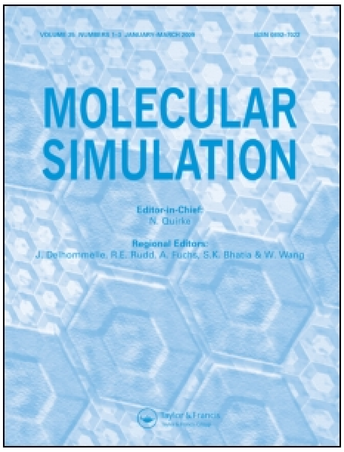

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Adsorption equilibria of single gas and gas mixture on homogeneous surfaces: a unified approach based on statistical thermodynamics developments. Part II: extension to gas mixture adsorption

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

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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). In this paper, we present a statistical thermodynamics approach for the calculation of mixed gas adsorption equilibrium data on uniform surfaces. The non-ideality of both the mixed gas phase and the adsorbed phase is considered by using the Redlich–Kwong EOS associated to the classic Lorentz–Berthelot mixing rules. This is an interesting way to extend the model presented in Part I and to predict multicomponent gas adsorption equilibria for highly non-ideal systems from parameters deduced from pure gas data. We present mixture adsorption isotherms and selectivity curves calculated using our model.

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

1. Introduction

Prediction of multi-component adsorption equilibria using parameters deduced from single gas adsorption data is of great practical importance. Such equilibrium data are indeed required for process design purpose. Generally the experimental determination of such data is time-consuming. As for pure gases, a lot of models are derived from macroscopic thermodynamics development. The most useful predictive theories for multi-component adsorption equilibria are described in [1–11]. They are considered as efficient tools for engineers concerned with adsorption process design. Unfortunately they 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. Most of them are based on the generalization of the corresponding pure gas adsorption models.

This paper is the second part of a work dealing with statistical–thermodynamics approach to predict single and multi-component gas equilibria. In the first part, the single gas adsorption equation developments were described in details. We had defined the model parameters and the final expression of the equilibrium isotherm equation. This second paper reports the same theoretical developments for binary mixed, the aim of which is to provide a useful prediction tool for engineers for the assessment of multi-component adsorption information in a wide range of pressure and temperature. Both phases are described using simple statistical thermodynamics developments which lead to the expression of the chemical potential of each specie in each phase. The equality of the chemical potentials of a given specie in each phase allows to relate the macroscopic variables (temperature, pressure, surface concentration and phases composition) together. The model does not require any further parameter compared to the pure gas version.

2. Theoretical section

In this approach, we replace the mixture by a hypothetic pure component, the properties of which are indexed “mix”.

As for the single gas case, the adsorption equilibrium expression between the adsorbed and the gas phases is expressed by the equality of the chemical potentials of the

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adsorptives in each phase. The development of such an equation requires the microscopic modeling of each phase separately in order to obtain the expression of the chemical potentials using statistical thermodynamics developments.

2.1 Non-ideal gas phase modeling

The canonical partition function Q_{gmix} of a system composed of a mixture of N_{gB} molecules of a gas B (molecular mass m_{B}) and N_{gC} molecules of a gas C (molecular mass m_{C}) in a volume V_{gmix} at temperature T is given by:

$$Q_{\mathrm{gmix}} = \frac{q_{\mathrm{gB}}^{N_{\mathrm{gB}}}\, q_{\mathrm{gC}}^{N_{\mathrm{gC}}}}{N_{\mathrm{gB}}!N_{\mathrm{gC}}!} \tag{1}$$

with, $N_{\mathrm{gmix}} = N_{\mathrm{gB}} + N_{\mathrm{gC}}$

q_{gB} and q_{gC} are respectively the partition function of one molecule of B (or C) and are expressed as:

$$q_{\mathrm{gB}} = q_{\mathrm{gB\,trans}}\, q_{\mathrm{gB\,rot}}\, q_{\mathrm{gB\,vibi}}\, q_{\mathrm{gB\,e}} \exp\left(\frac{-U'_{\mathrm{int\,mix}}}{2kT}\right) \tag{2}$$

$$q_{\mathrm{gC}} = q_{\mathrm{gC\,trans}}\, q_{\mathrm{gC\,rot}}\, q_{\mathrm{gC\,vibi}}\, q_{\mathrm{gC\,e}} \exp\left(\frac{-U'_{\mathrm{int\,mix}}}{2kT}\right) \tag{3}$$

where

- $q_{\mathrm{gB\,trans}}$ and $q_{\mathrm{gC\,trans}}$ are, respectively, the translation contributions to the partition functions q_{gB} and q_{gC} (three degrees of freedom of the mass centre of the molecule);
- $q_{\mathrm{gB\,rot}}$ and $q_{\mathrm{gC\,rot}}$ are, respectively, the rotational contributions to the partition functions q_{gB} and q_{gC};
- $q_{\mathrm{gB\,vibi}}$ and $q_{\mathrm{gC\,vibi}}$ are, respectively, the contributions to the partition functions q_{gB} and q_{gC} due to the internal vibrations in the molecule;
- $q_{\mathrm{gB\,e}}$ and $q_{\mathrm{gC\,e}}$ are, respectively, the electronic contributions to the partition functions q_{gB} and q_{gC};

The translation contribution to the partition function of component j may be written:

$$q_{\mathrm{g}j\,\mathrm{trans}} = \left[\frac{2\pi m_j kT}{h^2}\right]^{3/2} V_{\mathrm{fmix}} = \frac{V_{\mathrm{fmix}}}{\Lambda_j^3} \tag{4}$$

With,

$$\Lambda_j^{-1} = \left[\frac{2\pi m_j kT}{h^2}\right]^{1/2} \tag{5}$$

in which, suffix j means molecules B or C; Λ_j is the thermal de Broglie wavelength of molecule j; h is the Planck constant; m_j is the mass of molecule j; and k is the Boltzmann constant; V_{fmix} is the real volume available to the molecules in the mixture.

The contribution to the molecular partition function due to the interactions between the molecules is $\exp(-U'_{\mathrm{int\,mix}}/2kT)$, in which, $U'_{\mathrm{int\,mix}}$ is the potential energy of interaction between any molecule and all the others in the mixture;

$U'_{\mathrm{int\,mix}}$ may be calculated by:

$$U'_{\mathrm{int\,mix}} = -\int_{d_{\mathrm{mix}}}^{\infty} u'(r)\frac{N_{\mathrm{gmix}}}{V_{\mathrm{gmix}}} g'(r) 4\pi r^2 \mathrm{d}r \tag{6}$$

in which d_{gmix} is the molecular diameter of an hypothetic molecule in the gas phase representing the mixture.

Following the works of Vera and Prausnitz [12], the same developments as in part I may be done for the gas mixture, using similar expressions of equations (7)–(13) (Part I). We obtain,

$$U'_{\mathrm{int\,mix}} = -\frac{4\pi d_{\mathrm{gmix}}^3}{b_{\mathrm{mix}}} C'_{\mathrm{mix}} \sqrt{\frac{T_{\mathrm{cmix}}}{T}} \ln\left(1 + \frac{N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \tag{7}$$

T_{cmix} is the critical temperature of the hypothetic component; C'_{mix} is an energetic constant of the hypothetic component in the gas phase; b_{mix} is a parameter which characterizes the fluid. It may be considered as the volume of the molecule of the hypothetic component.

If we set $a_{\mathrm{mix}} = 2\pi d_{\mathrm{gmix}}^3 C'_{\mathrm{mix}} \sqrt{T_{\mathrm{cmix}}}$, a_{mix} is defined as the molecular attraction parameter of the hypothetic component.

The parameters of mixture (a_{mix} and b_{mix}) will be calculated thereafter using the pure component parameters and appropriate mixing rules.

Equation (7) becomes:

$$U'_{\mathrm{int\,mix}} = -\frac{2a_{\mathrm{mix}}}{kT\sqrt{T}b_{\mathrm{mix}}} \ln\left(1 + \frac{N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \tag{8}$$

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

$$\begin{aligned} Q_{\mathrm{gmix}} = {} & \frac{V_{\mathrm{fmix}}^{N_{\mathrm{gB}}}}{\Lambda_{\mathrm{B}}^{3N_{\mathrm{gB}}} N_{\mathrm{gB}}!} \frac{V_{\mathrm{fmix}}^{N_{\mathrm{gc}}}}{\Lambda_{\mathrm{C}}^{3N_{\mathrm{gC}}} N_{\mathrm{gC}}!} \\ & \times \left(q_{\mathrm{gB\,rot}} q_{\mathrm{gB\,vibi}}\, q_{\mathrm{gB\,e}} \exp\left(\frac{-U'_{\mathrm{int\,mix}}}{2kT}\right)\right)^{N_{\mathrm{gB}}} \\ & \times \left(q_{\mathrm{gC\,rot}}\, q_{\mathrm{gC\,vibi}}\, q_{\mathrm{gC\,e}} \exp\left(\frac{-U'_{\mathrm{int\,mix}}}{2kT}\right)\right)^{N_{\mathrm{gC}}} \end{aligned} \tag{9}$$

in which V_{fmix} may be calculated by

$$V_{\mathrm{fmix}} = V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}} \tag{10}$$

Combining equations (8)–(10) leads to

$$\begin{aligned}\ln Q_{\mathrm{gmix}} = {} & N_{\mathrm{gB}} \ln(V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}) - N_{\mathrm{gB}} \ln \Lambda_{\mathrm{B}}^{3} \\ & - N_{\mathrm{gB}} \ln N_{\mathrm{gB}} + N_{\mathrm{gB}} + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,rot}} \\ & + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,vibi}} + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,e}} \\ & + \frac{N_{\mathrm{gB}} a_{\mathrm{mix}}}{kT\sqrt{T} b_{\mathrm{mix}}} \ln\left(\frac{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \\ & + N_{\mathrm{gC}} \ln(V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}) \\ & - N_{\mathrm{gC}} \ln \Lambda_{\mathrm{C}}^{3} - N_{\mathrm{gC}} \ln N_{\mathrm{gC}} + N_{\mathrm{gC}} \\ & + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,rot}} + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,vibi}} \\ & + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,e}} + \frac{N_{\mathrm{gC}} a_{\mathrm{mix}}}{kT\sqrt{T} b_{\mathrm{mix}}} \\ & \times \ln\left(\frac{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \end{aligned} \tag{11}$$

Then

$$\begin{aligned}\ln Q_{\mathrm{gmix}} = {} & N_{\mathrm{gmix}} \ln(V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}) \\ & - N_{\mathrm{gB}} \ln \Lambda_{\mathrm{B}}^{3} - N_{\mathrm{gB}} \ln N_{\mathrm{gB}} + N_{\mathrm{gB}} \\ & + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,rot}} + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,vibi}} \\ & + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,e}} - N_{\mathrm{gC}} \ln \Lambda_{C}^{3} \\ & - N_{\mathrm{gC}} \ln N_{\mathrm{gC}} + N_{\mathrm{gC}} + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,rot}} \\ & + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,vibi}} + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,e}} \\ & + \frac{N_{\mathrm{gmix}} a_{\mathrm{mix}}}{kT\sqrt{T} b_{\mathrm{mix}}} \ln\left(\frac{V_{\mathrm{mix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \end{aligned} \tag{12}$$

We apply the classical mixing rules,

$$\begin{aligned} a_{\mathrm{mix}} &= a_{\mathrm{B}} y_{\mathrm{B}}^{2} + a_{\mathrm{C}} y_{\mathrm{C}}^{2} + 2 y_{\mathrm{B}} y_{\mathrm{C}} a_{\mathrm{B,C}} \\ &= a_{\mathrm{B}} \left(\frac{N_{\mathrm{gB}}}{N_{\mathrm{gmix}}}\right)^{2} + a_{\mathrm{C}} \left(\frac{N_{\mathrm{gC}}}{N_{\mathrm{gmix}}}\right)^{2} + 2 \frac{N_{\mathrm{gB}} N_{\mathrm{gC}}}{N_{\mathrm{gmix}}^{2}} a_{\mathrm{B,C}} \end{aligned} \tag{13}$$

$$b_{\mathrm{mix}} = b_{\mathrm{B}} y_{\mathrm{B}} + b_{\mathrm{C}} y_{\mathrm{C}} = b_{\mathrm{B}} \frac{N_{\mathrm{gB}}}{N_{\mathrm{gmix}}} + b_{\mathrm{C}} \frac{N_{\mathrm{gC}}}{N_{\mathrm{gmix}}} \tag{14}$$

in which,

- a_{B} and a_{C} are respectively the intermolecular attraction parameters between B and B and between C and C in the gas phase;
- y_{B} and y_{C} are respectively the mole fractions of the component B and C in the gas phase;
- b_{B} and b_{C} are the geometric parameters of pure components B and C;
- $a_{\mathrm{B,C}}$ is the attraction parameter between B and C in the gas phase; $a_{\mathrm{B,C}}$ may be calculated from a_{B} and a_{C} with quadratic mixing rule $a_{\mathrm{B,C}} = \sqrt{a_{\mathrm{B}} a_{\mathrm{C}}}$

Substituting equations (13) and (14) in equation (12), we have

$$\begin{aligned}\ln Q_{\mathrm{gmix}} = {} & N_{\mathrm{gmix}} \ln(V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}) \\ & - N_{\mathrm{gB}} \ln \Lambda_{\mathrm{B}}^{3} - N_{\mathrm{gB}} \ln N_{\mathrm{gB}} + N_{\mathrm{gB}} \\ & + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,rot}} + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,vibi}} \\ & + N_{\mathrm{gB}} \ln q_{\mathrm{gB\,e}} - N_{\mathrm{gC}} \ln \Lambda_{\mathrm{C}}^{3} \\ & - N_{\mathrm{gC}} \ln N_{\mathrm{gC}} + N_{\mathrm{gC}} + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,rot}} \\ & + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,vibi}} + N_{\mathrm{gC}} \ln q_{\mathrm{gC\,e}} \\ & + \frac{N_{\mathrm{gmix}} \left[a_{\mathrm{B}} \left(\frac{N_{\mathrm{gB}}}{N_{\mathrm{gmix}}}\right)^{2} + a_{\mathrm{C}} \left(\frac{N_{\mathrm{gC}}}{N_{\mathrm{gmix}}}\right)^{2} + 2 \frac{N_{\mathrm{gB}} N_{\mathrm{gC}}}{N_{\mathrm{gmix}}^{2}} a_{\mathrm{B,C}} \right]}{kT\sqrt{T} \left(\frac{N_{\mathrm{gB}}}{N_{\mathrm{gmix}}} b_{\mathrm{gB}} + \frac{N_{\mathrm{gC}}}{N_{\mathrm{gmix}}} b_{\mathrm{C}} \right)} \\ & \times \ln\left(\frac{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \end{aligned} \tag{15}$$

The chemical potential of component B in the mixture of B and C is obtained by differentiating $\ln Q_{\mathrm{gmix}}$ with respect to N_{gB}:

$$\mu_{\mathrm{gB}} = -kT \left(\frac{\partial \ln Q_{\mathrm{gmix}}}{\partial N_{\mathrm{gB}}} \right)_{T, V_{\mathrm{gmix}}, N_{\mathrm{gC}}} \tag{16}$$

$$\begin{aligned} \mu_{\mathrm{gB}} = -kT \Bigg[& \ln(V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}) - \frac{N_{\mathrm{gm}} b_{\mathrm{B}}}{V_{\mathrm{mix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}} - \ln \Lambda_{\mathrm{B}}^{3} - \ln N_{\mathrm{gB}} + \ln q_{\mathrm{gB\,rot}} + \ln q_{\mathrm{gB\,vibi}} + \ln q_{\mathrm{gB\,e}} \\ & + \frac{1}{kT\sqrt{T}} \frac{\left(\frac{2N_{\mathrm{gB}}(N_{\mathrm{gB}}+N_{\mathrm{gC}}) - N_{\mathrm{gB}}^{2}}{(N_{\mathrm{gB}}+N_{\mathrm{gC}})^{2}} a_{\mathrm{B}} - \frac{N_{\mathrm{gC}}^{2}}{(N_{\mathrm{gB}}+N_{\mathrm{gC}})^{2}} a_{\mathrm{C}} + \frac{2N_{\mathrm{gC}}(N_{\mathrm{gB}}+N_{\mathrm{gC}}) - 2N_{\mathrm{gB}} N_{\mathrm{gC}}}{(N_{\mathrm{gB}}+N_{\mathrm{gC}})^{2}} a_{\mathrm{B,C}} \right)}{b_{\mathrm{mix}}} \\ & - \frac{1}{kT\sqrt{T}} \frac{a_{\mathrm{mix}} (N_{\mathrm{gB}} + N_{\mathrm{gC}}) \left(\frac{N_{\mathrm{gB}}+N_{\mathrm{gC}}-N_{\mathrm{gB}}}{(N_{\mathrm{gB}}+N_{\mathrm{gC}})^{2}} b_{\mathrm{B}} - \frac{N_{\mathrm{gC}}}{(N_{\mathrm{gB}}+N_{\mathrm{gC}})^{2}} b_{\mathrm{C}} \right)}{b_{\mathrm{mix}}^{2}} \ln\left(\frac{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right) \\ & + \frac{N_{\mathrm{gmix}} a_{\mathrm{mix}}}{kT\sqrt{T} b_{\mathrm{mix}}} \frac{b_{\mathrm{B}}}{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}} \Bigg] \end{aligned} \tag{17}$$

Then

$$\begin{aligned}\mu_{\mathrm{gB}}=&-kT\Bigg[\ln(V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}})-\frac{N_{\mathrm{gmix}}b_{B}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}\\&-\ln\Lambda_{\mathrm{B}}^{3}-\ln N_{\mathrm{B}}+\ln q_{\mathrm{gB\,rot}}+\ln q_{\mathrm{gB\,vibi}}+\ln q_{\mathrm{gB\,e}}+\frac{1}{kT\sqrt{T}}\\&\times\Bigg[\frac{\left(2y_{\mathrm{B}}a_{\mathrm{B}}+2y_{\mathrm{C}}a_{\mathrm{B,C}}-y_{\mathrm{B}}^{2}a_{\mathrm{B}}-y_{\mathrm{C}}^{2}a_{\mathrm{C}}-2y_{\mathrm{B}}y_{\mathrm{C}}a_{\mathrm{B,C}}\right)}{b_{\mathrm{mix}}}\\&-\frac{a_{\mathrm{mix}}[y_{\mathrm{C}}b_{\mathrm{B}}+y_{\mathrm{B}}b_{\mathrm{B}}-b_{\mathrm{mix}}]}{b_{\mathrm{mix}}^{2}}\Bigg]\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&+\frac{N_{\mathrm{gmix}}a_{\mathrm{mix}}}{kT\sqrt{T}b_{\mathrm{mix}}}\frac{b_{\mathrm{B}}}{V_{\mathrm{mix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}\Bigg]\end{aligned}\tag{18}$$

Using expressions (13) and (14), we may write:

$$\begin{aligned}\mu_{\mathrm{gB}}=&-kT\Bigg[\ln(V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}})-\frac{N_{\mathrm{gmix}}b_{\mathrm{B}}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}\\&-\ln\Lambda_{\mathrm{B}}^{3}-\ln N_{\mathrm{B}}+\ln q_{\mathrm{gB\,rot}}+\ln q_{\mathrm{gB\,vibi}}+\ln q_{\mathrm{gB\,e}}\\&+\frac{2y_{\mathrm{B}}a_{\mathrm{B}}+2y_{\mathrm{C}}a_{\mathrm{B,C}}}{kT\sqrt{T}b_{\mathrm{mix}}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{a_{\mathrm{mix}}}{kT\sqrt{T}b_{\mathrm{mix}}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{a_{\mathrm{mix}}b_{\mathrm{B}}}{kT\sqrt{T}b_{\mathrm{mix}}^{2}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&+\frac{a_{\mathrm{mix}}}{kT\sqrt{T}b_{\mathrm{mix}}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&+\frac{N_{\mathrm{gmix}}a_{\mathrm{mix}}}{kT\sqrt{T}b_{\mathrm{mix}}}\frac{b_{\mathrm{B}}}{V_{\mathrm{mix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}\Bigg]\end{aligned}\tag{19}$$

Then

$$\begin{aligned}\mu_{\mathrm{gB}}=&-kT\Bigg[\ln\frac{(V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}})}{N_{\mathrm{gmix}}}-\frac{N_{\mathrm{gmix}}b_{\mathrm{B}}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}\\&-\ln\Lambda_{\mathrm{B}}^{3}-\ln y_{\mathrm{B}}+\ln q_{\mathrm{gB\,rot}}+\ln q_{\mathrm{gB\,vibi}}+\ln q_{\mathrm{gB\,e}}\\&+\frac{2y_{\mathrm{B}}a_{\mathrm{B}}+2y_{\mathrm{C}}a_{\mathrm{B,C}}}{kT\sqrt{T}b_{\mathrm{mix}}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{a_{\mathrm{mix}}b_{\mathrm{B}}}{kT\sqrt{T}b_{\mathrm{mix}}^{2}}\Bigg[\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}\Bigg]\Bigg]\end{aligned}\tag{20}$$

The total pressure p may be calculated from the canonical partition function of the mixture

$$p=kT\left(\frac{\partial\ln Q_{\mathrm{gmix}}}{\partial V_{\mathrm{gmix}}}\right)_{T,N_{\mathrm{gB}},N_{\mathrm{gC}}}\tag{21}$$

$$\begin{aligned}\frac{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}{N_{\mathrm{gmix}}}=\frac{kT}{p}\Bigg[&\frac{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\\&\times\Bigg(\frac{V_{\mathrm{gmix}}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}\\&-\frac{N_{\mathrm{gmix}}a_{\mathrm{mix}}}{kT\sqrt{T}\left(V_{\mathrm{mix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}\right)}\Bigg)\Bigg]\end{aligned}\tag{22}$$

Substituting equation (22) in equation (20) we obtain:

$$\begin{aligned}\mu_{\mathrm{gB}}=&-kT\Bigg[\ln\frac{(q_{\mathrm{gB\,rot}}q_{\mathrm{gB\,vibi}}q_{\mathrm{gB\,e}})kT}{\Lambda_{\mathrm{B}}^{3}}\\&-\ln py_{\mathrm{B}}+\ln\frac{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}-\frac{N_{\mathrm{gmix}}b_{\mathrm{B}}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}\\&+\frac{2y_{\mathrm{B}}a_{\mathrm{B}}+2y_{\mathrm{C}}a_{\mathrm{B,C}}}{kT\sqrt{T}b_{\mathrm{mix}}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{a_{\mathrm{mix}}b_{\mathrm{B}}}{kT\sqrt{T}b_{\mathrm{mix}}^{2}}\Bigg[\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}\Bigg]+\ln\Bigg(\frac{V_{\mathrm{gmix}}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}\\&-\frac{N_{\mathrm{gmix}}a_{\mathrm{mix}}}{kT\sqrt{T}(V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}})}\Bigg)\Bigg]\end{aligned}\tag{23}$$

The final expression of the chemical potential is,

$$\begin{aligned}\mu_{\mathrm{gB}}=&-kT\ln\frac{(q_{\mathrm{gB\,rot}}q_{\mathrm{gB\,vibi}}q_{\mathrm{gB\,e}})kT}{\Lambda_{\mathrm{B}}^{3}}\\&+kT\ln py_{\mathrm{B}}+kT\ln\Phi_{\mathrm{B}}'\end{aligned}\tag{24}$$

with

$$\mu_{\mathrm{gB}}^{0}=-kT\left[\ln kT\frac{q_{\mathrm{gB\,rot}}\,q_{\mathrm{gB\,e}}\,q_{\mathrm{gB\,vibi}}}{\Lambda_{\mathrm{B}}^{3}}\right]\tag{25}$$

$$\begin{aligned}\ln\Phi_{\mathrm{B}}'=&\frac{N_{\mathrm{gmix}}b_{\mathrm{B}}}{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}-\ln\frac{V_{\mathrm{gmix}}-N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\\&-\frac{2y_{\mathrm{B}}a_{\mathrm{B}}+2y_{\mathrm{C}}a_{\mathrm{B,C}}}{kT\sqrt{T}b_{\mathrm{mix}}}\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&+\frac{a_{\mathrm{mix}}b_{B}}{kT\sqrt{T}b_{\mathrm{mix}}^{2}}\Bigg[\ln\left(\frac{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)\\&-\frac{N_{\mathrm{gmix}}b_{\mathrm{mix}}}{V_{\mathrm{gmix}}+N_{\mathrm{gmix}}b_{\mathrm{mix}}}\Bigg]-\ln\left(\frac{PV_{\mathrm{gmix}}}{kT}\right)\end{aligned}\tag{26}$$

or

$$\Phi'_{\mathrm{B}} = \frac{kT}{pV_{\mathrm{gmix}}} \frac{V_{\mathrm{gmix}}}{V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}} \exp\left(\frac{N_{\mathrm{gmix}} b_{\mathrm{B}}}{V_{\mathrm{gmix}} - N_{\mathrm{gmix}} b_{\mathrm{mix}}}\right)$$
$$\times \left(\frac{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)^{\left(\frac{2y_{\mathrm{B}} a_{\mathrm{B}} + 2y_{\mathrm{C}} a_{\mathrm{B,C}}}{kT\sqrt{T} b_{\mathrm{mix}}}\right)}$$
$$\times \left(\frac{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}}}\right)^{\left(\frac{a_{\mathrm{mix}} b_{\mathrm{B}}}{kT\sqrt{T} b_{\mathrm{mix}}^2}\right)}$$
$$\times \exp\left(-\frac{a_{\mathrm{mix}} b_{\mathrm{B}}}{kT\sqrt{T} b_{\mathrm{mix}}^2} \frac{N_{\mathrm{gmix}} b_{\mathrm{mix}}}{V_{\mathrm{gmix}} + N_{\mathrm{gmix}} b_{\mathrm{mix}}}\right) \tag{27}$$

μ^0_{gB} is the standard chemical potential of component B, and Φ'_{B} is the 3D fugacity coefficient of component B in the mixture.

We obtain,

$$\mu_{\mathrm{gB}} = \mu^0_{\mathrm{gB}}(T, 1) + kT \ln p y_{\mathrm{B}} + kT \ln \Phi'_{\mathrm{B}} \tag{28}$$

The same expression may be derived for component C:

$$\mu_{\mathrm{gC}} = \mu^0_{\mathrm{gC}}(T, 1) + kT \ln p y_{\mathrm{C}} + kT \ln \Phi'_{\mathrm{C}} \tag{29}$$

2.2 Non-ideal adsorbed phase modeling

We consider now a system composed of N_{aB} molecules of a compound B and N_{aC} molecules of a component C adsorbed on a surface A at temperature T. The molecules may interact with each others. $U_{0\mathrm{B}}$ and $U_{0\mathrm{C}}$ are the adsorption energies (minimum of $u_{\mathrm{ads}}(r)$). Only one layer of molecules B and C can be adsorbed. The adsorbed molecules can move on the surface (mobile adsorption).

The canonical partition function Q_{amix} is given by:

$$Q_{\mathrm{amix}} = \frac{q_{\mathrm{aB}}^{N_{\mathrm{aB}}} q_{\mathrm{aC}}^{N_{\mathrm{aC}}}}{N_{\mathrm{aB}}! N_{\mathrm{aC}}!} \tag{30}$$

with $N_{\mathrm{amix}} = N_{\mathrm{aB}} + N_{\mathrm{aC}}$

$$q_{\mathrm{aB}} = q_{\mathrm{aB\,trans}}\, q_{\mathrm{aB\,vib}}\, q_{\mathrm{aB\,rot}}\, q_{\mathrm{aB\,vibi}}\, q_{\mathrm{aB\,e}} \times \exp\left(\frac{-U_{\mathrm{int\,mix}}}{2kT}\right) \exp\left(\frac{-U_{0\mathrm{B}}}{kT}\right) \tag{31}$$

$$q_{\mathrm{aC}} = q_{\mathrm{aC\,trans}}\, q_{\mathrm{aC\,vib}}\, q_{\mathrm{aC\,rot}}\, q_{\mathrm{aC\,vibi}}\, q_{\mathrm{aC\,e}} \times \exp\left(\frac{-U_{\mathrm{int\,mix}}}{2kT}\right) \exp\left(\frac{-U_{0\mathrm{C}}}{kT}\right) \tag{32}$$

in which,

- $q_{\mathrm{aB\,trans}}$ and $q_{\mathrm{aC\,trans}}$ are, respectively, the translational contributions to the partition functions q_{aB} and q_{aC} (two degrees of freedom of the mass centre of the molecule);
- $q_{\mathrm{aB\ vib}}$ and $q_{\mathrm{aC\ vib}}$ are, respectively, the contributions to the partition functions q_{aB} and q_{aC}, due to the vibrations of the molecule perpendicularly to the surface;
- $q_{\mathrm{aB\,rot}}$ and $q_{\mathrm{aB\,rot}}$ are, respectively, the rotational contributions to the partition functions q_{aB} and q_{aC};
- $q_{\mathrm{aB\,vibi}}$ and $q_{\mathrm{aC\,vibi}}$ are, respectively, the contributions to the partition functions q_{aB} and q_{aC}, due to the internal vibrations in the molecule;
- $q_{\mathrm{aB\,e}}$ and $q_{\mathrm{aC\,e}}$ are respectively the electronic contribution to the partition functions q_{aB} and q_{aC};
- $\exp(-(U_{0j}/kT))$ is the contribution of the adsorption energy of component j, with $j = \mathrm{B}$ or C.

The translation contribution to the partition function of component j may be written:

$$q_{aj\,\mathrm{trans}} = \left[\frac{2\pi m_j kT}{h^2}\right] A_{\mathrm{fmix}} = \frac{A_{\mathrm{fmix}}}{\Lambda_j^2} \tag{33}$$

in which A_{fmix} is the free surface available to the adsorbed molecules;

The contribution to the molecular partition function due to the interactions between the adsorbed molecules is $\exp(-(U_{\mathrm{int\,mix}}/2kT))$. $U_{\mathrm{int\,mix}}$ is the potential energy of interaction between any molecule of the adsorbed phase and all the others in the mixture.

It may be calculated by

$$U_{\mathrm{int\,mix}} = -\int_{d_{\mathrm{amix}}}^{\infty} u(r) \frac{N_{\mathrm{amix}}}{A} g(r) 2\pi r \mathrm{d}r \tag{34}$$

in which, d_{amix} is the molecular diameter of the hypothetic molecule in the adsorbed phase.

The same developments as in the previous section may be done in the case of the adsorbed phase mixture. Using expressions similar to equations (34)–(40) (Part I)

$$U_{\mathrm{int mix}} = -\frac{\pi d_{\mathrm{amix}}^2}{b_{\mathrm{amix}}} C_{\mathrm{mix}} \sqrt{\frac{T_{\mathrm{amix}}}{T}} \ln\left(1 + \frac{N_{\mathrm{amix}} b_{\mathrm{amix}}}{A}\right) \tag{35}$$

in which:

- T_{amix} is the critical temperature of the hypothetic component representing the mixture (adsorbed phase);
- C_{mix} is an energetic constant of the hypothetic component in the adsorbed phase;
- b_{amix} is a parameter which characterizes the mixed adsorbed phase. It may be considered as the surface of the hypothetic molecule:

If we set then $a_{\mathrm{amix}} = \pi d_{\mathrm{amix}}^2 C_{\mathrm{mix}} \sqrt{T_{\mathrm{amix}}}$, which is defined as the 2D molecular attraction parameter of the hypothetic component.

The mixture parameters (b_{amix} and b_{amix}) will be calculated thereafter using the pure component parameters of and appropriate mixing rules.

Equation (35) becomes

$$U_{\text{int mix}} = -\frac{a_{\text{amix}}}{kT\sqrt{T}b_{\text{amix}}}\ln\left(1+\frac{N_{\text{amix}}b_{\text{amix}}}{A}\right) \tag{36}$$

By setting

$$A_{\text{fmix}} = A - N_{\text{amix}}b_{\text{amix}} \tag{37}$$

Expression (30) becomes

$$\begin{aligned}Q_{\text{amix}} = {} & \frac{(A-N_{\text{amix}}b_{\text{amix}})^{N_{\text{aB}}}}{\Lambda_{\text{B}}^{2N_{\text{aB}}}N_{\text{aB}}!}\frac{(A-N_{\text{amix}}b_{\text{amix}})^{N_{\text{aC}}}}{\Lambda_{\text{C}}^{2N_{\text{aC}}}N_{\text{aC}}!}\\ & \times\left(q_{\text{aB rot}}\,q_{\text{aB vib}}\,q_{\text{aB vibi}}\,q_{\text{aB e}}\exp\left(\frac{-U_{\text{int mix}}}{2kT}\right)\right.\\ & \left.\times\exp\left(\frac{-U_{0\text{B}}}{kT}\right)\right)^{N_{\text{aB}}}\left(q_{\text{aC rot}}\,q_{\text{aC vib}}\,q_{\text{aC vibi}}\,q_{\text{aC e}}\right.\\ & \left.\times\exp\left(\frac{-U_{\text{int mix}}}{2kT}\right)\exp\left(\frac{-U_{0\text{C}}}{kT}\right)\right]^{N_{\text{sC}}}\end{aligned} \tag{38}$$

Combining equations (36)–(38) leads to

$$\begin{aligned}\ln Q_{\text{amix}} = {} & N_{\text{aB}}\ln(A-N_{\text{amix}}b_{\text{amix}}) - N_{\text{aB}}\ln\Lambda_{\text{B}}^2\\ & - N_{\text{aB}}\ln N_{\text{aB}} + N_{\text{aB}} + N_{\text{aB}}\ln q_{\text{aB rot}}\\ & + N_{\text{aB}}\ln q_{\text{aB vib}} + N_{\text{aB}}\ln q_{\text{aB vibi}}\\ & + N_{\text{aB}}\ln q_{\text{aB e}} + \frac{N_{\text{aB}}a_{\text{amix}}}{kT\sqrt{T}b_{\text{amix}}}\\ & \times\ln\left(\frac{A+N_{\text{amix}}b_{\text{amix}}}{A}\right) - \frac{N_{\text{aB}}U_{0\text{B}}}{kT}\\ & + N_{\text{aC}}\ln(A-N_{\text{amix}}b_{\text{amix}}) - N_{\text{aC}}\ln\Lambda_{\text{C}}^2\\ & - N_{\text{aC}}\ln N_{\text{aC}} + N_{\text{aC}} + N_{\text{aC}}\ln q_{\text{aC rot}}\\ & + N_{\text{aC}}\ln q_{\text{aC vib}} + N_{\text{aC}}\ln q_{\text{aC vibi}} + N_{\text{aC}}\ln q_{\text{aC e}}\\ & + \frac{N_{\text{C}}a_{\text{amix}}}{kT\sqrt{T}b_{\text{amix}}}\ln\left(\frac{A+N_{\text{amix}}b_{\text{amix}}}{A}\right) - \frac{N_{\text{aC}}U_{0\text{C}}}{kT}\end{aligned} \tag{39}$$

The chemical potential of component B in the adsorbed phase is obtained by differentiating $\ln Q_{\text{amix}}$ with respect to N_{aB} using the same Lorentz–Berthelot mixing rules as in equations (13) and (14) but in adsorbed phase

$$\begin{aligned}a_{\text{mix}} & = a_{\text{aB}}x_{\text{B}}^2 + a_{\text{aC}}x_{\text{C}}^2 + 2x_{\text{B}}x_{\text{C}}a_{\text{aB,C}}\\ & = a_{\text{aB}}\left(\frac{N_{\text{aB}}}{N_{\text{amix}}}\right)^2 + a_{\text{ac}}\left(\frac{N_{\text{aC}}}{N_{\text{amix}}}\right)^2 + 2\frac{N_{\text{aB}}N_{\text{aC}}}{N_{\text{amix}}^2}a_{\text{aB,C}}\end{aligned} \tag{40}$$

$$b_{\text{mix}} = b_{\text{aB}}x_{\text{B}} + b_{\text{aC}}x_{\text{C}} = b_{\text{aB}}\frac{N_{\text{aB}}}{N_{\text{amix}}} + b_{\text{aC}}\frac{N_{\text{aC}}}{N_{\text{amix}}} \tag{41}$$

in which,

- a_{aB} and a_{aC} are, respectively, the intermolecular attraction parameters between B and B and between C and C in the adsorbed phase;
- x_{B} and x_{C} are respectively the mole fractions of the component B and C in the adsorbed phase;
- b_{aB} and b_{aC} are the geometric parameters of pure components B and C in adsorbed phase;
- $a_{\text{aB,C}}$ is the attraction parameter between B and C in the adsorbed phase.

$a_{\text{aB,C}}$ may be calculated from a_{aB} and a_{aC} by $a_{\text{aB,C}} = \sqrt{a_{\text{aB}}a_{\text{aC}}}$.

The total spreading pressure Π may be calculated from the canonical partition function of the mixture

$$\Pi = kT\left(\frac{\partial\ln Q_{\text{amix}}}{\partial A_{\text{amix}}}\right)_{T,N_{\text{aB}},N_{\text{aC}}} \tag{42}$$

The final expression of the chemical potential is then:

$$\begin{aligned}\mu_{aB} = -kT & \left[\ln\frac{(q_{aB\text{rot}}q_{aB\text{vib}}q_{aB\text{vibi}}q_{aBe})kT}{\Lambda_B^2} - \frac{U_{0B}}{kT}\right.\\ & - \ln\Pi x_{\text{B}} + \ln\frac{1/\Gamma_{\text{mlmix}} - b_{\text{amix}}}{1/\Gamma_{\text{mlmix}}} - \frac{b_{\text{aB}}}{1/\Gamma_{\text{mlmix}} - b_{\text{amix}}}\\ & + \frac{2x_{\text{B}}a_{\text{aB}} + 2x_{\text{C}}a_{\text{aB,C}}}{kT\sqrt{T}b_{\text{amix}}}\ln\left(\frac{1/\Gamma_{\text{mlmix}} + b_{\text{amix}}}{1/\Gamma_{\text{mlmix}}}\right)\\ & - \frac{a_{\text{amix}}b_{\text{aB}}}{kT\sqrt{T}b_{\text{amix}}^2}\left[\ln\left(\frac{1/\Gamma_{\text{mlmix}} + b_{\text{amix}}}{1/\Gamma_{\text{mlmix}}}\right) - \frac{b_{\text{amix}}}{1/\Gamma_{\text{mlmix}} + b_{\text{amix}}}\right]\\ & \left. + \ln\left(\frac{1/\Gamma_{\text{mlmix}}}{1/\Gamma_{\text{mlmix}} - b_{\text{amix}}} - \frac{a_{\text{amix}}}{kT\sqrt{T}(1/\Gamma_{\text{mlmix}} + b_{\text{amix}})}\right)\right]\end{aligned} \tag{43}$$

in which $\Gamma_{\text{ml mix}}$ is the molecular surface concentration of the mixture defined as:

$$\Gamma_{\text{mlmix}} = \frac{N_{\text{amix}}}{A} \tag{44}$$

Or

$$\begin{aligned}\mu_{\text{sB}} = {} & -kT\ln\frac{(q_{\text{sBrot}}q_{\text{sBvib}}q_{\text{sBvibi}}q_{\text{sBe}})kT}{\Lambda_{\text{B}}^2}\\ & + U_{0\text{B}} + kT\ln\Pi x_{\text{B}} + kT\ln\Phi_{\text{B}}\end{aligned} \tag{45}$$

with

$$\mu_{\text{aB}}^0 = -kT\ln\frac{(q_{\text{aBrot}}q_{\text{aBvib}}q_{\text{aBvibi}}q_{\text{aBe}})kT}{\Lambda_{\text{B}}^2} + U_{0\text{B}} \tag{46}$$

$$\begin{aligned}\ln\Phi_{\text{B}} = {} & \ln\frac{1/\Gamma_{\text{mix}}}{1/\Gamma_{\text{mix}} - b_{\text{amix}}} + \frac{b_{\text{aB}}}{1/\Gamma_{\text{mix}} - b_{\text{amix}}}\\ & - \frac{2x_{\text{B}}a_{\text{aB}} + 2x_{\text{C}}a_{\text{aB,C}}}{kT\sqrt{T}b_{\text{amix}}}\ln\left(\frac{1/\Gamma_{\text{mix}} + b_{\text{amix}}}{1/\Gamma_{\text{mix}}}\right)\\ & + \frac{a_{\text{amix}}b_{\text{aB}}}{kT\sqrt{T}b_{\text{amix}}^2}\left[\ln\left(\frac{1/\Gamma_{\text{mix}} + b_{\text{amix}}}{1/\Gamma_{\text{mix}}}\right)\right.\\ & \left. - \frac{b_{\text{amix}}}{1/\Gamma_{\text{mix}} + b_{\text{amix}}}\right] - \ln\left(\frac{\Pi}{kT}\frac{1}{\Gamma_{\text{mix}}}\right)\end{aligned} \tag{47}$$

μ_{aB}^0 is the standard chemical potential of pure component B in the adsorbed phase and Φ_{B} is the 2D fugacity coefficient of component B in the mixture.

Finally, we obtain:

$$\mu_{\mathrm{aB}} = \mu^0_{\mathrm{aB}}(T,1) + kT\ln\Pi x_{\mathrm{B}} + kT\ln\Phi_{\mathrm{B}} \tag{48}$$

The same expression may be derived for component C:

$$\mu_{\mathrm{aC}} = \mu^0_{\mathrm{aC}}(T,1) + kT\ln\Pi x_{\mathrm{C}} + kT\ln\Phi_{\mathrm{C}} \tag{49}$$

2.3 Adsorption equilibrium

The adsorption equilibrium is obtained by the equality of the chemical potentials of both compounds in the adsorbed and gas phases.

$$\mu_{\mathrm{aB}} = \mu_{\mathrm{gB}} \tag{50}$$

$$\mu_{\mathrm{aC}} = \mu_{\mathrm{gC}} \tag{51}$$

$$\begin{aligned}&\mu^0_{\mathrm{aB}}(T,1) + kT\ln\Pi x_{\mathrm{B}} + kT\ln\Phi_{\mathrm{B}}\\ &\quad= \mu^0_{\mathrm{gB}}(T,1) + kT\ln p y_{\mathrm{B}} + kT\ln\Phi'_{\mathrm{B}}\end{aligned} \tag{52}$$

$$\begin{aligned}&\mu^0_{\mathrm{aC}}(T,1) + kT\ln\Pi x_{\mathrm{C}} + kT\ln\Phi_{\mathrm{C}}\\ &\quad= \mu^0_{\mathrm{gC}}(T,1) + kT\ln p y_{\mathrm{C}} + kT\ln\Phi'_{\mathrm{C}}\end{aligned} \tag{53}$$

$$\begin{aligned}\Phi_{\mathrm{B}} x_{\mathrm{B}} \Gamma_{\mathrm{ml\,mix}} &= \frac{\Lambda_{\mathrm{B}}(q_{\mathrm{aB\,vib}}\, q_{\mathrm{aB\,rot}}\, q_{\mathrm{aB\,e}}\, q_{\mathrm{aB\,vibi}})}{Z_{\mathrm{ml\,mix}} kT(q_{\mathrm{gB\,rot}}\, q_{\mathrm{gB\,e}}\, q_{\mathrm{gB\,vibi}})}\\ &\quad\times\exp\left(\frac{-U_{0\mathrm{B}}}{kT}\right) p y_{\mathrm{B}} \Phi'_{\mathrm{B}}\end{aligned} \tag{54}$$

$$\begin{aligned}\Phi_{\mathrm{C}} x_{\mathrm{C}} \Gamma_{\mathrm{ml\,mix}} &= \frac{\Lambda_{\mathrm{C}}(q_{\mathrm{aC\,vib}}\, q_{\mathrm{aC\,rot}}\, q_{\mathrm{aC\,e}}\, q_{\mathrm{aC\,vibi}})}{Z_{\mathrm{ml\,mix}} kT(q_{\mathrm{gC\,rot}}\, q_{\mathrm{gC\,e}}\, q_{\mathrm{gC\,vibi}})}\\ &\quad\times\exp\left(\frac{-U_{0\mathrm{C}}}{kT}\right) p y_{\mathrm{C}} \Phi'_{\mathrm{C}}\end{aligned} \tag{55}$$

where Z_{mlmix} is the molecular compressibility factor in the adsorbed phase:

$$Z_{\mathrm{ml\,mix}} = \frac{\Pi}{kT}\frac{1}{\Gamma_{\mathrm{ml\,mix}}}$$

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

$$\begin{aligned}&\frac{1}{1-\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}}}\exp\left(\frac{\Gamma_{\mathrm{mix}} b_{\mathrm{aB\,mol}}}{1-\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}}}\right)\\
&\quad\times(1+\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}})^{\left(\frac{2x_{\mathrm{B}} a_{\mathrm{aB\,mol}}+2x_{\mathrm{C}} a_{\mathrm{aB,C\,mol}}}{RT\sqrt{T}b_{\mathrm{amix}}}\right)}\\
&\quad\times(1+\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}})^{\left(\frac{a_{\mathrm{amix\,mol}} b_{\mathrm{aB\,mol}}}{RT\sqrt{T}b^2_{\mathrm{amix\,mol}}}\right)}\\
&\quad\times\exp\left(-\frac{a_{\mathrm{amix\,mol}} b_{\mathrm{aB\,mol}}}{RT\sqrt{T}b_{\mathrm{amix\,mol}}}\frac{\Gamma_{\mathrm{mix}}}{1+\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}}}\right)\Gamma_{\mathrm{mix}} x_{\mathrm{B}}\\
&= \frac{hN_0}{RT\sqrt{2\pi M_{\mathrm{B}} RT}}\frac{\exp(-(hv_{z\mathrm{B}}/2RT))}{1-\exp(-(hv_{z\mathrm{B}}/RT))}\\
&\quad\times\exp\left(\frac{-U_{0\mathrm{B}}}{RT}\right) p\frac{RT}{Pv_{\mathrm{mix}}}\frac{v_{\mathrm{mix}}}{v_{\mathrm{mix}}-b_{\mathrm{mix\,mol}}}\\
&\quad\times\exp\left(\frac{b_{\mathrm{B\,mol}}}{v_{\mathrm{mix}}-b_{\mathrm{mix\,mol}}}\right)\\
&\quad\times\left(\frac{v_{\mathrm{mix}}+b_{\mathrm{mix\,mol}}}{v_{\mathrm{mix}}}\right)^{\left(\frac{2y_{\mathrm{B}} a_{\mathrm{B\,mol}}+2y_{\mathrm{C}} a_{\mathrm{B,C\,mol}}}{RT\sqrt{T}b_{\mathrm{mix\,mol}}}\right)}\\
&\quad\times\left(\frac{v_{\mathrm{mix}}+b_{\mathrm{mix\,mol}}}{v_{\mathrm{mix}}}\right)^{\left(\frac{a_{\mathrm{mix\,mol}} b_{\mathrm{B\,mol}}}{RT\sqrt{T}b^2_{\mathrm{mix\,mol}}}\right)}\\
&\quad\times\exp\left(-\frac{a_{\mathrm{mix\,mol}} b_{\mathrm{B\,mol}}}{RT\sqrt{T}b^2_{\mathrm{mix\,mol}}}\frac{b_{\mathrm{mix\,mol}}}{v_{\mathrm{mix}}+b_{\mathrm{mix\,mol}}}\right) y_{\mathrm{B}}\end{aligned} \tag{56}$$

$$\begin{aligned}&\frac{1}{1-\Gamma_{\mathrm{mix\,mol}} b_{\mathrm{smix\,mol}}}\exp\left(\frac{\Gamma_{\mathrm{mix}} b_{\mathrm{aC\,mol}}}{1-\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}}}\right)\\
&\quad\times(1+\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}})^{\left(\frac{2x_{\mathrm{C}} a_{\mathrm{aC\,mol}}+2x_{B} a_{\mathrm{aB,C\,mol}}}{RT\sqrt{T}b_{\mathrm{amix}}}\right)}\\
&\quad\times(1+\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}})^{\left(\frac{a_{\mathrm{amix\,mol}} b_{\mathrm{ac\,mol}}}{RT\sqrt{T}b^2_{\mathrm{amix\,mol}}}\right)}\\
&\quad\times\exp\left(-\frac{a_{\mathrm{amix\,mol}} b_{\mathrm{aC\,mol}}}{RT\sqrt{T}b_{\mathrm{amix\,mol}}}\frac{\Gamma_{\mathrm{mix}}}{1+\Gamma_{\mathrm{mix}} b_{\mathrm{amix\,mol}}}\right)\Gamma_{\mathrm{mix}} x_{\mathrm{C}}\\
&= \frac{hN_0}{RT\sqrt{2\pi M_{\mathrm{C}} RT}}\frac{\exp\left(-\frac{h\nu_{z\mathrm{C}}}{2RT}\right)}{1-\exp\left(-\frac{h\nu_{z\mathrm{C}}}{RT}\right)}\exp\left(\frac{-U_{0\mathrm{C}}}{RT}\right) p\\
&\quad\times\frac{RT}{pv_{\mathrm{mix}}}\frac{v_{\mathrm{mix}}}{v_{\mathrm{mix}}-b_{\mathrm{mix\,mol}}}\exp\left(\frac{b_{\mathrm{C\,mol}}}{v_{\mathrm{mix}}-b_{\mathrm{mix\,mol}}}\right)\\
&\quad\times\left(\frac{v_{\mathrm{mix}}+b_{\mathrm{mix\,mol}}}{v_{\mathrm{mix}}}\right)^{\left(\frac{2y_{\mathrm{C}} a_{\mathrm{C\,mol}}+2y_{\mathrm{B}} a_{\mathrm{B,C\,mol}}}{RT\sqrt{T}b_{\mathrm{smix}}}\right)}\\
&\quad\times\left(\frac{v_{\mathrm{mix}}+b_{\mathrm{mix\,mol}}}{v_{\mathrm{mix}}}\right)^{\left(\frac{a_{\mathrm{mix\,mol}} b_{\mathrm{C\,mol}}}{RT\sqrt{T}b^2_{\mathrm{mix\,mol}}}\right)}\\
&\quad\times\exp\left(-\frac{a_{\mathrm{mix\,mol}} b_{\mathrm{C\,mol}}}{RT\sqrt{T}b^2_{\mathrm{mix\,mol}}}\frac{b_{\mathrm{mix\,mol}}}{v_{\mathrm{mix}}+b_{\mathrm{mix\,mol}}}\right) y_{\mathrm{C}}\end{aligned} \tag{57}$$

where

- Γ_{mix} is the molar surface concentration;
- $a_{\mathrm{mix\,mol}}$, $b_{\mathrm{mix\,mol}}$, $a_{\mathrm{amix\,mol}}$, $b_{\mathrm{amix\,mol}}$, $a_{\mathrm{B\,mol}}$, $b_{\mathrm{B\,mol}}$, $a_{\mathrm{C\,mol}}$, $\mathrm{b}_{\mathrm{C\,mol}}$, $a_{\mathrm{aB\,mol}}$, $b_{\mathrm{aB\,mol}}$, $a_{\mathrm{aC\,mol}}$, $b_{\mathrm{aC\ \,mol}}$, $a_{\mathrm{aB,C\,mol}}$ are, respectively, the molar expression corresponding to the molecular ones a_{mix}, b_{mix}, a_{amix}, b_{amix}, a_{B}, b_{B}, a_{C}, b_{C}, a_{aB}, b_{aB}, a_{aC}, b_{aC}, $a_{\mathrm{aB,C}}$;
- M_{B} and M_{C} are, respectively, the molar mass of B and C;
- v_{mix} is the molar volume of the gas phase;
- N_0 is the Avogadro number.

For given temperature T, pressure p and gas composition y_B equations (56) and (57) allow the calculation of Γ_{mix} as well as of the adsorbed phase composition x_{B}.

As in the case of pure gases adsorption equilibria, the final expression may be obtained from purely macroscopic thermodynamics developments using the concept of fugacity coefficient calculated from the equations of state.

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 binary mixture of adsorbates on a given non-porous homogenous adsorbents at 283 K and at 400 kPa. We used the Lennard-Jones potential model to describe the adsorbate–adsorbent interaction and adequate 3D and 2D energetic and geometric parameters for each adsorbate [13]. For the gas phase model these parameters can be easily calculated from the critical parameters of the pure adsorbate, the adsorbed phase model parameters can be derived from adsorption experimental data (pure isotherms data).

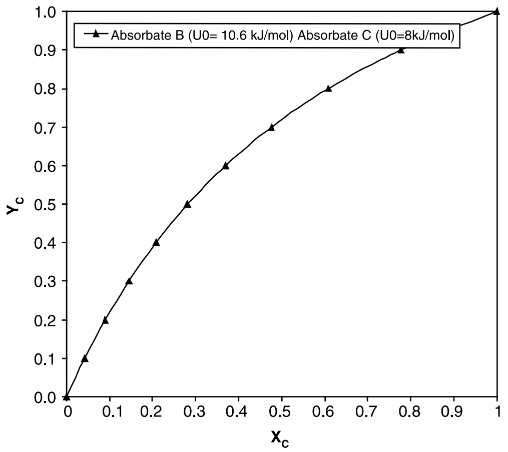

Figure 2. Selectivity curve of C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ($a_{\mathrm{B\,mol}}$, 3.217 J m^3 mol^{-2}; $b_{\mathrm{B\,mol}}$, 2.95 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aB\,mol}}$, 4.18 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aB\,mol}}$, 4.45 × 10^4 m^2 mol^{-2}; $a_{\mathrm{C\,mol}}$, 1.554 J m^3 mol^{-2}; $b_{\mathrm{C\,mol}}$, 2.67 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aC\,mol}}$, 8.10 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aC\,mol}}$, 7.88 × 10^4 m^2 mol^{-2}).

In figure 1 we show the computed surface concentration of adsorbates B and C in the binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa as a function of x_{C}. The corresponding selectivity curve is presented in figure 2

From these figures it appears that B is more adsorbed that as a consequence of the higher value of $U_{0\mathrm{B}}$.

We compute the surface concentration and selectivity curves using different sets of parameter values ($U_{0\mathrm{B}}$ and $U_{0\mathrm{C}}$) for a given set of $a_{\mathrm{aB\,mol}}$, $a_{\mathrm{aC\,mol}}$, $b_{\mathrm{aB\,mol}}$ and $b_{\mathrm{aC\,mol}}$. The results are illustrated in figures 3 and 4.

The selectivity (figure 4) depends of the ratio between $U_{0\mathrm{B}}$ and U_0, the selectivity can be overturned if the ratio is reversed. From figure 3, we can see that the curve change significantly for different values of the energy of interaction between the adsorbate and the surface. If the ratio is reversed, the shape of the surface concentration curves varies.

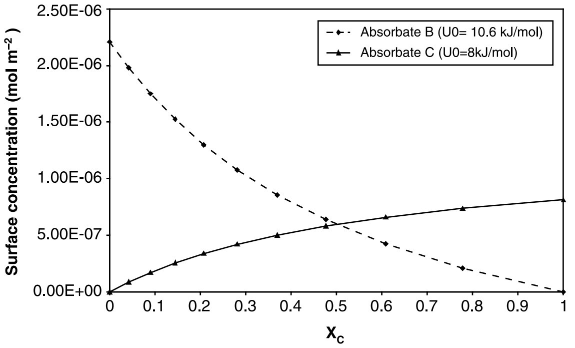

Figure 1. Adsorption isotherms of given adsorbates B and C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ($a_{\mathrm{B\,mol}}$, 3.217 J m^3 mol^{-2}; $b_{\mathrm{B\,mol}}$, 2.95 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aB\,mol}}$, 4.18 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aB\,mol}}$, 4.45 × 10^4 m^2 mol^{-2}; $a_{\mathrm{C\,mol}}$, 1.554 J m^3 mol^{-2}; $b_{\mathrm{C\,mol}}$, 2.67 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aC\,mol}}$, 8.10 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aC\,mol}}$, 7.88 × 10^4 m^2 mol^{-2}).

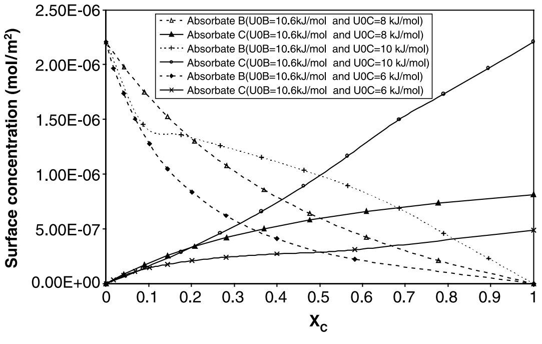

Figure 3. Adsorption isotherms of given adsorbates B and C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ($a_{\mathrm{B\,mol}}$, 3.217 J m^3 mol^{-2}; $b_{\mathrm{B\,mol}}$, 2.95 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aB\,mol}}$, 4.18 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aB\,mol}}$, 4.45 × 10^4 m^2 mol^{-2}, $a_{\mathrm{C\,mol}}$, 1.554 J m^3 mol^{-2}; $b_{\mathrm{C\,mol}}$, 2.67 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aC\,mol}}$, 8.10 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aC\,mol}}$, 7.88 × 10^4 m^2 mol^{-2}): Influence $U_{0\mathrm{B}}$ and $U_{0\mathrm{C}}$.

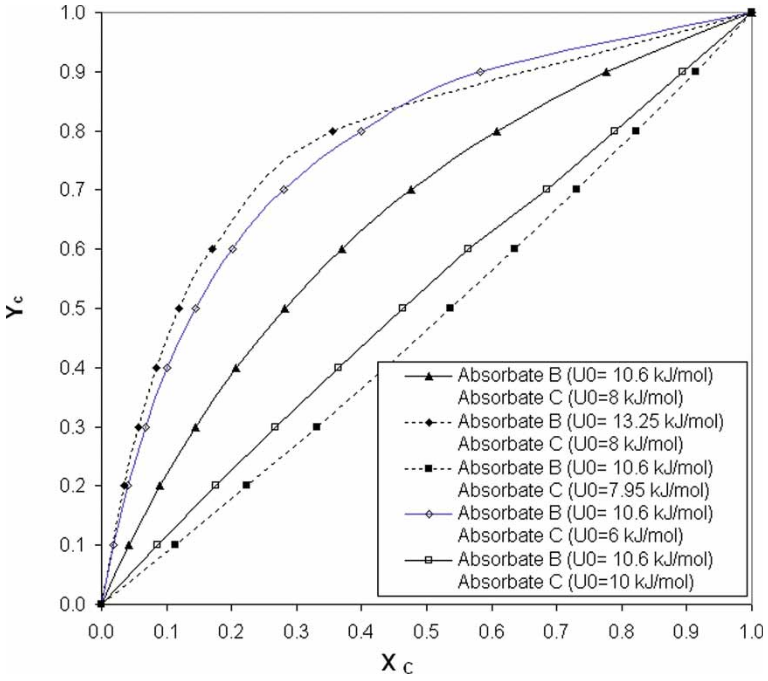

Figure 4. Selectivity curves of C in a binary mixture on a homogenous non-porous adsorbent at 283 K and 400 kPa. ($a_{\mathrm{B\,mol}}$, 3.217 J m^3 mol^{-2}; $b_{\mathrm{B\,mol}}$, 2.95 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aB\,mol}}$, 4.18 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aB\,mol}}$, 4.45 × 10^4 m^2 mol^{-2}, $a_{\mathrm{C\,mol}}$, 1.554 J m^3 mol^{-2}; $b_{\mathrm{C\,mol}}$, 2.67 × 10^{-5} m^3 mol^{-2}; $a_{\mathrm{aC\,mol}}$, 8.10 × 10^9 J m^2 mol^{-2}; $b_{\mathrm{aC\,mol}}$, 7.88 × 10^4 m^2 mol^{-2}): Influence $U_{0\mathrm{B}}$ and $U_{0\mathrm{C}}$.

4. Conclusion

The prediction of multicomponent adsorption equilibria using single-component adsorption data is one of the most challenging problems in adsorption studies. We propose a consistent new model, which may be obtained from macroscopic thermodynamics developments although it relies on a statistical thermodynamic description of both phases. The methodology assumes a non-ideal Redlich–Kwong behaviour for both the gas and adsorbed phases. According to this approach, the prediction of multicomponent adsorption equilibria from single component data would require no extra parameters. The theoretical developments show that the concept of fugacity coefficient may be defined for the adsorbed phase as well as for gas phase. It appears that the expression of the fugacity coefficient in the adsorbed phase may be calculated in the same way as for the gas phase by replacing the molar volume by the inverse of the surface concentration and by replacing the pressure by the spreading pressure. Such expressions of the fugacity coefficients are coherent with those provided by macroscopic thermodynamics developments which required the equation of state of the studied phase.

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