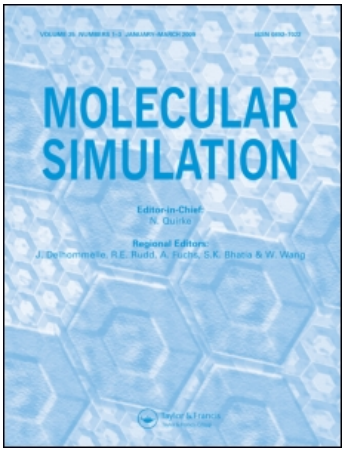

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Adsorption equilibria of single gas and gas mixture on homogeneous surfaces: a unified approach based on statistical thermodynamics developments. Part I: single gas adsorption

Y. Belmabkhout[a]; M. Frere[a]; G. De Weireld[a]
[a] Thermodynamics department, Faculté Polytechnique de Mons, Mons, Belgium

To cite this Article Belmabkhout, Y. , Frere, M. and De Weireld, G.(2006) 'Adsorption equilibria of single gas and gas mixture on homogeneous surfaces: a unified approach based on statistical thermodynamics developments. Part I: single gas adsorption', Molecular Simulation, 32: 7, 495 — 502
To link to this Article: DOI: 10.1080/08927020600851944
URL: http://dx.doi.org/10.1080/08927020600851944

Molecular Simulation, Vol. 32, No. 7, 15 June 2006, 495–502

Taylor & Francis
Taylor & Francis Group

Adsorption equilibria of single gas and gas mixture on homogeneous surfaces: a unified approach based on statistical thermodynamics developments. Part I: single gas adsorption

Y. BELMABKHOUT, M. FRERE* and G. DE WEIRELD

Thermodynamics department, Faculté Polytechnique de Mons, 31 bd Dolez, 7000 Mons, Belgium

(Received November 2005; in final form December 2005)

Theoretical description of single gas and gas mixture adsorption equilibria can be achieved in many different ways depending on the kind of approach (microscopic or macroscopic) and on the physical assumptions related to the nature of the adsorbent–adsorbate systems studied as well as temperature and pressure conditions. In this paper, a detailed statistical thermodynamics development is presented. It leads to a generalized expression of adsorption isotherms for pure gases on homogeneous surfaces. The non-ideality of both gas and adsorbed phases are taken into account using the Redlich–Kwong equations of state (EOS) which is adapted for two-dimension phases. Such an approach leads to a symmetrical treatment of both phases resulting in similar expressions of their EOS and of their fugacity coefficients. It allows an easy extension to gas mixtures adsorption equilibria. We present adsorption isotherms calculated using our model, the influence of the non-idealities are presented and discussed.

Keywords: Adsorption; Homogenous surface; Statistical thermodynamics; Equation of state

1. Introduction

Physical adsorption of gases and vapours in microporous media is a complex phenomenon which is difficult to tackle on a theoretical point of view, due to the heterogeneity of the adsorbent, the nature of interactions between the adsorptive and the adsorbent on the one hand and between the adsorptive molecules in the gas phase and in the adsorbed phase on the other hand. The temperature and the pressure conditions play also an important role in the final representation of equilibrium data.

As a consequence, it is generally more convenient to develop specific theoretical models for each kind of adsorptive–adsorbent system. Such models are simple because they are based on assumptions which are considered acceptable for the system of interest. They are often derived from macroscopic thermodynamic developments [1–2] and are considered as efficient tools for engineers concerned with adsorption process design. Unfortunately, these simple models fail at predicting experimental data in a wide range of conditions and do not allow a physical understanding of the adsorptive–adsorbent behaviour at the molecular level. Developing a "universal" model for single gas adsorption equilibria with adaptable sub-models of the potential energy functions and porous structure would be of great practical importance.

Some theoretical approaches are able to deal with the complexity of the adsorption phenomenon: molecular simulation methods like the grand canonical Monte-Carlo method (GCMC) [3] which is based on an equilibrium statistical treatment of the system or the density functional theory (DFT) [4] which is an approximate statistical mechanics method.

These very powerful methods are well-known for their ability to describe the behaviour of the adsorptive molecules in the porous structure of the adsorbent. They lead to interesting prediction performances as far as all kinds of interactions are correctly described. Their use in adsorption process simulation tools is not possible due to the prohibitive calculation times required for complex industrial systems. The calculations involved in such methods are based on a perfect description of the adsorbent structure which is only possible for homogeneous and well-known solids.

Using macroscopic thermodynamics based on statistical thermodynamic developments involving reasonable

*Corresponding author. Tel.: + 32 65 37 42 05. Fax: + 32 65 37 42 09. Email: marc.frere@fpms.ac.be

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020600851944

general assumptions may lead to simplest and efficient models. If such models are developed for homogeneous and non-porous adsorbents, they may remain sufficiently general. The only challenge is then the description of the non-idealities in both phases which may be taken into account by using classical theories developed for gases and liquids. Finally, these models may be extended to complex porous structures using the concept of integral adsorption equation [5–7].

In this paper, a rigorous "universal" model is presented for single gas adsorption equilibria: (1) it takes into accounts the non-ideality of both the gas and the adsorbed phases, (2) it can be easily extended to multicomponent adsorption equilibria; (3) it is thermodynamically consistent as it reduces to the Henry's law at low pressure; and (4) both the gas and the adsorbed phases are described in the same way.

2. Theoretical section

The adsorption equilibrium between the adsorbed and the gas phases is expressed by the equality of the chemical potentials of the adsorbate in each phase. This expression leads to an equation relating the adsorbed quantity to the pressure and temperature. The development of such an equation requires the microscopic modeling of each phase separately in order to obtain the expression of the chemical potential for each phase using statistical thermodynamics developments.

2.1 Non-ideal gas phase modeling

We consider a polyatomic molecule B composed (mass m) and a three-dimension system composed of N_g independent and indistinguishable molecules of B in a volume V_g at temperature T. The molecules may interact with each other.

The canonical partition function of the system composed of these N_g (independent and indistinguishable molecules) of B is:

$$Q_g = \frac{q_g^{N_g}}{N_g!} \tag{1}$$

in which q_g is the partition function of one molecule of the system and:

$$q_g = q_{g\,trans}\, q_{g\,rot}\, q_{g\,vibi}\, q_{g\,e}\, q_{g\,int} \tag{2}$$

in which:

- $q_{g\ trans}$ is the translational contribution to the partition function (3 degrees of freedom for the mass centre of the molecule);
- $q_{g\ rot}$ is the rotational contribution to the partition function;
- $q_{g\ vibi}$ is the contribution to the partition function due to the internal vibrations in the molecule;
- $q_{g\ e}$ is the electronic contribution to the partition function; and
- $q_{g\ int}$ is the contribution to the partition function due to the interactions between the molecules.

The translation contribution to the partition function reads:

$$q_{g\,trans} = \left[\frac{2\pi mkT}{h^2}\right]^{3/2} \quad V_f = \frac{V_f}{\Lambda^3} \tag{3}$$

with

$$\Lambda^{-1} = \left[\frac{2\pi mkT}{h^2}\right]^{1/2} \tag{4}$$

in which:

- Λ is the thermal de Broglie wavelength;
- h is the Planck constant;
- k is the Boltzmann constant; and
- V_f is the real volume available to the molecules.

The contribution to the molecular partition function due to the interactions between the molecules reads:

$$q_{g\,int} = \exp\left(-\frac{U'_{int}}{2kT}\right) \tag{5}$$

in which:

- U'_{int} is the potential energy of interaction between one molecule and all the other ones in the system.The determination of U'_{int} requires the knowledge of the potential energy of interaction $u'(r)$ between two molecules; r being the distance between their mass centres.

$$U'_{int} = -\int_{d_g}^{\infty} u'(r)\frac{N_g}{V_g} g'(r) 4\pi r^2 \mathrm{d}r \tag{6}$$

in which:

- $g'(r)$ is the radial repartition function;
- $(N_g/V_g)\ g'(r)$ expresses the local concentration of the gas at a distance r from the central molecule being considered;
- d_g is the molecular diameter (in the gas phase).

If we set $\eta = r/d_g$, equation (6) becomes:

$$U'_{int} = -4\pi\frac{N_g}{V_g} d_g^3 \int_1^{\infty} u(\eta) g(\eta) \eta^2 \mathrm{d}\eta \tag{7}$$

By setting

$$I' = \int_1^{\infty} u(\eta) g(\eta) \eta^2 \mathrm{d}\eta \tag{8}$$

Equation (7) becomes:

$$U'_{int} = -4\pi\frac{N_g}{V_g} d_g^3 I' \tag{9}$$

I' may be expressed by:

$$I' = C' G'(V_g) J'(T) \tag{10}$$

in which:

- C' is an energetic characteristic constant of the fluid;
- $G'(V_g)$ and $J'(T)$are the volume and temperature contribution functions to the non-ideality of the gas phase.

Depending on the mathematical expression of $G'(V_g)$ and $J'(T)$ we can obtain several well-kwon equations of state (EOS). Vera and Prausnitz [8] proposed different expressions for the calculation of these terms. We retain the following expressions:

$$G'(V_g) = \frac{V_g}{N_g b} \ln\left(1 + \frac{N_g b}{V_g}\right) \tag{11}$$

$$J'(T) = \sqrt{\frac{T_c}{T}} \tag{12}$$

In which:

- T_c is the critical temperature of the fluid;
- b is a parameter which characterizes the fluid. It may be considered as the volume of the molecule.

Combining equations (9)–(12) leads to:

$$U'_{int} = -\frac{4\pi d_g^3}{b} C' \sqrt{\frac{T_c}{T}} \ln\left(1 + \frac{N_g b}{V_g}\right) \tag{13}$$

Considering equations (1)–(3) leads to:

$$Q_g = \frac{V_f^{N_g}}{\Lambda^{3N_g}} \frac{1}{N_g!} \left(q_{g\,rot}\, q_{g\,vibi}\, q_{g\,e} \exp\left(\frac{-U'_{int}}{2kT}\right)\right)^{N_g} \tag{14}$$

in which V_f may be calculated by:

$$V_f = V_g - N_g b \tag{15}$$

Combining equations (13)–(15) leads to:

$$\begin{aligned} \ln Q_g = {} & N_g \ln\left(\frac{V_g - N_g b}{\Lambda^3}\right) - N_g \ln N_g + N_g \\ & + N_g \ln q_{g\,rot} + N_g \ln q_{g\,vibi} + N_g \ln q_{g\,e} \\ & + \frac{N_g 2\pi d_g^3 C'}{bkT} \sqrt{\frac{T_c}{T}} \ln\left(1 + \frac{N_g b}{V_g}\right) \end{aligned} \tag{16}$$

The chemical potential of the adsorbed phase is then obtained by differentiating ln Q_g with respect to N_g at constant temperature and volume:

$$\mu_g = -kT \left(\frac{\partial \ln Q_g}{\partial N_g}\right)_{T,V_g} \tag{17}$$

$$\begin{aligned} \mu_g = -kT \Bigg[& \ln\left(\frac{V_g - N_g b}{N_g}\right) - \ln \Lambda^3 + \ln q_{g\,rot} + \ln q_{g\,vibi} \\ & + \ln q_{g\,e} - \frac{N_g b}{V_g - N_g b} + \left[\frac{2\pi d_g^3 C'}{bkT} \sqrt{\frac{T_c}{T}} \ln\left(1 + \frac{N_g b}{V_g}\right)\right] \\ & + \left[\frac{N_g 2\pi d_g^3 C'}{bkT} \sqrt{\frac{T_c}{T}} \frac{b}{V_g + N_g b}\right]\Bigg] \end{aligned} \tag{18}$$

The pressure p of the system may also be computed from the canonical partition function:

$$\begin{aligned} p &= kT \left(\frac{\partial \ln Q_g}{\partial V_g}\right)_{T,N_g} \\ &= kT \frac{N_g}{V_g - N_g b} \left[1 - \frac{2\pi d_g^3 C'}{kT} \sqrt{\frac{T_c}{T}} \frac{N_g (V_g - N_g b)}{V_g (V_g + N_g b)}\right] \end{aligned} \tag{19}$$

$$\begin{aligned} \frac{V_g - N_g b}{N_g} = \frac{kT}{p} \Bigg[& \frac{V_g - N_g b}{V_g} \\ & \times \left(\frac{V_g}{V_g - N_g b} - \frac{2\pi d_g^3 C' \sqrt{T_c} N_g}{kT\sqrt{T}(V_g + N_g b)}\right)\Bigg] \end{aligned} \tag{20}$$

Finally, substituting equation (20) in equation (18) leads to:

$$\begin{aligned} \mu_g = -kT \Bigg[& \ln kT \frac{q_{g\,rot} q_{g\,vibi} q_{g\,e}}{\Lambda^3} - \ln p \\ & + \ln\left(\frac{V_g}{V_g - N_g b} - \frac{2\pi d_g^3 C' \sqrt{T_c} N_g}{kT\sqrt{T}(V_g + N_g b)}\right) \\ & + \ln \frac{V_g - N_g b}{V_g} - \frac{N_g b}{V_g - N_g b} \\ & + \left[\frac{2\pi d_g^3 C' \sqrt{T_c}}{bkT\sqrt{T}} \ln\left(\frac{V_g + N_g b}{V_g}\right)\right] \\ & + \left[\frac{N_g b}{V_g + N_g b} \frac{2\pi d_g^3 C' \sqrt{T_c}}{bkT\sqrt{T}}\right]\Bigg] \end{aligned} \tag{21}$$

If we set $a = 2\pi d_g^3 C' \sqrt{T_c}$, the final expression of the chemical potential is:

$$\begin{aligned} \mu_g = -kT \Bigg[& \ln kT \frac{q_{g\,rot} q_{g\,vibi} q_{g\,e}}{\Lambda^3} \\ & - \ln p + \ln \frac{pV_g}{kTN_g} + \ln \frac{V_g - N_g b}{V_g} - \frac{N_g b}{V_g - N_g b} \\ & + \left[\frac{a}{bkT\sqrt{T}} \ln\left(\frac{V_g + N_g b}{V_g}\right)\right] + \left[\frac{N_g b}{V_g + N_g b} \frac{a}{bkT\sqrt{T}}\right]\Bigg] \end{aligned} \tag{22}$$

Equation (22) may be written as:

$$\mu_g = \mu_g^0(T, 1) + kT \ln p + kT \ln \Phi' \tag{23}$$

with:

$$\mu_g^0 = -kT \left[\ln kT \frac{q_{g\,rot}\, q_{g\,e}\, q_{g\,vibi}}{\Lambda^3}\right] \tag{24}$$

$$\begin{aligned} \ln \Phi' = {} & -\ln \frac{pV_g}{kTN_g} + \ln \frac{V_g}{V_g - N_g b} + \frac{N_g b}{V_g - N_g b} \\ & - \frac{a}{bkT\sqrt{T}} \left[\ln\left(\frac{V_g + N_g b}{V_g}\right) + \frac{N_g b}{V_g + N_g b}\right] \end{aligned} \tag{25}$$

μ_g^0 is the standard chemical potential and Φ' is the fugacity coefficient of fluid.

The same developments may be done for an ideal gas. In such a case, U'_{int} is equal to zero and the molecular volume b may be neglected with respect to V_g.

The expression of the chemical potential is then:

$$\mu_{g\,IDEAL} = -kT\left[\ln kT\frac{q_{g\,rot}\,q_{g\,e}\,q_{g\,vibi}}{\Lambda^3} - \ln p\right] \quad (26)$$

Or:

$$\mu_{g\,IDEAL} = \mu_g^0(T,1) + kT\ln p \quad (27)$$

in which μ_g^0 is given by equation (24).

Equation (27) shows that μ_g^0 is the chemical potential of the gas, considered as ideal (perfect gas), at temperature T and at pressure $p = 1$. Equations (23) and (27) show that ln Φ' takes into account the interactions between the molecules as well as the non-ideality of the gas phase resulting from the molecular volume.

It should be noticed that equation (20) may be rearranged to obtain the following expression:

$$\frac{pV_g}{kTN_g} = \frac{V_g}{V_g - N_g b} - \frac{a\,N_g}{kT\sqrt{T}(V_g + N_g b)} \quad (28)$$

Which is the Redlich–Kwong EOS. The parameters a and b may be calculated from the critical temperature and pressure and from the acentric factor of the adsorbate [9–10].

2.2 Non-ideal adsorbed phase modeling

We consider a system composed of N_a molecules of B (mass m) adsorbed on a surface A at temperature T. The molecules may interact with each others. We assume that the potential energy of interaction $u_{ads}(r)$ between a molecule of B located at a distance r from the surface of the adsorbent does not depend on the location point on the surface (the surface of the adsorbent is considered to be homogeneous). U_0 is the adsorption energy (minimum of $u_{ads}(r)$). Only one layer of molecules B can be adsorbed. The adsorbed molecules can move on the surface (mobile adsorption).

The canonical partition function of this system is then:

$$Q_s = \frac{q_a^{N_a}}{N_a!} \quad (29)$$

in which q_a may be expressed as:

$$q_a = q_{a\,trans}\,q_{a\,vib}\,q_{a\,rot}\,q_{a\,e}\,q_{a\,vibi}\,q_{a\,int}\exp\left(\frac{-U_0}{kT}\right) \quad (30)$$

in which:

- $q_{a\ trans}$ is the translational contribution to the partition function (2 degrees of freedom for the mass centre of the molecule);
- $q_{a\ rot}$ is the rotational contribution to the partition function;
- $q_{a\ vibi}$ is the contribution to the partition function due to the internal vibrations in the molecule;
- $q_{a\ vib}$ is the contribution to the partition function due to the vibration of the molecule perpendicularly to the surface;
- $q_{a\ e}$ is the electronic contribution to the partition function;
- $q_{a\ int}$ is the contribution to the partition function due to the interactions between the molecules; and
- U_0 is the energy of interaction between an adsorbed molecule of B and the surface A.

$q_{a\ trans}$ and $q_{a\ int}$ may be expressed by:

$$q_{a\,trans} = \left[\frac{2\pi mkT}{h^2}\right]A_f = \frac{A_f}{\Lambda^2} \quad (31)$$

$$q_{a\,int} = \exp\left(-\frac{U_{int}}{2kT}\right) \quad (32)$$

in which:

- A_f is the free surface available to the adsorbed molecules;
- U_{int} is the potential energy of interaction between one molecule in the adsorbed phase and all the other ones in the system.

The determination of U_{int} requires the knowledge of the potential energy of interaction $u(r)$ between two adsorbed molecules; r being the distance between their mass centres.

$$U_{int} = -\int_{d_a}^{\infty} u(r)\frac{N_a}{A}g(r)2\pi r\,dr \quad (33)$$

in which:

- $g(r)$ is the radial repartition function, $(N_a/A)g(r)$ expresses the local surface concentration at a distance r from a central molecule being considered for the calculation of U_{int};
- d_a is the molecular diameter (in the adsorbed phase).

If we take $\eta = r/d_a$, equation (33) becomes:

$$U_{int} = -2\pi\frac{N_a}{A}d_a^2\int_1^{\infty} u(\eta)g(\eta)\eta\,d\eta \quad (34)$$

By setting:

$$I = \int_1^{\infty} u(\eta)g(\eta)\eta\,d\eta \quad (35)$$

equation (34) becomes:

$$U_{int} = -2\pi\frac{N_s}{A}d_a^2 I \quad (36)$$

in which I may be expressed as:

$$I = C\,G(A)J(T) \tag{37}$$

- C is an energetic characteristic constant of the fluid;
- $G(A)$ and $J(T)$are the surface and temperature contribution functions to the non-ideality of the adsorbed phase.

By analogy to equations (11) and (12), we set:

$$G(A) = \frac{A}{N_a b_a}\ln\left(1+\frac{N_a b_a}{A}\right) \tag{38}$$

$$J(T) = \sqrt{\frac{T_{ca}}{T}} \tag{39}$$

in which:

- T_{ca} is the two-dimension critical temperature of fluid;
- b_a is a parameter which characterizes the fluid. It may be considered as the surface occupied by a molecule in the adsorbed phase.

Combining equation (32) with equation (36)–(39) leads to:

$$q_{a\,int} = \exp\left(\frac{\pi d_s^2}{b_a kT}C\sqrt{\frac{T_{ca}}{T}}\ln\left(1+\frac{N_a b_a}{A}\right)\right) \tag{40}$$

By setting:

$$A_f = A - N_a b_a \tag{41}$$

Equations (29)–(31), (40) and (41) lead to:

$$\begin{aligned}\ln Q_a = {} & N_a \ln\frac{A-N_a b_a}{\Lambda^2} - N_a \ln N_a + N_a \\ & + N_a \ln(q_{a\,vib}\,q_{a\,rot}\,q_{a\,e}\,q_{a\,vibi}) \\ & + \frac{N_a \pi d_a^2}{b_a kT}C\sqrt{\frac{T_{ca}}{T}}\ln\left(1+\frac{N_a b_a}{A}\right) - \frac{N_a U_0}{kT}\end{aligned} \tag{42}$$

The chemical potential of the adsorbed phase is obtained by differentiating $\ln Q_a$ with respect to N_a at constant surface and temperature:

$$\mu_a = -kT\left(\frac{\partial \ln Q_a}{\partial N_a}\right)_{T,A} \tag{43}$$

The spreading pressure Π may also be calculated from the canonical partition function:

$$\Pi = kT\left(\frac{\partial \ln Q_a}{\partial A}\right)_{T,N_a} \tag{44}$$

Equations (42) and (44) lead to:

$$\begin{aligned}\frac{A-N_a b_a}{N_a} = {} & \frac{kT}{\Pi}\left(\frac{A-N_a b_a}{A}\left(\frac{A}{A-N_a b_a}\right.\right. \\ & \left.\left. - \frac{\pi d_a^2 C}{b_a kT}\sqrt{\frac{T_{ca}}{T}}\frac{N_a}{(A+N_a b_a)}\right)\right)\end{aligned} \tag{45}$$

Combining equations (42)–(45) leads to:

$$\begin{aligned}\mu_a = {} & -kT\left[\ln kT\frac{q_{a\,vib}\,q_{a\,rot}\,q_{a\,e}\,q_{a\,vibi}}{\Lambda^2} - \frac{U_0}{kT}\right. \\ & -\ln\Pi + \ln\frac{\Pi}{kT}\frac{1}{\Gamma_{ml}} + \ln\frac{1/\Gamma_{ml}-b_a}{1/\Gamma_{ml}} - \frac{b_a}{1/\Gamma_{ml}-b_a} \\ & \left. + \frac{\pi d_a^2}{b_a kT}C\sqrt{\frac{T_{ca}}{T}}\left(\ln\left(\frac{1/\Gamma_{ml}+b_a}{1/\Gamma_{ml}}\right)+\frac{b_a}{1/\Gamma_{ml}+b_a}\right)\right]\end{aligned} \tag{46}$$

in which Γ_{ml} is the surface molecular concentration defined as:

$$\Gamma_{ml} = \frac{N_a}{A} \tag{47}$$

If we set $a_a = \pi d_a^2 C\sqrt{T_{ca}}$, the final expression of the chemical potential is:

$$\begin{aligned}\mu_a = {} & -kT\left[\ln kT\frac{q_{a\,vib}\,q_{a\,rot}\,q_{a\,e}\,q_{a\,vibi}}{\Lambda^2}\right] + U_0 \\ & + kT\ln\Pi - kT\ln\frac{\Pi}{kT}\frac{1}{\Gamma_{ml}} \\ & - kT\ln\frac{1/\Gamma_{ml}-b_a}{1/\Gamma_{ml}} + \frac{kTb_a}{1/\Gamma_{ml}-b_a} \\ & - \frac{a_a}{b_a\sqrt{T}}\left(\ln\left(\frac{1/\Gamma_{ml}+b_a}{1/\Gamma_{ml}}\right)+\frac{b_a}{1/\Gamma_{ml}+b_a}\right)\end{aligned} \tag{48}$$

Equation (48) may also be written as:

$$\mu_a = \mu_a^0(T,1) + kT\ln\Pi + kT\ln\Phi \tag{49}$$

with:

$$\mu_a^0 = -kT\left[\ln kT\frac{q_{a\,vib}\,q_{a\,rot}\,q_{a\,e}\,q_{a\,vibi}}{\Lambda^2}\right] + U_0 \tag{50}$$

$$\begin{aligned}\ln\Phi = {} & -\ln\frac{\Pi}{kT}\frac{1}{\Gamma_{ml}} + \ln\frac{1/\Gamma_{ml}}{1/\Gamma_{ml}-b_a} + \frac{b_a}{1/\Gamma_{ml}-b_a} \\ & - \frac{a_a}{kT\sqrt{T}b_a}\left[\ln\left(\frac{1/\Gamma_{ml}+b_a}{1/\Gamma_{ml}}\right)+\frac{b_a}{1/\Gamma_{ml}+b_a}\right]\end{aligned} \tag{51}$$

μ_s^0 is the standard chemical potential and Φ is the two-dimension fugacity coefficient.

If we consider an ideal adsorbed phase, that is to say that U_{int} and b_a are equal to zero, equation (48) reduces to:

$$\mu_{\text{a IDEAL}} = -kT\left[\ln kT\frac{q_{\text{a vib}}\,q_{\text{a rot}}\,q_{\text{a e}}\,q_{\text{a vibi}}}{\Lambda^2}\right] + U_0 + kT\ln\Pi \tag{52}$$

As a consequence:

$$\mu_{\text{a IDEAL}} = \mu_{\text{a}}^0(T,1) + kT\ln\Pi \tag{53}$$

In which μ_{a}^0 is given by equation (50).

Equation (53) shows that μ_{a}^0 is the chemical potential of the adsorbed phase, considered as ideal, at temperature T and for a spreading pressure $\Pi = 1$. Equations (49) and (52) show that $\ln\Phi$ takes into account the non-ideality due to the molecular surface and to the attractions between the adsorbed molecules.

Rearranging equation (45) leads to:

$$\frac{\Pi}{kT}\frac{1}{\Gamma_{\text{ml}}} = \frac{1/\Gamma_{\text{ml}}}{1/\Gamma_{\text{ml}} - b_{\text{a}}} - \frac{a_{\text{a}}}{kT\sqrt{T}(1/\Gamma_{\text{ml}} + b_{\text{a}})} \tag{54}$$

This could be considered as the two-dimension Redlich–Kwong EOS. a_{a} and b_{a} appear to be its coefficients. Their calculation by similar rules as those used for the gas phase would require the knowledge of the two-dimension critical temperature and pressure as well as the corresponding acentric factor of the fluid, which is not possible. As a consequence, these parameters should be determined by an optimization procedure between simulated and experience data.

If we retain other valid expressions of $G(V_{\text{g}})$ (equation (38)) and $J(T)$ (equation (39)), we can obtain other two-dimension EOS.

2.3 Non-ideal adsorption isotherm model

Considering adsorption equilibrium between the adsorbed phase and the gas phase leads to:

$$\mu_{\text{g}} = \mu_{\text{a}} \tag{55}$$

$$\mu_{\text{a}}^0(T,1) + kT\ln\Pi + kT\ln\Phi = \mu_{\text{g}}^0(T,1) + kT\ln p + kT\ln\Phi' \tag{56}$$

$$\Phi\Gamma_{\text{ml}} = \frac{\Lambda(q_{\text{a vib}}\,q_{\text{a rot}}\,q_{\text{a e}}\,q_{\text{a vibi}})}{Z_{\text{ml}}kT(q_{\text{g rot}}\,q_{\text{g e}}\,q_{\text{g vibi}})}\exp\left(\frac{-U_0}{kT}\right)p\Phi' \tag{57}$$

in which $Z_{\text{ml}} = (\Pi/kT)\,(1/\Gamma_{\text{ml}})$.

If we suppose that there is no change in the rotational, internal, vibration and electronic contributions when the molecules migrate from the gas phase to the adsorbed phase and by converting the expression to its molar form, we obtain:

$$\left[\frac{RT\Gamma}{N_0\Pi}\frac{1/\Gamma}{1/\Gamma - b_{\text{amol}}}\exp\left(\frac{b_{\text{amol}}}{1/\Gamma - b_{\text{amol}}}\right)\left[\frac{1/\Gamma + b_{\text{amol}}}{1/\Gamma}\right]^{-\frac{N_0 a_{\text{amol}}}{RT\sqrt{T}b_{\text{amol}}}} \times\exp\left(-\frac{N_0 a_{\text{amol}}}{RT\sqrt{T}}\frac{1}{1/\Gamma + b_{\text{amol}}}\right)\right]\Gamma = \frac{hN_0}{ZRT\sqrt{2\pi MRT}}\frac{\exp\left(-\frac{N_0 h\nu_z}{2RT}\right)}{1-\exp\left(-\frac{N_0 h\nu_z}{RT}\right)}\exp\left(\frac{-N_0 U_0}{RT}\right)p \times\left[\begin{array}{l}\frac{RT}{P\nu}\frac{\nu}{\nu - b_{\text{mol}}}\exp\left(\frac{b_{\text{mol}}}{\nu - b_{\text{mol}}}\right) \\ \left[\frac{\nu + b_{\text{mol}}}{\nu}\right]^{-\frac{N_0 a_{\text{mol}}}{RT\sqrt{T}b_{\text{mol}}}}\exp\left(-\frac{N_0 a_{\text{mol}}}{RT\sqrt{T}}\frac{1}{\nu + b_{\text{mol}}}\right)\end{array}\right] \tag{58}$$

where:

- Γ is the molar surface concentration of the fluid;
- a_{mol}, b_{mol}, a_{amol}, b_{amol}, Z are respectively the molar expression corresponding to the molecular ones a, b, a_{a}, b_{a}, Z_{ml};
- M is the molar mass;
- ν is the molar volume of the gas phase; and
- N_0 is the Avogadro number.

The molar expression of the local model is then:

$$\Gamma\left[\frac{1}{1-\Gamma b_{\text{amol}}}\exp\left(\frac{\Gamma b_{\text{amol}}}{1-\Gamma b_{\text{amol}}}\right)[1+\Gamma b_{\text{amol}}]^{-\frac{N_0 a_{\text{amol}}}{RT\sqrt{T}b_{\text{amol}}}} \times\exp\left(-\frac{N_0\Gamma a_{\text{amol}}}{RT\sqrt{T}}\frac{1}{1+\Gamma b_{\text{amol}}}\right)\right] = \frac{hN_0}{RT\sqrt{2\pi MRT}}\frac{\exp\left(-\frac{N_0 h\nu_z}{2RT}\right)}{1-\exp\left(-\frac{N_0 h\nu_z}{RT}\right)}\exp\left(\frac{-N_0 U_0}{RT}\right)p \times\left[\begin{array}{l}\frac{RT}{P\nu}\frac{\nu}{\nu - b_{\text{mol}}}\exp\left(\frac{b_{\text{mol}}}{\nu - b_{\text{mol}}}\right) \\ \left[\frac{\nu + b_{\text{mol}}}{\nu}\right]^{-\frac{N_0 a_{\text{mol}}}{RT\sqrt{T}b_{\text{mol}}}}\exp\left(-\frac{N_0 a_{\text{mol}}}{RT\sqrt{T}}\frac{1}{\nu + b_{\text{mol}}}\right)\end{array}\right] \tag{59}$$

where:

$$\left[\frac{1}{1-\Gamma b_{\text{amol}}}\exp\left(\frac{\Gamma b_{\text{amol}}}{1-\Gamma b_{\text{amol}}}\right)[1+\Gamma b_{\text{amol}}]^{-\frac{N_0 a_{\text{amol}}}{RT\sqrt{T}b_{\text{amol}}}} \times\exp\left(-\frac{N_0\Gamma a_{\text{amol}}}{RT\sqrt{T}}\frac{1}{1+\Gamma b_{\text{amol}}}\right)\right]$$

takes into account the non-ideality of the adsorbed phase.

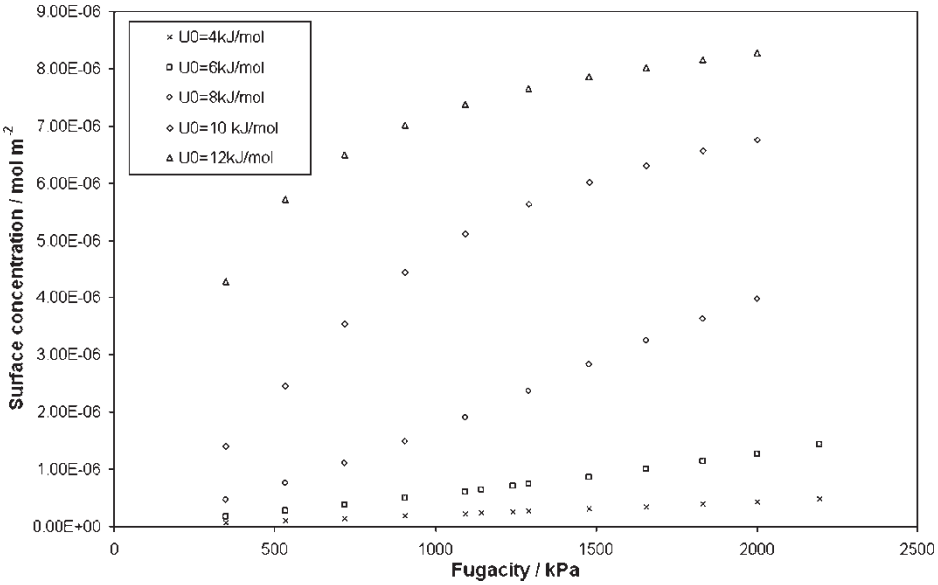

Figure 1. Adsorption isotherms of a given adsorbate at 283 K on a homogenous non-porous adsorbent (a_{mol}: 1.554 J m^3 mol^{-2}; b_{mol}: 2.67 × 10^{-5} m^3 mol^{-2}; a_{amol}: 8.10 × 10^9 J m^2 mol^{-2}; and b_{amol}: 7.88 × 10^4 m^2 mol^{-2}): influence of U_0.

The treatment of the ideal case leads to the following expression:

$$\Gamma = \frac{hN_0}{RT\sqrt{2\pi MRT}} \frac{\exp\left(-\frac{N_0 h\nu_z}{2RT}\right)}{1-\exp\left(-\frac{N_0 h\nu_z}{RT}\right)} \exp\left(\frac{-N_0 U_0}{RT}\right) p \tag{60}$$

This last equation is the expression of the Henry's Law

3. Results and discussion

We present some results of the surface concentration computed using the model developed above. These computations were carried out considering a given adsorbate on a given non-porous homogenous adsorbents at 283 K and in a pressure range up to 2.5 MPa. We used the Lennard-Jones potential model to describe the adsorbate–adsorbent interaction and adequate three-dimension and two-dimension energetic and geometric parameters [11]. For the gas phase model, these parameters can be easily calculated from the critical parameters of the adsorbate, the adsorbed phase model parameters (a_{amol} and b_{amol}) can be derived only from adsorption experimental data.

The influence of U_0 value is shown in figure 1 showing the computed surface concentration on different homogenous non-porous adsorbent at 283 K as a function of gas fugacity.

From this figure, we can see that the shape of the curve varies significantly for different values of the energy of interaction between the adsorbate and the surface in the whole fugacity range. For high values of U_0, the surface concentration Γ increases quickly with fugacity. For low values of energy, the surface concentration Γ increases linearly with fugacity.

The influence of the local model parameters on the adsorption isotherms were also studied at 283 K and in a pressure range up to 2.5 MPa

We compute the surface concentration ($U_0 = 8$ kJ/mol) using different sets of parameter values (a_{amol} and b_{amol}). The results are illustrated in figures 2 and 3.

A rise of a_{amol} or a decrease of b_{amol} leads to higher surface concentrations which is physically consistent with the meaning of these parameters. From these figures, we can see that the shape of the surface concentration curves varies significantly for an increase of a_{amol} or a decrease of b_{amol}. High values of a_{amol} correspond to strong interactions between the adsorbated molecules (in comparison to the adsorbate–surface interactions); the mass uptake is thus low at low gas fugacity and increase more quickly with the fugacity when the coverage ration increases.

Low values of b_{amol} lead to high surface concentrations at saturation due to the fact that the molecules have a lower surface.

4. Conclusions

We developed a general model for the calculation of equilibrium surface concentrations as a function of temperature and pressure. This model relating macroscopic data, which characterize the equilibrium of adsorption of pure gases on homogeneous surfaces, is based on simple statistical thermodynamics developments. It leads to a symmetrical approach of both the adsorbed and the gas phases in terms of EOS and fugacity coefficient calculations. This model is based on the Redlich–Kwong EOS in order to take into account the non-ideality of both phases. Other expressions of the isotherm equation could be deduced using other equations of state and using purely macroscopic developments.

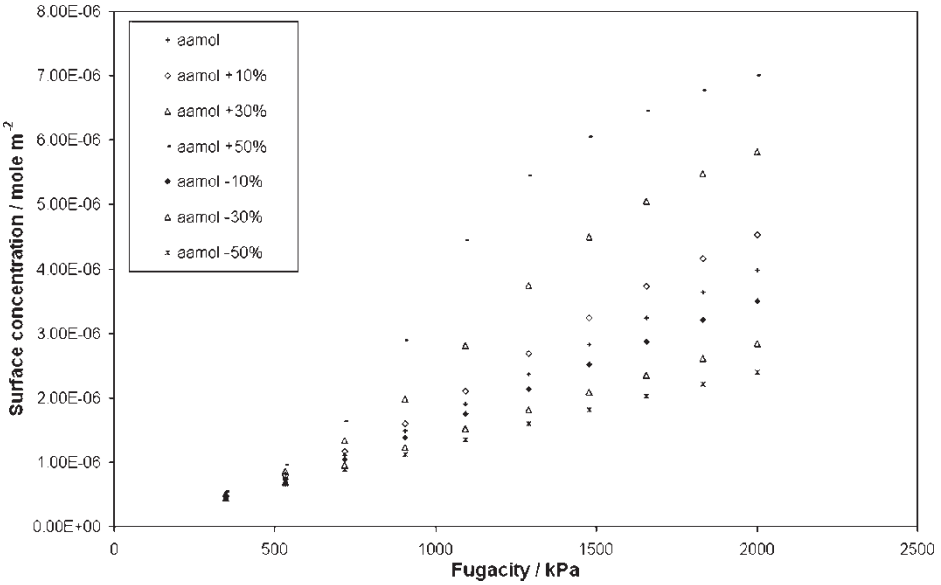

Figure 2. Adsorption isotherms of a given adsorbate at 283 K on a homogenous non-porous adsorbent (U_0: 8 kJ; a_{mol}: 1.554 J m^3 mol^{-2}; b_{mol}: 2.67 × 10^{-5} m^3 mol^{-2}; a_{amol}: 8.10 × 10^9 J m^2 mol^{-2}; and b_{amol}: 7.88 × 10^4 m^2 mol^{-2}): influence of a_{amol}.

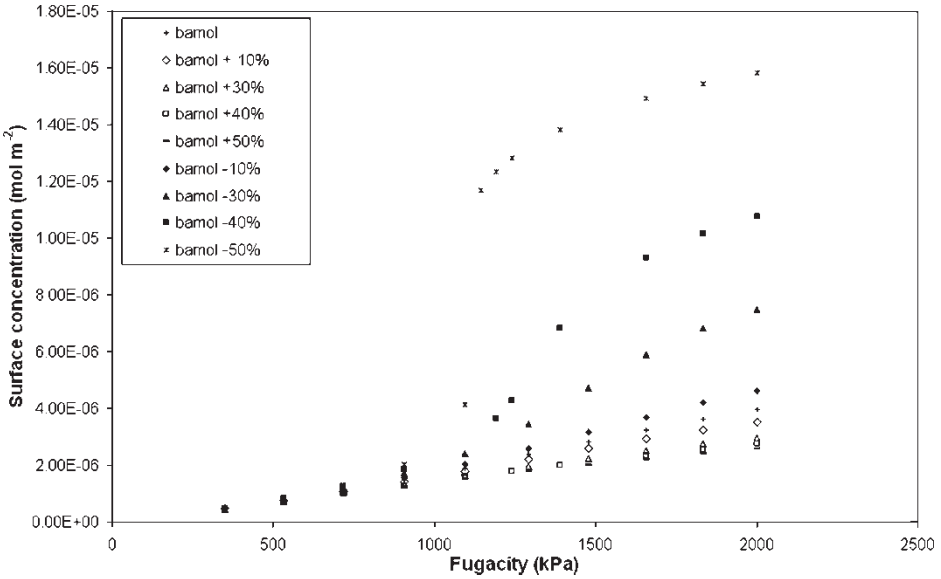

Figure 3. Adsorption isotherms of a given adsorbate at 283 K on a homogenous non-porous adsorbent (U_0: 8 kJ; a_{mol}: 1.554 J m^3 mol^{-2}; b_{mol}: 2.67 × 10^{-5} m^3 mol^{-2}; a_{amol}: 8.10 × 10^9 J m^2 mol^{-2}; and b_{amol}: 7.88 × 10^4 m^2 mol^{-2}): influence of b_{amol}.

The influence of each macroscopic parameter was studied; the computations provide meaningful results.

References

[1] T.L. Hill. *An Introduction to Statistical Thermodynamics*, Addison-Wesley, London (1960).
[2] D.M. Ruthven. *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York (1983).
[3] K. Grabowski, A. Patrykiejew, S. Sokolowski. Monte Carlo simulation of adsorption on preadsorbed layers. *Surf. Sci.*, **506**, 47 (2005).
[4] P.I. Ravikovitch, A. Vishnyakov, A.V. Neimark. Density functional theories and molecular simulations of adsorption and phase transitions in nanopores. *Phys. Rev. E*, **64**(011602) (2001).
[5] S. Ross, J.P. Olivier. *On Physical Adsorption*, Interscience, New York (1964).
[6] J. Jagiello, J.A. Schwarz. *Langmuir*, **9**, 2513 (1993).
[7] M. Frère, J. Bougard, R. Jadot. Determination of the micropore volume distribution function of activated carbons by gas adsorption. *Adsorption*, **3**, 55 (1996).
[8] J.H. Vera, J. Prausnitz. Generalized van der Waals theory for dense fluids. *Chem. Eng. J.*, **3**, 1 (1972).
[9] J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, New Jersey (1999).
[10] R. Jadot. A comparative study of four equations of state to calculate the thermodynamic properties of halogenated hydrocarbons and their mixtures. *Int. J. Refrig.*, **4**(2), 61 (1981).
[11] G. De Weireld, M. Frère. Study of the buoyancy effect on high pressure and high temperature adsorption isotherms measurements. *Proceeding of 7th International Conference on Fundamentals of Adsorption*, pp. 693–699, IK International, Ltd, Chiba city (2001).