



# On the use of the dual process Langmuir model for binary gas mixture components that exhibit single process or linear isotherms

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## Abstract

Two methodologies were developed to predict adsorption equilibria of a binary system when one of the components is described by the dual-process Langmuir (DPL) model and the other component is described by either the single process Langmuir (SPL) or linear isotherm (LI) model. Energetic site matching with the DPL–SPL model considered perfect positive (PP), perfect negative (PN) and unselective (US) correlations, and that with the DPL–LI model considered PP and PN correlations. A consistent set of single and binary isotherms for O<sub>2</sub> and N<sub>2</sub> on 5A zeolite were used to successfully demonstrate these concepts. For the DPL–SPL binary system, PP meant O<sub>2</sub> adsorbed only on the N<sub>2</sub> low energy site, PN meant O<sub>2</sub> adsorbed only on the N<sub>2</sub> high energy site, and US meant O<sub>2</sub> adsorbed on both sites with the ratio of its saturation capacity on each site the same as that for N<sub>2</sub>. For this case, the PP model predicted the binary data well and correctly predicted that O<sub>2</sub> only adsorbed on the low energy site of N<sub>2</sub>; the PN model predicted the data poorly and US was close but not as good as PP. The binary predictions from the DPL–SPL model that require only single component information to obtain the single component DPL and SPL parameters were nearly as good as those obtained from a non-predictive formulation similar to the US correlation but that utilized all the single and binary data to obtain the single component DPL and SPL parameters. For the DPL–LI binary system, with O<sub>2</sub> having an affinity for only one site, PN meant O<sub>2</sub> interacted solely with the high energy site of N<sub>2</sub> and PP meant O<sub>2</sub> interacted solely with the low energy site of N<sub>2</sub>; and because O<sub>2</sub> exhibited a linear isotherm (i.e., the Henry's law constants from the SPL parameters), it did not affect the adsorption of N<sub>2</sub> on its sites, but N<sub>2</sub> did affect the adsorption of O<sub>2</sub> on its sites. For this case, the PP model predicted the binary data well and correctly predicted that O<sub>2</sub> did not affect the adsorption of N<sub>2</sub>, but that N<sub>2</sub> did affect the adsorption of O<sub>2</sub> on the low energy site of N<sub>2</sub>; the PN model predicted the data poorly.

**Keywords** Mixed-gas adsorption equilibria · Dual process Langmuir · Single process Langmuir · Linear isotherm · Dual site Langmuir

## List of symbols

A	Component A	$K_{j,i}$	Henry's law constant for component $i$ (= A or B) on Site $j$ (= 1 or 2), mol kg <sup>-1</sup> kPa <sup>-1</sup>
$b_{j,i}$	Affinity parameter of component $i$ (= A or B) on Site $j$ (= 1 or 2), kPa <sup>-1</sup>	$K_{o_{j,i}}$	Henry's law constant pre-exponential factor of component $i$ (= A or B) on Site $j$ (= 1 or 2), kPa <sup>-1</sup>
$b_{o_{j,i}}$	Pre-exponential factor of component $i$ (= A or B) on Site $j$ (= 1 or 2), kPa <sup>-1</sup>	$n$	Total amount adsorbed from single gas or gas mixture, mol kg <sup>-1</sup>
B	Component B	$n_i$	Amount adsorbed of component $i$ (= A or B) from single gas, mol kg <sup>-1</sup>
$E_{j,i}$	Adsorption energy of component $i$ (= A or B) on Site $j$ (= 1 or 2), kJ mol <sup>-1</sup>	$n_{i,m}$	Amount adsorbed of component $i$ (= A or B) from gas mixture, mol kg <sup>-1</sup>
		$n_{j,i}^s$	Saturation capacity of component $i$ (= A or B) on Site $j$ (= 1 or 2), mol kg <sup>-1</sup>
		$n_j^s$	Saturation capacity on Site $j$ (= 1 or 2), mol kg <sup>-1</sup>
		$N$	Number of data points
		$P$	Absolute pressure, kPa
		$R$	Universal gas constant, kJ mol <sup>-1</sup> K <sup>-1</sup>

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$T$	Absolute temperature, K
$x_i$	Adsorbed phase mole fraction of component $i$ (= A or B)
$y_i$	Gas phase mole fraction of component $i$ (= A or B)
$z_e$	Experimental quantity in Eq. 24
$z_p$	Predicted quantity in Eq. 24

## 1 Introduction

The Langmuir model (Langmuir 1918), unquestionably, is the most famous and widely used equilibrium adsorption isotherm model known. It is simple and easy to use but only contains two parameters which limits its ability to fit single component experimental data over wide ranges of pressures and temperatures. However, Irving Langmuir asserted over 100 years ago (Langmuir 1918), if you apply his constant energy two parameter isotherm on each type of homogeneous patch of a multi-patch adsorbent with each type of patch having a different energy and sum over all the patches, then you obtain the total coverage on a heterogeneous adsorbent. He was correct, but it seems just two types of patches or sites is good enough (Ritter et al. 2011).

This two site model is referred to as the dual process Langmuir (DPL) model. It has four parameters, two for each type of site, which greatly expands its ability to fit single component experimental data. It also accurately predicts experimental mixed gas adsorption equilibria from only single component information, including azeotropes (Ritter et al. 2011). This unique ability arises from it easily accounting for either perfect positive (PP) or perfect negative (PN) behavior by simply organizing the two types of sites appropriately with the affinity parameters, i.e., adsorbate–adsorbent free energies, of each adsorbate.

The two types of sites that each component adsorbs on in the DPL model gives rise to four adsorbate–adsorbent free energies for a binary system: two free energies for component one and two free energies for component two (one each on each type of site). When both components see *Site 1* as a high free energy site and *Site 2* as a low free energy site, then their adsorbate–adsorbent free energies correlate in a PP fashion. When component one sees *Site 1* as a high free energy site and component two sees *Site 1* as a low free energy site and vice versa for *Site 2*, then their adsorbate–adsorbent free energies correlate in a PN fashion. This energetic site matching concept based on PP and PN correlations has been discussed in detail elsewhere (Tien 1994), but never for the DPL model until Ritter et al. (2011) showed how to formulate and use it properly.

In fact, the DPL model has been used to predict mixed gas adsorption equilibria for some time, even as early as 1983 (Myers 1983), without ever mentioning or accounting for the energetic site matching concept in the PP or PN

formulations. In other words, the DPL model was, in some cases, unintentionally used improperly, potentially and unknowingly obtaining erroneous results because the sites were not properly matched with each pair of adsorbates. The potential erroneous results are revealed very clearly by Ritter et al. (2011) by noting the vastly different mixed gas adsorption equilibria predictions they obtained from the PP and PN formulations for the same mixed gas system, with only one formulation correctly predicting the experimental behavior. To highlight this point about when and if the DPL model was being used properly for predicting or correlating mixed gas adsorption equilibria, a non-exhaustive review of the literature (Wilkins and Rajendran 2019; Purdue 2018; Jahromi et al. 2018a, b; Erden et al. 2018a, b; Farmahini et al. 2018; Goel et al. 2016; Erden and Erden 2017; Rocha et al. 2017; Goel et al. 2017; Pahinkar and Garimella 2017; Pahinkar et al. 2017; Awadallah-F et al. 2017; Khurana and Farooq 2016; Perez et al. 2016; Mohammadi et al. 2016; Brunchi et al. 2014; Caldwell et al. 2015; Pahinkar et al. 2015; Krishnamurthy et al. 2014a, b; Awadallah-F and Al-Muhtaseb 2013; Swisher et al. 2013; García et al. 2013; Khalighi et al. 2012; Nikolaidis et al. 2018; Gholami et al. 2010; Gholami and Talaie 2010; Rezaei et al. 2010; Xiao et al. 2008; Ko et al. 2005; Brandani and Ruthven 2003; Liu et al. 1999, 2000a, b; Dreisbach et al. 1999; Do and Do 1999; Mathias et al. 1996) was performed. A summary is provided in Table 1.

The review in Table 1 shows that prior to the work of Ritter et al. (2011), no one used the DPL model appropriately (Nikolaidis et al. 2018; Gholami et al. 2010; Gholami and Talaie 2010; Rezaei et al. 2010; Xiao et al. 2008; Ko et al. 2005; Brandani and Ruthven 2003; Liu et al. 1999, 2000a, b; Dreisbach et al. 1999; Do and Do 1999; Mathias et al. 1996), including his own group (Liu et al. 1999, 2000a, b). However, even after their work appeared in the literature, only about two-thirds of those using the DPL model realized they needed to consider PP or PN behavior. The remaining third simply did not consider energetic site matching in their mixed gas predictions. Ritter et al. (2011) also overlooked two interesting cases associated with the use of the DPL model for predicting mixed gas adsorption equilibria.

These two cases arise when one of the components in a gas mixture is described by the DPL model and the other component is described by either the SPL model or the LI model. Very recently the DPL–SPL case was properly analyzed with energetic site matching by Wilkins and Rajendran (2019). A similar, more detailed analysis is offered herein. The DPL–SPL was also indirectly considered by Mathias et al. (1996), and Do and Do (1999), but both without considering energetic site matching. Ritter et al. (2011), when commenting about the work of Mathias et al. (1996), incorrectly stated that because one of the components can be described by the SPL model, the energetic

**Table 1** Summary of the use of the dual process Langmuir (DPL) model for predicting mixed-gas adsorption equilibria, with consideration of energetic site matching in perfect positive (PP), perfect negative (PN) and unselective (US) correlations

Adsorbates	Adsorbent	Energetic site matching considered?	PP, PN or US correlations?	Reference
CO <sub>2</sub> -N <sub>2</sub>	13X zeolite	Yes	DPL for CO <sub>2</sub> , SPL PP, PN, US for N <sub>2</sub>	Wilkins and Rajendran (2019)
CO <sub>2</sub> -H <sub>2</sub> O-N <sub>2</sub>	13X Zeolite	Yes	PP, PN, US; depended on model used	Purdue (2018)
CH <sub>4</sub> -N <sub>2</sub>	13X zeolite	No	PP	Jahromi et al. (2018a)
CO <sub>2</sub> -Dry air	13X zeolite	Yes	US for dry air	Erden et al. (2018a)
CH <sub>4</sub> -N <sub>2</sub>	13X zeolite	Yes	PP	Jahromi et al. (2018b)
CH <sub>4</sub> -N <sub>2</sub>	BPL activated carbon	Yes	PP	Erden et al. (2018b)
CO <sub>2</sub> -N <sub>2</sub>	13X zeolite and reference	No	Procedure 1: PN; Procedures 2 and 3: DPL for CO <sub>2</sub> , LI US for N <sub>2</sub>	Farmahini et al. (2018)
CO <sub>2</sub> -N <sub>2</sub>	MF-700	Yes	PP	Goel et al. (2016)
CO <sub>2</sub> -CH <sub>4</sub>	13X zeolite	Yes	PP and PN	Erden and Erden (2017)
CO <sub>2</sub> -CH <sub>4</sub>	Carbon molecular sieve	No	PP	Rocha et al. (2017)
CO <sub>2</sub> -N <sub>2</sub>	Resorcinol-formaldehyde carbon	No	PP	Goel et al. (2017)
CO <sub>2</sub> -N <sub>2</sub>	5A zeolite	No	PP	Pahinkar and Garimella (2017)
CH <sub>4</sub> -CO <sub>2</sub> -N <sub>2</sub>	5A zeolite in poly(etherimide) membrane	No	PP: CH <sub>4</sub> -N <sub>2</sub> ; PN: CH <sub>4</sub> -CO <sub>2</sub> , N <sub>2</sub> -CO <sub>2</sub>	Pahinkar et al. (2017)
CO <sub>2</sub> -CH <sub>4</sub> , CH <sub>4</sub> -N <sub>2</sub> , CO <sub>2</sub> -N <sub>2</sub>	Resorcinol-formaldehyde activated carbon xerogel	No	PN: CH <sub>4</sub> -CO <sub>2</sub> , CH <sub>4</sub> -N <sub>2</sub> ; PP: CO <sub>2</sub> -N <sub>2</sub>	Awadallah-F et al. (2017)
CO <sub>2</sub> -N <sub>2</sub>	74 adsorbents: Activated carbon, MOF-177, Mg-MOF-74, UTSA-16, 13X zeolite	No	PP, PN, US; depended on adsorbent	Khurana and Farooq (2016)
C <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub>	Na-ETS-10, Microcarbon, Macrocarbon, BPL activated carbon, AC1, AC2	Yes	PP: Na-ETS-10, Microcarbon, Macrocarbon, AC1 and AC2; PN: BPL activated carbon	Perez et al. (2016)
O <sub>2</sub> -Ar, O <sub>2</sub> -Ar-N <sub>2</sub>	Carbon molecular sieve	Yes	PP	Mohammadi et al. (2016)
CO <sub>2</sub> -N <sub>2</sub> , CO <sub>2</sub> -C <sub>3</sub> H <sub>8</sub>	Hypothetical silica Zeolite, silica mordenite	Yes	PP: CO <sub>2</sub> -N <sub>2</sub> ; PN: CO <sub>2</sub> -C <sub>3</sub> H <sub>8</sub>	Brunchi et al. (2014)
CO <sub>2</sub> -N <sub>2</sub>	Activated carbon phenolic resins: modified, unmodified	Yes	PP	Caldwell et al. (2015)
CH <sub>4</sub> -CO <sub>2</sub> -N <sub>2</sub> , CO <sub>2</sub> -N <sub>2</sub>	5A zeolite, 13X zeolite	No	5A zeolite: PP: CH <sub>4</sub> -N <sub>2</sub> ; PN: CH <sub>4</sub> -CO <sub>2</sub> , N <sub>2</sub> -CO <sub>2</sub> ; 13X zeolite: PP: N <sub>2</sub> -CO <sub>2</sub>	Pahinkar et al. (2015)
CO <sub>2</sub> -N <sub>2</sub>	13X zeolite	Yes	PP	Krishnamurthy et al. (2014a)
CO <sub>2</sub> -N <sub>2</sub> , CO <sub>2</sub> -H <sub>2</sub> O	13X zeolite, silica gel	Yes	PN: CO <sub>2</sub> -N <sub>2</sub> -13X; PP: H <sub>2</sub> O-CO <sub>2</sub> -13X, CO <sub>2</sub> -N <sub>2</sub> -silica gel	Krishnamurthy et al. (2014b)
CH <sub>4</sub> -CO <sub>2</sub> -N <sub>2</sub>	Resorcinol-formaldehyde activated carbon xerogel	No	PN: CO <sub>2</sub> -CH <sub>4</sub> , CO <sub>2</sub> -N <sub>2</sub> ; PP: CH <sub>4</sub> -N <sub>2</sub>	Awadallah-F and Al-Muhtaseb (2013)
CO <sub>2</sub> -N <sub>2</sub> , CO <sub>2</sub> -C <sub>3</sub> H <sub>8</sub>	Hypothetical zeolites, H-MOR zeolite, 13X zeolite	Yes	PP: CO <sub>2</sub> -N <sub>2</sub> ; PN: CO <sub>2</sub> -C <sub>3</sub> H <sub>8</sub>	Swisher et al. (2013)
CO <sub>2</sub> -N <sub>2</sub> -H <sub>2</sub>	Activated carbon phenolic resin	Yes	Considered all correlations: PN: CO <sub>2</sub> -H <sub>2</sub> , CO <sub>2</sub> -N <sub>2</sub> ; PP: N <sub>2</sub> -H <sub>2</sub> best	García et al. (2013)
C <sub>3</sub> H <sub>8</sub> -C <sub>3</sub> H <sub>6</sub>	4A zeolite	Yes	PP	Khalighi et al. (2012)
CO <sub>2</sub> -N <sub>2</sub>	13X zeolite	No	DPL for CO <sub>2</sub> , SPL US for N <sub>2</sub>	Nikolaidis et al. (2018)

**Table 1** (continued)

Adsorbates	Adsorbent	Energetic site matching considered?	PP, PN or US correlations?	Reference
H <sub>2</sub> O–CO <sub>2</sub> –CH <sub>4</sub> –N <sub>2</sub>	Zeolite	No	PP: H <sub>2</sub> O–CH <sub>4</sub> , H <sub>2</sub> O–N <sub>2</sub> , CH <sub>4</sub> –N <sub>2</sub> ; PN: H <sub>2</sub> O–CO <sub>2</sub> , CH <sub>4</sub> –CO <sub>2</sub> , N <sub>2</sub> –CO <sub>2</sub>	Gholami et al. (2010)
H <sub>2</sub> O–CO <sub>2</sub> –CH <sub>4</sub> –N <sub>2</sub>	5A zeolite	No	PP: H <sub>2</sub> O–CH <sub>4</sub> , H <sub>2</sub> O–N <sub>2</sub> , CH <sub>4</sub> –N <sub>2</sub> ; PN: H <sub>2</sub> O–CO <sub>2</sub> , CH <sub>4</sub> –CO <sub>2</sub> , N <sub>2</sub> –CO <sub>2</sub>	Gholami and Talaie (2010)
CO <sub>2</sub> –N <sub>2</sub>	C5400, C5900, NaX zeolite	No	PP: C5400: DPL for CO <sub>2</sub> , SPL for O <sub>2</sub> ; PP: C5900 and NaX zeolite	Rezaei et al. (2010)
CO <sub>2</sub> –N <sub>2</sub> –O <sub>2</sub>	13X zeolite	No	PP: CO <sub>2</sub> –O <sub>2</sub> ; PN: CO <sub>2</sub> –N <sub>2</sub> , N <sub>2</sub> –O <sub>2</sub>	Xiao et al. (2008)
CO <sub>2</sub> –N <sub>2</sub>	13X zeolite	No	DPL for CO <sub>2</sub> , SPL US for N <sub>2</sub>	Ko et al. (2005)
CO <sub>2</sub> –C <sub>2</sub> H <sub>4</sub> , CO <sub>2</sub> –C <sub>3</sub> H <sub>8</sub>	NaLSX, NaX, CaX, CaA	No	PP: CO <sub>2</sub> –N <sub>2</sub> –NaLSX, CO <sub>2</sub> –C <sub>3</sub> H <sub>8</sub> –CaX and CaA; PN: CO <sub>2</sub> –C <sub>3</sub> H <sub>8</sub> –NaLSX and NaX	Brandani and Ruthven (2003)
nC <sub>4</sub> H <sub>10</sub> –nC <sub>7</sub> H <sub>16</sub> –N <sub>2</sub>	BAX activated carbon	No	PP: C <sub>4</sub> H <sub>10</sub> –C <sub>7</sub> H <sub>16</sub> ; PN: C <sub>4</sub> H <sub>10</sub> –N <sub>2</sub> , C <sub>7</sub> H <sub>16</sub> –N <sub>2</sub>	Liu et al. (2000a)
nC <sub>4</sub> H <sub>10</sub> –C <sub>6</sub> H <sub>6</sub> –nC <sub>7</sub> H <sub>16</sub> –N <sub>2</sub>	BAX activated carbon	No	PP: C <sub>4</sub> H <sub>10</sub> –C <sub>7</sub> H <sub>16</sub> , C <sub>6</sub> H <sub>6</sub> –C <sub>4</sub> H <sub>10</sub> , C <sub>6</sub> H <sub>6</sub> –C <sub>7</sub> H <sub>16</sub> ; PN: C <sub>4</sub> H <sub>10</sub> –N <sub>2</sub> , C <sub>7</sub> H <sub>16</sub> –N <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> –N <sub>2</sub>	Liu et al. (2000b)
nC <sub>4</sub> H <sub>10</sub> –N <sub>2</sub>	BAX activated carbon	No	PN	Liu et al. (1999)
CH <sub>4</sub> –N <sub>2</sub> , CH <sub>4</sub> –CO <sub>2</sub> , CO <sub>2</sub> –N <sub>2</sub> , CH <sub>4</sub> –CO <sub>2</sub> –N <sub>2</sub>	Norit activated carbon	No	PP for all mixtures	Dreisbach et al. (1999)
Hypothetical	Hypothetical	No	PN	Do and Do (1999)
O <sub>2</sub> –N <sub>2</sub>	5A zeolite	No	DPL for N <sub>2</sub> , SPL US for O <sub>2</sub>	Mathias et al. (1996)

site-matching issue is completely circumvented. It is shown herein that this statement is incorrect. In contrast, the DPL–LI case was considered only recently by Farmani et al. (2018), but only cursorily without energetic site matching considerations. Therefore, the objective of this work is to show how to properly treat both of these cases.

For the DPL–SPL case, the objective is to describe a methodology based on three approaches to predict the mixed gas adsorption equilibria of a binary system, with one of the components described by the DPL model (usually the heavier component) and other component described by the SPL model (usually the lighter component). The three approaches differ on how the individual processes of the isotherms correlate, i.e., in PP, PN or unselective (US) fashion. For the DPL–LI case, the objective is to describe a methodology based on two approaches to predict the mixed gas adsorption equilibria of a binary system, with one of the components described by the DPL model (the heavier component) and other component described by the LI model (the lighter component). The two approaches again differ on how the individual processes of the isotherms correlate, i.e., in PP or PN

fashion. For both cases, a consistent set of single and binary adsorption equilibria (Talu et al. 1996) is used to demonstrate these concepts.

## 2 Dual process Langmuir (DPL) formulations

### 2.1 Unary equilibria

The single gas DPL model (Ritter et al. 2011) describes the adsorption of component *i* on a heterogeneous adsorbent that is comprised of two types of homogeneous but energetically different patches (or sites). Assuming that the adsorbate–adsorbent free energy on each type of patch is constant, the amount adsorbed  $n_i$  of component *i* is given by

$$n_i = \left( \frac{n_{1,i}^s b_{1,i} P}{1 + b_{1,i} P} \right)_{\text{Site 1}} + \left( \frac{n_{2,i}^s b_{2,i} P}{1 + b_{2,i} P} \right)_{\text{Site 2}} \quad (1)$$

where  $n_{1,i}^s$  and  $b_{1,i}$  are respectively the saturation capacity and affinity parameter on *Site 1*,  $n_{2,i}^s$  and  $b_{2,i}$  are respectively

the saturation capacity and affinity parameter on *Site 2*, and  $P$  is the absolute pressure. All of the assumptions of the Langmuir model apply on each type of patch, and the two types of patches do not interact with each other (Langmuir 1918). The affinity parameter or free energy for each type of site is expressed as

$$b_{j,i} = b_{o_{j,i}} \exp\left(\frac{E_{j,i}}{RT}\right) \tag{2}$$

where the subscript  $j$  represents the free energy level of *Site 1* or *2*,  $E_{j,i}$  is the adsorption energy of component  $i$  on *Site j*,  $b_{o_{j,i}}$  is the pre-exponential factor or adsorption entropy of component  $i$  on *Site j*, and  $T$  is temperature.

There are two limiting cases of Eq. 1. First, if the adsorption of component  $i$  on an adsorbent is comprised of just one homogeneous site, then Eq. 1 reduces to the single process Langmuir (SPL) model, i.e.,

$$n_i = \left(\frac{n_{j,i}^s b_{j,i} P}{1 + b_{j,i} P}\right)_{Site j} \tag{3}$$

where the subscript  $j$  now represents *Site 1* or *2* for mixed gas adsorption. Second, if the adsorption of component  $i$  on an adsorbent exhibits a linear isotherm, where it follows from Eq. 1 that

$$(b_{1,i} P)_{Site 1} \ll 1, (b_{2,i} P)_{Site 2} \ll 1 \tag{4}$$

with the affinity parameters given by Eq. 2. Then Eq. 1 reduces to

$$n_i = (n_{1,i}^s b_{1,i} P)_{Site 1} + (n_{2,i}^s b_{2,i} P)_{Site 2} = (K_{1,i} P)_{Site 1} + (K_{2,i} P)_{Site 2} \tag{5}$$

written in terms of the Henry’s law constants  $K_{j,i}$ , because there is no way to distinguish between  $n_{j,i}^s$  and  $b_{j,i}$ . The temperature dependence of  $K_{j,i}$  is given by Eq. 2 with  $b_{j,i}$  and  $b_{o_{j,i}}$  respectively replaced with  $K_{j,i}$  and  $K_{o_{j,i}}$ . Equation 5 is a two site linear isotherm (LI) model. For the SPL case, Eq. 5 reduces to

$$n_i = (K_{j,i} P)_{Site j} \tag{6}$$

i.e., a one site LI model. The subscript  $j$  again represents *Site 1* or *2*. It is noteworthy that Eq. 5 reduces to Eq. 6 only for the special case where  $b_{1,i} = b_{2,i}$ , as discussed by Farmahini et al. (2018)

### 2.2 Binary equilibria

In the DPL model, there are two types of sites that each component adsorbs on, which gives rise to four adsorbate–adsorbent free energies: two free energies for component A, i.e., one on each type of site, and two free energies for component B, i.e., one on each type of site. These free energies must be correlated in either the PP or PN fashion through the single component affinity parameters, i.e., the  $b_{j,i}$  values in the mixed gas form of the DPL model. When components A and B obey the PP correlation for energetic site matching, the corresponding amount adsorbed for each component from a binary gas mixture is given by (Ritter et al. 2011)

$$\begin{aligned} n_{A,m} &= \left(\frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A} + P y_B b_{1,B}}\right)_{Site 1} + \left(\frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A} + P y_B b_{2,B}}\right)_{Site 2} \tag{7} \\ n_{B,m} &= \left(\frac{n_{1,B}^s P y_B b_{1,B}}{1 + P y_A b_{1,A} + P y_B b_{1,B}}\right)_{Site 1} + \left(\frac{n_{2,B}^s P y_B b_{2,B}}{1 + P y_A b_{2,A} + P y_B b_{2,B}}\right)_{Site 2} \tag{8} \end{aligned}$$

When components A and B obey the PN correlation for energetic site matching, the corresponding amount adsorbed for each component from a binary gas mixture is given by (Ritter et al. 2011)

$$\begin{aligned} n_{A,m} &= \left(\frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A} + P y_B b_{1,B}}\right)_{Site 1} + \left(\frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A} + P y_B b_{2,B}}\right)_{Site 2} \tag{9} \\ n_{B,m} &= \left(\frac{n_{1,B}^s P y_B b_{1,B}}{1 + P y_A b_{2,A} + P y_B b_{1,B}}\right)_{Site 1} + \left(\frac{n_{2,B}^s P y_B b_{2,B}}{1 + P y_A b_{1,A} + P y_B b_{2,B}}\right)_{Site 2} \tag{10} \end{aligned}$$

where  $y_A$  and  $y_B$  are the gas phase mole fractions of components A and B, and  $n_{A,m}$  and  $n_{B,m}$  are the amounts adsorbed of components A and B from the binary gas mixture. The total amount adsorbed is simply the sum of  $n_{A,m}$  and  $n_{B,m}$ . The adsorbed phase mole fractions of components A and B, i.e.,  $x_A$  and  $x_B$ , are given by

$$x_A = \frac{n_{A,m}}{n_{A,m} + n_{B,m}} \tag{11}$$

$$x_B = \frac{n_{B,m}}{n_{A,m} + n_{B,m}} \tag{12}$$

In this formulation, the saturation capacity for each component on each type of site is allowed to be different with minimal consequences, as shown elsewhere (Ritter et al. 2011).

The difference between Eqs. 7 and 9, and similarly the difference between Eqs. 8 and 10 lies only in the ordering of the affinity parameter  $b_{j,i}$  on each type of site. Notice that for the PP correlation (Eqs. 7, 9),  $j = 1$  for both components on *Site 1*, meaning both components see *Site 1* as a high free energy site, and  $j = 2$  for both components on

*Site 2*, meaning both components see *Site 2* as a low free energy site. However, notice that for the PN correlation (Eqs. 9, 10),  $j=2$  for component A and  $j=1$  for component B on *Site 1*, meaning component A sees *Site 1* as a low free energy site and component B sees *Site 1* as a high free energy site, and  $j=2$  for component B and  $j=1$  for component A on *Site 2*, meaning component B sees *Site 2* as a low free energy site and component A sees *Site 2* as a high free energy site.

### 2.3 Binary equilibria: DPL–SPL case

For the DPL–SPL case, when component A in a binary gas mixture is described by the DPL model and component B in this binary gas mixture is described by the SPL model, three possibilities arise. Component B, which has an affinity for one type of site only, can interact solely with the high free energy site of component A or solely with the low free energy site of component A, or component B can interact with both types of sites of component A with the same affinity on each type of site. When component B interacts only with one of the sites of component A, then component B does not adsorb at all on the other site of component A. When component B interacts with both sites of component A, then logically it can be assumed that the ratio of the saturation capacities on each site is the same for each component.

When component B only adsorbs on the low free energy site of component A, the corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A} + P y_B b_B} \right)_{\text{Site 1}} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A}} \right)_{\text{Site 2}} \quad (13)$$

$$n_{B,m} = \left( \frac{n_B^s P y_B b_B}{1 + P y_A b_{1,A} + P y_B b_B} \right)_{\text{Site 1}} \quad (14)$$

where it is assumed that *Site 1* is the low energy site and *Site 2* is the high energy site. When component B only adsorbs on *Site 2*, i.e., the high free energy site of component A, the corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A}} \right)_{\text{Site 1}} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A} + P y_B b_B} \right)_{\text{Site 2}} \quad (15)$$

$$n_{B,m} = \left( \frac{n_B^s P y_B b_B}{1 + P y_A b_{2,A} + P y_B b_B} \right)_{\text{Site 2}} \quad (16)$$

The designation of PP or PN in these cases depends on the two adsorbates and the adsorbent under consideration. This is discussed in more detail later. When component B interacts with both sites of component A, this is an unselective (US) correlation with the ratio of the saturation capacities on each site being the same. The corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A} + P y_B b_B} \right)_{\text{Site 1}} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A} + P y_B b_B} \right)_{\text{Site 2}} \quad (17)$$

$$n_{B,m} = \left( \frac{n_{1,B}^s P y_B b_B}{1 + P y_A b_{1,A} + P y_B b_B} \right)_{\text{Site 1}} + \left( \frac{n_{2,B}^s P y_B b_B}{1 + P y_A b_{2,A} + P y_B b_B} \right)_{\text{Site 2}} \quad (18)$$

where

$$\frac{n_{1,B}^s}{n_{2,B}^s} = \frac{n_{1,A}^s}{n_{2,A}^s} = \frac{n_B^s - x}{x} \quad (19)$$

ensures the ratio of the saturation capacities of each component on each site is equal. Solving for  $x$  provides the values of  $n_{1,B}^s$  and  $n_{2,B}^s$  to use in Eq. 18.

### 2.4 Binary equilibria: DPL–LI cases

In the formulation considered herein, a linear isotherm (LI) can have either one or two types of sites. For the DPL–LI one site case, when component A in a binary gas mixture is described by the DPL model and component B in this binary gas mixture is described by the LI one site model (Eq. 6), two possibilities arise. Component B, which has an affinity for only one site, can interact solely with the high free energy site of component A. The corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A}} \right)_{\text{Site 1}} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A}} \right)_{\text{Site 2}} \quad (20)$$

$$n_{B,m} = \left( \frac{n_B^s P y_B b_B}{1 + P y_A b_{2,A}} \right)_{\text{Site 2}} = \left( \frac{K_{2,B} P y_B}{1 + P y_A b_{2,A}} \right)_{\text{Site 2}} \quad (21)$$

Or, component B can interact solely with the low free energy site of component A. The corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A}} \right)_{\text{Site 1}} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A}} \right)_{\text{Site 2}} \quad (22)$$



$$n_{B,m} = \left( \frac{n_B^s P y_B b_B}{1 + P y_A b_{1,A}} \right)_{Site 1} = \left( \frac{K_{1,B} P y_B}{1 + P y_A b_{1,A}} \right)_{Site 1} \quad (23)$$

However, because component B exhibits a linear isotherm, it does not affect the adsorption of component A on either of its sites because of the relationship in Eq. 4; whereas, component A does affect the adsorption of component B on either of its sites. Again, the designation of PP or PN in these cases depends on the two adsorbates and the adsorbent under consideration. Note there is no unselective correlation to consider for the DPL–LI one site case because there is no way to differentiate  $n_{j,i}^s$  and  $b_{j,i}$  from  $K_{ij}$  in Eq. 6.

For the DPL–LI two site case, when component A in a binary gas mixture is described by the DPL model and component B in this binary gas mixture is described by the LI two site model (Eq. 5), two possibilities also arise. Component B, which now has high and low free energy sites just like component A, can interact in either a PP or PN fashion with component A. This is respectively analogous to Eqs. 7 and 8 and Eqs. 9 and 10. For the PP case, the corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A}} \right)_{Site 1} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A}} \right)_{Site 2} \quad (24)$$

$$n_{B,m} = \left( \frac{K_{1,B} P y_B}{1 + P y_A b_{1,A}} \right)_{Site 1} + \left( \frac{K_{2,B} P y_B}{1 + P y_A b_{2,A}} \right)_{Site 2} \quad (25)$$

For the PN case, the corresponding amount adsorbed for each component is given by

$$n_{A,m} = \left( \frac{n_{1,A}^s P y_A b_{1,A}}{1 + P y_A b_{1,A}} \right)_{Site 1} + \left( \frac{n_{2,A}^s P y_A b_{2,A}}{1 + P y_A b_{2,A}} \right)_{Site 2} \quad (26)$$

$$n_{B,m} = \left( \frac{K_{2,B} P y_B}{1 + P y_A b_{1,A}} \right)_{Site 1} + \left( \frac{K_{1,B} P y_B}{1 + P y_A b_{2,A}} \right)_{Site 2} \quad (27)$$

Notice Eqs. 20, 22, 24 and 26 are not only the same, but they are also the same as Eq. 1, i.e., the single gas DPL model. This is because there is no influence of component B on the adsorption of component A when component B exhibits a linear isotherm. Notice the denominators in Eqs. 21, 23, 25 and 27 do not include any contribution from component B, as Eq. 4 holds true.

### 2.5 Mathias-Talu (MT) correlation (Mathias et al. 1996)

Mathias et al. (1996) considered a more restrictive case of the US case given by Eqs. 17 and 18. They correlated component

A with the DPL model and component B with the SPL model. They also assumed the saturation capacities of components A and B on Site 1 were equal and the saturation capacities of components A and B on Site 2 were equal, i.e.,  $n_{1,A}^s = n_{1,B}^s = n_1^s$  and  $n_{2,A}^s = n_{2,B}^s = n_2^s$ . The corresponding amount adsorbed for each component is thus given by

$$n_{A,m} = \left( \frac{n_1^s P y_A b_{1,A}}{1 + P y_A b_{1,A} + P y_B b_B} \right)_{Site 1} + \left( \frac{n_2^s P y_A b_{2,A}}{1 + P y_A b_{2,A} + P y_B b_B} \right)_{Site 2} \quad (28)$$

$$n_{B,m} = \left( \frac{n_1^s P y_B b_B}{1 + P y_A b_{1,A} + P y_B b_B} \right)_{Site 1} + \left( \frac{n_2^s P y_B b_B}{1 + P y_A b_{2,A} + P y_B b_B} \right)_{Site 2} \quad (29)$$

More details about their analysis are provided below.

## 3 Results and discussion

### 3.1 Single component correlations

To illustrate the utility of the DPL–SPL and DPL–LI formulations, a consistent set of single and binary isotherms from the literature were selected, i.e., O<sub>2</sub> and N<sub>2</sub> on 5A zeolite (Talu et al. 1996). Moreover, to further show the utility of the DPL–SPL formulation, comparisons were made with the correlations of the same data produced by Mathias et al. (1996) It must be pointed out that they fitted simultaneously all the single component and binary data to obtain their single component DPL and SPL parameters. In doing so, they also assumed that the saturation capacity for O<sub>2</sub> and N<sub>2</sub> was the same on each site, a thermodynamic constraint that is usually ignored (Ritter et al. 2011). These respectively made their analysis non-predictive and more restrictive compared to what was done in this work, as discussed below.

Based on what Mathias et al. (1996) showed it was surmised that N<sub>2</sub> would require two processes and O<sub>2</sub> would require only one process to describe the corresponding isotherms. Hence, to determine if one or two processes were needed the single component equilibrium adsorption isotherms for O<sub>2</sub> and N<sub>2</sub> on 5A zeolite were fitted to the single component DPL model using Eqs. 1 and 2 and the SPL model using Eqs. 2 and 3. For each adsorbate, the isotherms measured at two temperatures were fitted simultaneously to each model using Excel Solver with the fitting parameters scaled so their magnitudes ranged between 0.1 and 10 for Solver to work most effectively. The results are summarized in Table 2 and Figs. 1 and 2. For comparison, the correlations of the single component isotherms from Mathias et al. (1996) are included in the table and figures.

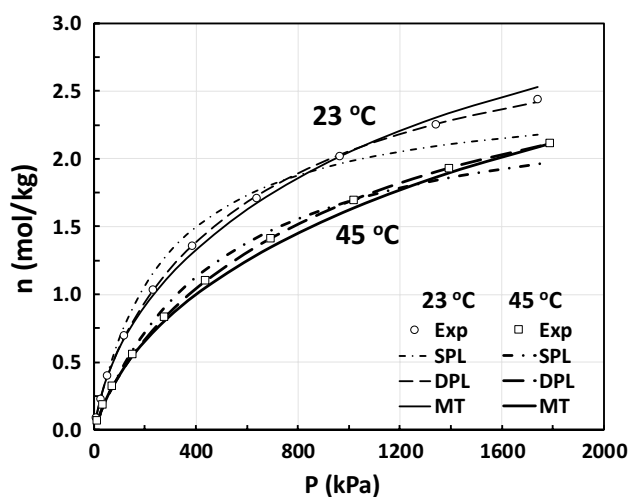
The goodness of the fit of each model was judged by the average relative error (ARE) defined as

$$ARE = \frac{100}{N} \sum_k^N abs \left( \frac{z_e - z_p}{z_e} \right)_k \quad (30)$$

**Table 2** Single-process Langmuir (SPL) and dual-process Langmuir (DPL) model parameters and average relative errors (AREs) obtained from fitting single component adsorption isotherms of O<sub>2</sub> and N<sub>2</sub> on 5A zeolite (Talu et al. 1996)

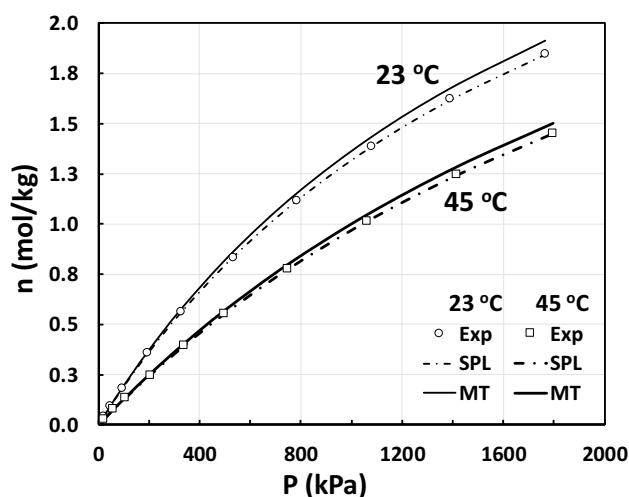
Model	Adsorbate	$b_{o_1}$ (kPa <sup>-1</sup> )	$b_{o_{12}}$ (kPa <sup>-1</sup> )	$E_1$ (kJ mol <sup>-1</sup> )	$E_2$ (kJ mol <sup>-1</sup> )	$n_1^s$ (kJ mol <sup>-1</sup> )	$n_2^s$ (kJ mol <sup>-1</sup> )	ARE (%)
SPL	O <sub>2</sub>	$9.407 \times 10^{-7}$	–	15.551	–	3.853	–	0.45
SPL	N <sub>2</sub>	$7.127 \times 10^{-7}$	–	21.028	–	2.521	–	6.59
DPL	O <sub>2</sub>	$4.988 \times 10^{-7}$	$9.069 \times 10^{-7}$	9.366	15.733	1.843	3.639	0.45
DPL	N <sub>2</sub>	$2.745 \times 10^{-7}$	$1.180 \times 10^{-6}$	27.605	17.543	0.356	2.882	0.47
SPL–US	O <sub>2</sub>	$9.407 \times 10^{-7}$	$9.407 \times 10^{-7}$	15.551	15.551	0.424	3.429	–
DPL–US	N <sub>2</sub>	$2.745 \times 10^{-7}$	$1.180 \times 10^{-6}$	27.605	17.543	0.356	2.882	–
SPL–MT <sup>a</sup>	O <sub>2</sub>	$9.238 \times 10^{-7}$	$9.238 \times 10^{-7}$	15.552	15.552	0.69	3.34	3.12
DPL–MT <sup>a</sup>	N <sub>2</sub>	$1.132 \times 10^{-6}$	$5.192 \times 10^{-7}$	22.852	17.849	0.69	3.34	2.21

<sup>a</sup>SPL–MT and DPL–MT parameters obtained from Mathias et al. (1996) noting that they have an error in their Table 3. The  $b^o$  and  $d^o$  values in that table are actually  $b$  and  $d$  at 296.15 K

**Fig. 1** Single gas equilibrium adsorption isotherms for N<sub>2</sub> on 5A zeolite fitted to the SPL and DPL models, and correlations from Mathias, et al. (MT) (1996)

where  $N$  is the total number of data points for each adsorbate, and  $z_e$  and  $z_p$  are respectively the experimental and predicted quantities of interest, in this case the amount adsorbed  $n$ . It was clear from the AREs that the N<sub>2</sub> isotherms required two processes to achieve a good fit, while the O<sub>2</sub> isotherms only required one process. It was also clear from the AREs that the correlations of the single component isotherms from Mathias et al. (1996) did not fit the data well (as they admitted) because they regressed all the single and binary data simultaneously.

Predictions from these models, plotted along with the experimental isotherms in Figs. 1 and 2 respectively for N<sub>2</sub> and O<sub>2</sub>, reflect very well the AREs in Table 1. Nearly perfect agreement was obtained for each isotherm of N<sub>2</sub> using the DPL model and for each isotherm of O<sub>2</sub> using the SPL model. Notice the AREs from the SPL and DPL models are

**Fig. 2** Single gas equilibrium adsorption isotherms for O<sub>2</sub> on 5A zeolite fitted to the SPL model and correlations from Mathias et al. (MT) (1996)

the same for O<sub>2</sub>, indicating the SPL model was good enough. The correlations of the single component isotherms from (Mathias et al. 1996) were reasonable but not as good. The SPL model was not capable of fitting the N<sub>2</sub> isotherms, with an ARE of over 6% and with most of the data points being over and under predicted.

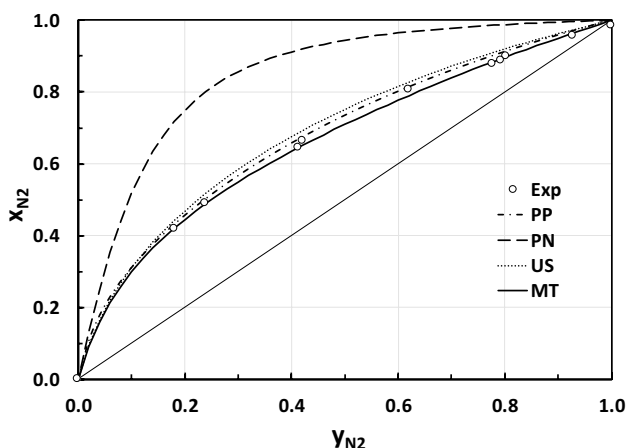
### 3.2 DPL–SPL model predictions

For the DPL–SPL N<sub>2</sub>–O<sub>2</sub> 5A zeolite binary system, it was assumed for energetic site matching that PP implies O<sub>2</sub> adsorbs only on the N<sub>2</sub> low energy *Site 1*, PN implies O<sub>2</sub> adsorbs only on the N<sub>2</sub> high energy *Site 2*, and US implies O<sub>2</sub> adsorbs on both sites with the ratio of its saturation capacity on each site the same as that for N<sub>2</sub>. This designation is based on N<sub>2</sub> having a quadrupole moment (Yang

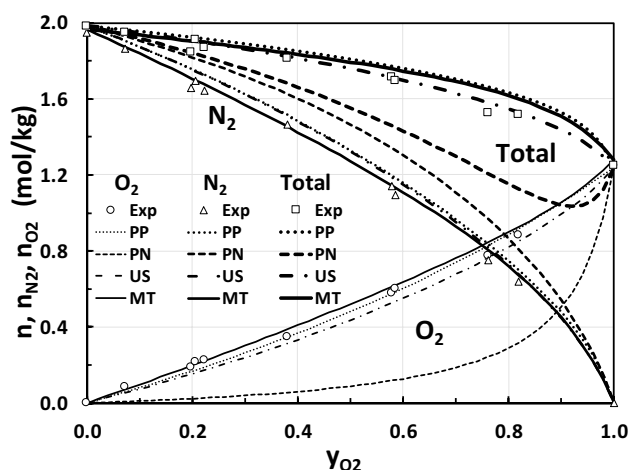


2003), while O<sub>2</sub> does not. As an aside, it was interesting that for the DPL–SPL CO<sub>2</sub>–N<sub>2</sub> 13X zeolite system, where CO<sub>2</sub> and N<sub>2</sub> both have quadrupole moments (Yang 2003), Wilkins and Rajendran (2019) considered the opposite designation. In their case, PP implied N<sub>2</sub> adsorbed only on the CO<sub>2</sub> high energy site and PN implied N<sub>2</sub> adsorbed only on the CO<sub>2</sub> low energy site. Figures 3, 4 and 5 respectively show the binary predictions of the experimental *x*–*y*, *n*–*y* and *n*–*P* diagrams for O<sub>2</sub> and N<sub>2</sub> on 5A zeolite (Talu et al. 1996) by the DPL<sub>N<sub>2</sub></sub>–SPL<sub>O<sub>2</sub></sub> model for PP, PN, US and correlations from Mathias et al. (1996) The corresponding AREs calculated from Eq. 30 are provided in Table 3.

The *x*–*y* diagram in Fig. 3 shows that except for the PN predictions by the DPL–SPL model, the predictions from the PP and US DPL–SPL models and the correlation from Mathias et al. (1996) all agreed well with the binary experimental data. The AREs in Table 3 show MT was better than PP but not significantly, and PP was better than US but not significantly. The *n*–*y* and *n*–*P* diagrams in Figs. 4 and 5 show essentially the same trends, with MT being better than PP, PP being better than US and PN providing poor predictions. The AREs in Table 3 for MT and PP were much closer in magnitude for the binary experimental data for these diagrams compared to the *x*–*y* diagram. This was good news because from a dynamic adsorption process modeling point of view the most important information obtained from the mixed-gas equilibrium adsorption model are the predicted amounts adsorbed of each component from the binary gas mixture. The AREs in Table 3 reflect all these trends, with the AREs for N<sub>2</sub> compared to O<sub>2</sub> always being significantly lower. This was due the adsorption of N<sub>2</sub> always being significantly greater than the adsorption of O<sub>2</sub>, i.e., for these



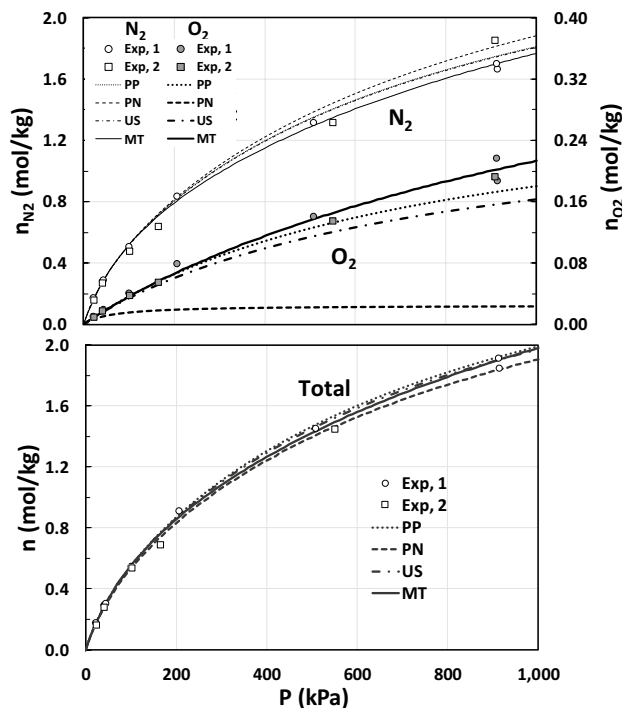
**Fig. 3** Binary predictions of *x*–*y* mixed gas adsorption equilibria for O<sub>2</sub> and N<sub>2</sub> on 5A zeolite at *T*=23.2 °C and *P*=915 kPa by the DPL<sub>N<sub>2</sub></sub>–SPL<sub>O<sub>2</sub></sub> model: *PP* perfect positive, *PN* perfect negative, *US* unselective, *MT* correlations from Mathias et al. (1996)



**Fig. 4** Binary predictions of *n*–*y* mixed gas adsorption equilibria for O<sub>2</sub> and N<sub>2</sub> on 5A zeolite at *T*=23.2 °C and *P*=915 kPa by the DPL<sub>N<sub>2</sub></sub>–SPL<sub>O<sub>2</sub></sub> model: *PP* perfect positive, *PN* perfect negative, *US* unselective, *MT* correlations from Mathias et al. (1996)

binary data, the reported N<sub>2</sub> to O<sub>2</sub> selectivity varied between 1.7 and 4.7 (Mathias et al. 1996).

It was also clear from these DPL–SPL model predictions that the PP formulation with O<sub>2</sub> adsorbing only on the N<sub>2</sub> low energy *Site 1* was the correct energetic site matching



**Fig. 5** Binary predictions of *n*–*P* mixed gas adsorption equilibria for O<sub>2</sub> and N<sub>2</sub> on 5A zeolite at *T*=23.2 °C and *y*<sub>O<sub>2</sub></sub>~0.2 by the DPL<sub>N<sub>2</sub></sub>–SPL<sub>O<sub>2</sub></sub> model: *PP* perfect positive, *PN* perfect negative, *US* unselective, *MT* correlations from Mathias et al. (1996)

**Table 3** Average relative errors (AREs) for the PP, PN, US and MT predictions/correlations from the DPL–SPL and DPL–LI models shown in the  $x$ – $y$ ,  $n$ – $y$  and  $n$ – $P$  diagrams (Figs. 3, 4, 5, 6) for the binary adsorption equilibria of  $O_2$  and  $N_2$  on 5A zeolite (Talu et al. 1996)

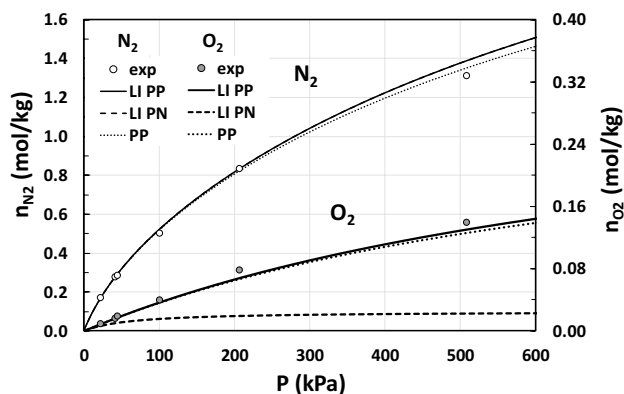
ARE (%)				
	PP	PN	US	MT
x–y Diagram DPL–SPL				
$N_2$	2.17	30.16	3.91	0.78
$O_2$	11.29	78.14	16.84	4.44
n–y Diagram DPL–SPL				
$N_2$	3.86	9.68	3.25	1.63
$O_2$	6.54	52.36	10.23	4.45
Total	2.40	6.46	0.79	1.82
n–P Diagram DPL–SPL				
$N_2$	6.14	6.85	6.03	5.27
$O_2$	6.43	59.83	10.89	5.67
Total	5.05	4.54	4.70	4.64
n–P Diagram DPL–LI				
	PP–LI	PN–LI		PP
$N_2$	2.13	2.13		1.71
$O_2$	4.12	52.90		5.07

correlation for this binary system. The PN formulation with  $O_2$  adsorbing only on the  $N_2$  high energy *Site 2* produced large AREs particularly for  $O_2$ . This result showed that for the PN DPL–SPL model, with  $O_2$  and  $N_2$  both adsorbing on the high energy site of  $N_2$ ,  $O_2$  did not affect the adsorption of  $N_2$  on its high energy site, but that  $N_2$  did significantly and incorrectly suppress the adsorption of  $O_2$  on the high energy site of  $N_2$ . In contrast, the US formulation with  $O_2$  adsorbing on both sites with the ratio of its saturation capacity on each site the same as that for  $N_2$  provided reasonable predictions but not as good as PP in most cases except for the total amount adsorbed. Of course, the MT correlation, which is similar in principle to the US correlation, provided the lowest AREs for all three diagrams. This was expected since Matthias et al. (1996) used all the single component and also binary data to obtain their single component DPL and SPL parameters, as stated earlier. This made the MT model a correlation instead of a predictive model. In contrast, the DPL–SPL model formulated in this work was strictly predictive as it did not require any binary information to obtain the single component DPL and SPL parameters. It only required specifying the energetic site matching as PP, PN or US.

### 3.3 DPL–LI one site model predictions

For the one site DPL–LI binary system, it was assumed for energetic site matching that with  $O_2$  having an affinity for only one site, PN implies  $O_2$  interacts solely with the high energy site of  $N_2$  and PP implies  $O_2$  interacts solely with

the low energy site of  $N_2$ . In addition, because  $O_2$  exhibits a linear isotherm simply produced from the Henry's law constants from the SPL parameters listed in Table 2, it does not affect the adsorption of  $N_2$  on either of its sites, but  $N_2$  does affect the adsorption of  $O_2$  on either of its sites. Figure 6 shows the binary predictions of the experimental  $n$ – $P$  diagram for  $O_2$  and  $N_2$  on 5A zeolite (Talu et al. 1996) by the  $DPL_{N_2-LI_{O_2}}$  model for PP–LI and PN–LI. The corresponding AREs calculated from Eq. 30 are also provided in Table 3. The PP predictions from the DPL–SPL model were included in this figure and table for comparison. Note that this is the same experimental data as in Fig. 5 but limited to about 500 kPa since for  $O_2$  the predictions were



**Fig. 6** Binary predictions of  $n$ – $P$  mixed gas adsorption equilibria for  $O_2$  and  $N_2$  on 5A zeolite at  $T=23.2$  °C and  $y_{O_2} \sim 0.2$  by the  $DPL_{N_2-LI_{O_2}}$  model: *PP* perfect positive, *PN* perfect negative

based on its linear isotherm. The  $x$ - $y$  and  $n$ - $y$  diagrams were not considered in this analysis of the DPL–LI model because the pressure of all that binary data at 915 kPa was too high.

The  $n$ - $P$  diagram in Fig. 6 shows the PP–LI predictions from the DPL–LI model were nearly as good as the PP predictions from the DPL–SPL model for both O<sub>2</sub> and N<sub>2</sub>. Not surprisingly, slight deviations between these two PP models began to appear as the pressure increased. The AREs in Table 3 reflect these trends, with the AREs for N<sub>2</sub> compared to O<sub>2</sub> always being significantly lower, for the same reason as given above. In contrast, the PN predictions from the DPL–LI model deviated significantly from the binary experimental data for O<sub>2</sub> but not for N<sub>2</sub>. For N<sub>2</sub>, the PP and PN predictions essentially overlapped. These results showed the PP DPL–LI model correctly predicted that O<sub>2</sub> did not affect the adsorption of N<sub>2</sub> on its high energy site, but that N<sub>2</sub> did affect the adsorption of O<sub>2</sub> on the low energy site of N<sub>2</sub> in a PP fashion. Just like with the PN DPL–SPL model for this binary system, these results further showed that for the PN DPL–LI model, with O<sub>2</sub> and N<sub>2</sub> both adsorbing on the high energy site of N<sub>2</sub>, O<sub>2</sub> did not affect the adsorption of N<sub>2</sub> on its high energy site, but that N<sub>2</sub> did significantly and incorrectly suppress the adsorption of O<sub>2</sub> on the high energy site of N<sub>2</sub>.

## 4 Conclusion

Two detailed methodologies were developed to predict mixed gas adsorption equilibria of a binary system when one of the components is described by the DPL model and the other component is described by either the SPL or LI model. Energetic site matching with the DPL–SPL model considered PP, PN and US correlations. Energetic site matching with the DPL–LI model considered PP and PN correlations; there was no way to formulate an US correlation for the DPL–LI model.

For both cases, a consistent set of single and binary isotherms from the literature were used to successfully demonstrate these concepts, i.e., O<sub>2</sub> and N<sub>2</sub> on 5A zeolite. For the DPL–SPL binary system, PP meant O<sub>2</sub> adsorbed only on the N<sub>2</sub> low energy site, PN meant O<sub>2</sub> adsorbed only on the N<sub>2</sub> high energy site, and US meant O<sub>2</sub> adsorbed on both sites with the ratio of its saturation capacity on each site the same as that for N<sub>2</sub>. For this case, the DPL–SPL model predicted the binary experimental data well in terms of  $x$ - $y$ ,  $n$ - $y$  and  $n$ - $P$  diagrams, and it correctly predicted that O<sub>2</sub> only adsorbed on the low energy site of N<sub>2</sub> in a PP fashion. The PN predictions were markedly different than the binary experimental data, and the US predictions were close to but not as good as the PP predictions.

The binary predictions from the DPL–SPL model only required single component information to obtain the single component DPL and SPL parameters. These predictions were nearly as good as those obtained from a non-predictive formulation similar to the US correlation but that utilized all the single and binary experimental data to obtain the single component DPL and SPL parameters. For this non-predictive correlation, the average of all the AREs when predicting the  $x$ - $y$ ,  $n$ - $y$  and  $n$ - $P$  diagrams of this binary system was 3.59%, while that for the predictive PP DPL–SPL model was 5.49%, quite close indeed.

For the DPL–LI binary system, with O<sub>2</sub> having an affinity for only one site, PN meant O<sub>2</sub> interacted solely with the high energy site of N<sub>2</sub> and PP meant O<sub>2</sub> interacted solely with the low energy site of N<sub>2</sub>. Because O<sub>2</sub> exhibited a linear isotherm produced from the Henry's law constants from the SPL parameters, it did not affect the adsorption of N<sub>2</sub> on either of its sites, but N<sub>2</sub> did affect the adsorption of O<sub>2</sub> on either of its sites. For this case, the DPL–LI model predicted the binary experimental data well in terms of the  $n$ - $P$  diagram, and it correctly predicted that O<sub>2</sub> did not affect the adsorption of N<sub>2</sub>, but that N<sub>2</sub> did affect the adsorption of O<sub>2</sub> on the low energy site of N<sub>2</sub> in a PP fashion. The PN predictions deviated significantly from the experimental data. In fact, the PP DPL–LI model did as well as the PP DPL–SPL model in predicting the  $n$ - $P$  diagram of this binary system, with the average of the AREs for O<sub>2</sub> and N<sub>2</sub> being 3.13% and 3.39% respectively for the PP DPL–LI and PP DPL–SPL models.

Overall, these formulations are the proper ones to use when one of the components in a binary gas mixture is described by the DPL model and the other component is described by either the SPL or LI model. The options to consider for energetic site matching are different compared to when both components in a binary gas mixture are described by the DPL model. For the DPL–SPL model, PP, PN and US correlations must be considered, while for the DPL–LI model, PP and PN correlations must be considered. In both cases, as with any mixed-gas formulation of the DPL model, careful consideration must be given to the assignment of the adsorbate–adsorbent free energies to each site.

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## Compliance with ethical standards

**Conflict of interest** The authors declare they have no conflicts of interest.

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