption data from the corresponding pure gas data.

Unfortunately, until now there does not exist any model which is able to predict pure gas adsorption data from tabulated parameters concerning the adsorbate on the one hand and the adsorbent on the other hand. This poor state of the art is mainly due to the complexity of the phenomenon. Indeed, most of the microscopic parameters of the theoretical models are difficult to determine by direct measurement: the surfacic behaviour of the adsorbed phase located in pores of molecular dimension, the heterogeneous structure of some adsorbents make it impossible. These parameters must be determined by minimization of the deviation between simulation results and experimental data. The physical validity of the parameters is connected to the adequacy of the model: different models may lead to different

values of the same parameters. Another problem is that some parameters are relevant to the binary system adsorbate-adsorbent so that it makes difficult any tabulation for prediction purpose. Last but not least, most of the theoretical models make too simple assumptions on the structure of the adsorbents. As a consequence, the effect of the structure of the adsorbent is not well described and the models fail at data prediction.

On the thermodynamic side, the most well known approaches of the theoretical simulation of pure gas adsorption data are the statistical thermodynamics developments, the macroscopic models based on the potential theory and the vacancy solution model. Among the models based on statistical thermodynamics, the most commonly used are the Langmuir, the B.E.T and the Fowler-Guggenheim theories (Langmuir, 1916; Brunauer et al., 1938; Fowler and Guggenheim, 1939; Hill, 1960; Lyklema, 1991 and 1994; Rudzinski and Everett, 1992). They derive from the calculation of the canonical partition function of the adsorbed phase which leads both to the determination of the equation of state and of the chemical potential. All of them require the knowledge of the same kinds of parameters: the specific surface area of the adsorbent, the molecular surface of the adsorbate, the adsorption energy and a last parameter taking into account the difference in the vibrational, translational and rotational behaviours of the adsorbate molecules when passing from he gaseous phase to the adsorbed phase. The B.E.T. and the Fowler-Guggenheim models require a supplementary parameter: the number of adsorbed layers (B.E.T.) and the attraction energy between adsorbed molecules (Fowler-Guggenheim). Unfortunately these models can be used only for non-porous materials with an homogeneous surface which is rarely the case for real adsorbents. Besides, even if these conditions are fulfilled, it is quite difficult to perform purely predictive calculations as the parameters are rarely known a priori: some of them like the adsorption energy are relevant to the binary system adsorbate-adsorbent, others like the specific surface area are characteristics of the adsorbent and thus are not tabulated. For some simple molecules such as nitrogen or argon and well known adsorbents such as non-porous graphite, it is possible to dispose of the parameters so that prediction can be performed.

All these models we have just mentioned make the assumption that the adsorbed molecules are fixed on the surface. Statistical thermodynamics developments may lead to other models when considering the adsorbed molecules to be mobile on the surface (de Boer, 1953; Hill, 1960; Lyklema, 1991 and 1994; Rudzinski and Everett, 1992). Such treatments require the knowledge of a potential energy function between adsorbed molecules and of a radial distribution function. Well known equations of state previously developed for gases can be applied to adsorbed layers. Anyway, the same remarks as the ones we did concerning the localised-adsorption models are still valid. No pure prediction is possible for the same reasons as previously.

A lot of studies have tried to generalize these models to heterogeneous surfaces introducing the concept of adsorption integral equation and adsorption energy distribution function (Ross and Olivier, 1964; Rudzinski and Everett, 1992). Although it is quite interesting, such an approach does not improve the performances of the models from the predictive point of view. Indeed each binary system adsorbate-adsorbent is characterized by its own energy distribution function. This function must be determined from experimental data for each new system. Evenmore, for some adsorbents like activated carbons, the heterogeneity is mainly to geometric origin.

Using stricter statistical thermodynamics methods such as the Monte Carlo procedure or the density functional theory, the physical significance of the parameters is generally more obvious (Baker and Henderson, 1976; Evans, 1979; Evans and Tarazona, 1984; Walton and Quirke, 1986; Panagiotopoulos, 1987). These methods primarily developed for homogeneous sorbents are now being used for the determination of pore volume distribution functions of heterogeneous adsorbents from pure gas adsorption data such as nitrogen or argon isotherms (Lastoskie et al., 1994; Olivier et al., 1994). However no example has shown that the obtained distribution function could be used to simulate adsorption data for other adsorbates. This is mainly due to the restrictive assumptions of these procedures.

Among the macroscopic models deriving from the potential theory, the Dubinin-Radushkevich isotherm equation is the most well known (Polanyi, 1932; Dubinin and Radushkevich, 1947). The parameters are the total pore volume of the adsorbent and the characteristic energy of the binary system adsorbate-adsorbent. This model developed for porous materials is powerful for the simulation of adsorption isotherms in a wide range of temperature once the two

parameters have been determined for the adsorbate-adsorbent system. Moreover it is possible to calculate the characteristic energy of any adsorbate from the characteristic energy of a reference adsorbate (very often benzene) on the same sorbent multiplied by an affinity factor which is a characteristic of the adsorbate (Dubinin and Timofeyev, 1948). These affinity factors are tabulated. The pore volume is assumed to be independent of the adsorbate so that only an adsorption isotherm of the reference adsorbate is required for the calculation of adsorption isotherms of any adsorbate. This model was first developed for homogeneous porous adsorbents. Some authors have proposed improvements which take into account the heterogeneity of adsorbents (Huber et al., 1978; Jaroniec and Piotrowska, 1986). Dubinin and Plavnik (1968) have shown that the characteristic energy of benzene could be related to the pore size of activated carbons. It is then possible to consider the heterogeneity of activated carbons by introducing in the model a pore volume distribution function (Dubinin, 1985). Such a function is determined from adsorption data for a given adsorbate (generally benzene). This function is then used for simulation purpose. This theory appears to be the only model which allows the adsorption isotherm prediction from tabulated parameters of the adsorbate (mainly the affinity factor) and predetermined parameters concerning the activated carbon.

The vacancy solution model is based on the work by Lucassen-Reynders (1972, 1973, 1976) for surfactant solutions adapted to adsorption by Suwanayuen and Danner (1980). The adsorbed phase is considered to be a binary surface phase. The two components are an hypothetical solvent called the vacancy and the adsorbate. Such a model leads to an equation of state for the adsorbed phase in which an activity coefficient appears. When introducing this equation of state in the Gibbs isotherm relation (Ross and Olivier, 1964; Ruthven, 1984; Lyklema, 1991) an isotherm equation is obtained. Its mathematical expression depends on the choice of the activity coefficient model. These isotherm equations look like the ones obtained by statistical thermodynamics developments. The macroscopic approach does not lead to a clear definition to the parameters on the microscopic point of view. These parameters must be determined from adsorption data for each new system adsorbate-adsorbent. Once these parameters are known for a given system, these models are particularly powerful for the calculation of adsorption data in a wide range of temperatures. Besides they make possible the prediction of gas mixtures adsorption data using only parameters for the corresponding pure compounds. Unfortunately, the heterogeneity of the adsorbent does not appear and it is impossible to predict pure gas adsorption data without preliminary experiments.

Simulation of pure gas adsorption data on heterogeneous solids from tabulated parameters and predetermined information concerning the structure of the adsorbent is still a problem. This is mainly due to the poor knowledge of the structure of adsorbents. In this paper, we present a method for the determination of the micropore volume distribution function of activated carbons. It is based upon a theoretical treatment of pure gas adsorption data. Once the micropore volume distribution function is known, the same theoretical model allows the determination of adsorption data (isotherms and heats) for different adsorbates at different temperatures using mainly parameters directly available in literature.

First of all, we have developed a theoretical model for the calculation of adsorption isotherms and adsorption heats on activated carbons. Using experimental data (adsorption isotherms of carbon dioxide and ethane on activated carbon—F30/470 CHEMVIRON CARBON—at 303 and 323 K), we have determined the unknown parameters of our model. These parameters characterize the structure of the activated carbon which has been used and the interaction between the adsorbed molecules and the pore surface. That is the reason why this model can be seen as a new method for the characterization of activated carbons. These parameters have then been used for the calculation of integral heats of adsorption of the same adsorbates on the same adsorbent at the same temperatures. The calculated values have been compared to experimental data. Afterwards using the same parameters for the absorbent, we have predicted adsorption data (adsorption isotherms and heats) for a third adsorbate (ethylene) at 303 and 323 K. We have ended this study by testing the performances of our model at very low temperature (233 and 273 K) for one of the adsorbates (ethane).

Theoretical Section

For a given adsorbate-adsorbent system, the adsorbed mass m and the integral heat of adsorption Q at given temperature T and pressure P are calculated by (Ross

and Olivier, 1964; Jagiello and Schwarz, 1993; Jagiello et al., 1994):

$$m(T, P) = \int_{H=0}^{H=\infty} M\Gamma(T, P, H)F_A(H)\,dH \quad (1)$$

$$Q(T, P) = \int_{H=0}^{H=\infty} Q_A(T, P, H)F_A(H)\,dH \quad (2)$$

in which:

H	is the pore diameter (m or Å);
M	is the molar mass of the adsorbate (kg mol^{-1});
$F_A(H)$	is the surface distribution function (m^2 $kg^{-1}Å^{-1}$) or ($m^2kg^{-1}m^{-1}$);
$\Gamma(T, P, H)$	is the surface concentration (mol m^{-2});
$Q_A(T, P, H)$	is the areal integral heat of adsorption (Jm^{-2}).

It is commonly assumed that activated carbons consist in packings of crystallites of which the structure is composed of parallel graphite planes. In these crystallites, the distance between two planes is not constant as it is the case for graphite. These voids resulting from the thermal treatment of activated carbons define slit-shaped micropores (Matranga et al., 1992; Bojan and Vernov, 1992; Cracknell et al., 1993). That is the reason why the surface distribution function F_A can be related to the volume distribution function $F_V(H)$ by:

$$F_A(H) = \frac{2F_V(H)}{H} \quad (3)$$

in which:

$F_V(H)$ is expressed in ($m^3kg^{-1}Å^{-1}$) or ($m^3kg^{-1}m^{-1}$);

$F_A(H)$ is the geometric surface distribution function. The factor 2 takes into account the two walls of the pore. In fact, it may occur in very narrow pores that only one layer of molecules can be adsorbed. For other pores, one layer can be adsorbed on each wall (two layers per pore) but the steric effects prevent from a complete filling of each surface. That is the reason why $F_A(H)$ is rather calculated by:

$$F_A(H) = \frac{x(H)F_V(H)}{H} \quad (4)$$

in which:

$F_A(H)$ is then the surface effectively available for the adsorbate molecules;

the function $x(H)$ takes into account the steric effect. $x(H)$ is equal to 1 for very narrow micropores, 2 for large micropores and has intermediate values in the other cases. x is calculated as a function of H for a given adsorbate molecule size.

In Eqs. (1) and (2), $\Gamma(T, P, H)$ and $Q_A(T, P, H)$ are calculated assuming the van der Waals and ideal gas equations of state are valid respectively for the adsorbed and gaseous phases:

$$P = \frac{RT\sqrt{2\pi MRT}}{hN_0} \frac{\left(1 - \exp\left(-\frac{hf_z(H)N_0}{RT}\right)\right)}{\exp\left(-\frac{1}{2}\frac{hf_z(H)N_0}{RT}\right)} \times \left(\exp\left(\frac{U(H)}{RT}\right)\right)\frac{\Gamma}{1 - b\Gamma}\exp\left(\frac{b\Gamma}{1 - b\Gamma}\right) \times \exp\left(-\frac{2a\Gamma}{RT}\right) \quad (5)$$

$$Q_A = -2a\Gamma^2 + U(H)\Gamma - \frac{RT}{2}\Gamma + \frac{hf_z(H)N_0}{2}\Gamma + \frac{hf_z(H)N_0}{\left(\exp\left(\frac{hf_z(H)N_0}{RT}\right) - 1\right)}\Gamma \quad (6)$$

in which:

R	is the ideal gas constant: $R = 8.314$ $Jmol^{-1}K^{-1}$;
h	is the Planck's constant: $h = 6.626$ 10^{-34} Js;
N_0	is the Avogadro's number: $N_0 = 6.022$ 10^{-23} mol^{-1};
a ($J\,m^2\,mol^{-2}$) and b ($m^2\,mol^{-1}$)	are the parameters of the two-dimension van der Waals equation.
$U(H)$	is the adsorption energy ($Jmol^{-1}$); its value depends on the pore dia meter H;
$f_z(H)$	is the vibration frequency of the absorbed molecules perpendicularly to the adsorption surface (Hz); its value also depends on the pore diameter H.

Equations (5) and (6) are known as the Hill-de Boer relations (de Boer, 1953). Using them involves the following assumptions:

— the gas is ideal;
— the adsorbed molecules are mobile on the adsorption surface;
— adsorption is monolayer;

— there is no change is the rotational and internal behaviours of the adsorbate molecules when passing from the gas phase to the adsorbed phase;
— adsorbed molecules interact between each other following a Sutherland's potential; they are randomly distributed on the surface;
— the adsorbed molecules are vibrating perpendicularly to the surface, they are considered to be harmonic oscillators.

The Hill-de Boer model is expected to be reliable at high temperatures (supercritical temperatures) at low pressures and for simple molecules for which the van der Waals parameters are known (Jagiello and Schwarz, 1993; Jagiello et al., 1994).

In Eqs. (5) and (6), a and b can be calculated from the corresponding parameters of the three-dimension equation a_v ($Jm^3\ mol^{-2}$) and b_v ($m^3 mol^{-1}$) (Ross and Olivier, 1964). These ones are available in literature (Lange, 1967).

$$u_0 = \frac{a_v}{b_v} \tag{7}$$

$$r_0 = \left(\frac{3}{2}\frac{b_v}{\pi N_0}\right)^{\frac{1}{3}} \tag{8}$$

$$a = \pi u_0 \frac{r_0^2}{4} N_0 \tag{9}$$

$$b = \pi \frac{r_0^2}{2} N_0 \tag{10}$$

in which:

u_0 is the minimum interaction energy between adsorbed molecules (taken positive) ($Jmol^{-1}$);
r_0 is the distance between two adsorbed molecules corresponding to the minimum value of the interaction energy (m).

In Eqs. (5) and (6), U and f_z appear to be functions of the pore diameter H. The calculation of these functions requires the knowledge of the potential energy function $U_{pot}(z, H)$ ($Jmol^{-1}$) of an adsorbate molecule located at a distance z (m or Å) of the first wall of a pore of diameter H. In this work, we assume that such a function can be expressed as a double Lennard-Jones potential (Matranga et al., 1992; Cracknell et al., 1992; Bojan and Vernov, 1992):

$$U_{pot}(z, H) = U_e \frac{5}{3}\left[\frac{2}{5}\left(\frac{\sigma_{ms}}{z}\right)^{10} - \left(\frac{\sigma_{ms}}{z}\right)^{4} + \frac{2}{5}\left(\frac{\sigma_{ms}}{H-z}\right)^{10} - \left(\frac{\sigma_{ms}}{H-z}\right)^{4}\right] \tag{11}$$

in which:

z is the distance between the adsorbate molecule and the first surface of the pore (m or Å);
$H - z$ is the distance between the adsorbate molecule and the second surface of the pore (m or Å);
σ_{ms} is the geometric Lennard-Jones parameter for the adsorbate molecule-surface system (m or Å);
U_e is the energetic parameter ($Jmol^{-1}$), it corresponds to the well depth of U_{pot} when H tends to ∞.

σ_{ms} is calculated by:

$$\sigma_{ms} = \frac{\sigma_{mm} + \sigma_{ss}}{2} \tag{12}$$

in which:

σ_{mm} is the geometric Lennard-Jones parameter of the adsorbate (m or Å), it is available in literature (Hirschfelder et al., 1954);
σ_{ss} is the corresponding parameter for the adsorption surface (m or Å), $\sigma_{ss} = 3.4$ Å for graphite.

The value of U_e is to be determined.

$U(H)$ is the well depth value of $U_{pot}(z, H)$:

$$\left(\frac{\partial U_{pot}}{\partial z}\right) = 0 \tag{13}$$

As to $f_z(H)$, it is calculated by:

$$f_z(H) = \frac{1}{2\pi}\sqrt{\left|\frac{1}{M}\left(\frac{\partial^2 U_{pot}}{\partial z^2}\right)_{z=z_{eq}}\right|} \tag{14}$$

in which:

z_{eq} is the z value at the minimum of U_{pot} (m or Å).

Using Eq. (11) for the potential energy function introduces a new assumption on the molecular structure of the adsorbate molecule. It must be non polar and spheric in shape.

Equations (1) and (2) allow the calculation of the adsorbed mass m and adsorption heat Q for a given temperature T and a given pressure P. Indeed, the knowledge of the micropore volume distribution function F_V allows the calculation of F_A by Eq. (4). Γ and Q_A are calculated by Eqs. (5) and (6) as functions of temperature and pressure; in these equations a and b are calculated from the tabulated van der Waals parameters thanks to Eqs. (7) and (10). As to $U(H)$ and $f_z(H)$,

they are deduced from Eqs. (13) and (14) using Eq. (11) for $U_{pot}(z, H)$. Such calculations require σ_{ms} (calculated by Eq. (12) from tabulated values of σ_{mm}) and U_e.

In fact the only unknown parameters are U_e and the pore volume distribution function. The first one is relevant to the binary system adsorbate-pore surface. The second one is a characteristic of the adsorbent which is independent of the adsorbate. It is thus possible to determine $F_V(H)$ and U_e from experimental adsorption data.

Experimental Section

The validation of our theory as a new method for the determination of the micropore volume distribution function of activated carbons but also as the first development of a new adsorption data prediction model requires the confrontation with experimental results. Two kinds of results are provided: adsorption isotherms and adsorption heat curves. Given some restrictive assumptions of the model, 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 use of the van der Waals equation of state as local model involves supercritical temperatures;
— the assumptions on gas ideality and on monolayer adsorption are valid at low pressure.

We have studied three adsorbates: carbon dioxide, ethane and ethylene at two temperatures: 303 and 323 K which are quasicritical or supercritical temperatures for these adsorbates. For ethane, measurements have been conducted at lower temperatures, namely 273 and 233 K. The maximum pressure was in all cases 100 kPa.

The measurement of adsorption isotherms and adsorption heat curves 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. In this work, it has been used in a static working. Even if the measurements principles are well known, the simultaneity of the heat flow and mass change measurement using such an apparatus is quite original. The complete experimental procedure will be presented in a paper to be published (Berlier and Frère, in press).

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 (<0.5%). However, the Archimedes' effect causes systematic errors in the mass measurement; the resulting highest relative error was 2% for ethylene at 323 K and 100 kPa with typical values of 0 to 1% in the other cases. 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. The experimental measurement error on adsorption heat is about 1% which is lower than the deviation observed between different runs of the same experiment (about 2%).

Results and Discussion

Using adsorption isotherms for carbon dioxide and ethane at 303 and 323 K, we have determined the adsorption energies U_{eCO_2} and $U_{eC_2H_4}$ for these adsorbates on a graphite surface and the micropore volume distribution function of the used activated carbon.

Assuming a Gaussian-like behaviour for this distribution function does not allow the simultaneous representation of the four adsorption isotherms. That is the reason why we have tried a double Gaussian-like function:

$$F_V(H) = \frac{V_{P1}}{\sqrt{2\pi}\sigma_1} \exp\left(-\frac{(H-m_1)^2}{2\sigma_1^2}\right) + \frac{V_{P2}}{\sqrt{2\pi}\sigma_2} \exp\left(-\frac{(H-m_2)^2}{2\sigma_2^2}\right) \quad (15)$$

in which:

m_1 is the average of the first contribution (m or Å);
σ_1 is the standard deviation of the first contribution (m or Å);
V_{P1} is the pore volume of the first contribution (m^3Kg^{-1});
m_2 is the average of the second contribution (m or Å);
σ_2 is the standard deviation of the second contribution (m or Å);
V_{P2} is the pore volume of the second contribution (m^3Kg^{-1});

Table 1. Parameters of the double Gaussian distribution function and adsorption energies of carbon dioxide and ethane on graphite.

m_1 (Å)	m_2 (Å)	σ_1 (Å)	σ_2 (Å)	V_{p1} (m^3kg^{-1})	V_{p2} (m^3kg^{-1})	$U_{e\,CO_2}$ ($Jmol^{-1}$)	$U_{e\,C_2H_6}$ ($Jmol^{-1}$)
10.366	7.473	0.772	0.010	$3.081\ 10^{-4}$	$0.749\ 10^{-4}$	12725.3	17450.6

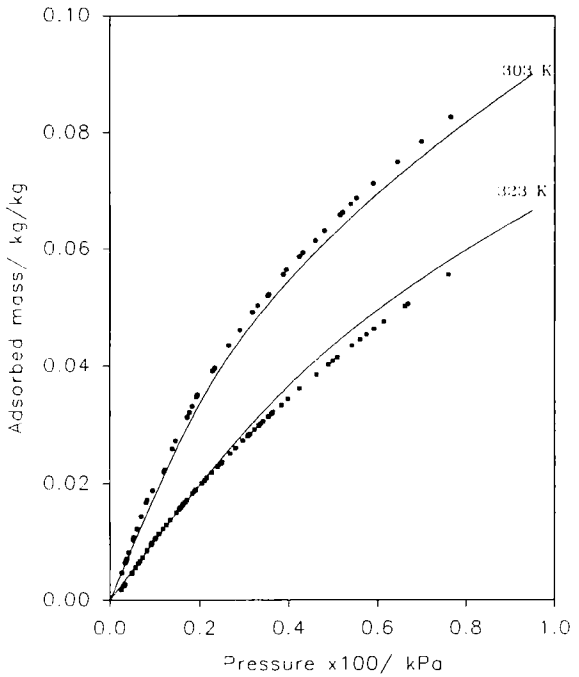

Figure 1. Adsorption isotherms of carbon dioxide (—: calculated 303 and 323 K, ●: experimental 303 K, ■: experimental 323 K).

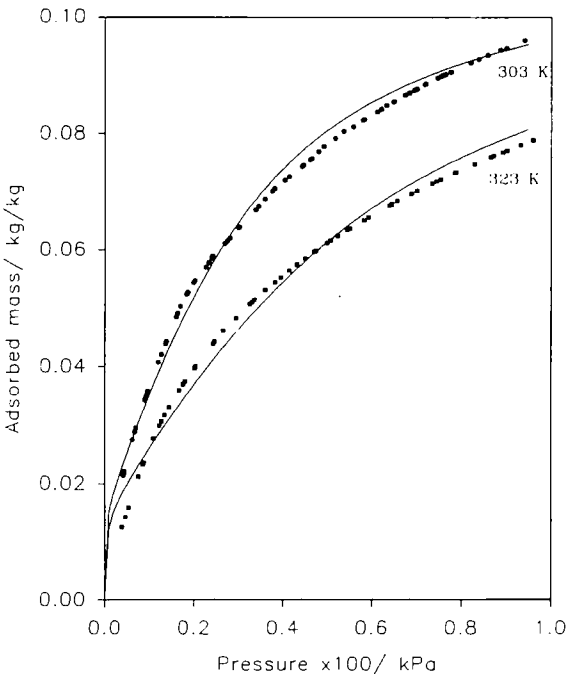

Figure 2. Adsorption isotherms of ethane (—: calculated 303 and 323 K, ●: experimental 303 K, ■: experimental 323 K).

Table 1 presents the parameters of the pore volume distribution function and the adsorption energies of carbon dioxide and ethane on graphite.

Figure 1 shows the confrontation between experimental and calculated isotherms of carbon dioxide at 303 and 323 K. Figure 2 shows the same isotherms for ethane. The mean deviations are respectively 3% and 4% for carbon dioxide and ethane.

The knowledge of m_1, m_2, σ_1, σ_2, V_{p1}, V_{p2}, $U_{e\,CO_2}$ and $U_{e\,C_2H_6}$ allows the calculation of the corresponding adsorption heat curves for carbon dioxide and ethane at 303 and 323 K. Figure 3 shows the comparison between experimental and calculated adsorption heats as a function of pressure for carbon dioxide at 303 and 323 K. Figure 4 shows the same comparison for ethane. The mean deviations are about 12% for carbon dioxide and 9% for ethane.

Using the same pore volume distribution function, we have tried to correlate our model to experimental data for ethylene. Using adsorption isotherms at 303 and 323 K of this adsorbate, we have determined the only unknown parameter, that is to say the adsorption energy of ethylene on graphite. We have found $U_{e\,C_2H_4} = 15376.2\ Jmol^{-1}$. Afterwards, we have calculated both adsorption isotherms and adsorption heat curves for ethylene at 303 and 323 K. Figure 5 shows the comparison between experimental and calculated isotherms. The mean deviation which has been observed is 2%. As to Figure 6, it presents the corresponding comparison for adsorption heat curves. The mean deviation is 13%.

As final step, we have calculated the adsorption isotherms of ethane at 233 and 273 K and we have compared them to the corresponding experimental data. The results are presented in Figure 7. Then mean deviation is about 15%. The same discrepancies arise for the three other adsorbates at very low temperatures.

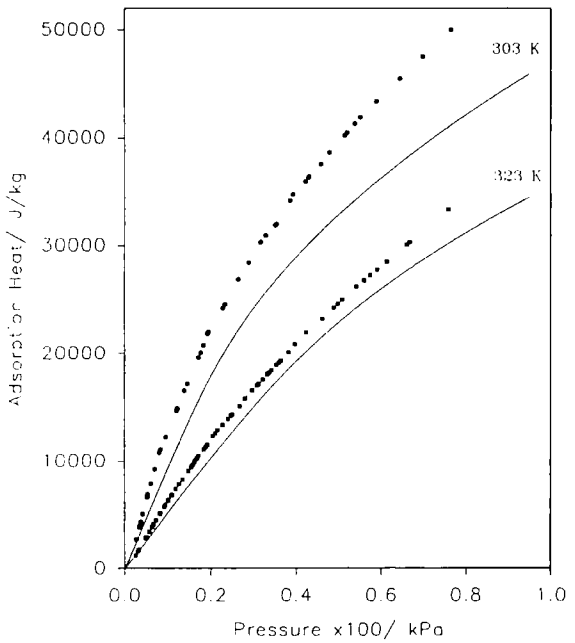

Figure 3. Adsorption heat curves of carbon dioxide (—: calculated 303 and 323 K, ●: experimental 303 K, ■: experimental 323 K).

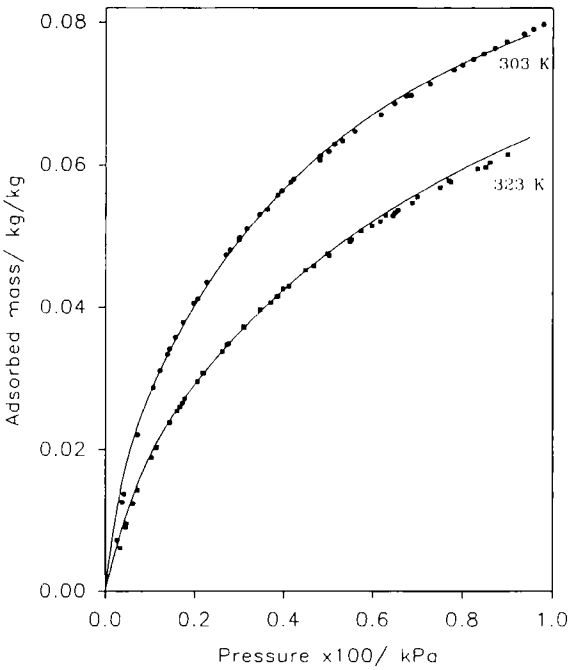

Figure 5. Adsorption isotherms of ethylene (—: calculated 303 and 323 K, ●: experimental 303 K, ■: experimental 323 K).

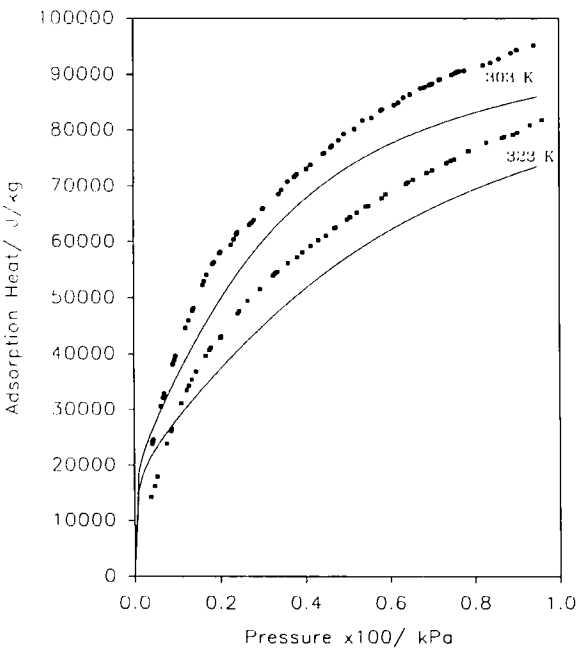

Figure 4. Adsorption heat curves of ethane (—: calculated 303 and 323 K, ●: experimental 303 K, ■: experimental 323 K).

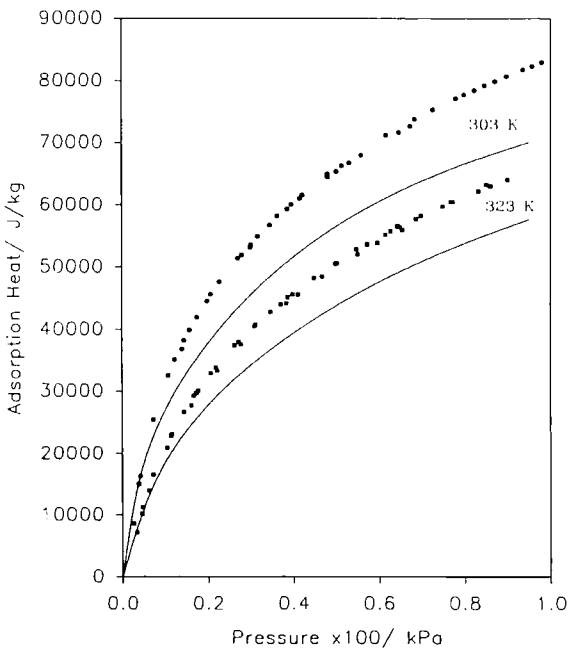

Figure 6. Adsorption heat curves of ethylene (—: calculated 303 and 323 K, ●: experimental 303 K, ■: experimental 323 K).

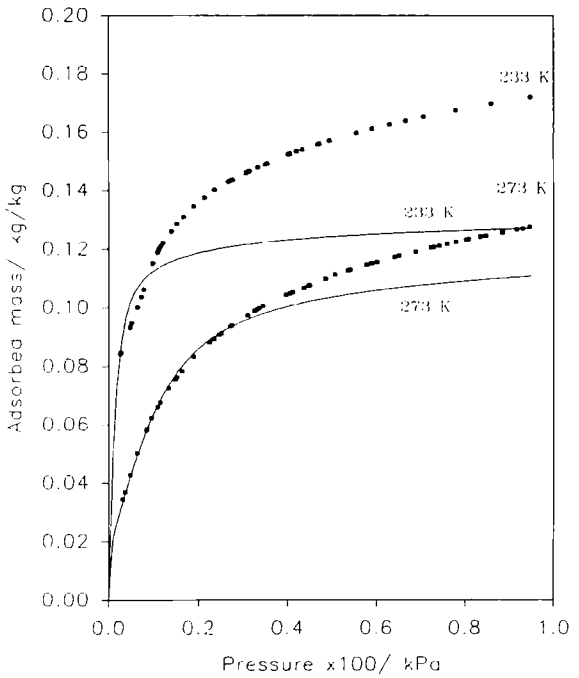

Figure 7. Adsorption isotherms of ethane (—: calculated 233 and 273 K, ●: experimental 233 K, ■: experimental 273 K).

Conclusions

In this paper, we have shown that the determination of the porous structure of adsorbents and the pure gas adsorption data prediction are linked problems. We have used a simple model such as the Hill-de Boer theory and introduced it in the integral adsorption equation. The geometric and energetic modelling of the porous structure of activated carbons has made possible the link between the energetic distribution function and the pore volume distribution function. We have obtained a model in which the parameters involved are clearly defined. Most of them are available in literature. The only unknown parameters are the geometric structure of the adsorbent (its pore volume distribution function) and the adsorption energy of the adsorbate molecule on graphite. Unfortunately this model is not general. It involves numerous assumptions linked to the choice of the local adsorption model (Hill-de Boer) but also to the geometric and energetic modelling of activated carbons. Using experimental data within the range of conditions in which the model is expected to be reliable, it is possible to determine the pore volume distribution function of the used adsorbent. The fact that the mathematical form of this function is fixed is a disadvantage. However, the validity of this function can be checked. Indeed, it must be possible to simulate adsorption data for different adsorbates at different temperatures with a unique distribution function. This procedure has been followed in our work. We have found that a double Gaussian was a good choice for the adsorbent we have studied. We have succeeded in the representation of adsorption isotherms at supercritical temperatures for three different adsorbates with deviations ranging from 2 to 4%. Another originality of this work is that we have also used calorimetric data (determined by direct measurement) which have been compared to the calculated values. The discrepancies have been estimated to be about 10%. Such results which seem to be poor are in fact encouraging for a first approach. In general the experimental and calculated adsorption heats are determined from the corresponding isotherms by the "isosteric procedure". The adequacy of the model to simulate adsorption data is then obviously linked to its performances at isotherms simulation. Unfortunately the model fails at describing experimental data at low temperatures. It is not surprising given the assumptions of the Hill-de Boer model.

As a conclusion, our model can be seen as a progress as it proves that it is possible to simulate adsorption data using parameters relevant to the molecular structure of the adsorbate on the one hand and of the structure of the adsorbent on the other hand. Indeed, the only parameter which is a characteristic of the binary system adsorbate-pore surface is the adsorption energy U_e. That is the reason why it can be used for the determination of the micropore volume distribution function of activated carbons. On the other hand, its use as a predictive model requires further developments. It is not powerful at low temperature and the energetic parameter must be determined from experiments. The development of the local models used in the integral adsorption equation (Hill-de Boer, Lennard-Jones potential) should lead to a wider range of conditions in which it could be used. The introduction of mixing rules for the calculation of U_e or the systematic tabulations of its values (U_e being function of the adsorbate for a given kind of surface) would be interesting for prediction.

Nomenclature

a	energetic parameter of the two-dimension van der Waals equation of state	Jm^2mol^{-2}

b	geometric parameter of the two-dimension van der Waals equation of state	m^2mol^{-1}
a_v	energetic parameter of the three-dimension van der Waals equation of state	Jm^3mol^{-2}
b_v	geometric parameter of the three-dimension van der Waals equation of state	m^3mol^{-1}
f_z	vibrational frequency of the adsorbed molecules perpendicularly to the adsorption surface	Hz
F_A	surface distribution function	$m^2kg^{-1}m^{-1}$ or $m^2kg^{-1}Å^{-1}$
F_V	volume distribution function	$m^3kg^{-1}m^{-1}$ or $m^3\ kg^{-1}\ Å^{-1}$
h	Planck's constant $h = 6.626\ 10^{-34}$ Js	
H	pore diameter	m or Å
$H - z$	distance between the adsorbate molecule and the second surface of the pore	m or Å
m	adsorbed mass	kg adsorbate kg^{-1} adsorbent
m_1	average of the first contribution of the pore volume distribution function	m or Å
m_2	average of the second contribution of the pore volume distribution function	m or Å
M	molar mass of the adsorbate	$kgmol^{-1}$
N_0	Avogadro's number $N_0 = 6.022\ 10^{23}\ mol^{-1}$	
P	pressure	kPa
Q	integral adsorption heat	Jkg^{-1}
Q_A	areal integral heat of adsorption	Jm^{-2}
R	ideal gas constant $R = 8.314\ Jmol^{-1}K^{-1}$	
r_0	distance between two adsorbed molecules corresponding to the minimum value of the interaction energy	m
T	temperature	K
u_0	minimum interaction energy between adsorbed molecules (taken positive)	$Jmol^{-1}$
U	minimum value of U_{pot} for a given H	$Jmol^{-1}$
U_e	minimum value of U_{pot} when H tends to ∞	$Jmol^{-1}$
$U_{e\,CO_2}$	U_e value for the binary system carbon dioxide-graphite	$Jmol^{-1}$
$U_{e\,C_2H_6}$	U_e value for the binary system ethane-graphite	$Jmol^{-1}$
$U_{e\,C_2H_4}$	U_e value for the binary system ethylene-graphite	$Jmol^{-1}$
U_{pot}	potential energy function of an adsorbate molecule located in a pore	$Jmol^{-1}$
V_{P1}	pore volume of the first contribution of the pore volume distribution function	m^3kg^{-1}
V_{P2}	pore volume of the second contribution of the pore volume distribution function	m^3kg^{-1}
x	weighing factor for the surface filling	
z	distance between the adsorbate molecule and the first surface of the pore	m or Å
z_{eq}	z value at the minimum of U_{pot} for a given H	m or Å
Γ	surface concentration	$mol\ m^{-2}$
σ_{mm}	geometric Lennard-Jones parameter of the adsorbate	m or Å
σ_{ms}	geometric Lennard-Jones parameter of the adsorbate molecule-surface system	m or Å
σ_{ss}	geometric Lennard-Jones parameter of the adsorption surface	m or Å
σ_1	standard deviation of the first contribution of the pore volume distribution function	m or Å
σ_2	standard deviation of the second contribution of the pore volume distribution function	m or Å.

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