Adsorption (2024) 30:1593–1601
https://doi.org/10.1007/s10450-023-00430-x

On adsorption azeotropy and a classification based on the dual site Langmuir isotherm

Stefano Brandani[1]

Received: 15 December 2022 / Revised: 16 December 2022 / Accepted: 24 October 2023 / Published online: 21 November 2023

Abstract

Adsorption azeotropy is a phenomenon that has been known for nearly a century, yet few properties have been formally proven. Here four general properties of adsorption azeotropy in porous materials are discussed and shown to apply irrespective of the isotherm, including the fact that there is always a lower bound on the pressure at which an azeotrope may be present. As molecules of different size will favour the occurrence of an azeotrope, this study considers in detail the thermodynamically consistent dual site Langmuir model, where azeotropy is solely the result of the adsorbent heterogeneity. Six categories of adsorption azeotropes, which can be grouped into three pairs of mirror cases, are formally identified for this model. Dimensionless ratios allow to determine formally each category and the analysis also includes a discussion of the crossing of the pure component isotherms. The heterogeneity of the adsorbent is shown to lead to azeotropes that can include an upper bound on pressure; that can occur even if the pure component isotherms do not cross; and can be present below the pressure at which the pure component isotherms cross. Finally, the analysis allows to identify also the ranges of parameters for which the pure component isotherms cross but an azeotrope is not present.

Keywords Adsorption azeotropy · Dual site Langmuir isotherm · Thermodynamic consistency

List of symbols

b_{Ai}	Affinity of component i in site A, Pa^{-1}
b_{Bi}	Affinity of component i in site B, Pa^{-1}
B	Coefficient of quadratic equation defined in Eq. 26, –
C	Coefficient of quadratic equation defined in Eq. 26, –
K_{Pi}	Henry law constant of component i, Pa^{-1}
f	Fugacity, Pa
F	Function defined in Eq. 12, –
G	Gibbs energy of the system, J
n_i	Moles of component i in the fluid phase, mol
n_i^{Ads}	Moles of component i in the adsorbed phase, mol
P	Pressure, Pa
P_{Az}	Pressure at the azeotrope, Pa
P_{Cross}	Pressure at which the pure component isotherms cross, Pa
q_i	Adsorbed amount of component i, mol m^{-3}
q_i^0	Pure component adsorbed amount of component i, mol m^{-3}
q_{Si}	Saturation capacity of component i, mol m^{-3}
q_{AS}	Saturation capacity of site A, mol m^{-3}
q_{BS}	Saturation capacity of site B, mol m^{-3}
V_S	Volume of the solid, m^3
x	Mole fraction of component 1 in the adsorbed phase, –
x_i	Mole fraction of component i in the adsorbed phase, –
y	Mole fraction of component 1 in the fluid phase, –
y_i	Mole fraction of component i in the fluid phase, –
y_{Az}	Mole fraction at the azeotrope of component 1 in the fluid phase, –

Greek letters

α	Dimensionless group defined in Eq. 12, –
Γ_i	Ratio of affinities of the different sites for component i, –
Γ_A	Ratio of affinities of the components on site A, –
Γ_B	Ratio of affinities of the components on site B, –
ϕ	Fraction of total sites of type A, –
μ_S	Chemical potential of the solid (volume basis), J m^{-3}

✉ Stefano Brandani
s.brandani@ed.ac.uk

[1] School of Engineering, University of Edinburgh, Edinburgh EH9 3FB, UK

μ_i	Chemical potential of component i in the fluid phase, J mol^{-1}
μ_i^{Ads}	Chemical potential of component i in the adsorbed phase, J mol^{-1}
χ	Ratio of differences of site Henry law constants, defined in Eq. 19, –
Ψ_i^0	Pure component reduced grand potential, mol m^{-3}

1 Introduction

Adsorption azeotropy has been found in many systems, with the earliest examples nearly a century ago [1, 2]. Damkohler [3] discussed these earlier results and measured data for argon and nitrogen on silica gel at 89 K, which exhibits an azeotrope. These data have been tested for thermodynamic consistency [4], confirming unambiguously the existence of a binary azeotrope. Brunauer in his book [5] links the occurrence of the azeotrope in [3] with multilayer adsorption, but this is not a requirement as shown by Cook and Basmadjian [6].

The existence of an azeotrope was originally associated with the crossing of the pure component adsorption isotherms [6, 7], but systems have been identified that exhibit azeotropy without this feature [8–11], including data from Talu on hydrogen sulphide and propane on mordenite for which thermodynamic consistency was demonstrated [9]. It is interesting to note that Hyun and Danner [8] also showed a case where the isotherms crossed but an azeotrope was not present (Ethylene-Isobutane on 13X at 373 K).

The effect of an azeotrope on adsorption column dynamics was investigated by Basmadjan [12] and examples of breakthrough curves for such systems can also be found [13, 14].

There are many occurrences of adsorption azeotropy in the literature and good recent accounts can be found in [15, 16]. Luberti et al. [15] show a range of azeotropic systems and correlate the data with the multisite Langmuir isotherm, demonstrating that the heterogenous ideal adsorbed solution theory [17] provides a reasonable approach to predicting binary systems, but improved correlations are possible introducing mixture activity coefficient models, see also [18]. Jiang et al. [16] attempt to develop a systematic characterization of the possible cases encountered with the dual site Langmuir (DSL) model. Their focus is on a numerical exploration aimed at finding suitable parameters of the DSL model for both the case of thermodynamic consistency [17] and inconsistency, i.e. the more general case that allows the saturation capacities of the sites to vary with the adsorbate. In [16] examples are given for cases where the pure component isotherms do not cross but an azeotrope is present. Furthermore, they concluded that the thermodynamically consistent DSL model has an azeotrope when the pure component isotherms cross, while for the more general case crossing isotherms could have no azeotrope. A more recent study by the same group [19] expanded the exploration of possible cases to consider whether it was possible to predict azeotropy at a pressure below the pressure at which the pure component isotherms cross, concluding that this was the case, citing also Talu's system of carbon dioxide and propane on mordenite [9] as an example.

The aim of this contribution is to provide a set of proofs for general properties of adsorption azeotropy valid for any adsorption isotherm and subsequently investigate the behaviour of the thermodynamically consistent DSL model, as this contribution is part of a collection of papers in honour of Orhan Talu, who in his publications has always insisted on ensuring thermodynamic consistency. The analysis that follows provides formal proofs to several observations made in [16, 19], but also demonstrates some gaps and inconsistencies in what was reported.

2 General properties of adsorption azeotropy

A simple definition of adsorption azeotropy is that the mole fractions of the adsorbed phase and the fluid phase are equal, $x_i = y_i$, and $dx_i/dy_i \neq 1$. These conditions imply that on an x–y diagram the equilibrium curve crosses the diagonal at the azeotrope.

It is also possible to relate the azeotrope to a maximum or minimum of the chemical potential of the solid [15]. As this is something that to the author's knowledge has not been demonstrated in previous work a short proof will be given.

The Gibbs energy of a closed cell containing a gas phase and an adsorbent that is maintained at constant pressure (moving piston) is given by

$$G = V_S\mu_S + \sum_i\left(n_i\mu_i + n_i^{Ads}\mu_i^{Ads}\right) \tag{1}$$

For a system at equilibrium $\mu_i = \mu_i^{Ads}$. We can write the differential of the Gibbs energy and incorporate the equilibrium relationship

$$dG = V_S d\mu_S + \sum_i\left(n_i + n_i^{Ads}\right)d\mu_i + \sum_i\mu_i d\left(n_i + n_i^{Ads}\right) \tag{2}$$

The last term on the RHS is zero since the cell is a closed system. Therefore, at equilibrium

$$-V_S d\mu_S = \sum_i\left(n_i + n_i^{Ads}\right)d\mu_i \tag{3}$$

Defining $n_T = \sum_i\left(n_i + n_i^{Ads}\right)$, for a system at an azeotrope ($x_i = y_i$) at constant temperature and pressure

$$-V_S d\mu_S = n_T\sum_i y_i d\mu_i = 0 \tag{4}$$

At constant temperature and pressure the term on the RHS is zero from the Gibbs-Duhem equation for the gas phase, *q.e.d.*

It is therefore possible to state that: **at constant temperature and pressure, at the azeotrope the chemical potential of the solid and as a result the reduced grand potential are either a maximum or a minimum with respect to composition**. This can be seen as the equivalent of the case in vapour-liquid equilibrium, where the azeotrope results in either a maximum or minimum of the total pressure. It is therefore possible to identify the presence of an azeotrope in terms of the derivatives with respect to composition of the reduced grand potential at infinite dilution. The infinite dilution activity coefficient can also be used for this purpose as shown by Siperstein [18]. While the reduced grand potential of a mixture is not directly available experimentally, this approach for determining the presence of an azeotrope may prove to be useful in molecular simulations and in the analysis of multicomponent mixture models. As this is a general property of adsorption azeotropy, which is independent of the model adopted, it can be seen as the thermodynamic necessary and sufficient condition for the existence of an adsorption azeotrope.

Given that the reduced grand potential at low pressure reduces to $\sum_i y_i P K_{Pi}$, with K_{Pi} the pure component Henry law constants, **there is always a lower bound on the pressure at which an adsorption azeotrope can occur**.

A third general property of adsorption azeotropy is related to the crossing of the pure component reduced grand potentials. Simply stated: **if the pure component reduced grand potentials cross an azeotrope is present**. This is only a sufficient condition for adsorption azeotropy and Siperstein and Myers [11] have shown that it is possible to have an azeotrope even when the pure component reduced grand potentials do not cross. This third property can be proven formally.

At the intersection of the pure component reduced grand potentials the Ideal Adsorbed Solution Theory [20] gives as the solution

$$x_i = y_i \tag{5}$$

for all compositions, as in this case the reference pressures of both components are equal to the total pressure. The IAST predicts selectivity reversal at the point where the pure component reduced grand potentials cross. This does not mean that the IAST predicts an azeotrope in the sense of the definition used here as in this case $dx_i/dy_i = 1$, and it is equivalent to an ideal liquid mixture with two components that have the same vapour pressure.

Any thermodynamically consistent mixture model will cross the IAST predictions [21, 22], therefore at the crossing of the reduced grand potentials there will be an azeotrope, *q.e.d.*

A final general property can be inferred from the previous one. The reduced grand potential of the pure components is obtained from the Gibbs isotherm [23, 24].

$$\psi_i^0 = \int_0^P q_i^0 d\ln f \tag{6}$$

where q_i^0 is the adsorbed amount for component i pure.

At low pressure, for a thermodynamically consistent isotherm model [21] Eq. 6 reduces to $\psi_i^0 = K_{Pi}P$, where K_{Pi} are the pure component Henry law constants.

At high pressure the adsorbed amount will become finite and equal to the saturation capacity q_{Si} and Eq. 6 will reduce to $\psi_i^0 = C_i + q_{Si}\ln f$, with C_i a constant.

If we define component 1 such that $K_{P1} > K_{P2}$ the pure component reduced grand potentials will cross if $q_{S2} > q_{S1}$ and an azeotrope will be present. Note that in this case also the pure component isotherms cross. Therefore, the final general property can be stated as: **define component 1 such that $K_{P1} > K_{P2}$, the pure component isotherms and the reduced grand potentials will cross if $q_{S2} > q_{S1}$ and an azeotrope will be present**.

This final condition is actually quite important as it shows that adsorption azeotropy is always present for differently sized molecules where van der Waals forces dominate (all non-polar molecules) as the Henry law constant will follow the size of the molecules and the saturation capacity will be in the opposite order. Consider for example adsorption of propane (1) and methane (2) on any microporous adsorbent. Due to the difference in size of the molecules the final condition will apply to this pair of adsorbates, albeit the pressure at which the azeotrope will begin to occur may be high as enough methane will have to adsorb before this can happen.

In what follows the focus is on the thermodynamically consistent dual site Langmuir (DSL) isotherm, which ensures that both molecules have the same saturation capacity and as a result the final general property of adsorption azeotropy does not apply. Hence, this model will highlight the conditions that result in an azeotrope due to the heterogeneity of the adsorbent and not size differences of the molecules. As most adsorption separations focus on separating molecules that are similar to each other, this in itself is an important special case to study in detail.

3 Adsorption azeotropy and the dual site Langmuir isotherm

Consider an adsorbent that can be described by a DSL isotherm. Assume that the isotherm is locally thermodynamically consistent, i.e. the saturation capacities for different molecules are the same for each site [17]. The binary adsorbed amounts, q_1 and q_2, are given by

$$q_1 = q_{AS}\frac{b_{A1}Py}{1 + b_{A1}Py + b_{A2}P(1-y)} + q_{BS}\frac{b_{B1}Py}{1 + b_{B1}Py + b_{B2}P(1-y)} \tag{7}$$

$$q_2 = q_{AS}\frac{b_{A2}P(1-y)}{1 + b_{A1}Py + b_{A2}P(1-y)} + q_{BS}\frac{b_{B2}P(1-y)}{1 + b_{B1}Py + b_{B2}P(1-y)} \tag{8}$$

where y is the mole fraction of component 1 in the gas phase and P is the total pressure of the system. Note that in the notation letters identify the sites and numbers identify the adsorbates.

The ratio of the mole fraction in the adsorbed phase to that in the gas phase is given by

$$\frac{x}{y} = \frac{q_{AS}\frac{b_{A1}P}{1+b_{A1}Py+b_{A2}P(1-y)} + q_{BS}\frac{b_{B1}P}{1+b_{B1}Py+b_{B2}P(1-y)}}{q_{AS}\frac{b_{A1}Py+b_{A2}P(1-y)}{1+b_{A1}Py+b_{A2}P(1-y)} + q_{BS}\frac{b_{B1}Py+b_{B2}P(1-y)}{1+b_{B1}Py+b_{B2}P(1-y)}} \tag{9}$$

For an azeotrope to occur this ratio must be 1.

This relationship can be rearranged to give

$$q_{AS}\frac{b_{A1} - b_{A2}}{1 + b_{A1}Py + b_{A2}P(1-y)} + q_{BS}\frac{b_{B1} - b_{B2}}{1 + b_{B1}Py + b_{B2}P(1-y)} = 0 \tag{10}$$

We can see that if molecule 1 is more strongly adsorbed on both sites $b_{A1} > b_{A2}$ and $b_{B1} > b_{B2}$ no azeotrope can be present. The only case that needs to be considered is $b_{A1} > b_{A2}$ and $b_{B1} < b_{B2}$, since site A can be defined as the one for which molecule 1 has a larger affinity.

Introducing a set of dimensionless parameters.

$$\phi = \frac{q_{AS}}{q_{AS} + q_{BS}}; \Gamma_A = \frac{b_{A1}}{b_{A2}} > 1; \Gamma_B = \frac{b_{B1}}{b_{B2}} < 1; \Gamma_2 = \frac{b_{A2}}{b_{B2}} \tag{11}$$

where ϕ is the fraction of sites of type A, while the Γ parameters represent the ratios of the affinities.

Equation 10 can be rewritten as

$$\alpha = \frac{(1-\phi)\left(1-\Gamma_B\right)}{\phi\left(\Gamma_A - 1\right)} = \frac{\Gamma_2 + b_{A2}P\left[1 - y\left(1-\Gamma_B\right)\right]}{1 + b_{A2}P\left[1 + y\left(\Gamma_A - 1\right)\right]} = F(P,y) \tag{12}$$

which leads to the pressure at which an azeotrope will occur

$$b_{A2}P_{Az} = \frac{\alpha - \Gamma_2}{1 - y\left(1-\Gamma_B\right) - \alpha\left[1 + y\left(\Gamma_A - 1\right)\right]} \tag{13}$$

and the composition at which an azeotrope will occur

$$y_{Az} = \frac{\Gamma_2 + b_{A2}P - \alpha\left(1 + b_{A2}P\right)}{\left[\alpha\left(\Gamma_A - 1\right) + \left(1 - \Gamma_B\right)\right]b_{A2}P} \tag{14}$$

The term on the LHS of Eq. 12 is a constant, α. Therefore the condition for the existence of an azeotrope can be analysed by inspecting the function on the RHS, F. To understand if an azeotrope will be present one has to consider the dependence of this function on mole fraction and pressure.

$$\left.\frac{\partial F}{\partial y}\right|_P = -\frac{b_{A2}P\left(1-\Gamma_B\right)}{1 + b_{A2}P\left[1 + y\left(\Gamma_A - 1\right)\right]} - \frac{b_{A2}P\left(\Gamma_A - 1\right)\left\{\Gamma_2 + b_{A2}P\left[1 - y\left(1 - \Gamma_B\right)\right]\right\}}{\left\{1 + b_{A2}P\left[1 + y\left(\Gamma_A - 1\right)\right]\right\}^2} \tag{15}$$

By inspection $\left.\frac{\partial F}{\partial y}\right|_P < 0$ apart for $P = 0$ where $\left.\frac{\partial F}{\partial y}\right|_0 = 0$.

$$\left.\frac{\partial F}{\partial P}\right|_y = -\frac{b_{A2}\left[\Gamma_2 - 1 + y\left[1 - \Gamma_B + \Gamma_2\left(\Gamma_A - 1\right)\right]\right]}{\left\{1 + b_{A2}P\left[1 + y\left(\Gamma_A - 1\right)\right]\right\}^2} \tag{16}$$

This function is more complex as $\left.\frac{\partial F}{\partial P}\right|_y$ changes sign when

$$y = y_I = \frac{1 - \Gamma_2}{1 - \Gamma_B + \Gamma_2\left(\Gamma_A - 1\right)} \tag{17}$$

$y_I = 0$ when $\Gamma_2 = 1$. If $\Gamma_2 > 1$, y_I is always negative and there will not be a change of sign. By inspection $\left.\frac{\partial F}{\partial P}\right|_y < 0$ when $\Gamma_2 \geq 1$.

$y_I = 1$ when $\Gamma_2 = \Gamma_B/\Gamma_A$. If $\Gamma_2 < \Gamma_B/\Gamma_A$, y_I is always greater than 1 and there will not be a change of sign. By inspection $\left.\frac{\partial F}{\partial P}\right|_y > 0$ when $\Gamma_2 < \Gamma_B/\Gamma_A$.

If $\Gamma_B/\Gamma_A < \Gamma_2 < 1$ there will be a change of sign with $\left.\frac{\partial F}{\partial P}\right|_y > 0$ for $y < y_I$, and $\left.\frac{\partial F}{\partial P}\right|_y < 0$ for $y > y_I$, and $F\left(P, y_I\right) = \Gamma_2$.

As a result of the considerations above it is possible to state:

1. If $\Gamma_2 > 1$, $F(P,y)$ has a maximum at $F(0{,}0) = \Gamma_2$ and a minimum at $F(\infty,1) = \frac{\Gamma_B}{\Gamma_A}$. An azeotrope will exist if $\Gamma_2 > \alpha > \frac{\Gamma_B}{\Gamma_A}$
2. If $1 > \Gamma_2 > \Gamma_B/\Gamma_A$, $F(P,y)$ has a maximum at $F(\infty,0) = 1$ and a minimum at $F(\infty,1) = \frac{\Gamma_B}{\Gamma_A}$. In this case an azeotrope will exist if$1 > \alpha > \frac{\Gamma_B}{\Gamma_A}$
3. If $\Gamma_2 < \Gamma_B/\Gamma_A$, $F(P,y)$ has a maximum at $F(\infty,0) = 1$ and a minimum at $F(0{,}1) = \Gamma_2$. In this case an azeotrope will exist if$1 > \alpha > \Gamma_2$

From Eq. 14

$$b_{A2}\frac{\partial P_{Az}}{\partial y} = \frac{\left(\alpha - \Gamma_2\right)\left[\left(1 - \Gamma_B\right) + \alpha\left(\Gamma_A - 1\right)\right]}{\left\{1 - y\left(1 - \Gamma_B\right) - \alpha\left[1 + y\left(\Gamma_A - 1\right)\right]\right\}^2} \tag{18}$$

Table 1 Summary of relationships for binary adsorption azeotropy with the dual site Langmuir isotherm. Site A is the adsorption site for which molecule 1 is more strongly adsorbed

Isotherm	$q_1 = q_{AS}\frac{b_{A1}Py}{1+b_{A1}Py+b_{A2}P(1-y)} + q_{BS}\frac{b_{B1}Py}{1+b_{B1}Py+b_{B2}P(1-y)}$ $q_2 = q_{AS}\frac{b_{A2}P(1-y)}{1+b_{A1}Py+b_{A2}P(1-y)} + q_{BS}\frac{b_{B2}P(1-y)}{1+b_{B1}Py+b_{B2}P(1-y)}$
Define	$\phi = \frac{q_{AS}}{q_{AS}+q_{BS}}; \Gamma_A = \frac{b_{A1}}{b_{A2}} > 1; \Gamma_B = \frac{b_{B1}}{b_{B2}} < 1; \Gamma_2 = \frac{b_{A2}}{b_{B2}}; \alpha = \frac{(1-\phi)(1-\Gamma_B)}{\phi(\Gamma_A-1)}$
Azeotrope	$\alpha = \frac{\Gamma_2+b_{A2}P[1-y(1-\Gamma_B)]}{1+b_{A2}P[1+y(\Gamma_A-1)]}$
Given *P*	$y_{Az} = \frac{\Gamma_2+b_{A2}P-\alpha(1+b_{A2}P)}{[\alpha(\Gamma_A-1)+(1-\Gamma_B)]b_{A2}P}$
Given *y*	$b_{A2}P_{Az} = \frac{\alpha-\Gamma_2}{1-y(1-\Gamma_B)-\alpha[1+y(\Gamma_A-1)]}$
Requirement for azeotrope	$\Gamma_2 > \alpha > \frac{\Gamma_B}{\Gamma_A}$ if $\Gamma_2 \geq 1$ $1 > \alpha > \frac{\Gamma_B}{\Gamma_A}$ if $1 > \Gamma_2 \geq \frac{\Gamma_B}{\Gamma_A}$ $1 > \alpha > \Gamma_2$ if $\frac{\Gamma_B}{\Gamma_A} > \Gamma_2$
Category 1	$\Gamma_2 > \alpha$ and $\alpha > 1\,\frac{\alpha-\Gamma_2}{1-\alpha} > b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha}$ $\frac{\alpha-\Gamma_2}{1-\alpha} > b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha}$ any y Crossing isotherms $P_{Cross} < P_{Az}$
Category 2	$\Gamma_2 \geq 1$ and $\frac{\Gamma_B}{\Gamma_A} < \alpha < 1\, b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha} 1 > y_{Az} > \frac{1-\alpha}{1-\Gamma_B+\alpha(\Gamma_A-1)}$ Crossing isotherms $P_{Cross} < P_{Az}$
Category 3	$\alpha > \Gamma_2 > \frac{\Gamma_B}{\Gamma_A}$ and $1 > \alpha\, b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{1-\alpha} 0 < y_{Az} < \frac{1-\alpha}{1-\Gamma_B+\alpha(\Gamma_A-1)}$ Non-crossing isotherms possible $P_{Cross} > P_{Az}$ is possible
Category 4	1 Non-crossing isotherms possible $P_{Cross} > P_{Az}$ is possible
Category 5	$\Gamma_2 < \frac{\Gamma_B}{\Gamma_A}$ and $1 > \alpha > \frac{\Gamma_B}{\Gamma_A} b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{1-\alpha} 0 < y_{Az} < \frac{1-\alpha}{1-\Gamma_B+\alpha(\Gamma_A-1)}$ Crossing isotherms $P_{Cross} < P_{Az}$
Category 6	$\Gamma_2 < \frac{\Gamma_B}{\Gamma_A}$ and $\frac{\Gamma_B}{\Gamma_A} > \alpha > \Gamma_2 \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha} > b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{1-\alpha}$ any y Crossing isotherms $P_{Cross} < P_{Az}$

When $\Gamma_2 > 1, \alpha < \Gamma_2$ and $\frac{\partial P_{Az}}{\partial y} < 0$. This leads to a very interesting behaviour:

4. If $\alpha > 1$ the azeotrope will only appear in a limited pressure range:$\frac{\alpha-\Gamma_2}{1-\alpha} > b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha}$
5. If $\alpha \leq 1$, then $b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha}$, while the concentration range will be limited to

When $\frac{\Gamma_B}{\Gamma_A} < \Gamma_2 < 1$ there will be two further cases to consider.

6. If $\alpha > \Gamma_2, \frac{\partial P_{Az}}{\partial y} > 0$ and the pressure will be $b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{1-\alpha}$ as $\alpha > \frac{\Gamma_B}{\Gamma_A}$. The concentration range will be limited to $0 < y_{Az} < \frac{1-\alpha}{1-\Gamma_B+\alpha(\Gamma_A-1)}$.
7. If $\alpha < \Gamma_2, \frac{\partial P_{Az}}{\partial y} < 0$ and $b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha}$, while the concentration range will be limited to$1 > y_{Az} > \frac{1-\alpha}{1-\Gamma_B+\alpha(\Gamma_A-1)}$

When $\Gamma_2 < \frac{\Gamma_B}{\Gamma_A}$ there will be two final cases to consider.

8. If $\alpha > \Gamma_2, \frac{\partial P_{Az}}{\partial y} > 0$ and the pressure will be $b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{1-\alpha}$ when $\alpha > \frac{\Gamma_B}{\Gamma_A}$. The concentration range will be limited to$0 < y_{Az} < \frac{1-\alpha}{1-\Gamma_B+\alpha(\Gamma_A-1)}$
9. If $\alpha > \Gamma_2, \frac{\partial P_{Az}}{\partial y} > 0$ and when $\alpha < \frac{\Gamma_B}{\Gamma_A}$ the azeotrope will be present only in a limited pressure range:$\frac{\alpha-\Gamma_2}{\Gamma_B-\Gamma_A\alpha} > b_{A2}P_{Az} > \frac{\alpha-\Gamma_2}{1-\alpha}$

All these conditions allow the definition of six categories of azeotropes that can be obtained from the thermodynamically consistent DSL isotherm. These are summarised in Table 1 along with all the expressions useful for the study of an azeotrope with the DSL isotherm. The six categories are ordered in decreasing value of Γ_2 and depend on which bounds limit the pressure and the concentration as well as whether azeotropes can be present when the isotherms do not cross.

Categories 1–3 are the mirrors of categories 6 – 4 obtained by inverting both the order of the sites and that of the adsorbates. Categories 1 and 6 are both characterized by a finite range of pressures for azeotropes, something first observed by Cook and Basmadjian [6]. Categories 2 and 5 have only a lower bound in pressure and a limited range of compositions possible, but when an azeotrope is present the pure component isotherms cross. Categories 3 and 4 have only a lower bound in pressure and a limited range of compositions possible, but allow azeotropes even when the pure component isotherms do not cross, and when the pure component isotherms cross the bound on the azeotrope pressure is lower that the pressure at which the pure component isotherms cross.

4 Relationship to previous work on the DSL model

Do and Do [7] analysed a subset of the possible cases presented here as they considered that only the more weakly adsorbed component on site A could adsorb on site B. Therefore, the particular case considered in [7] can be obtained from the previous analysis setting $b_{B1} = 0$ or $\Gamma_B = 0$, and note that the pure component isotherms always cross.

In the analysis of azeotropy and the DSL isotherm presented recently [16, 19] a dimensionless parameter was introduced based on the differences of the Henry law constants of the sites.

$$\chi = \frac{K_{PB2} - K_{PB1}}{K_{PA1} - K_{PA2}} = \frac{b_{B2} - b_{B1}}{b_{A1} - b_{A2}} \frac{q_{BS}}{q_{AS}} \tag{19}$$

In terms of the dimensionless groups used here

$$\chi = \frac{\alpha}{\Gamma_2} \tag{20}$$

According to [16, 19] the condition for azeotropy requires

$$1 > \chi > 0 \tag{21}$$

While, defining $\frac{1}{\Gamma_1} = \frac{\Gamma_B}{\Gamma_A \Gamma_2} = \frac{b_{B1}}{b_{A1}}$, the analysis presented here indicates that in fact

$$1 > \chi > \frac{1}{\Gamma_1} \text{ If } \Gamma_2 > 1 \tag{22}$$

When $\Gamma_2 > 1, 1 > \frac{1}{\Gamma_1} > 0$, therefore, there will be a range of values of χ where this condition is met.

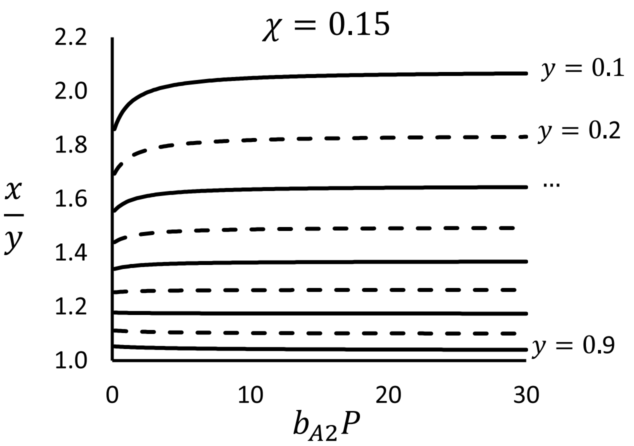

Fig. 1 System for which $\chi > 0$ but there is no azeotrope as in all cases $\frac{x}{y} > 1$. $\Gamma_2 = 0.2$; $\Gamma_A = 2.5$; $\Gamma_B = 0.1$; $\alpha = 0.03$; $\frac{1}{\Gamma_1} = 0.2$. Pure component isotherms do not cross

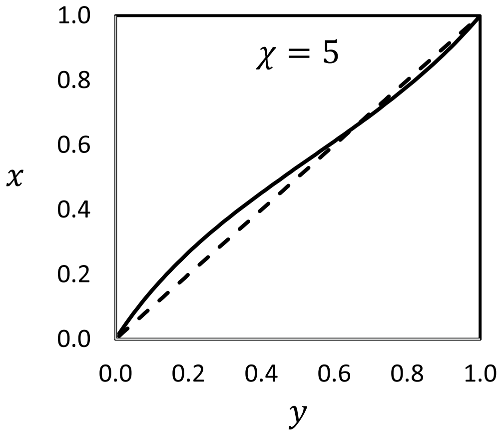

Fig. 2 System (category 5) for which $\chi > 1$ and there is an azeotrope. $\Gamma_2 = 0.05$; $\Gamma_A = 3$; $\Gamma_B = 0.4$; $\alpha = 0.25$; $b_{A2}P = 7.5$

$$\frac{1}{\Gamma_2} > \chi > \frac{1}{\Gamma_1} \text{ If } 1 > \Gamma_2 > \frac{\Gamma_B}{\Gamma_A} \tag{23}$$

and

$$\frac{1}{\Gamma_2} > \chi > 1 \text{ If } \Gamma_2 < \frac{\Gamma_B}{\Gamma_A} \tag{24}$$

When $\Gamma_2 < 1, \frac{1}{\Gamma_1} < \frac{1}{\Gamma_2}$, therefore, there will be a range of values of χ where the conditions in Eqs. 23, 24 are met.

It is easy to generate sets of parameters for the different categories. One can start by setting b_{A2} and b_{B2} to obtain Γ_2 in the range of interest, i.e. below or above 1. Suitable values of the remaining affinities can then be set ensuring $\Gamma_A > 1$ and $\Gamma_B < 1$. As the fraction of total sites of type A, ϕ, can be changed arbitrarily between 0 and 1 it is possible to obtain any value for α.

Figure 1 shows an example where $\frac{1}{\Gamma_1} > \chi > 0$ and an azeotrope is not present.

Figure 2 shows an example where $\chi > 1$. Therefore, there are conditions of adsorption azeotropy for the thermodynamically consistent DSL model that have not been identified previously in [16, 19] as the search for viable parameter values started by ensuring that the constraint given by Eq. 21 was met.

5 Crossing of pure component isotherms

While crossing of the pure component isotherms is not a requirement for adsorption azeotropy, it is a potential indicator that the mixture can have an azeotrope. It is therefore useful to complete the analysis of the thermodynamically consistent DSL model and discuss whether the six categories for azeotropy will always have crossing isotherms or not.

The condition for the presence of an intersection of the pure component isotherms is given by

$$q_{AS}\frac{b_{A1}P}{1+b_{A1}P} + q_{BS}\frac{b_{B1}P}{1+b_{B1}P} = q_{AS}\frac{b_{A2}P}{1+b_{A2}P} + q_{BS}\frac{b_{B2}P}{1+b_{B2}P} \tag{25}$$

After some algebraic manipulation it is possible to recast this condition as the solution of the quadratic equation.

$$\left(b_{A2}P\right)^2 + Bb_{A2}P + C = 0 \tag{26}$$

where

$$B = \Gamma_2\frac{\Gamma_B + 1 - \alpha\left(\Gamma_A + 1\right)}{\Gamma_B - \Gamma_A\Gamma_2\alpha} \text{ and } C = \Gamma_2\frac{\Gamma_2 - \alpha}{\Gamma_B - \Gamma_A\Gamma_2\alpha}$$

One positive $b_{A2}P_{Cross}$ value, $\left(-B + \sqrt{B^2 - 4C}\right)/2$, fulfils the crossing of the isotherms condition when $C < 0$. This results in the following condition

$$\frac{\Gamma_B}{\Gamma_2\Gamma_A} > \alpha > \Gamma_2 \text{ or } \frac{\Gamma_B}{\Gamma_2\Gamma_A} < \alpha < \Gamma_2 \tag{27}$$

If $\Gamma_2 > 1$ the condition for $C < 0$ is wider than that of the azeotrope.

If $\Gamma_2 < \frac{\Gamma_B}{\Gamma_A}$ the condition for $C < 0$ is wider than that of the azeotrope. Therefore, this case is similar to the previous one.

Categories 1, 2, 5 and 6 in Table 1 will always have crossing isotherms when an azeotrope is present, but there will be ranges of parameters where the isotherms will cross but there will not be an azeotrope, contrary to what was stated in [16]. Figure 3 shows an example of crossing isotherms but no azeotrope.

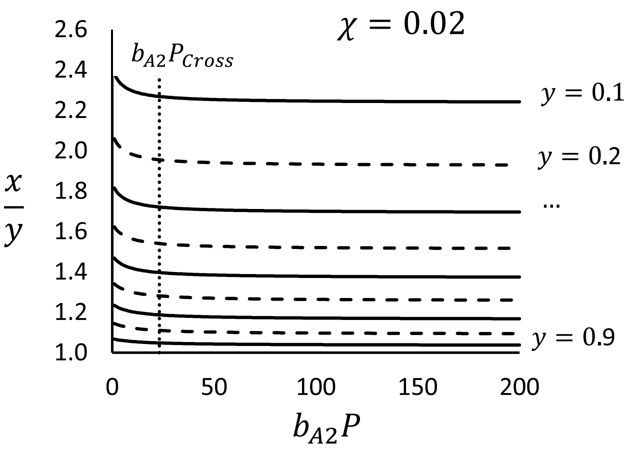

Fig. 3 System for which pure component isotherms cross but there is no azeotrope as in all cases $\frac{x}{y} > 1$. $\Gamma_2 = 2.5$; $\Gamma_A = 3$; $\Gamma_B = 0.25$; $\alpha = 0.05$; $\frac{1}{\Gamma_1} = 0.033$

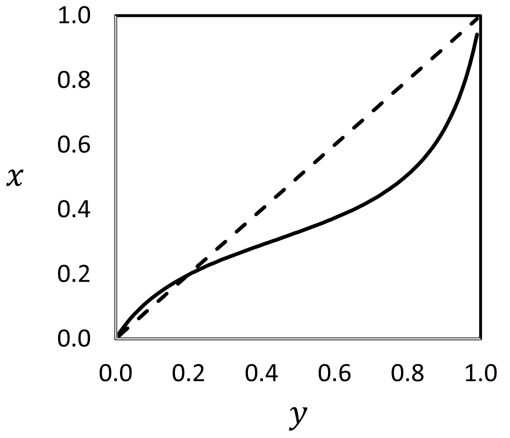

Fig. 4 System (category 3) where the pure component isotherms do not cross and there is an azeotrope. $\Gamma_2 = 0.067$; $\Gamma_A = 7.5$; $\Gamma_B = 0.1$; $\alpha = 0.3$; $b_{A2}P = 1.67$

If $1 > \Gamma_2 > \frac{\Gamma_B}{\Gamma_A}$ the condition for $C < 0$ is more stringent than that of the azeotrope.

It is necessary to consider also the case of $B < 0$ and $C > 0$

$$\frac{\Gamma_B}{\Gamma_2\Gamma_A} > \alpha > \frac{\Gamma_B + 1}{\Gamma_A + 1} \text{and} \Gamma_2 > \alpha \text{ or } \frac{\Gamma_B}{\Gamma_2\Gamma_A} < \alpha < \frac{\Gamma_B + 1}{\Gamma_A + 1} \text{ and } \Gamma_2 < \alpha \tag{28}$$

Of these only the subset that fulfils $B^2 > 4C$ will result in pure component isotherms that cross twice.

Categories 3 and 4 in Table 1 can have an azeotrope when the isotherms do not cross as the conditions for crossing of the isotherms are more stringent that those

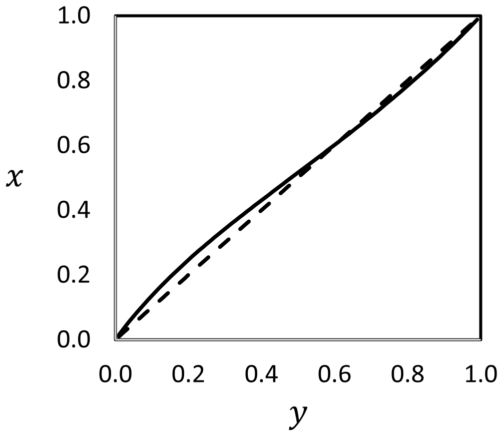

Fig. 5 System (category 4) with pure component isotherms crossing twice and the azeotrope can present below crossing pressure. $\Gamma_2 = 0.095$; $\Gamma_A = 25$; $\Gamma_B = 0.381$; $\alpha = 0.071$; $b_{A2}P = 0.05$

that lead to an azeotrope. Figure 4 shows an example of isotherms not crossing but an azeotrope is present.

For azeotropes belonging to categories 3 and 4 it has been observed that when the isotherms cross the lower bound of the azeotrope pressure is less than that of the crossing of the pure component isotherms. As an example consider the case where $B^2 \approx 4C$. Selecting parameters that will give a denominator of B close to 0 allows to increase $b_{A2}P_{Cross} \approx -B$. Figure 5 shows an example of an azeotrope belonging to category 4 where the azeotrope can be present below the pressure at which the pure component isotherms cross. In the case shown $b_{A2}P_{Az}$ is half of $b_{A2}P_{Cross} = 0.099$ (second value is 0.11), while the pressure at which an azeotrope will first occur corresponds to $b_{A2}P_{Az}(y = 1) = 0.017$.

6 Conclusions

A formal proof has been provided for the following properties valid for adsorption in a porous material (finite saturation capacity) irrespective of the adsorption isotherm:

1. At constant temperature and pressure, at the azeotrope the chemical potential of the solid and as a result the reduced grand potential are either a maximum or a minimum with respect to composition.
2. There is always a lower bound on the pressure at which an adsorption azeotrope can occur.
3. If the pure component reduced grand potentials cross an azeotrope is present.
4. Define component 1 such that $K_{P1} > K_{P2}$, the pure component isotherms and the reduced grand potentials will cross if $q_{S2} > q_{S1}$ and an azeotrope will be present.

The thermodynamically consistent DSL model has been used to show that heterogeneity of the adsorbent can lead to different categories of azeotropes that can be grouped into three mirror pairs. A formal analysis based on dimensionless ratios allows to define the category to which a system belongs and a discussion of the relationship of the azeotropes and the crossing of the pure component isotherms was included.

The condition for adsorption azeotropy for the thermodynamically consistent DSL model has been shown to be different from what was previously reported in the literature [16, 19], allowing to identify cases where previously it was thought that an azeotrope would not occur as well as cases where one would have predicted the existence of an azeotrope when in fact this would not be the case.

A concise overview of the analysis carried out for the thermodynamically consistent DSL model has been provided in Table 1. This includes a complete set of relationships that clarify if an azeotrope can occur with an upper bound on pressure; if there is a lower or upper bound on the mole fraction in the fluid phase; if an azeotrope can be present if the pure component isotherms cross; if the isotherms can cross without the presence of an azeotrope; and if the azeotrope pressure can be lower that the pressure at which the pure component isotherms cross.

Author contributions SB carried out the analysis and wrote and reviewed the manuscript.

Funding None.

Data availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethical approval Not applicable.

References

1. Lorenz, R., Wiedbrauck, E.: Über Adsorption Nr. 6. Adsorptionsgleichgewichte bei anwesenheit zweier gase. Z Anorg. Allgem. Ch. **143**, 268–276 (1925)
2. Klosky, S., Woo, L.P.L.: Adsorption of mixtures of easily condensable gases. J. Phys. Chem. **32**, 1387–1395 (1928)
3. Damkohler, G.: Über die adsorption von N_2-Ar-gemischen. Z Phys. Chem. **B23**, 69–88 (1933)
4. Broughton, D.B.: Adsorption isotherms for binary gas mixtures. Ind. Eng. Chem. **40**, 1506–1508 (1948)
5. Brunauer, S.: The adsorption of gases and vapours. In: Physical adsorption, p. 489. Oxford University Press, Oxford (1944)
6. Cook, W.H., Basmadjian, D.: The prediction of binay adsorption equilibria from pure component isotherms. Can. J. Chem. Eng. **43**, 78–83 (1965)
7. Do, D.D., Do, H.D.: On the azeotropic behaviour of adsorption systems. Adsorption **5**, 319–329 (1999)
8. Hyun, S.H., Danner, R.P.: Equilibrium adsorption of ethane, ethylene, isobutane, carbon dioxide, and their binary mixtures on 13X molecular sieves. J. Chem. Eng. Data **27**, 196–200 (1982)
9. Talu, O., Zwiebel, I.: Multicomponent adsorption equilibria of nonideal mixtures. AIChE J. **32**, 1263–1276 (1986)
10. Zheng, Y., Gu, T.: Modified van der Waals equation for the prediction of multicomponent isotherms. J. Colloid Interface Sci. **206**, 457–463 (1998)
11. Siperstein, F., Myers, A.L.: Mixed-gas adsorption. AIChE J. **47**, 1141–1159 (2001)
12. Basmadjian, D., Coroyannakis, P., Karayannopoulos, C.: Equilibrium theory revisited. Isothermal fixed-bed sorption of binary systems – II. Non-langmuir solutes with type I parent isotherms: azeotropic systems. Chem. Eng. Sci. **42**, 1737–1752 (1987)
13. Toyoda, I., Adachi, N., Kato, S., Kawasaki, J.: Simulation of fixed-bed adsorption of CO_2–C_2H_4-zeolite 5A system with azeotropic behavior. J. Chem. Eng. Jpn. **20**, 434–437 (1987)
14. Persichini, C., Mersmann, A.: Breakthrough behaviour of a binary gas mixture with azeotropic adsorption equilibrium. Chem. Eng. Tech. **13**, 8–14 (1990)
15. Luberti, M., Mennitto, R., Brandani, S., Santori, G., Sarkisov, L.: Activity coefficient models for accurate prediction of adsorption azeotropes. Adsorption **27**, 1191–1206 (2021)
16. Jiang, H., Ebner, A.D., Ritter, J.A.: Theoretical analysis of the necessary and sufficient conditions for the formation of adsorption azeotropes in binary gas mixtures. Langmuir **37**, 12584–13594 (2021)
17. Myers, A.L.: Activity coefficients of mixtures adsorbed on heterogeneous surfaces. AIChE J. **29**, 691–693 (1983)
18. Siperstein, F.: Determination of azeotropic behavior in adsorbed mixtures. Adsorption. **11**, 55–59 (2005)
19. Jiang, H., Ebner, A.D., Ritter, J.A.: Theoretical analysis of the pressure regions where adsorption azeotropes exist in binary gas mixtures. ACS Omega **7**, 43242–43254 (2022)
20. Myers, A.L., Prausnitz, J.M.: Thermodynamics of mixed-gas adsorption. AIChE J. **11**, 121–127 (1965)
21. Talu, O., Myers, A.L.: Rigorous thermodynamic treatment of gas adsorption. AIChE J. **34**, 1887–1893 (1988)
22. Brandani, S.: The rigid adsorbent lattice fluid model: thermodynamic consistency and relationship to the real adsorbed solution theory. Membranes **12**, 1009 (2022)
23. Ruthven, D.M.: Principles of adsorption and adsorption processes. Wiley, New York (1984)
24. Myers, A.L., Monson, P.: Physical adsorption of gases: the case for absolute adsorption as the basis for thermodynamic analysis. Adsorption **20**, 591–622 (2014)