

Comments on practical use of Langmuir gas adsorption isotherm model

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Abstract The physical and thermodynamic characteristics of the Langmuir adsorption isotherm model for pure gas and gas mixtures as well as the constraints on the saturation adsorption capacity of the gases by this model are discussed. Arbitrary violation of these constraints, viz. temperature dependence of the saturation capacity and unequal saturation capacities for the components of a mixed gas, may lead to unrealistic heat of adsorption and unreliable predictions of mixed gas equilibria. Several physically and thermodynamically consistent analytical models for pure and mixed gas adsorption isotherms, which were developed using the Langmuir model as backbone, and which account for unequal -sized adsorbates, lateral interactions between adsorbed molecules, multi-layer adsorption, and adsorbent heterogeneity, are briefly reviewed. These models can be practically very useful to describe experimental isotherm data and for adsorptive process modeling.

Keywords Langmuir gas adsorption model · Physical and thermodynamic consistencies · Restrictions on model parameters · Beyond Langmuir

1 Introduction

The classic Langmuir adsorption isotherm model was originally used to describe chemisorption of a pure gas on a non-porous surface (Langmuir 1918; Young and Crowell 1962; Trapnell and Hayward 1964). Subsequently the

model has been popular to describe physisorption of a pure gas or a gas mixture on micro-mesoporous adsorbents of practical interest such as activated carbons, zeolites, alumina and silica gels, polymeric adsorbents, and others (Gregg and Sing 1967; Ruthven 1984; Yang 1987).

The Langmuir model is based on the assumption that (a) the adsorbent surface consists of a collection of adsorption sites of identical energy of adsorption (energetically homogeneous), (b) one adsorbed molecule occupies one site, and (c) there is no lateral interaction between the adsorbed molecules (Fowler 1935; Young and Crowell 1962; Trapnell and Hayward 1964). The adsorption sites are primarily located inside the porous network (consisting of micro, meso, and macro-pores) inside a practical adsorbent particle. The maximum extent of adsorption on an adsorbent is governed by the total number of sites in the adsorbent.

The Langmuir model for describing the equilibrium adsorption isotherm of a pure gas i on a solid surface (adsorbent) at a pressure P (atm) and temperature T (K) is frequently expressed analytically as (Gregg and Sing 1967; Ruthven 1984; Yang 1987).

$$\theta_i^0 = \frac{b_i P}{1 + b_i P} = \frac{n_i^0}{m_i}; \quad b_i P = \frac{\theta_i^0}{1 - \theta_i^0} \quad (1)$$

where n_i^0 is the specific amount (mol/g) of the pure gas i adsorbed from a superincumbent gas at pressure P (atm) and temperature T (K) in equilibrium with the adsorbent. The parameter m_i (mole/g) represents the saturation adsorption capacity of pure gas i on the adsorbent (capacity when all sites are filled). It is also termed ‘mono-layer capacity’ for adsorption on a non-porous adsorbent (Young and Crowell 1962). The variable θ_i^0 is the fraction of the available adsorption sites for pure component i which are

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occupied by the adsorbed molecules at P and T. The variable b_i (atm^{-1}) is the Langmuir gas-site interaction parameter for pure gas i on an energetically homogeneous adsorbent.

The corresponding extended Langmuir model for a mixed gas adsorption isotherm from a gas mixture of i components (mole fraction of component $i = y_i$) at P and T is described by (Markham and Benton 1931; Trapnell and Hayward 1964; Ruthven 1984; Yang 1987):

$$\theta_i = \frac{n_i}{m_i} = \frac{b_i P y_i}{1 + \sum_j b_j P y_j}; \quad b_i P y_i = \frac{\theta_i}{(1 - \sum_j \theta_j)} \quad (2)$$

where n_i (mol/g) is the specific equilibrium amount of component i adsorbed from a gas mixture of N_c components ($j = 1, 2, \dots, N_c$) at P, T and y_i . The variable θ_i is the fraction of the adsorption sites of component i occupied by that component at P, T and y_i . It follows from Eq. (2) that n_i (or θ_i) from a gas mixture can be estimated by knowing the pure gas Langmuir parameters (m_i and b_i) of the components.

The number of adsorption sites does not change with the system temperature for a physically and chemically inert adsorbent (all practical adsorbents for gas separation application). Thus, according to the basic assumptions of the Langmuir model, m_i cannot be a function of T since it is determined by the specific number of sites on the inert adsorbent surface.

Equations (1) and (2) do not account for complex issues like surface irregularities, nature of adsorbate and adsorbent molecules, orientation and physical nature of the adsorbed molecules and interactions between them, micro-meso porosity of the adsorbent, energetic heterogeneity of the surface, etc., which are often associated with real systems (Gregg and Sing 1967; Avnir et al. 1992; Jaroniec 1995; Rouquerol et al. 1999). Yet they are frequently used in modelling of Pressure Swing Adsorption (PSA) and Thermal Swing Adsorption (TSA) processes for gas separation and purification because they empirically describe experimentally measured pure and multicomponent gas adsorption isotherms for many adsorption systems of practical interest over the pressure, temperature, and composition ranges of interest. Furthermore, they provide analytical and mathematically simple equations which facilitate data interpolation and extrapolation as well as numerical simulation of adsorptive process models.

The traditional solution thermodynamics model can be used in conjunction with the Langmuir isotherm model for estimating the isosteric heat of adsorption of a gas, the surface potential of a gas, and for correlating mixed gas and pure gas adsorption isotherms using the Ideal Adsorbed Solution Theory (Myers and Prausnitz 1965). It is assumed that the adsorbed phase is a homogeneous solution in this approach.

It should be pointed out that the Gibbsian surface excess (GSE) is the true experimental variable for measurement of the extent of adsorption (Sircar 1999) while Eqs. (1) and (2) use actual amount adsorbed (AAA) as the variables to define the extent of adsorption. The GSE and the AAA are approximately equal when the gas density is low. That is the case for many practical PSA and TSA process systems. Otherwise, one needs to assume an adsorbed phase volume to translate GSE to AAM. Interestingly, it is a common practice to loosely call GSE as AAA and use the Langmuir model at high pressure if the model fits the data.

2 Isosteric heats of adsorption for Langmuir model

The isosteric heats of adsorption of a pure gas i (q_i^0 , KJ/mole) and that of component i of a gas mixture (q_i , KJ/mole) can be estimated from the pure gas and multi-component gas adsorption isotherms at different temperatures by using the following thermodynamic equations (Sircar 1991a; Sircar et al. 1999):

$$q_i^0(n_i^0) = RT^2 \left[\frac{\partial \ln P}{\partial T} \right]_{n_i^0}; \quad \text{Pure gas } i \quad (3)$$

$$q_i(n_i) = RT^2 \left[\frac{\partial \ln p_i}{\partial T} \right]_{n_i}; \quad \text{Component } i \text{ of a mixed gas} \quad (4)$$

where p_i ($= P y_i$) is the partial pressure of component i in the equilibrium gas phase. The gas phase is assumed to be an ideal gas. The isosteric heat of adsorption a pure gas or that of component i from a gas mixture is independent of the adsorbate loadings for an energetically homogeneous adsorbent.

Equations (1)–(4) can be combined to show that for a Langmuir isotherm:

$$q_i^0(n_i^0) = q_i(n_i) = -RT^2 \left[\frac{d \ln b_i}{dT} \right] = q_i^* = \text{constant} \quad (5)$$

According to Eq. (5), neither q_i^0 nor q_i are functions of adsorbate loadings for the Langmuir isotherm model, which is consistent with the properties of an energetically homogeneous adsorbent. The parameter q_i^* is a characteristic isosteric heat of adsorption for the adsorbent.

3 Limiting characteristics of Langmuir isotherm model

The limiting forms of Eqs. (1) and (2) in the low pressure region ($P \rightarrow 0$) are as follows:

$$n_i^0 \rightarrow m_i b_i P = K_i^0(T)P \quad \text{as } P \rightarrow 0 \tag{6}$$

$$n_i \rightarrow m_i b_i P y_i = K_i^0(T)P y_i \quad \text{as } P \rightarrow 0 \tag{7}$$

Equations (6) and (7) show that the Langmuir model correctly exhibits the Henry’s Law limits as $P \rightarrow 0$ for a pure gas or a gas mixture, as required by adsorption thermodynamics (Hill 1960; Gregg and Sing 1967). The equilibrium amount adsorbed of a pure gas i at temperature T is proportional to the total gas pressure and the equilibrium amount adsorbed of component i from a gas mixture at temperature T is proportional to the partial pressure of that component in the gas phase in the Henry’s Law region. Thus, the pure and mixed gas adsorption isotherms are linear in that region. The proportionality constant $K_i^0 (= m_i b_i)$ is called the Henry’s law constant (moles/g/atm) for pure gas at temperature T . The isosteric heat of adsorption of a pure gas in the Henry’s Law region (q_i^0) can be easily obtained by combining Eqs. (3) and (6) as:

$$\frac{d \ln K_i^0}{dT} = \left[\frac{d \ln b_i}{dT} \right] = - \left[\frac{q_i^0}{RT^2} \right] \tag{8}$$

Equation (8) assumes that m_i is not a function of T as required by the basic assumptions of the Langmuir model. It may be seen from Eqs. (5) and (8) that $q_i^0 = q_i^*$. It follows that K_i^0 and b_i are exponential functions of T :

$$K_i^0(T) = K_i^* \exp \left[\frac{q_i^0}{RT} \right]; \quad b_i(T) = b_i^* \exp \left[\frac{q_i^0}{RT} \right] \tag{9}$$

where K_i^* and b_i^* are constants.

It should be noted that the Langmuir model for mixed gas adsorption (Eq. 2) at constant P and T exhibits linear isotherms in the limit of infinite dilution of a component ($y_i \rightarrow 0$), where n_i is proportional to p_i :

$$n_i = \frac{m_i b_i P y_i}{1 + \sum_{j \neq i} b_j P y_j} = K_i^m P y_i; \quad K_i^m = \frac{K_i^0(T)}{[1 + \sum_{j \neq i} b_j P y_j]} \tag{10}$$

where $K_i^m (P, T, y_{j \neq i})$ is the Henry’s constant for component i of a gas mixture at infinite dilution of that component. It is a function of P , T and y_i .

For adsorption of a binary gas mixture ($y_1 + y_2 = 1$) at constant P and T :

$$K_1^m = \frac{K_1^0(T)}{[1 + b_2 P]}; \quad y_1 \rightarrow 0, \quad K_2^m = \frac{K_2^0(T)}{[1 + b_1 P]}; \quad y_2 \rightarrow 0 \tag{11}$$

The limiting forms of Eqs. (1) and (2) in the high pressure region ($P \rightarrow \infty$) are as follows:

$$n_i^0 \rightarrow m_i, \theta_i^0 \rightarrow 1, \text{ for pure gas;}$$

$$n_i = \frac{m_i b_i y_i}{\sum_i b_i y_i}, \theta_i = \frac{b_i y_i}{\sum_i b_i y_i} < 1, \text{ for gas mixture} \tag{12}$$

The isotherm approaches the upper limits described by Eq. (12) asymptotically as $P \rightarrow \infty$. It should be noted that according to the Langmuir model, the upper limit of amount adsorbed of a component of a gas mixture at constant y_i and T is less than its saturation capacity, and the limiting value depends on its composition.

4 Type I adsorption isotherm

The over-all isotherm shape of a pure gas or the components of a gas mixture are characterized by Eqs. (6), (7) and (12). The isotherm has a linear section in the Henry’s Law region and it asymptotically levels off in the high pressure region. This shape is classified as Type I isotherm by the Brunauer classification (Trapnell and Hayward 1964; Gregg and Sing 1967), which is exhibited by many meso-microporous adsorbents of practical interest.

Consequently, the analytical Langmuir isotherm model is very popular for describing experimental isotherm data and for numerical simulation of adsorptive separation processes as well as for parametric study of the processes (Hyun and Danner 1982; Kumar and Sircar 1986; Rege and Yang 1997; Liu and Ritter 1998; Barg et al. 2000; Waldron and Sircar 2000; Simo et al. 2008; Casas et al. 2012; Vemula et al. 2015). The primary reason is the relative simplicity of the Langmuir isotherm model which can mimic a Type I isotherm shape.

5 Empirical assumption of temperature dependence of m_i

The basic tenet of temperature independent saturation capacity (m_i) of the Langmuir model is often ignored in order to better fit experimental adsorption isotherms (Rege and Yang 1997; Liu and Ritter 1998; Barg et al. 2000; Simo et al. 2008; Casas et al. 2012). Empirical temperature dependence of m_i (exponential or reciprocal) is generally introduced in the model so that m_i decreases with increasing T [$\frac{dm_i}{dT} < 0$] which is often observed experimentally.

It can be shown by using Eqs. (1), (3) and (8) that the assumption of temperature dependent m_i makes the isosteric heat of adsorption of a pure gas (q_i^{**}) a function of the fractional adsorbate loading (θ_i^0):

$$\frac{[q_i^{**} - q_i^0]}{RT^2} = - \frac{\theta_i^0}{[1 - \theta_i^0]} \frac{d \ln m_i}{dT} \tag{13}$$

where $q_i^{**}(\theta_i^0)$ is the isosteric heat of adsorption of pure gas i under the assumption of $m_i = m_i(T)$. q_i^0 is the isosteric heat of adsorption of pure gas i in the Henry's Law region.

Equation (13) indicates that (a) $q_i^{**} \rightarrow q_i^0$ at the limit of $\theta_i^0 \rightarrow 0$, and then it increases monotonically as θ_i^0 is increased, reaching the limit of infinity, when $\theta_i^0 \rightarrow 1$ when $\frac{dm_i}{dT} < 0$, and (b) $q_i^{**} \leq q_i^0$, and it decreases monotonically as θ_i^0 is increased, reaching the limit of negative infinity, when $\theta_i^0 \rightarrow 1$, when $\frac{dm_i}{dT} > 0$. Both scenarios are inconsistent with the original basis of the Langmuir model. The patterns of isosteric heat vs adsorbate loadings are characteristics of lateral interactions between the adsorbed molecules (case a) and adsorption of a gas on an energetically heterogeneous adsorbent (case b). Furthermore, the limits of infinite heats are physically absurd. Thus, $m_i \neq m_i(T)$ is the only consistent choice for the Langmuir model.

The above-described artificial loading dependence of isosteric heat of adsorption of a pure gas introduced by the empirical assumption of temperature dependence of m_i is often ignored and an average constant heat of adsorption is used in process design (Rege and Yang 1997; Liu and Ritter 1998; Barg et al. 2000; Simo et al. 2008; Casas et al. 2012). The validity of such assumption is, however, debatable, and it can lead to large error in estimation of adsorptive process performance (Hartzog and Sircar 1995).

6 Gurvitsch rule

The Gurvitsch rule is based on the assumption that the pores of a micro-mesoporous solid are filled with a liquid adsorbate when the saturation adsorption capacity of the adsorbate (m_i , mol/g) is reached, particularly for adsorption of a pure condensable vapor at $T (< T_C)$, where T_C is the

critical temperature of the adsorbate. Thus, one gets (Gregg and Sing 1967):

$$m_i v_i^L = v^p \tag{14}$$

where v_i^L (cm³/mol) is the molar volume of the liquid adsorbate at temperature T , and v^p (cm³/g) is the pore volume of the adsorbent. The rule has been experimentally verified for many adsorbate-adsorbent systems (Gregg and Sing 1967). Since v^p is not dependent on T , and v_i^L is a very weak function of T ($\frac{dv_i^L}{dT} \geq 0$), Eq. (14) indicates that:

$$\frac{d \ln m_i}{dT} = - \frac{d \ln v_i^L}{dT} \leq 0 \tag{15}$$

In other words, the validity of the Gurvitsch rule supports the condition that m_i is not a function (or a very weak function) of T as required by the Langmuir isotherm model.

7 Thermodynamic consistency between pure-gas and binary-gas Langmuir isotherm models

Adsorption thermodynamics provides (a) two consistency tests between the binary gas and pure gas adsorption isotherms, and (b) two tests for internal consistency of the binary gas isotherms (Rao and Sircar 1999). They are described in Table 1. The left hand sides of Eqs. (16) and (17) can be estimated using binary gas isotherm data while the right hand sides of these equations can be estimated using pure gas isotherm data. Hence they provide consistency tests of type (a). Equations (18) and (19), on the other hand, provide thermodynamic relationships between binary gas isotherms measured at constant T , y_1 and T , P . Hence they are examples of type (b) consistency tests.

It can be shown that all of these consistency tests are satisfied by the Langmuir isotherm models only under the

Table 1 Thermodynamic consistency tests for pure and binary gas isotherms

Integral test Binary at constant T & P Pure gas at constant T	$\int_0^1 \frac{[n_1 y_2 - n_2 y_1]}{y_1 y_2} dy_1 = \int_0^P \frac{n_1^0}{P} dP - \int_0^P \frac{n_2^0}{P} dP \tag{16}$
Differential test Binary at constant T & P Pure gas at constant T	$n(P, T, y_1) - P \frac{\partial}{\partial P} \left[\int_0^{y_1} \left\{ \frac{n_1 y_2 - n_2 y_1}{y_1 y_2} \right\}_{P,T} dy_1 \right]_{T,y_1} = n_2^0(P, T) \tag{17}$
	$n(P, T, y_1) + P \frac{\partial}{\partial P} \left[\int_0^1 \left\{ \frac{n_1 y_2 - n_2 y_1}{y_1 y_2} \right\}_{P,T} dy_1 \right]_{T,y_1} = n_1^0(P, T)$
Internal consistency test Binary at constant T , y_1 and T , P	$n_1(P, T, y_1) = y_1 n(P, T, y_1) + y_1 y_2 \frac{\partial}{\partial y_1} \left\{ \int_0^P n d \ln P \right\}_{T, y_1, P, T} \tag{18}$
Internal consistency test Binary at constant T , y_1 and constant T , P	$\left[\frac{\partial n}{\partial y_1} \right]_{T,P} = \frac{P}{y_1 y_2} \left[y_2 \left(\frac{\partial n_1}{\partial P} \right)_{T,y_1} - y_1 \left(\frac{\partial n_2}{\partial P} \right)_{T,y_1} \right] \tag{19}$

constraint of $m_i = m$ (Rao and Sircar 1999). In other words, the saturation capacities of different components of a gas mixture must be equal for the mixed gas Langmuir isotherm model to be thermodynamically consistent. Otherwise, the quality of prediction of multi-component adsorption equilibrium by mixed-gas Langmuir model using the pure gas Langmuir parameters may be questionable. The thermodynamic and physical unsoundness of the assumption of unequal m_i values in the mixed gas Langmuir model has also been pointed out earlier (Young and Crowell 1962). However, that conclusion was reached by only applying the integral consistency test to pure and binary gas adsorption isotherms. In fact, the same restriction satisfies all of the consistency tests summarized by Table 1, which is a more stringent proof in favor of the restriction. Examples of application of integral as well as internal thermodynamic consistency tests to actual experimental binary and pure gas isotherm data can be found elsewhere (Rao and Sircar 1999; Wu et al. 2014a).

Interestingly many publications do not follow this constraint and unrestricted values of m_i are used to fit pure gas Langmuir isotherms. (Yang 1987; Liu and Ritter 1998; Barg et al. 2000; Caldwell et al. 2015). The quality and reliability of the estimated binary or multi-component gas equilibrium data in the entire range of P, T, and y_i of interest by the mixed gas Langmuir model should be extensively verified using experimental mixed gas data in such a case, before using them in process models.

According to Eq. (10), the binary selectivity ($S_{ij} = n_i y_j / n_j y_i$) of adsorption of component i over component j of a gas mixture obeying the thermodynamically consistent form of mixed-gas Langmuir model is given by $S_{ij} = b_i / b_j$. Thus, S_{ij} is a function of T only. One example of such a system is adsorption of N_2 and O_2 on Na-Mordenite (Kumar and Sircar 1986).

The Honig-Nitta model (Table 2) can be used for cases where the adsorbates have different saturation capacities. The binary selectivity for this model can be functions of P, and y_i for a given T (Wu and Sircar 2016).

8 Example of error in using $m_i \neq m_j$ in mixed-gas Langmuir model

An example of the error in estimation of a binary gas adsorption isotherm by using unequal saturation capacities of the components in the mixed-gas Langmuir isotherm is presented below:

Figure 1 shows pure gas adsorption isotherms of two gases (components 1 and 2) which follow homogeneous Honig isotherm model (Table 2). The model parameters for adsorption of a pure gas i at a given temperature are (i) the saturation adsorption capacity (m_i , m moles/g), (ii) the

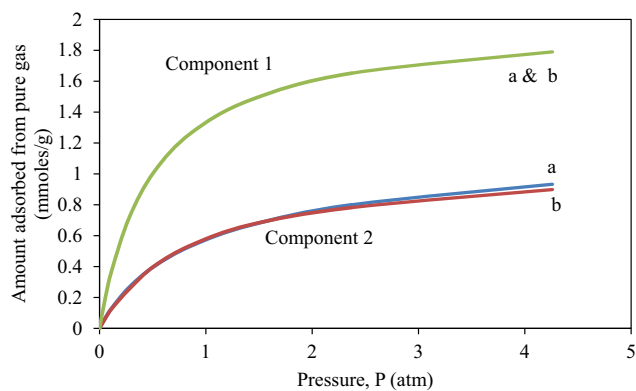


Fig. 1 Pure gas isotherms using Honig (a) and Langmuir (b) models

number of adsorption sites occupied by each molecule (a_i), and (iii) the gas–solid interaction parameter (b_i , atm^{-1}). Thermodynamic consistency requires that $[a_i m_i = \text{constant}]$. The Honig isotherm reduces to the Langmuir model when $a_i = 1$ [$m_i = m$]. The model parameters used for generating the isotherms of Fig. 1 are ($m_1 = 2.0$, $a_1 = 1.0$, $b_1 = 2.0$) for component 1 and ($m_2 = 1.333$, $a_2 = 1.5$, $b_2 = 1.0$) for component 2. Thus, $a_i m_i$ is a constant (= 2.0). The selectivity [$S_{12} = m_1 b_1 / m_2 b_2$] of adsorption of component 1 over component 2 is 3.0.

The component 1 pure gas isotherm in Fig. 1 can be generated by using identical values of m_1 and b_1 for either Honig (a) or Langmuir (b) model since $a_1 = 1.0$. Interestingly, the Figure shows that the component 2 pure gas isotherm generated by the Honig model (a) can also be described very well by the Langmuir model (b) using artificial values of m_{2L} (= 1.081 m moles/g) and b_{2L} (= 1.156 atm^{-1}). Thus one may justify the use of mixed-gas Langmuir model with unequal m_i values for estimation of binary gas isotherm for these gases since the pure gas isotherms can apparently be fitted by Langmuir model (albeit using artificial parameters).

Figure 2 compares the binary gas isotherms corresponding to the pure gas isotherms of Fig. 1 at a total gas pressure of 2.0 atm, calculated using (A) the thermodynamically consistent extension of Honig model to binary gas by Nitta et al. (Table 2b), which provides the correct prediction of binary gas isotherm for these gases, and (B) the mixed gas Langmuir model with unequal values of m_i (Eq. 2). It may be seen that model B significantly underestimates the amount adsorbed of the more selectively adsorbed component and overestimates the amount adsorbed of the less selectively adsorbed component at all gas phase compositions. This exercise, therefore, demonstrates the misleading nature of using thermodynamically inconsistent mixed gas Langmuir model with unequal m_i values even when the pure gas isotherms can apparently be described using that assumption.

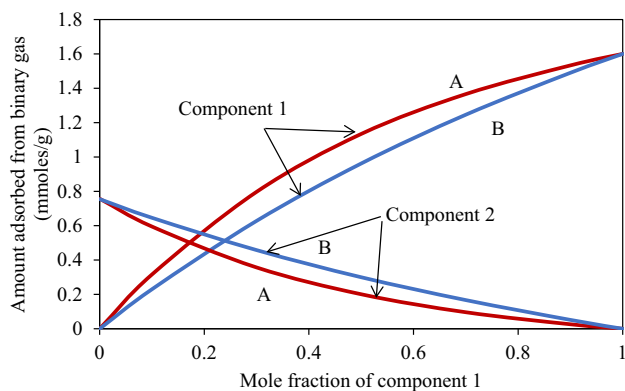


Fig. 2 Binary gas adsorption isotherms at a total gas pressure $P = 2.0$ atm (A Thermodynamically consistent Nitta Model; B Mixed-gas Langmuir model with unequal m_i values)

9 Ideal adsorbed solution theory (IAST) and Langmuir model

The ideal adsorbed solution theory can be used to estimate the equilibrium amount adsorbed $[n_i(P, T, y_i)]$ from a multicomponent gas (mole fraction of component $i = y_i$) at pressure P , temperature T , using the corresponding pure gas adsorption isotherms $[n_i^0(P, T)]$ at T . The relevant mathematical formulations for IAST are as follows (Myers and Prausnitz 1965):

$$P y_i = P_i^* x_i; x_i = \frac{n_i}{\sum_i n_i}; \sum \frac{x_i}{n_i^*} = \frac{1}{n}; n = \sum_i n_i \quad (20)$$

where P_i^* is the pressure of pure gas i at which the surface potential of that component ($\varphi_i^* = RT \int_0^{P_i^*} \frac{n_i^0}{P} dP$) is equal to the surface potential (φ^*) of the mixture at P, T and y_i , and n_i^* $[= n_i^0(P_i^*, T)]$ is the equilibrium amount adsorbed of pure gas at P_i^* and T . The relationship between P_i^* of different components of the mixture at constant T is given by:

$$\frac{\varphi_i^*}{RT} = \int_0^{P_i^*} \frac{n_i^0}{P} dP = \frac{\varphi^*}{RT} \quad (21)$$

Equation (21) can be used in conjunction with the pure gas Langmuir model Eq. (1) under the constraint $[m_i = m]$ to obtain an analytical relationship between P_i^* and P_j^* :

$$b_i P_i^* = b_j P_j^* \quad (22)$$

Hence it follows that:

$$\begin{aligned} (a) \quad n_i^* = n_j^* = n &= \frac{m \sum_j b_j P y_j}{1 + \sum_j b_j P y_j}; & (b) \quad x_i &= \frac{b_i P y_i}{\sum_j b_j P y_j}; \\ (c) \quad n_i = (n x_i) &= \frac{m b_i P y_i}{1 + \sum_j b_j P y_j} \end{aligned} \quad (23)$$

Equation (23c) describing n_i as a function of P and y_i at a constant T is identical with the mixed gas Langmuir isotherm model (Eq. 2) under the constraint ($m_i = m$). Thus, the thermodynamically consistent mixed gas Langmuir model can be analytically derived by applying IAST to the corresponding pure gas Langmuir model.

10 Beyond Langmuir isotherm models

The Langmuir model has been extensively used as the foundation for developing more sophisticated models which include the effects of (a) unequal adsorbate sizes ($m_i \neq m_j$), (b) lateral interaction between the adsorbed molecules, (c) multi-layer adsorption, and (d) adsorbent heterogeneity. Several analytical, pure and multicomponent gas adsorption isotherm models have been published in the literature with one or more of the above described attributes. Thus, these models can be used under conditions beyond the basic assumptions of the Langmuir model. All of these models reduce to the original Langmuir model form when the additional attributes are removed.

Table 2 lists the models developed for a homogeneous adsorbent:

- (a) The original Langmuir model Eq. (2) is reproduced here in a form that is comparable with (b) and (c).
- (b) Honig (1966), and Nitta and coworkers (1984), respectively, proposed a multisite Langmuir model for adsorption of a pure and a mixed gas on an energetically homogeneous adsorbent which relaxes the basic Langmuir concept of adsorption of one adsorbed molecule per site, in order to account for adsorbate size differences. The model is capable of describing different variations of binary gas adsorption selectivity with adsorbate loading, including the extreme case of adsorption azeotrope (Sircar 1995). The parameter a_i represents the number of adsorption sites per molecule of component i .
- (c) Martinez and Basmadjian (1996) proposed a model for pure and mixed gas adsorption on a homogeneous adsorbent where the adsorbate sizes can be different and lateral interaction between adsorbed molecules can exist. The isosteric heat of adsorption increases with increased adsorbate loading due to lateral interaction between adsorbed molecules.
- (d) Sircar (1985) proposed a new model for adsorption of a pure vapor ($T < T_c = \text{critical } T$) on a homogeneous adsorbent where the isotherm is Type II in shape (multi-layer formation) by assuming that adsorption takes place in stacks of Langmuir-type mono layers at all values of x . The model provides

Table 2 Beyond Langmuir: models developed for homogeneous adsorbent

Isotherm models	Pure gas	Multi-component gas	Constraints
(a) Langmuir (Young and Crowell 1962)	$b_i P = \frac{\theta_i^0}{[1 - \theta_i^0]}$ $\theta_i^0 = \frac{n_i^0}{m_i}$	$b_i P y_i = \frac{\theta_i}{[1 - \sum_i \theta_i]}$ $\theta_i = \frac{n_i}{m}$	$m_i \neq m_i(T)$ $m_i = m$
(b) Honig (1966), Nitta et al (1984) (Unequal adsorbate size)	$b_i P = \frac{\theta_i^0}{[1 - \theta_i^0]^{a_i}}$ $\theta_i^0 = \frac{n_i^0}{m_i}$	$b_i P y_i = \frac{\theta_i}{[1 - \sum_i \theta_i]^{a_i}}$ $\theta_i = \frac{n_i}{m}$	$m_i \neq m_i(T)$
(c) Martinez and Basmadjian (1996) (Lateral interaction)	$b_i P = \frac{\theta_i^0}{[1 - \theta_i^0]^{a_i}} e^{-\frac{a_i w_{ij} \theta_i^0}{RT}}$ $\theta_i^0 = \frac{n_i^0}{m_i}$	$b_i P y_i = \frac{\theta_i}{[1 - \sum_i \theta_i]^{a_i}} e^{-\frac{\sum_j a_j w_{ij} \theta_j}{RT}}$ $\theta_i = \frac{n_i}{m}$	$m_i \neq m_i(T)$ $a_i m_i = a_j m_j$ $w_{ij} = 0$
(d) Sircar (1985) (Multilayer)	$\theta_i^0(x) = \frac{n_i^0(x)}{m} = \frac{C_1 x [1 + (C_\infty - 1)x]}{(1-x)[1 + (C_1 - 1)x]}$ $x = \frac{P}{P^*}; C_1(T) = C_1^0 \exp\left[\frac{q_1^0}{RT}\right];$ $C_\infty = C_\infty(T)$ $n_i^0 \rightarrow m C_1 x \text{ as } x \rightarrow 0;$ $n_i^0 \rightarrow \infty \text{ as } x \rightarrow 1$	Not derived	$m \neq m(T)$

$b_i = b_i^0 \exp[q_i^0/RT]$ is the Langmuir gas-site interaction parameter (models a–c) for component i ; q_i^0 is the isosteric heat of adsorption of component i in the Henry’s Law region; b_i^0 is a constant. m_i is the saturation capacity of component i ; a_i is the number of sites occupied by each molecule of component i ; w_{ij} is the lateral interaction parameter between component i and j . $P^*(T)$ is vapor pressure of condensable adsorbate (vapor) at T

better fit of experimental Type II isotherm than the classic BET model (Young and Crowell 1962).

(a) The dual site Langmuir (DSL) model [Table 3(a1)], is based on an original Langmuir idea that a heterogeneous adsorbent consists of a collection of adsorption sites of different adsorption energies and

Table 3 lists models developed for a heterogeneous adsorbent:

Table 3 Beyond Langmuir: models developed for heterogeneous adsorbent

Isotherm models	Pure gas	Multi-component gas	Constraints
(a) (1) Langmuir Dual-site (DSL) model (Langmuir 1918) (Heterogeneous)	$\theta_i^0 = \frac{z b_{iA} P}{[1 + b_{iA} P]} + \frac{(1-z) b_{iB} P}{[1 + b_{iB} P]}$ $\theta_i^0 = \frac{n_i^0}{m}; m = m_A + m_B; \alpha = \frac{m_A}{m}$ $X = A, B: \text{two sites of DSL model}$	$\theta_i = \frac{z b_{iA} P y_i}{[1 + \sum_i b_{iA} P y_i]} + \frac{(1-z) b_{iB} P y_i}{[1 + \sum_i b_{iB} P y_i]}$ $\theta_i = \frac{n_i}{m}$	$m_{iA} = m_{jA}$ $m_{iB} = m_{jB}$ $m_A, m_B \neq f(T)$
(2) Sircar and Myers (1984) Discret two-site Langmuir model (Heterogeneous)	$\theta_i^0 = \frac{C P}{2} \times \left[\frac{1}{C P + \exp(-\frac{\mu}{RT})} + \frac{1}{C P + \exp(+\frac{\mu}{RT})} \right]$ $C = C^0 \exp[\mu/RT]$	Not derived	$m \neq m(T)$
(b) Toth (1962) and Jaroniec and Toth (1976) isotherm Models (Heterogeneous)	$b_i P = \frac{\theta_i^0}{[1 - (\theta_i^0)^{k_i}]^{1/k_i}}$	$b_i P y_i = \frac{\theta_i}{\left[1 - \left(\sum_i \theta_i\right)^{k_i}\right]^{1/k_i}}$	$m_i = m \neq m(T)$ $k_i = k$
(c) Sircar (1991b) (Heterogeneous)	$\theta_i^0 = \theta_{iH}^0 \left[1 - \frac{(1 - \theta_{iH}^0)}{\theta_{iH}^0} f(z_i^0) \right];$ $\theta_i^0 = \frac{n_i^0}{m_i}; \theta_{iH}^0 = \frac{\mu_i P}{[1 + \mu_i P]}$ $z_i^0 = \psi_i \theta_{iH}^0;$ $f(z_i^0) = \frac{1}{2\sigma_i} \ln \frac{1 + z_i^0}{1 - z_i^0} - 1$	$\theta_i = \theta_{iH} \left[1 - \frac{(\psi_i - z)}{z} f(z) \right];$ $\theta_i = \frac{n_i}{m_i}; \theta_{iH} = \frac{\mu_i P y_i}{1 + \sum_i \mu_i P y_i}$ $z = \sum_i \psi_i \theta_{iH}$ $f(z) = \frac{1}{2\sigma} \ln \frac{1+z}{1-z} - 1$	$m_i = m \neq m(T)$ $0 \leq \psi_i(T) < 1$ $\frac{d\psi_i}{dT} < 0$

$\mu_i = \mu_i^* \exp [q_i^*/RT]$ and $\sigma_i = \sigma_i^* \exp [q_i^*/RT]$ are, respectively, the mean and the dispersion of the uniform distribution of Henry’s constants on the adsorbent for component i at T ; μ and σ are, respectively, the mean and variance of the two site discret energy distribution; $\psi_i = \sqrt{3} [\sigma/\mu_i]$ is the degree of heterogeneity (Sircar Model) for component i at T ; k_i is the degree of heterogeneity (Toth model); b_{iX} is the Langmuir gas–solid interaction parameter for component i on site X ; q_{iX}^0 is the corresponding Henry’s Law isosteric heat of adsorption

that the over-all isotherm of a gas is obtained by adding the contributions of each site (Langmuir 1918; Young and Crowell 1962). The DSL model assumes only two different types of sites in the adsorbent. The model is popular because of flexibility introduced by six adjustable parameters in the model. On the other hand, a very large volume of experimental isotherm data (pure and mixture) may be necessary to reliably ascertain these parameters. Another analytical formulation of dual site Langmuir model, where two discreet energy sites on an adsorbent surface are described by two delta functions, was proposed by Sircar and Myers (1984). Table 3(a2) shows the pure gas isotherm expression for this model. The model uses only four adjustable parameters, yet capable of describing pure gas isotherms very well.

- (b) The empirical isotherm model proposed by Toth (1962) for adsorption of a pure gas on a heterogeneous adsorbent and an extension of the model for mixed gases by Jaroniec and Toth (1976) are frequently used to describe pure and mixed gas isotherm data. An analytical expression for the energy distribution on a heterogeneous surface (patch-wise homogeneous) has also been obtained for the Toth model by inverting the ‘Fredholm integral of first kind’ using the Langmuir isotherm model as the local homogeneous isotherm (kernel) in the integral (Sircar and Myers 1984; Sircar and Myers 1988). In other words, the Toth model can be derived by integrating the homogeneous Langmuir isotherm model with the above-mentioned site energy distribution.

It should be pointed out that (a) the isosteric heat of adsorption of a pure gas approaches negative infinity at the limit of $\theta_i^0 \rightarrow 1$ according to the Toth model, which is a serious weakness of the model, and (b) the mixed gas Toth model is thermodynamically consistent only when the degrees of heterogeneity of the components (k_i) are the same.

- (c) Sircar (1991b) proposed a model for a heterogeneous adsorbent by assuming that the energetic heterogeneity of the surface for a gas is accounted for by a uniform distribution of Henry’s Law constants of the gas on different patches of same energy (patch-wise homogeneous concept) while the local adsorption isotherm on a patch is given by the Langmuir model. The model is capable of describing the same or different degrees of heterogeneity for different components of a gas mixture (Sircar 1991b; Wu et al. 2014b).

These models are practically very useful because they provide analytical expressions for (a) pure and multi-gas

adsorption isotherms, and (b) isosteric heats of adsorption of pure gas and components of a gas mixture. In particular, the heat of adsorption of a component of a gas mixture can be a complex function of adsorbate loadings and the availability of an analytical model is very welcome (Sircar 1991a, b; Hartzog and Sircar 1995). Such analytical models facilitate the numerical modeling of non-isothermal, cyclic adsorptive gas separation processes such as Pressure or Thermal Swing Adsorption, and reduce the CPU time for model solutions. Tables 2 and 3 provides examples of a few of these models which are thermodynamically and physically consistent, and exhibit Henry’s Law behavior in the low pressure region.

All but one of the models of Tables 2 and 3 analytically describe Type I isotherm for a pure gas isotherm or a gas mixture. The corresponding analytical expressions for pure gas or binary gas isosteric heats of adsorption can be found elsewhere (Sircar 1991a; Sircar and Myers 2003; Wu et al. 2014b). These models have also been successfully tested using various experimental isotherm data, sometimes extensively. Thus, their practical value is evident. The multi-layer (Type II isotherm) model of Table 2 overcomes some of the deficiencies of many existing multi-layer pure gas isotherm models. It has also been successfully tested using experimental data on many different systems.

11 Conclusions

- The saturation adsorption capacity (m) of an adsorbate, which is a key variable in the homogeneous Langmuir isotherm model for pure or mixed gas adsorption, is constrained by the physics and thermodynamics of adsorption as follows:
 - (i) The variable m cannot be a function of temperature; arbitrary introduction of temperature dependence of m in the model creates an artificial dependence of the isosteric heat of adsorption (q) of a gas on adsorbate loading (n). The function $q(n)$ increases with increasing n and the limiting value of q , when $n \rightarrow m$, is infinity, which is physically absurd.
 - (ii) The saturation capacities of different components of a gas mixture (m_i) must be equal ($m_i = m_j$) in the mixed gas Langmuir model for satisfying various integral, differential, and internal thermodynamic consistencies by the model. Thus, estimation of multi-component gas adsorption equilibria from pure gas adsorption isotherms, which are fitted with arbitrary

selection (unequal) of pure gas m_i values, may not be reliable and should be extensively tested with actual experimental data prior to practical use like process modeling and design.

- The mixed gas Langmuir isotherm model can be analytically derived by the application of IAST concept to the pure gas Langmuir isotherms.
- Various analytical pure and mixed-gas adsorption isotherm models, which are developed using the classic Langmuir model as the backbone, and which include the effects (individually or some combination) of (a) different adsorbate sizes, (b) lateral interactions between adsorbed molecules, (c) multi-layer adsorption, and (d) adsorbent heterogeneity are available. These models are (a) thermodynamically consistent (under some constraints) and (b) exhibit Henry's Law region at low pressures. They also provide analytical expressions for isotherms and the corresponding pure and mixed gas isosteric heats of adsorption as functions of adsorbate loadings, which facilitate numerical modeling of adsorptive processes. It is recommended that these models should be examined for modeling purposes.
- The thermodynamically consistent multi-site occupancy model of Nitta et al. (1984), which extends the classic Langmuir model to describe adsorption isotherm from a gas mixture containing adsorbates of different sizes ($m_i \neq m_j$), is particularly recommended to be used as a basic isotherm model for adsorption on a homogeneous adsorbent because of its practical outreach (Golden and Sircar 1994a, b; Sircar and Rao 1999). This model should be used instead of empirically using the original Langmuir model with different m_i values.

Compliance with ethical standards

Conflict of interest The author declares no competing financial interest.

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