

Theoretical Analysis of the Pressure Regions Where Adsorption Azeotropes Exist in Binary Gas Mixtures

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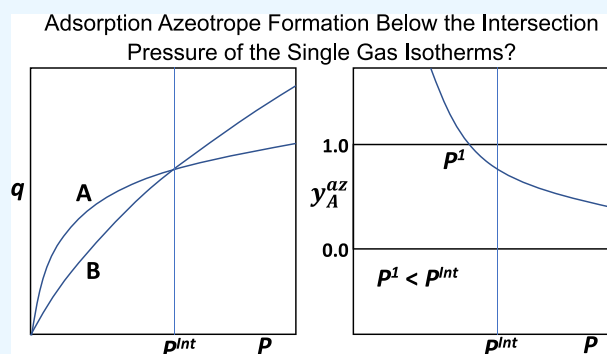
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ABSTRACT: This work confirmed theoretically whether adsorption azeotropes can form in a binary gas mixture at a pressure P below the intersection pressure of the corresponding single-gas isotherms. The thermodynamically consistent dual-process Langmuir (DPL) model with equal component i saturation capacities $q_{i,j}^s$ on site j and the general DPL model with nonequal $q_{i,j}^s$ on site j were used for this purpose. Relationships derived from both DPL models, in terms of the single-gas isotherm DPL model parameters, were used to answer this question. When the P range where adsorption azeotropes always exist is infinite beyond the onset P of adsorption azeotropic formation, both DPL models and experimental data showed that it is possible to form adsorption azeotropes in the corresponding binary gas mixture at pressures not only above but even below the single-gas isotherm intersection P . When the P range where adsorption azeotropes always exist is finite beyond the onset P of adsorption azeotropic formation, only the general DPL model predicts the onset P of this finite P range can be below the intersection P of the corresponding single-gas isotherms. Without theoretical proof, the thermodynamically consistent DPL model seemingly restricts this P range to be equal to or greater than the intersection P of the corresponding single-gas isotherms. For a finite P region where adsorption azeotropes always exist in a binary gas mixture, the binary selectivity inverts when traversing from below the lower onset P to the higher cessation P . Both models also showed, counterintuitively, that perfect positive energetic site matching can result in the formation of adsorption azeotropes in binary gas mixtures, not just perfect negative energetic site matching. Overall, this work provides some confirmation that it is indeed possible to form adsorption azeotropes in a binary gas mixture at pressures below the intersection P of the corresponding single-gas isotherms based on two physically sound formulations of the DPL model.



INTRODUCTION

Azeotropic behavior in binary vapor–liquid equilibria (VLE)¹ and adsorption azeotropic behavior in gas–solid adsorption equilibria^{2–38} are very similar with both being quite common, as noted recently by Jiang et al.³⁹ An adsorption azeotrope occurs when the gas (y_i) and adsorbed (x_i) phase mole fractions in a binary gas mixture are equal at a given temperature (T) and pressure (P), i.e., when they intersect the 45° diagonal on an x – y diagram at constant T and P . Just like in VLE, this means that the selectivity $S_{12} = (x_1/y_1)/(x_2/y_2) = 1.0$ at this point.

Numerous articles are reported in the literature on the experimental formation of adsorption azeotropes in binary gas mixtures for a variety of adsorbate–adsorbent systems.^{2,3,8,9,12,14,15,33,35–37} Numerous articles are also reported in the literature on the development of models or correlations that predict adsorption azeotrope behavior.^{4–14,17,18,20–26,29–32,34–36,38,39} The most recent work by Jiang et al.³⁹ theoretically assessed the necessary and sufficient conditions for the formation of an adsorption azeotrope in a binary gas mixture when this mixture exhibits either

intersecting or nonintersecting single-gas isotherms. However, none of these articles have ever clearly answered the question of whether adsorption azeotropes can form in a binary gas mixture below the intersection P of the corresponding single-gas isotherms.

Cook and Basmadjian¹³ may have been the first to reveal with their model that, for intersecting single-gas isotherms, a specific P range exists where the corresponding binary gas mixture always exhibits an adsorption azeotrope. Based on speculative extrapolation of their theoretical analysis with the data of Damkohler,² they inferred that this P range is above the intersection P of the corresponding single-gas isotherms. With no proof or reference for substantiation, Dunne and Myers⁴⁰

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proclaimed that adsorption azeotropes in a binary gas mixture form only at pressures above the intersection P of the corresponding single-gas isotherms. This statement could be conjectured from earlier work by Kidnay and Myers,²³ where they stated selectivity reversal would occur in an ideal adsorbed solution of a binary gas mixture only at pressures above the intersection P of the corresponding single-gas isotherms and necessarily at the intersection P of the corresponding single-gas spreading pressures. Do and Do¹⁹ derived a theoretical relationship for the threshold P of a binary gas mixture, above which an adsorption azeotrope is always exhibited. However, they did not state where this threshold P lies relative to the intersection P of the corresponding single-gas isotherms. Subsequently, Nguyen and Do²¹ also asserted without any justification that this threshold P of a binary gas mixture corresponds to the intersection P of the corresponding single-gas isotherms, a statement in stark contrast to the argument posed by Kidnay and Myers.²³ Clearly, from these limited sources, the question of whether adsorption azeotropes can form in a binary gas mixture below the intersection P of the corresponding single-gas isotherms has not been answered.

Therefore, to provide resolution to this puzzling question, the objective of this work is to confirm theoretically whether adsorption azeotropes can form in a binary mixture below the intersection P of the corresponding single-gas isotherms. Like in the previous work by the authors,³⁹ which showed that an adsorption azeotrope may form in a binary gas mixture when this mixture exhibits nonintersecting or may not form when exhibiting intersecting single-gas isotherms, the thermodynamically consistent and general dual-process Langmuir (DPL) models are used for this purpose. Relationships derived from both DPL models, in terms of the single-gas isotherm DPL model parameters, are used to find examples that disclose the P region in a binary gas mixture where adsorption azeotropes always exist relative to the intersection P of the single-gas isotherms. The upshot is that the relationship between the intersection P of the single-gas isotherms and the P range over which adsorption azeotropes form in the corresponding binary gas mixture is revealed by both DPL models and also by experimental data from the literature when applied to the general DPL model. The relationship between energetic site matching based on the single-gas isotherm DPL model parameters and adsorption azeotrope formation in the corresponding binary gas mixture is also examined with these DPL models.

METHODS

To evaluate the relationship between the P region in a binary gas mixture where an adsorption azeotrope always exists and the intersection P of the corresponding single-gas isotherms, the DPL model is utilized in two different formulations. The first formulation is called the thermodynamically consistent DPL model, and the second formulation is called the general DPL model, which is thermodynamically inconsistent.³¹ However, the errors associated with using the later DPL model are typically small⁴¹ and offset by its effectiveness for predicting mixed-gas adsorption equilibria, including adsorption azeotropes.³¹

Do and Do¹⁹ carried out a similar but very limited analysis of adsorption azeotrope formation in a binary gas mixture using a DPL model for one of the components and a single-process Langmuir (SPL) model for the other component. However, they did not consider the relationship between the

single-gas isotherm intersection P and the P range for which the corresponding binary gas mixture always exhibits an adsorption azeotrope. In the ensuing analysis with the DPL model applied to both components, the relationship between the single-gas isotherm intersection P and the P range for which the corresponding binary gas mixture always exhibits an adsorption azeotrope is evaluated.

General DPL Model. The general DPL model for single (pure) gases is given by

$$q_i^P = \frac{K_{i,1}P}{1 + b_{i,1}P} + \frac{K_{i,2}P}{1 + b_{i,2}P} \quad (1)$$

where K_{ij} is the Henry's law constant and given by

$$K_{i,j} = q_{i,j}^s b_{i,j} \quad (2)$$

$i = A$ or B , and $q_{i,j}^s$ and $b_{i,j}$ are respectively the saturation capacities (or loadings) and the affinities of component i for process or site j . Without loss of generality, it is assumed that component A is the more strongly adsorbed species in the Henry's law region, i.e.,

$$K_A > K_B \quad (3)$$

where

$$K_i = K_{i,1} + K_{i,2} \quad (4)$$

and where for site 1, the following is always assumed,

$$K_{A,1} - K_{B,1} > 0 \quad (5)$$

For a binary gas mixture, the corresponding general DPL model is given by

$$q_i = \frac{K_{i,1}P y_i}{1 + b_{A,1}P y_A + b_{B,1}P y_B} + \frac{K_{i,2}P y_i}{1 + b_{A,2}P y_A + b_{B,2}P y_B} \quad (6)$$

For this general DPL model formulation, the saturation loadings of each component i on site j are not equal, i.e., $q_{A,j}^s \neq q_{B,j}^s$. At the adsorption azeotrope,

$$y_i = x_i \quad (7)$$

where $x_i = \frac{q_i}{q_A + q_B}$. Applying eq 6 to eq 7 leads to

$$\frac{-K_{A,1} + K_{B,1}}{1 + b_{A,1}P y_A + b_{B,1}P y_B} = \frac{K_{A,2} - K_{B,2}}{1 + b_{A,2}P y_A + b_{B,2}P y_B} \quad (8)$$

Notice that $K_{A,1} - K_{B,1}$ and $K_{A,2} - K_{B,2}$ in eq 8 must be opposite in sign to satisfy the condition for the existence of an adsorption azeotrope. The value of y_A that satisfies eq 8, which is defined as y_A^{az} , is given by

$$y_A^{az} = \frac{(1 + b_{B,2}P) - \chi(1 + b_{B,1}P)}{\chi(b_{A,1} - b_{B,1}) - (b_{A,2} - b_{B,2})P} \quad (9)$$

where

$$\chi = \frac{(K_{B2} - K_{A2})}{(K_{A1} - K_{B1})} \quad (10)$$

An adsorption azeotrope exists only when $0 < y_A^{az} < 1$. Also, because $K_{A,1} - K_{B,1}$ and $K_{A,2} - K_{B,2}$ must be opposite in sign for an adsorption azeotrope to exist, eqs 3 and 5 lead to

$$0 < \chi < 1 \quad (11)$$

When $\chi = 1$, an adsorption azeotrope can form but it is not guaranteed. When $\chi \leq 0$, an adsorption azeotrope does not exist. It is important to identify the bounding pressures P^0 and P^1 for which y_A^{az} is respectively equal to 0 and 1. These expressions are obtained directly from eq 9, as

$$P^0 = \frac{1 - \chi}{\chi b_{B1} - b_{B2}} \quad (12)$$

$$P^1 = \frac{1 - \chi}{\chi b_{A1} - b_{A2}} \quad (13)$$

For a given P , the condition for the intersection of the single-gas isotherms is given by

$$q_A^P = q_B^P \quad (14)$$

where

$$P = P_A = P_B \quad (15)$$

Equations 1, 14, and 15 lead to the following expression,

$$\begin{aligned} q_A^P - q_B^P &= \frac{K_{A,1}}{1 + b_{A,1}P} + \frac{K_{A,2}}{1 + b_{A,2}P} - \frac{K_{B,1}}{1 + b_{B,1}P} \\ &\quad - \frac{K_{B,2}}{1 + b_{B,2}P} \\ &= 0 \end{aligned} \quad (16)$$

or

$$\begin{aligned} &[(q_{A,1}^s b_{A,1} - q_{B,1}^s b_{B,1}) + b_{A,1} b_{B,1} P (q_{A,1}^s - q_{B,1}^s)](1 + b_{A,2}P) \\ &\quad (1 + b_{B,2}P)P + \\ &[(q_{A,2}^s b_{A,2} - q_{B,2}^s b_{B,2}) + b_{A,2} b_{B,2} P (q_{A,2}^s - q_{B,2}^s)](1 + b_{A,1}P) \\ &\quad (1 + b_{B,1}P)P \\ &= 0 \end{aligned} \quad (17)$$

The left hand side (LHS) of eq 17 is a fourth-order expression in P , with one of its roots being the trivial solution $P = 0$. After canceling the common P terms and simplifying, eq 17 becomes a third-order expression in P , i.e.,

$$f(P) = a_f P^3 + b_f P^2 + c_f P + d_f = 0 \quad (18)$$

where

$$a_f = b_{A,1} b_{A,2} b_{B,1} b_{B,2} (q_A^s - q_B^s) \quad (19)$$

$$\begin{aligned} b_f &= b_{A,1} b_{A,2} ((b_{B,1} + b_{B,2}) q_A^s - K_B) \\ &\quad - b_{B,1} b_{B,2} ((b_{A,1} + b_{A,2}) q_B^s - K_A) \end{aligned} \quad (20)$$

$$\begin{aligned} c_f &= b_{A,1} b_{A,2} q_A^s - b_{B,1} b_{B,2} q_B^s + (b_{B,1} + b_{B,2}) K_A \\ &\quad - (b_{A,1} + b_{A,2}) K_B \end{aligned} \quad (21)$$

$$d_f = K_A - K_B \quad (22)$$

with

$$q_i^s = q_{i,1}^s + q_{i,2}^s \quad (23)$$

and with its discriminant given by

$$\Delta_f = 18a_f b_f c_f d_f - 4b_f^3 d_f^2 + b_f^2 c_f^2 - 4a_f c_f^3 - 27a_f^2 d_f^2 \quad (24)$$

All the possible cases of intersecting and nonintersecting single-gas isotherms resulting from eq 18 are depicted elsewhere.³⁹ It suffices to state here that nonintersecting single-gas isotherms are granted only when both $a_f > 0$ and $\Delta_f < 0$ and that it is not possible to have nonintersecting single-gas isotherms when $a_f < 0$. These conditions are revisited later in this work.

Thermodynamically Consistent DPL Model. The thermodynamically consistent DPL model for single (pure) gases is still given by eqs 1 and 2. The thermodynamically consistent DPL model for a binary gas mixture is also given by eq 6, but now with the stipulation that the saturation loadings of each component i on site j are identical, i.e.,

$$q_{A,j}^s = q_{B,j}^s = q_j^s \quad (25)$$

As before, component A is assumed to be the more strongly adsorbed species in the Henry's law region, i.e.,

$$K_A > K_B \quad (26)$$

where

$$K_i = K_{i,1} + K_{i,2} \quad (27)$$

Equations 26 and 27 are the same as eqs 3 and 4. Also, for site 1, the following is always assumed

$$b_{A,1} - b_{B,1} > 0 \quad (28)$$

while noting that, for the thermodynamically consistent DPL model, the affinities (b_{ij}) can be used instead of the Henry's law constants (K_{ij}) (eq 5) because the saturation capacities ($q_{i,j}^s$) on each site cancel out.

According to the adsorption azeotrope condition in eq 7, the adsorption azeotrope relationship for this thermodynamically consistent DPL model is given by

$$\frac{-b_{A,1} + b_{B,1}}{1 + b_{A,1} P y_A + b_{B,1} P y_B} = \frac{b_{A,2} - b_{B,2}}{1 + b_{A,2} P y_A + b_{B,2} P y_B} \frac{q_2^s}{q_1^s} \quad (29)$$

with y_A^{az} given by

$$y_A^{az} = \frac{\chi(1 + b_{B,1}P) - (1 + b_{B,2}P) \frac{1}{P}}{\left(1 + \frac{q_2^s}{q_1^s}\right)(b_{A,2} - b_{B,2})} \quad (30)$$

and χ given by

$$\chi = \frac{(b_{B2} - b_{A2}) q_2^s}{(b_{A1} - b_{B1}) q_1^s} \quad (31)$$

For this thermodynamically consistent DPL model, an adsorption azeotrope exists only when $b_{A,1} - b_{B,1}$ and $b_{A,2} - b_{B,2}$ are opposite in sign and just like with the general DPL model, when

$$0 < \chi < 1 \quad (32)$$

When $\chi = 1$, an adsorption azeotrope can form, but it is not guaranteed. When $\chi \leq 0$, an adsorption azeotrope does not exist. P^0 and P^1 are still given by eqs 12 and 13, respectively.

The condition for the intersection of single-gas isotherms is still given by eq 14. For this thermodynamically consistent DPL model, this condition, along with eqs 1 and 15, leads to

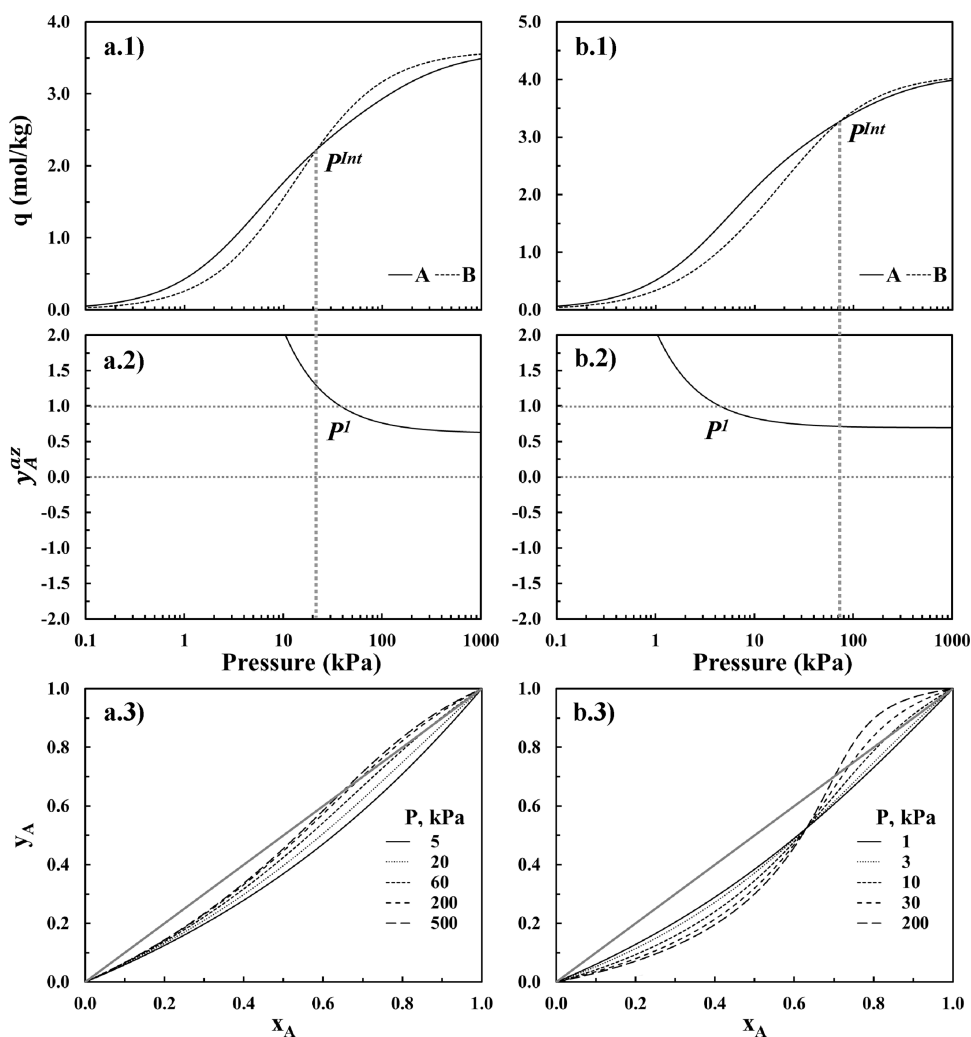


Figure 1. Thermodynamically consistent DPL model where two intersecting single-gas isotherms result in the formation of adsorption azeotropes in the corresponding binary gas mixtures (Cases 1 and 2 in Table 1): single-gas isotherms of components A and B for Cases 1 (a.1) and 2 (b.1), corresponding P regions for adsorption azeotrope existence in terms of y_A^{az} for Cases 1 (a.2) and 2 (b.2) with $P^{\text{int}} < P^1$ (Case 1) and $P^{\text{int}} > P^1$ (Case 2), and corresponding x - y diagrams for Cases 1 (a.3) and 2 (b.3).

$$q_A^P - q_B^P = q_1^s \left(\frac{b_{A,1}}{1 + b_{A,1}P} - \frac{b_{B,1}}{1 + b_{B,1}P} \right) + q_2^s \left(\frac{b_{A,2}}{1 + b_{A,2}P} - \frac{b_{B,2}}{1 + b_{B,2}P} \right) = 0 \quad (33)$$

or

$$q_1^s(b_{A,1} - b_{B,1})(1 + b_{A,2}P)(1 + b_{B,2}P)P + q_2^s(b_{A,2} - b_{B,2})(1 + b_{A,1}P)(1 + b_{B,1}P)P = 0 \quad (34)$$

The LHS of eq 34 is a third-order expression in P with one of its roots being the trivial solution $P = 0$. After canceling the common P terms and simplifying, eq 34 becomes a second-order expression in P , i.e.,

$$g(P) = a_g P^2 + b_g P + c_g = 0 \quad (35)$$

where

$$a_g = b_{A,2}b_{B,2}(b_{A,1} - b_{B,1})q_1^s + b_{A,1}b_{B,1}(b_{A,2} - b_{B,2})q_2^s \quad (36)$$

$$b_g = (b_{A,2} + b_{B,2})(b_{A,1} - b_{B,1})q_1^s + (b_{A,1} + b_{B,1})(b_{A,2} - b_{B,2})q_2^s \quad (37)$$

$$c_g = K_A - K_B \quad (38)$$

and with its discriminant given by

$$\Delta_g = b_g^2 - 4a_g c_g \quad (39)$$

Again, all the possible cases of intersecting and nonintersecting single-gas isotherms resulting from eq 35 are depicted elsewhere.³⁹ As previously noted with the general DPL model, nonintersecting single-gas isotherms are granted only when both $a_g > 0$ and $\Delta_g < 0$, and that it is not possible to have nonintersecting single-gas isotherms when $a_g < 0$. These important conditions are revisited later in this work.

RESULTS

The theoretical developments provide a framework to reveal whether an adsorption azeotrope can form in a binary gas

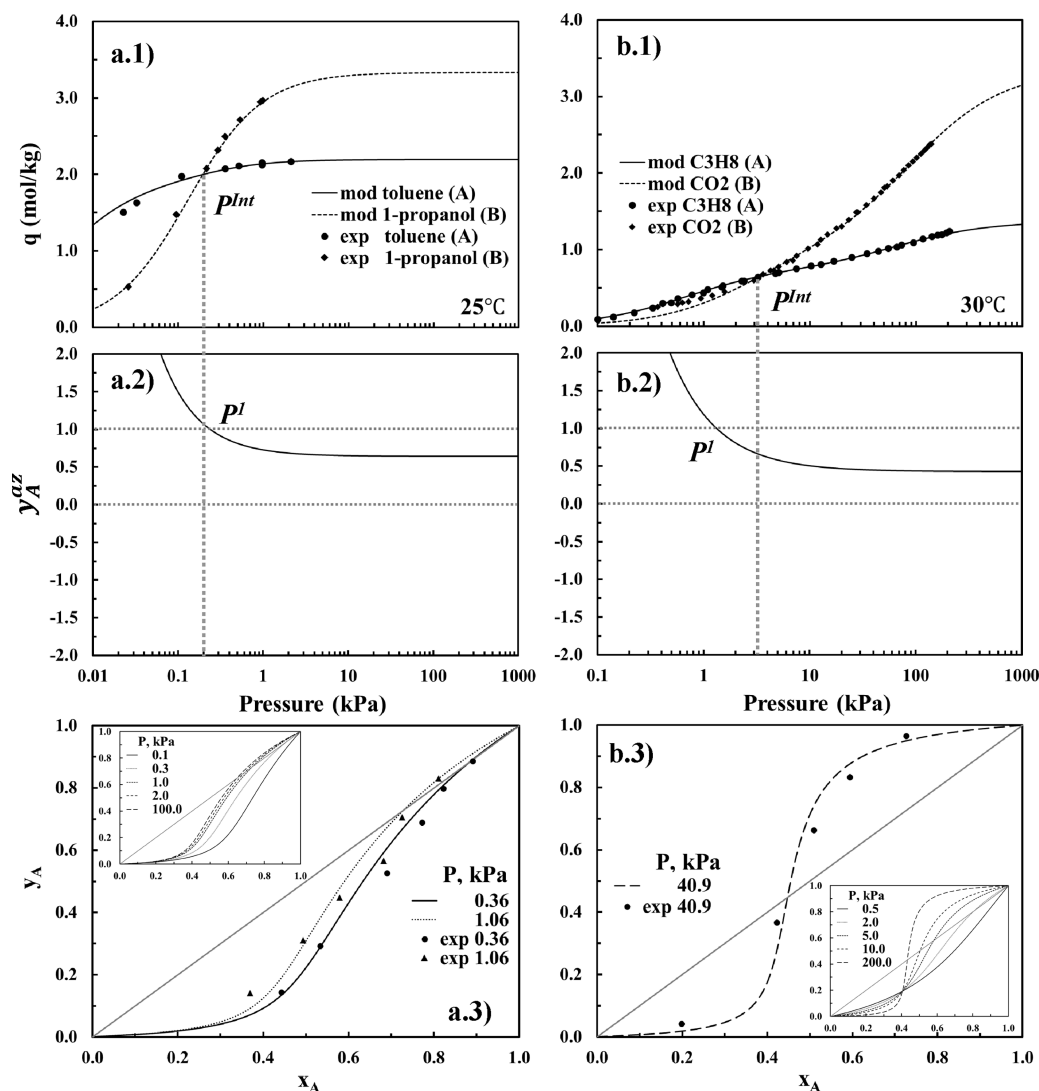


Figure 2. Experimental data for $\text{C}_6\text{H}_5\text{CH}_3$ (toluene) and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (1-propanol) on dealuminated Y (DAY) zeolite at 25 °C⁸ (a.1–a.3) and C_3H_8 (propane) and CO_2 (carbon dioxide) on H-mordenite at 30 °C⁹ (b.1–b.3) where two intersecting single-gas isotherms result in the formation of adsorption azeotropes in the corresponding binary gas mixtures (Cases 3 and 4 in Table 1): single-gas isotherms for $\text{C}_6\text{H}_5\text{CH}_3$ – $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ on DAY zeolite (a.1) and C_3H_8 – CO_2 on H-mordenite (b.1) fitted to the general DPL model (lines), corresponding P regions for adsorption azeotrope existence in terms of y_A^{az} with $P^{\text{int}} < P^1$ (Case 3) and $P^{\text{int}} > P^1$ (Case 4), and corresponding x – y diagrams for $\text{C}_6\text{H}_5\text{CH}_3$ – $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ on DAY zeolite (a.3) and C_3H_8 – CO_2 on H-mordenite (b.3), along with general DPL model predictions for the experimental P and several different P shown in the inserts.

mixture at pressures below the intersection P of the corresponding single-gas isotherms. Several cases are considered to prove or disprove this notion using the thermodynamically consistent and general DPL models. To further validate the findings, the general DPL model is also applied to two experimental systems in the literature that exhibit intersecting single-gas isotherms while the corresponding binary gas mixtures exhibit adsorption azeotropes.

Ten different cases are considered that answer the question on the single-gas isotherm intersection P relative to the P region where adsorption azeotropes exist in the corresponding binary gas mixture. All of the cases are demonstrated with examples, where the single-gas isotherm parameters are determined by trial and error while using the established constraints from the theoretical developments for each DPL model, just like in the previous work.³⁹ The results from all 10 cases are displayed in Figures 1–5, with the corresponding

single-gas isotherm parameters and adsorption azeotrope existence parameters listed in Table 1.

Figures 1–5 each has top, middle, and bottom sets of panels that respectively display the single-gas isotherms of the individual gases in the binary gas mixture, y_A^{az} as a function of P for the corresponding binary gas mixture, and x – y diagrams for the binary gas mixture at a given T and several different P . The horizontal sets of panels in each figure display a different case for each situation. The results are provided below.

The notion is to prove that an adsorption azeotrope in a binary gas mixture can form at pressures below the intersection P of the corresponding single-gas isotherms. This could not be gleaned from the six scenarios analyzed in the previous work by the authors.³⁹ In that work, when an adsorption azeotrope in a binary gas mixture formed, the corresponding single-gas isotherms did not intersect, and when the single-gas isotherms

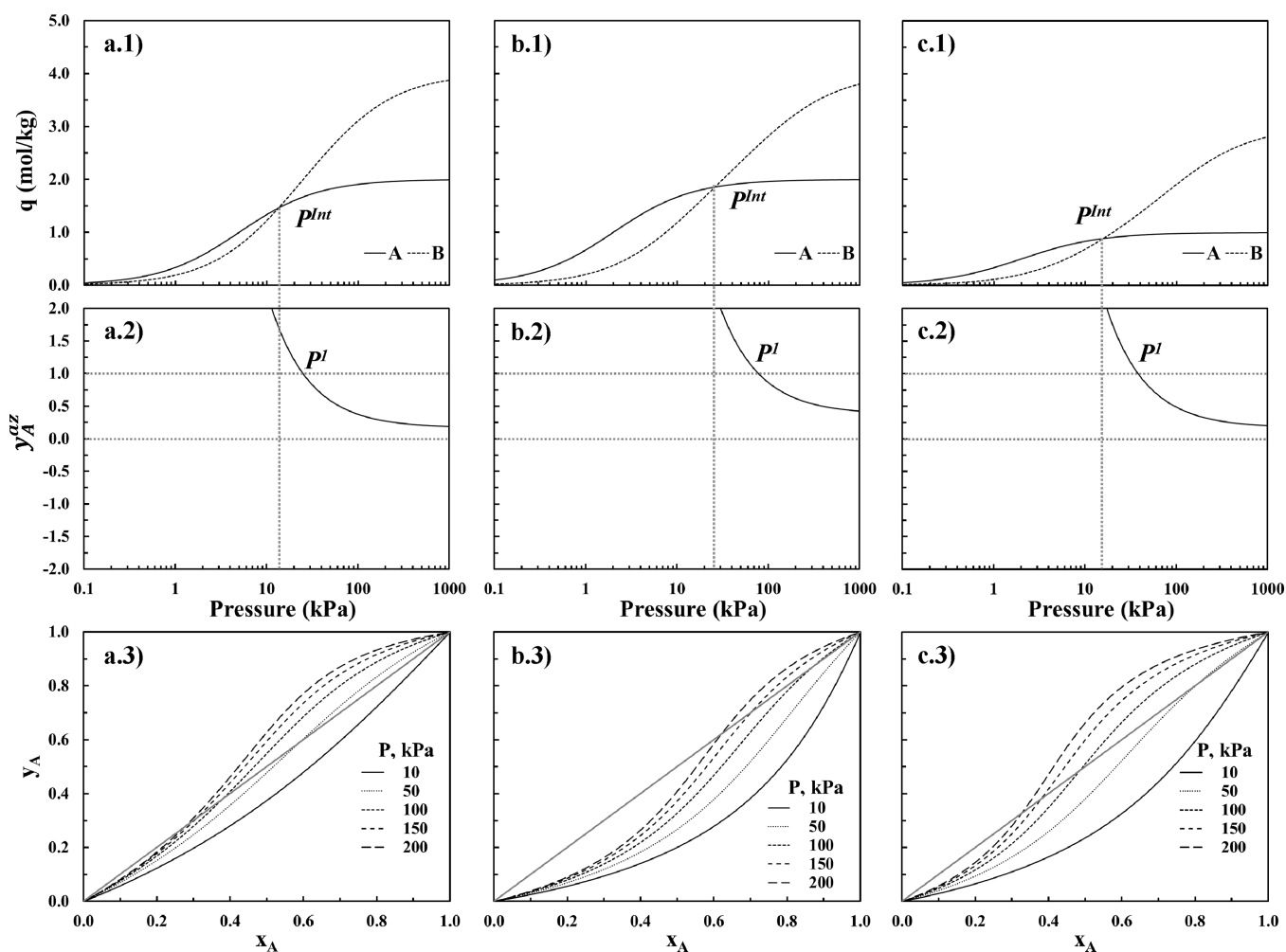


Figure 3. General DPL model where two intersecting single-gas isotherms result in the formation of adsorption azeotropes in the corresponding binary gas mixtures defined by Do and Do¹⁹ (Cases 5, 6, and 7 in Table 1): single-gas isotherms of components A and B for Cases 5 (a.1), 6 (b.1), and 7 (c.1), corresponding P regions for adsorption azeotrope existence in terms of y_A^{az} with $P^{int} < P^I$ for Cases 5 (a.2), 6 (b.2), and 7 (c.2), and corresponding x - y diagrams for Cases 5 (a.3), 6 (b.3), and 7 (c.3).

did intersect, an adsorption azeotrope did not form in the corresponding binary gas mixture.

To prove the notion above, the thermodynamically consistent DPL model was used first because intersecting single-gas isotherms ensure that the corresponding binary gas mixture exhibits an adsorption azeotrope.³⁹ Several sets of thermodynamically consistent DPL model parameters were found that prove adsorption azeotropes in binary gas mixtures can form at pressures above or below the intersection P of the corresponding single-gas isotherms. Just two of the numerous situations where y_A^{az} (eq 9) falls in between 0 and 1 are plotted in Figure 1. The DPL isotherm parameters and the corresponding values of χ , a_g , and Δ_g used to obtain these results, along with the resulting P^{int} , P^0 and P^I , are given in Table 1 (Cases 1 and 2). The parameters listed in Table 1 were obtained by trial and error, while ensuring a negative coefficient a_g (eq 36) and χ values between 0 and 1. The first constraint ensures the single-gas isotherms intersect, while the second constraint ensures an adsorption azeotrope does exist.

For Cases 1 and 2, Figure 1a.1,b.1 and the parameter values in Table 1 show that the isotherms do intersect each other. Figure 1a.2,b.2 also shows that the formation of adsorption azeotropes in these binary gas mixtures is possible only for

pressures $\geq P^I = 38.18$ kPa for Case 1 and $\geq P^I = 4.50$ kPa for Case 2. Both P^0 are negative in these cases (Table 1), and thus, neither has any real significance. For Case 1, the intersection P of the single-gas isotherms is 21.9 kPa (Figure 1b.1), which is below the onset P of azeotropic behavior in this binary gas mixture, which is 38.18 kPa (Figure 1b.2), and as pressure increases beyond P^I , y_A^{az} decreases to a constant value of about 0.73 at pressures larger than about 900 kPa with an adsorption azeotrope always existing as $P \rightarrow \infty$. In contrast, for Case 2, the intersection P of the single-gas isotherms is 70.7 kPa (Figure 1a.1), which is above the onset P of azeotropic behavior in this binary gas, which is 4.50 kPa (Figure 1a.2), and as pressure increases beyond P^I , y_A^{az} decreases to a constant value of about 0.73 at pressures larger than about 70 kPa, again with an adsorption azeotrope always existing as $P \rightarrow \infty$. Figure 1a.3,b.3 shows that the respective x_A - y_A curves intersect the 45° diagonal above P^I , i.e., in the adsorption azeotrope existence regions. Based on the thermodynamically consistent DPL model, these results prove that an adsorption azeotrope in a binary gas mixture can form at pressures either above or even below the intersection P of the corresponding single-gas isotherms.

Figure 2 provides two examples from the literature where experimental data are consistent with the results in Figure 1.

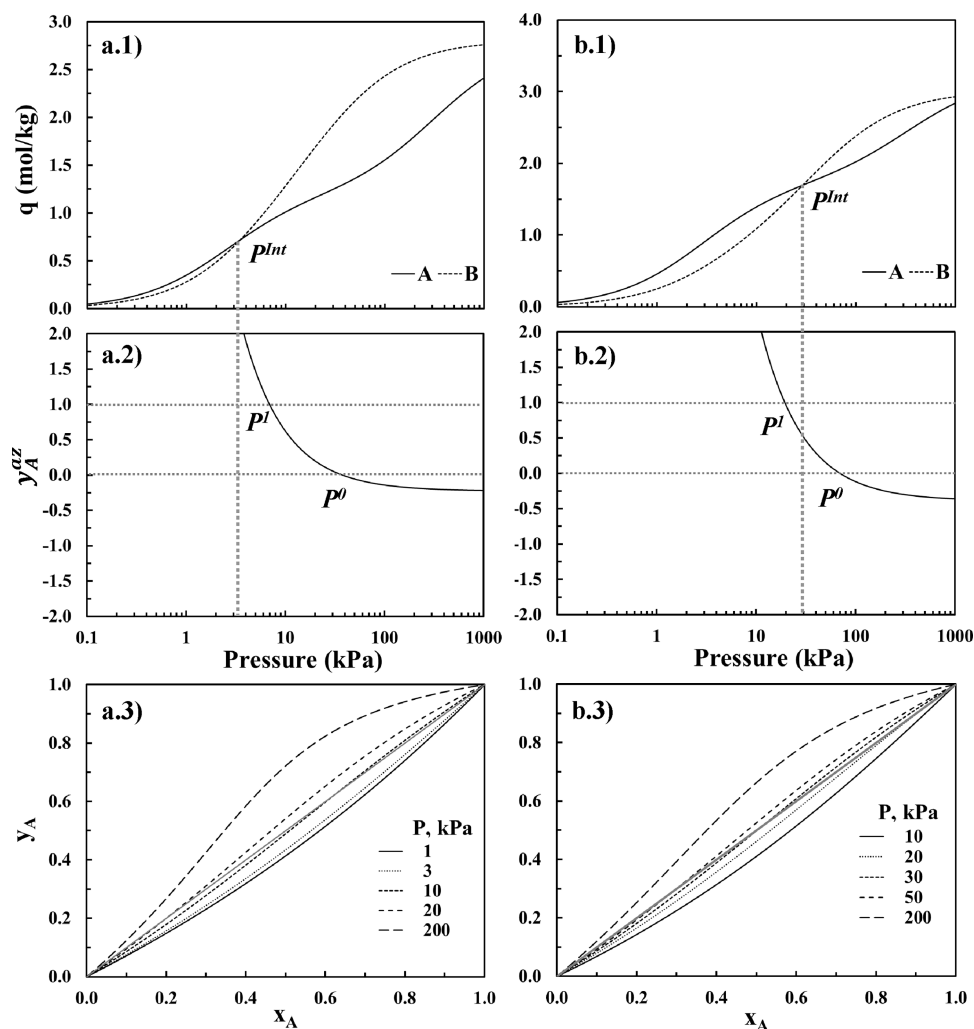


Figure 4. Thermodynamically consistent (a) and general (b) DPL models where two intersecting single-gas isotherms result in the formation of adsorption azeotropes in the corresponding binary gas mixtures (Cases 8 and 9 in Table 1): single-gas isotherms of components A and B for Cases 8 (a.1) and 9 (b.1), corresponding P regions for adsorption azeotrope existence in terms of y_A^{az} for Cases 8 (a.2) and 9 (b.2) with $P^{\text{int}} < P^1 < P^0$ (Case 8) and $P^1 < P^{\text{int}} < P^0$ (Case 9), and corresponding x - y diagrams for Cases 8 (a.3) and 9 (b.3).

Figure 2a shows the results for $\text{C}_6\text{H}_5\text{CH}_3$ (toluene) and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (1-propanol) on dealuminated Y (DAY) zeolite at 25°C ,⁸ and Figure 2b shows the results for C_3H_8 (propane) and CO_2 (carbon dioxide) on H-mordenite at 30°C .⁹ In both examples, the experimental single-gas isotherms intersect each other (Figure 2a.1,b.1), and the corresponding binary gas mixtures both exhibit experimental adsorption azeotropes (Figure 2a.3,b.3). Also in both examples, the experimental adsorption azeotropes occur at pressures above the intersection pressures of the corresponding single-gas isotherms; however, these narrow experimental conditions do not provide any information about the single-gas isotherm intersection P and the corresponding P region where adsorption azeotropes always exist in a binary gas mixture.

To resolve this issue, the general DPL model was applied to these two experimental data sets to determine the P regions where adsorption azeotropes always exist in these binary gas mixtures. The general DPL isotherm parameters and the corresponding values of χ , a_f , and Δ_f used to obtain these results, along with the resulting P^0 and P^1 , are given in Table 1 (Cases 3 and 4). Note that once the single-gas isotherm parameters for each gas were obtained independently by nonlinear regression with each experimental data set, the

constraint that a_f must be a negative coefficient (eq 36) to ensure the single-gas isotherms intersect and the constraint that χ must be in between 0 and 1 to ensure an adsorption azeotrope exists are determined strictly by the resulting DPL single-gas isotherm parameters, with no adjustments possible.

For Cases 3 and 4, Figure 2a.1,b.1 and the parameter values in Table 1 show that the general DPL model correlations agree very well with the experimental data sets and that the isotherms do intersect each other. Figure 2a.3,b.3 also shows that the general DPL model predicts the x - y diagrams very well for these two binary gas mixtures, including their adsorption azeotrope compositions. Figure 2a.2 and Table 1 reveal that the onset pressure P^0 of adsorption azeotrope formation in the $\text{C}_6\text{H}_5\text{CH}_3$ - $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ binary gas mixture on DAY zeolite occurs at pressures above the single-gas isotherm intersection P , in agreement with the theoretical results in Figure 1a. In contrast, Figure 2b.2 and Table 1 reveal that the onset pressure P^0 of adsorption azeotrope formation in the CO_2 - C_3H_8 binary gas mixture on H-mordenite occurs below the single-gas isotherm intersection P , in agreement with the theoretical results in Figure 1b. Based on the general DPL model, these results show theoretically, in conjunction with experimental data, that an adsorption azeotrope in a binary gas

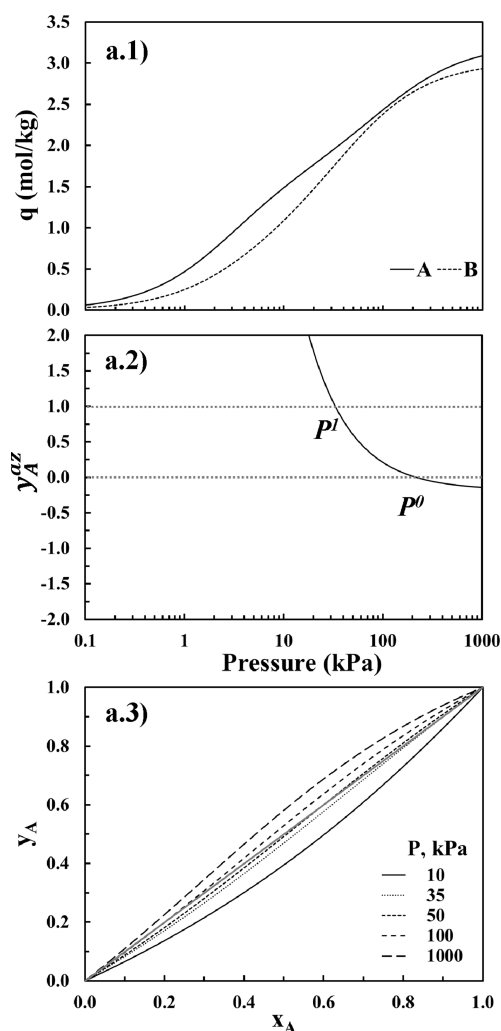


Figure 5. General DPL model where two nonintersecting single-gas isotherms result in the formation of adsorption azeotropes in the corresponding binary gas mixture (Case 10 in Table 1): single-gas isotherms of components A and B for Case 10 (a.1), corresponding P regions for adsorption azeotrope existence in terms of y_A^{az} for Case 10 (a.2), and corresponding x - y diagrams for Case 10 (a.3).

mixture can form at pressures either above or even below the intersection P of the corresponding single-gas isotherms.

It is interesting that for both experimental cases (Figure 2), as well as for the theoretical cases considered so far (Cases 1–4 in Table 1 and Figures 1 and 2), the y_A^{az} functions level off inside the binary gas mixture adsorption azeotropic existence P regions as $P \rightarrow \infty$. As mentioned earlier, this means for the binary gas mixtures that exhibit adsorption azeotropic behavior in these examples, they always exhibit an adsorption azeotrope above the onset or threshold P (either P^0 or P^1), providing an infinite range of pressures as $P \rightarrow \infty$ beyond these onset pressures where adsorption azeotropes always exist. The same behavior was observed when applying the three sets of DPL and SPL model parameters from the work of Do and Do¹⁹ to the theoretical developments herein, i.e., their three binary gas mixtures also exhibited an infinite range of pressures where adsorption azeotropes always exist once beyond the threshold pressures. These results are shown in Figure 3 and correspond to Cases 5, 6, and 7 in Table 1.

For Cases 5, 6, and 7, Figure 3a.1–c.1 and the parameter values in Table 1 show that the isotherms do intersect each

other. Figure 3a.2–c.2 also show that the formation of adsorption azeotropes in these binary gas mixtures is possible only for pressures $\geq P^1 = 25$ kPa for Case 5, $\geq P^1 = 78$ kPa for Case 6 and $\geq P^1 = 38$ kPa for Case 7. The P^0 are negative in these cases (Table 1) and thus do not have any real significance. For Case 5, the intersection P of the single-gas isotherms is 13.4 kPa (Figure 3a.1), which is below the onset P of azeotropic behavior in this binary gas mixture, which is 25 kPa (Figure 3a.2), and as pressure increases beyond P^1 , y_A^{az} decreases to a constant value of about 0.2 at pressures larger than about 1000 kPa with an adsorption azeotrope always existing as $P \rightarrow \infty$. For Case 6, the intersection P of the single-gas isotherms is 26 kPa (Figure 3b.1), which again is below the onset P of azeotropic behavior in this binary gas, which is 78 kPa (Figure 3b.2), and as pressure increases beyond P^1 , y_A^{az} decreases to a constant value of about 0.4 at pressures larger than about 1000 kPa, again with an adsorption azeotrope always existing as $P \rightarrow \infty$. For Case 7, the intersection P of the single-gas isotherms is 16 kPa (Figure 3c.1), which again is below the onset P of azeotropic behavior in this binary gas, which is 38 kPa (Figure 3c.2), and as pressure increases beyond P^1 , y_A^{az} decreases to a constant value of about 0.2 at pressures larger than about 1000 kPa, again with an adsorption azeotrope always existing as $P \rightarrow \infty$. Figure 3a.3–c.3 shows that the respective x_A - y_A curves intersect the 45° diagonal above P^1 , i.e., in the adsorption azeotrope existence regions. These results, based on the intersecting single-gas isotherms and corresponding azeotropic binary gas mixtures formulated by Do and Do,¹⁹ are consistent with Cases 1 and 3 in Table 1, which show the generally understood notion that an adsorption azeotrope in a binary gas mixture can form at pressures above the intersection P of the corresponding single-gas isotherms.

None of these cases cross through the binary gas mixture adsorption azeotrope existence P region. Crossing through the y_A^{az} region implies that above a certain P , an adsorption azeotrope ceases to exist but with the binary gas selectivity always being the inverse of that below the onset P , i.e., S_{12} changes to S_{21} . This situation, i.e., the existence of a finite P region where an adsorption azeotrope always exists in a binary gas mixture, has been suggested in the literature by only Cook and Basmadjian¹³ based on applying their theoretical analysis to the experimental data of Damkohler,² and it has also been shown but never mentioned by Nguyen and Do²¹ when predicting hypothetical binary gas adsorption equilibria using their new model based on corresponding hypothetical intersecting single-gas isotherms.

Figure 4 provides two examples that are consistent with the models of Cook and Basmadjian¹³ and Nguyen and Do²¹ wherein a finite P region instead of an infinite P region exists in a binary gas mixture where an adsorption azeotrope always exists. For the thermodynamically consistent DPL model, it was easy to find a finite P region for adsorption azeotrope existence in a binary gas mixture with the onset P of this region always being equal to or greater than the intersection P on the corresponding single-gas isotherms. However, it was not possible to find a finite P region with the onset P below the intersection P of the corresponding single-gas isotherms with the thermodynamically consistent DPL model. In contrast, it was relatively easy to find this region with the general DPL model, i.e., a finite P region for adsorption azeotrope existence in a binary gas mixture with the onset P being below the intersection P of the corresponding single-gas isotherms. The

Table 1. Single-Gas Isotherm Parameters and Intersection P , and Adsorption Azeotrope Existence Parameters and P Region

case	component	$q_{s1,mol}$ kg^{-1}	b_1,kPa^{-1}	$q_{s2,mol}$ kg^{-1}	b_2,kPa^{-1}	a_f or a_g	Δ_f or Δ_g	χ	P^{int},kPa	P^0,kPa	P^1,kPa	Figure
1 ^a	A	2.50	0.20	1.1	0.010	-6.55×10^{-4}	6.19×10^{-4}	0.16	21.9	-23.6	38.2	1a
	B	2.50	0.09	1.1	0.050							
2 ^a	A	3.00	0.20	1.1	0.010	-9.12×10^{-4}	4.56×10^{-3}	0.55	70.7	-2.0	4.5	1b
	B	3.00	0.04	1.1	0.250							
3	C ₆ H ₅ CH ₃	1.85	248.24	0.3	5.911	-1.05×10^5	4.40×10^{15}	0.04	0.2	-0.13	0.24	2a
	CH ₃ CH ₂ CH ₂ OH	0.68	8.30	2.7	7.571							
4	C ₃ H ₈	0.74	1.55	0.6	0.015	-1.87×10^{-4}	2.98×10^{-6}	0.33	3.4	-1.8	1.3	2b
	CO ₂	2.34	0.01	1.0	0.380							
5	A	2.00	0.20	0.00	0.00	0.00	2.26×10^{-10}	0.17	13.4	-125	25	3a
	B	2.00	0.08	2.00	0.02							
6	A	2.00	0.50	0.00	0.00	0.00	3.14×10^{-9}	0.03	26.0	-130	78	3b
	B	2.00	0.10	2.00	0.01							
7	A	1.00	0.50	0.00	0.00	0.00	1.58×10^{-9}	0.05	15.9	-190	38	3c
	B	1.00	0.10	2.00	0.01							
8 ^a	A	1.20	0.40	1.6	0.003	-5.20×10^{-3}	4.06×10^{-3}	0.27	3.5	37.4	6.9	4a
	B	1.20	0.22	1.6	0.040							
9	A	1.73	0.35	1.5	0.003	1.51×10^{-6}	3.95×10^{-8}	0.13	29.1	70.0	19.4	4b
	B	0.91	0.28	2.1	0.025							
10	A	1.73	0.35	1.50	0.01	5.17×10^{-6}	-4.25×10^{-9}	0.10		214	33	5
	B	0.91	0.28	2.11	0.02							

^aThermodynamically consistent DPL model.

DPL isotherm parameters and the corresponding values of χ , a_f , Δ_f , a_g , and Δ_g used to obtain these results, along with the resulting P^0 and P^1 , are given in Table 1 (Cases 8 and 9). The parameters listed in Table 1 were obtained by trial and error, while ensuring a negative coefficient a_f or a_g (eq 19 or eq 36) and χ values between 0 and 1. The first constraint ensures the single-gas isotherms intersect, as evident in Figure 4b.1,b.3, while the second constraint ensures an adsorption azeotrope does exist.

For Cases 8 and 9, Figure 4a.1,b.1 and the parameter values in Table 1 show that the isotherms do intersect each other. Figure 4a.2,b.2 shows that the formation of adsorption azeotropes in these binary gas mixtures is possible in finite P regions between $P^1 \geq 6.91$ kPa and $P^0 \leq 37.4$ kPa for Case 8 and between $P^1 \geq 19.44$ kPa and $P^0 \leq 70.0$ kPa for Case 9. For Case 8 (i.e., the thermodynamically consistent DPL model), the intersection P of the single-gas isotherms is 3.5 kPa (Figure 4b.1), which is below the onset P of azeotropic behavior in this binary gas mixture, which is 6.91 kPa (Figure 4b.2). In contrast, for Case 9 (i.e., the general DPL model), the intersection P of the single-gas isotherms is 29.1 kPa (Figure 4a.1), which is above the onset P of azeotropic behavior in this binary gas mixture, which is 19.44 kPa (Figure 4a.2). Figure 4a.3,b.3 shows that the respective x_A - y_A curves intersect the 45° diagonal only when in between P^1 and P^0 , i.e., in the finite adsorption azeotrope existence P regions. It is also clear from Figure 4a.3,b.3 that the binary selectivity S_{AB} inverts to S_{BA} when traversing outside this region from the lower onset pressures to the higher cessation pressures. These two cases show it is theoretically possible to have a finite P region where an adsorption azeotrope in a binary gas mixture always exists, with the onset P potentially always being equal to a greater than the corresponding single-gas isotherm intersection P for the thermodynamically consistent DPL model and even below the single-gas isotherm intersection P for the general DPL model.

As an aside and perhaps more suitable for the previous work by the authors,³⁹ Figure 5 provides one more interesting example wherein a finite P region instead of an infinite P region exists in a binary gas mixture where an adsorption azeotrope always exists but now for two corresponding nonintersecting single-gas isotherms. The general DPL isotherm parameters and the corresponding values of χ , a_f , and Δ_f used to obtain these results, along with the resulting P^0 and P^1 , are given in Table 1 (Case 10). The parameters listed in Table 1 were obtained by trial and error, while ensuring a positive coefficient a_f (eq 36) and χ values between 0 and 1. The first constraint ensures the single-gas isotherms do not intersect, while the second constraint ensures an adsorption azeotrope does exist.

For Case 10, Figure 5a.1 and the parameter values in Table 1 show that the isotherms do not intersect each other. Figure 5a.2 also shows that the formation of an adsorption azeotrope in this binary gas mixture is possible in a finite P region between $P^1 \geq 33.1$ kPa and $P^0 \leq 213.5$ kPa. Figure 5a.3 shows that the respective x_A - y_A curves intersect the 45° diagonal only when in between P^1 and P^0 , i.e., in the finite adsorption azeotrope existence P regions. Figure 5a.3 also shows that the binary selectivity S_{AB} inverts to S_{BA} when traversing outside this region from the lower onset pressures to the higher cessation pressures. This final case shows with the general DPL model that it is possible to have a finite P region where an adsorption azeotrope in a binary gas mixture always exists, even when the corresponding single-gas isotherms do not intersect.

DISCUSSION

It is interesting that the thermodynamically consistent DPL model proves it is theoretically possible to form adsorption azeotropes in binary gas mixtures at pressures above the intersection P of the corresponding single-gas isotherms, for either an infinite or finite adsorption azeotrope existence P region. This is the situation that is generally understood and reported in the literature. What is more intriguing, however, is that the thermodynamically consistent DPL model proves it is

theoretically possible to form adsorption azeotropes in binary gas mixtures even at pressures below the intersection P of the corresponding single-gas isotherms, but only for an infinite adsorption azeotrope existence P region, not for a finite P region. The general DPL model cautiously shows this is possible for both finite and infinite adsorption azeotrope existence P regions. Again, it is impossible to state which DPL formulation is correct.

The formation of adsorption azeotropes in binary gas mixtures below the intersection P of the corresponding single-gas isotherms is the situation that is generally not understood and has not been reported in the literature. In fact, it appears no one has ever tried to experimentally measure an adsorption azeotrope in a binary gas mixture below the intersection P of the corresponding single-gas isotherms because of the general belief that they exist only above the intersection P of the single-gas isotherms. In fact, the general DPL model shows it is possible to form an adsorption azeotrope in the binary gas mixture $C_3H_8-CO_2$ on H-mordenite at 30 °C below the intersection P of the corresponding single-gas isotherms. Hence, based on both DPL models, this analysis provides some confirmation that an adsorption azeotrope in a binary gas mixture may form even at pressures below the intersection P of the corresponding single-gas isotherms.

It is worth briefly discussing the perfect positive (PP) and perfect negative (PN) energetic site-matching correlations³¹ that resulted for Cases 1–4 and 8–10 in Table 1 (Cases 5–7 do not have a PP or PN distinction because component A in each case is characterized by the SPL isotherm model with only one energetic site). According to the affinity (b_{ij}) of each component on each site, PP means both components see one of the sites as a high-energy site and the other site as a low-energy site. PN means one of the components sees one of the sites as a high-energy site while the other component sees it as a low-energy site and vice versa for the other site. The parameters in Table 1 were obtained without consideration of this energetic site-matching construct; only adsorption azeotrope existence constraints were considered, as mentioned.

According to the alignment of the b_{ij} for each case in Table 1, only Cases 2 and 4 are PN. Cases 1, 3, 8, 9, and 10 are all PP. It is generally understood that PP behavior does not result in the formation of adsorption azeotropes, while PN behavior can result in the formation of adsorption azeotropes.³¹ It was interesting that PN behavior resulted in the formation of adsorption azeotropes even when the corresponding single-gas isotherms did not intersect (Cases 1, 2, 5, and 6 in Table 1 of the previous work by the authors³⁹ and Case 10 in Table 1 of this work). PN behavior also resulted in the formation of adsorption azeotropes when the corresponding single-gas isotherms did intersect (Cases 2 and 4 in Table 1 of this work). However, perhaps for the first time, these results showed that PP behavior can also result in the formation of adsorption azeotropes (Cases 1, 3, 8, 9, and 10), where each of these cases also had corresponding intersecting single-gas isotherms, except for Case 10. Even the experimental $C_6H_5CH_3-CH_3CH_2CH_2OH$ binary gas mixture on DAY zeolite (Case 3) showed that PP behavior can result in the formation of adsorption azeotropes based on the general DPL model. Cases 1 and 8, based on the thermodynamically consistent DPL model, showed also that PP behavior can result in the formation of adsorption azeotropes. These were interesting and unexpected results.

CONCLUSIONS

The aim of this work was to confirm theoretically whether adsorption azeotropes can form in a binary mixture at a P below the intersection P of the corresponding single-gas isotherms. The thermodynamically consistent and general DPL models were used for this purpose. Relationships derived from both DPL models, in terms of the single-gas isotherm DPL model parameters, were used to find examples to discern the relationship between the P region in a binary gas mixture where adsorption azeotropes always exist and the intersection P of the corresponding single-gas isotherms. The theoretical developments thus provided a framework to reveal whether an adsorption azeotrope can form in a binary gas mixture at pressures below the intersection P of the corresponding single-gas isotherms.

This work showed that an adsorption azeotrope in a binary gas mixture can form at pressures even below the intersection P of the corresponding single-gas isotherms. Both DPL models, along with experimental data fitted to the general DPL model, showed it is possible with the P range of adsorption azeotrope formation being infinite once the onset P of adsorption azeotrope formation is reached. Only the general DPL model showed that it is possible when a finite P range exists where adsorption azeotropes always exist. In contrast and without a theoretical proof, when a finite P range exists where adsorption azeotropes always exist, the thermodynamically consistent DPL model was seemingly restricted to forming adsorption azeotropes at pressures equal to or greater than the intersection P of the corresponding single-gas isotherms, never less than it. Both DPL models showed that when the P range where an adsorption azeotrope always exists is finite, the binary selectivity inverts when proceeding from the lower onset P to the higher cessation P of this range. Both DPL models also showed that perfect positive energetic site matching can result in the formation of adsorption azeotropes, an interesting and counterintuitive result. It was once thought that only perfect negative energetic site matching can result in the formation of adsorption azeotropes.

Overall, this work provided some confirmation that it is possible to form adsorption azeotropes in a binary gas mixture at pressures below the intersection P of the corresponding single-gas isotherms. Both DPL models provided evidence to support this notion with similar outcomes in most cases. However, more binary gas mixture adsorption azeotrope experimental data is needed to prove the correctness of these two physically sound DPL model formulations.

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NOMENCLATURE

a_f	constant defined in eq 19
a_g	constant defined in eq 36
b_f	constant defined in eq 20
b_g	constant defined in eq 37
b_i	affinity of species i (=A or B), kPa^{-1}
$b_{i,j}$	affinity of species i (=A or B) on site j , kPa^{-1}
c_f	constant defined in eq 21
c_f	constant defined in eq 38
d_f	constant defined in eq 22
$K_{i,j}$	Henry's law constant of species i (=A or B) on site j , $\text{mol kg}^{-1} \text{kPa}^{-1}$
K_i	Henry's law constant of species i (=A or B), $\text{mol kg}^{-1} \text{kPa}^{-1}$
P	absolute pressure, kPa
P^0	pressure when $y_A^{\text{az}} = 1.0$, kPa
P^1	pressure when $y_A^{\text{az}} = 0.0$, kPa
P^{int}	intersection pressure of the single-gas isotherms, kPa
q_i	amount adsorbed (loading) of species i (=A or B) in the binary gas mixture, mol kg^{-1}
q_i^{p}	amount adsorbed (loading) of pure (single gas) species i (=A or B), mol kg^{-1}
$q_{i,j}^{\text{s}}$	saturation amount adsorbed (loading) of species i (=A or B) on site j , mol kg^{-1}
q_j^{s}	saturation amount adsorbed (loading) of species A or B on site j , mol kg^{-1}
T	absolute temperature, K
x_i	adsorbed phase mole fraction of species i (=A or B)
y_i	gas phase mole fraction of species i (=A or B)
y_A^{az}	gas phase mole fraction of species A in the azeotropic region

Greek Symbols

α	event of single-gas isotherms intersecting
α^c	event of single-gas isotherms not intersecting
β	event of binary gas mixture forming an azeotrope
β^c	event of binary gas mixture not forming an azeotrope
Δ_f	discriminant expression of eq 18 defined in eq 24
Δ_g	discriminant expression of eq 35 defined in eq 39
χ	expression defined in eq 10

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