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# New Model That Describes Adsorption of Laterally Interacting Gas Mixtures on Random Heterogeneous Surfaces. 1. Parametric Study and Correlation with Binary Data

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Analytic expressions for the adsorption of a binary gas mixture that laterally interacts on a random heterogeneous surface are developed. The lateral interactions are of the Bragg–Williams type, and the surface heterogeneity is modeled via a random distribution of sites described by a uniform distribution of Henry's law constants. A parametric study shows that complex phase behavior can be predicted with this model, including azeotropes and sigmoidal-shaped  $x$ – $y$  diagrams. This model is also successfully correlated with binary data from the literature with average relative errors of less than 10% for both single-component and binary adsorption data.

## Introduction

The lattice gas concepts developed by Hill<sup>1</sup> for the adsorption of single gases, and extended by O'Brien and Myers<sup>2</sup> and more recently by Russell and LeVan<sup>3</sup> for the adsorption of gas mixtures can be very useful in discerning subtle information on the adsorption of gases and their mixtures. These lattice gas models are usually based on patchwise or random heterogeneous surfaces, and the lateral interactions are typically of the Bragg–Williams type. It has been shown in different studies that adsorption heterogeneity imparts changes in the binary selectivity, surface coverage, and adsorbed phase compositions significantly, as a result of altering the ratio of the component Henry's law constants and also because of excluded volume effects.<sup>4,5</sup> The effect of adsorption heterogeneity and lateral interactions on adsorption phenomena and the role of different distributions of energetic sites have also been studied and analyzed.<sup>3–17</sup>

The Bragg–Williams approximation for lateral interactions has been considered the most in these studies, with different themes used to describe the adsorption heterogeneity distribution. For example, Hill<sup>1</sup> employed a simple

uniform distribution of energies to describe the heterogeneous surface and obtained an analytic expression for single gas adsorption. O'Brien and Myers<sup>2</sup> chose a more complicated discrete distribution and obtained analytic expressions for mixed gas adsorption that contained cumbersome summation terms. A model similar to that of O'Brien and Myers<sup>2</sup> is developed in this study based on the simpler uniform distribution. This is accomplished by extending the models developed by Ritter et al.<sup>12</sup> and Kapoor et al.<sup>18</sup> to include the adsorption of gas mixtures and lateral interactions, respectively.

Ritter et al.<sup>12</sup> developed an analytical expression to describe the adsorption of single gases which laterally interact on a random heterogeneous surface according to the Bragg–Williams approximation and a uniform distribution of energies. The model is based on the rigorous theory of Hill<sup>1</sup> but is obtained using a method proposed by Jaroniec and Patrykiewicz.<sup>8</sup> Kapoor et al.<sup>18</sup> and also Sircar<sup>6</sup> extended the Langmuir model for adsorption of noninteracting gas mixtures on heterogeneous surfaces described by uniform distributions. However, to derive an explicit analytical expression, Kapoor et al.<sup>18</sup> assumed that the variance of the energy distribution is the same for all of the components in the gas mixture. Sircar<sup>6</sup> circumvented this assumption by integrating over a distribution of Henry's law constants to obtain an explicit analytical solution.

In this study, a uniform distribution of Henry's law constants<sup>6</sup> is utilized to describe a random heterogeneous surface, along with the Bragg–Williams approximation and a method suggested by Jaroniec et al.,<sup>19</sup> to develop a simple model for the adsorption of a binary gas mixture that laterally interacts on a random heterogeneous surface. A parametric study is performed, where the emphasis is placed on the engineering aspects as opposed to a thermodynamic description.<sup>2</sup> The coupled and sometimes competing effects of heterogeneity and attractive lateral interactions are disclosed. This new model is also successfully correlated with binary adsorption data from the literature.

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### Theory

Single and binary gas adsorption models are developed that account for surface heterogeneity as well as lateral interactions. There are four key assumptions made in the development of the models that allow for analytical expressions to be obtained: (1) A random heterogeneous surface allows the lateral interaction terms in the model to be functions only of the overall surface coverage.<sup>1</sup> (2) The heterogeneous surface is described by a distribution of Henry's law constants instead of energies.<sup>6</sup> (3) The distribution of Henry's law constants is represented by a uniform distribution; the adsorption isotherm is relatively insensitive to the shape of the distribution.<sup>10</sup> (4) The lateral interactions are of the Bragg–Williams type, a crude but simple approximation that qualitatively has the features of more rigorous treatments.<sup>1</sup>

**Single Gas Adsorption.** The single gas adsorption integral equation that accounts for lateral interactions on a random heterogeneous surface is written as

$$\theta_R = \int_{b_L}^{b_H} \theta_k [T, P, b_k, \Omega(\theta_R)] f(b_k) db_k \quad (1)$$

where  $\theta_k$  and  $\theta_R$  are the fractional surface coverages on constant-energy sites and a random heterogeneous surface, respectively,  $T$  is the absolute temperature,  $P$  is the pressure,  $b$  is Henry's law constant,  $\Omega$  is the lateral interaction term, and the subscripts L and H indicate low- and high-energy sites, respectively. The integration is performed over a distribution of Henry's law constants,<sup>6</sup> where the distribution function,  $f(b_k)$ , is normalized according to

$$\int_{b_L}^{b_H} f(b_k) db_k = 1 \quad (2)$$

and the subscript  $k$  denotes sites of constant Henry's law constants (or energy, see eq 4). The local isotherm used in this study is given by

$$\theta_k [T, P, b_k, \Omega(\theta_R)] = \frac{b_k P \Omega}{1 + b_k P \Omega} \quad (3)$$

where

$$b_k = b_0 \exp\left(\frac{\epsilon_k}{kT}\right) \quad (4)$$

$$\Omega = \exp\left(\frac{-z\omega\theta_R}{kT}\right) \quad (5)$$

$\epsilon$  is the energy of adsorption,  $k$  is Boltzmann's constant, and  $(-\omega)$  denotes attractive lateral interactions. Equation 3 is the Fowler and Guggenheim adsorption isotherm written for a random heterogeneous surface. The uniform distribution of Henry's law constants is defined by<sup>6</sup>

$$f(b_k) = \frac{1}{b_H - b_L} \quad b_L \leq b_k \leq b_H \quad (6)$$

$$f(b_k) = 0 \quad \text{elsewhere} \quad (7)$$

with the average Henry's law constant and square root of

variance given by

$$b = \frac{b_H + b_L}{2} \quad (8)$$

$$\sigma = \frac{b_H - b_L}{2\sqrt{3}} \quad (9)$$

The ratio,  $\sqrt{3}\sigma/b$ , or the degree of heterogeneity,<sup>6</sup> is always limited between zero and unity for completely homogeneous and completely heterogeneous surfaces, respectively. Combining eqs 3–9 with eq 1 and integrating yields

$$\theta_R = 1 - \frac{1}{2P\Omega\sigma\sqrt{3}} \ln \left[ \frac{1 + P\Omega(b + \sigma\sqrt{3})}{1 + P\Omega(b - \sigma\sqrt{3})} \right] \quad (10a)$$

A more convenient form of eq 10a for fitting experimental data is given by

$$n_R = m \left( 1 - \frac{1}{2P\Omega\sigma\sqrt{3}} \ln \left[ \frac{1 + P\Omega(b + \sigma\sqrt{3})}{1 + P\Omega(b - \sigma\sqrt{3})} \right] \right) \quad (10b)$$

where  $n$  is the amount adsorbed,  $m$  is the saturation limit, and  $b$ ,  $\Omega$ , and  $\sigma$  are defined by eqs 4, 5, and 9, respectively.

Equation 10 describes the adsorption of single gases that laterally interact on a random heterogeneous surface. This model has four parameters:  $V_m$ ,  $b$ ,  $\sigma$ , and  $\Omega$ . However, because of  $\Omega$ , eq 10 is implicit with respect to  $\theta_R$  and thus requires an iterative solution.

There are some unique characteristics of this model that are worth noting. It is easy to show, by expanding eq 10 into a Taylor series and taking the limit as  $P$  approaches zero, that the Henry's law region is linear and given by

$$\theta_R = bP \quad (11)$$

The interesting point is that by assuming a uniform distribution of Henry's law constants, the isotherm becomes independent of the heterogeneity parameter,  $\sigma$ . This is in contrast to a similarly derived isotherm based on a uniform distribution of energies,<sup>6</sup> where the Henry's law isotherm is given by

$$\theta = \frac{Pb}{s} \sinh(s) \quad (12)$$

where  $s$  is the equivalent heterogeneity parameter. The only plausible explanation for this surprising but, nevertheless, thermodynamically consistent result is that the effect of heterogeneity in the Henry's law region is already accounted for in the average Henry's law constant,  $b$ . Moreover, it is shown later that when  $\sigma$  is varied from zero to the maximum value of  $\sigma$  allowed by this model, the different isotherms do not cross and once out of the Henry's law region, progress to  $\theta = 1$  more slowly. In contrast, when a uniform distribution of energies is assumed, Ritter et al.<sup>12</sup> showed that according to eq 10, the Henry's law constant (slope of the isotherm) increases with increasing  $\sigma$  and that the isotherms eventually cross and only then progress more slowly toward  $\theta = 1$ , which is consistent with eq 12.

These differences in the two isotherm models, i.e., one based on a uniform distribution of energies and the other one based on a uniform distribution of Henry's law

constants, is manifest by the relationship between the distributions. Clearly, since

$$db_k = \frac{b_0}{kT} \exp\left(\frac{\epsilon}{kT}\right) d\epsilon \quad (13)$$

a uniform distribution of Henry's law constants corresponds to the following exponential distribution of energies:

$$f(\epsilon) = \left(\frac{1}{b_H - b_L}\right) \frac{b_0}{kT} \exp\left(\frac{\epsilon}{kT}\right) \quad (14)$$

It is noteworthy that similar exponential distributions have been used previously to describe heterogeneous surfaces.<sup>20,21</sup> Now the independence of heterogeneity in the Henry's law region is clear. For an exponential distribution of energies, the highest energies are also the most in number. Thus, any adsorption beyond the Henry's law region must necessarily correspond to lower energy sites that are less in number. So as  $\sigma$  decreases from  $\sigma_{\max}$  to zero, the isotherms do not cross. In contrast, for a uniform distribution of energies, the number distribution is equally weighted among the energies, which results in the crossing of the isotherms.<sup>12</sup>

**Binary Gas Adsorption.** The adsorption integral equation for component  $i$  of a binary mixture that laterally interacts on a random heterogeneous surface is written as

$$\theta_{i,R} = \int_{b_{i,L}}^{b_{i,H}} \theta_i(T, P, y_i, y_j, \alpha_i, \alpha_j, b_i, b_j) f(b_i, b_j) db_i db_j \quad (15)$$

A method referred to as energetic site matching,<sup>2,18,22</sup> i.e.,

$$\int_{b_{i,L}}^{b_i} f(b_i) db_i = \int_{b_{i,L}}^{b_j} f(b_j) db_j \quad (16)$$

is used to simplify eq 15. Equation 16 represents a functional relationship between components  $i$  and  $j$  of a binary gas mixture and implies the ordering of sites from low to high Henry's law constants is the same for all  $i$ . Combining eqs 15 and 16 according to Valenzuela et al.<sup>22</sup> yields a simplified adsorption integral equation for a binary mixture:

$$\theta_{i,R} = \int_{b_{i,L}}^{b_{i,H}} \theta_i(T, P, y_i, y_j, \alpha_i, \alpha_j, b_i) f(b_i) db_i \quad (17)$$

where  $j = 1, 2$ . The uniform distribution of Henry's law constants for component  $i$  of a gas mixture is given by

$$f(b) = \frac{1}{b_{i,H} - b_{i,L}} \quad b_{i,L} \leq b_i \leq b_{i,H} \quad (18)$$

$$f(b) = 0 \quad \text{elsewhere} \quad (19)$$

with the average Henry's law constant and square root of

variance given by

$$b_i = \frac{b_{i,H} + b_{i,L}}{2} \quad (20)$$

$$\sigma_i = \frac{b_{i,H} - b_{i,L}}{2\sqrt{3}} \quad (21)$$

For the local isotherm of eq 15 or 17, eq 3 is extended for a binary gas mixture:<sup>19</sup>

$$\theta_i(T, P, y_i, y_j, \alpha_i, \alpha_j, b_i) = \frac{b_i y_i P \beta_i}{1 + \sum_j b_j y_j P \beta_j} \quad (22)$$

where

$$\beta_i = \exp(-\alpha \theta_{i,R} - \alpha_{ij} \theta_{j,R}) \quad (23)$$

$$\alpha_{ij} = -(1 - k_{ij}) \sqrt{\alpha_i \alpha_j} \quad (24)$$

$$\alpha_i = \frac{z w_i}{kT} \quad i, j = 1, 2 \quad (i \neq j) \quad (25)$$

Substitution of eqs 18–25 into eq 17 and integrating yields

$$\theta_{i,R} = \frac{\sigma_i P \beta_i}{\sum_{j=1}^2 \sigma_j P \beta_j} + \frac{P \beta_i (\sigma_i + \sigma_i \sum_{j=1}^2 b_j P \beta_j - b_i \sum_{j=1}^2 \sigma_j P \beta_j)}{2\sqrt{3} (\sum_{j=1}^2 \sigma_j P \beta_j)^2} \times \ln \left( \frac{1 + \sum_{j=1}^2 (b_j - \sqrt{3} \sigma_j) P \beta_j}{1 + \sum_{j=1}^2 (b_j + \sqrt{3} \sigma_j) P \beta_j} \right) \quad (26)$$

where  $i, j = 1, 2$  and  $\beta_i, \alpha_{ij}, \alpha_i, b_i$  and  $\sigma_i$  are defined above.

Equation 26 describes the adsorption of component  $i$  of a binary gas mixture that laterally interacts on a random heterogeneous surface. It has four single gas parameters for each component of the gas mixture. It also has a binary interaction parameter,  $k_{ij}$ , which allows for significant deviation of  $\alpha_{ij}$  from the geometric mean; however,  $k_{ij}$  has to be obtained from binary mixture information. Moreover, because of  $\beta_i$ , eq 26 requires an iterative, simultaneous solution of a set of coupled algebraic equations. It is also noted that unless the monolayer capacities of each component of the mixture are the same ( $V_{m,i} = V_{m,j}$ ), eq 26 suffers slightly from a lack of thermodynamic consistency; however, the extent of the thermodynamic inconsistency has been shown to be insignificant for most practical applications.<sup>23</sup>

## Results and Discussion

**Parametric Study.** A parametric study is carried out to investigate the effects of pressure, Henry's law constant, surface heterogeneity, and attractive lateral interactions on single and binary gas adsorption isotherms. It also shows the relative importance of each of these properties with respect to relative adsorption affinities of each component in the binary mixture. Ranges of the parameters are selected to represent practical systems encoun-

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**Table 1. Fixed Parameters and Manipulated Variables for the Parametric Study**

variable	units	case 1	case 2	case 3	case 4	case 5	case 6
$b_1$	atm <sup>-1</sup>	0.6	0.6	0.6	0.6	0.6	0.6
$b_2$	atm <sup>-1</sup>	0.5	0.5	0.5	0.2	0.2	0.2
$\sigma_1$	atm <sup>-1</sup>	0.35	0.35	0.35	10 <sup>-5</sup> to 0.35	10 <sup>-5</sup> to 0.35	10 <sup>-5</sup>
$\sigma_2$	atm <sup>-1</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup>	10 <sup>-5</sup> to 0.12	10 <sup>-5</sup>	10 <sup>-5</sup> to 0.12
$\alpha_1$		-1.5	-1.5	0.0 to -2.0	0.0 to -2.0	0.0 to -2.0	0.0
$\alpha_2$		-2.0	-2.0	0.0 to -2.0	0.0 to -2.0	0.0	0.0 to -2.0
$k_{12}$		1.5	1.25 to -1.5	0.0	0.0	0.0	0.0
$P$	atm	0.1 to -2.5	5.0	5.0	5.0	5.0	5.0

tered in typical gas adsorption processes. The factors explored in this parametric study include the effect of pressure (case 1),  $k_{12}$  (case 2), lateral interactions (cases 3 and 4), and partial nonidealities of the heavy (case 5) and light (case 6) components. The values of the fixed parameters and the ranges of the manipulated variables for each of these cases are summarized in Table 1.

**Effect of Pressure (Case 1).** The parameters for the effect of pressure are given in case 1 of Table 1. For this case, component 1 is slightly more strongly adsorbed and considerably more heterogeneous than component 2, but it has slightly weaker lateral interactions. For the binary mixture,  $k_{12}$  is positive, which enhances the attractions between similar components (see below). The results for case 1 are shown in Figure 1.

Figure 1a shows that the two adsorption isotherms cross each other at  $P \approx 0.3$ , and at higher pressures the surface coverage of component 2 exceeds that of component 1. These results are due to a combination of the effects of heterogeneity and lateral interactions.<sup>12</sup> Figure 1b, which shows the relative selectivity to adsorb component 1 over component 2 at different compositions, indicates that this is a very nonideal system; for a similar ideal system  $S_{12}$  ( $=b_1/b_2$ ) = 1.2 and is independent of  $y_1$ . At low  $y_1$ ,  $S_{12}$  decreases with increasing  $P$ , whereas at high  $y_1$ , the opposite is true.

Also, at all but the lowest pressure investigated, an azeotrope exists, which is consistent with the single gas isotherms crossing each other at  $P \approx 0.3$  atm. For the lowest pressure, heterogeneity dominates and causes a slight deviation from ideal behavior. At higher pressures, the effects of lateral interactions dominate, as seen from the sigmoidal-shaped curve in Figure 1b, which results from the effects of a positive  $k_{12}$ . The  $x$ - $y$  diagram shown in Figure 1c shows this behavior very clearly; and so does Figure 1d, where component 1 exhibits a slightly higher surface coverage at  $P = 0.1$  atm when  $y_1 \rightarrow 1.0$  than component 2 when  $y_1 \rightarrow 0.0$ . This result is due to the larger Henry's law constant as well as the higher heterogeneity of component 1. However, at higher pressures, the trend is quite the opposite. This is explained by the slightly higher lateral interactions of component 2 which become more appreciable with increasing pressure until they tend to dominate the relative adsorption affinity of the two components.

**Effect of  $k_{12}$  (Case 2).** The parameters for the effect of  $k_{12}$  are given in case 2 of Table 1. For the binary mixture,  $k_{12}$  varies from being positive to negative. Therefore, as  $k_{12}$  decreases, the attractions between similar components gradual become attractions between dissimilar components. The results for case 2 are shown in Figure 2.

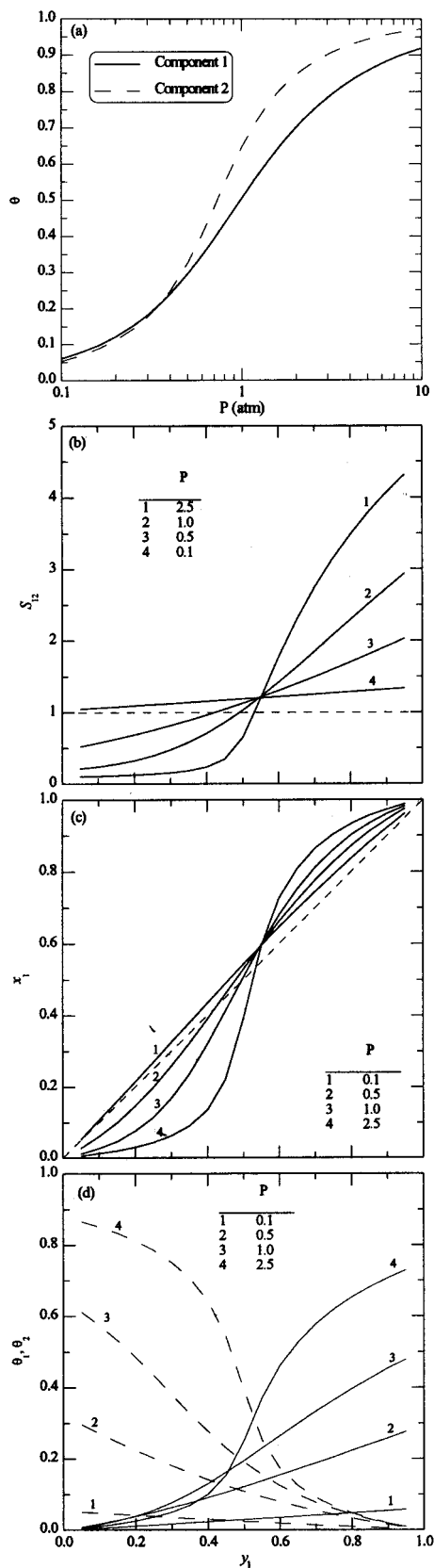
This case is similar to case 1 except that  $P$  is constant; thus, the single gas isotherms shown in Figure 2a are the same as those shown in Figure 1a. According to the selectivities shown in Figure 2b, an azeotrope occurs for every  $k_{12}$  except for  $k_{12} = 0$ . Therefore,  $k_{12}$  can cause azeotropic behavior. Moreover, Figure 2c shows that for

a large positive  $k_{12}$ , a sigmoidal-shaped curve results, and because of the attraction between similar components, at high  $y_2$  the surface is covered with component 2 and vice versa at high  $y_1$ , as seen in Figure 2d. For a large negative  $k_{12}$ , a sigmoidal-shaped curve still results, but with the opposite concavities; thus, selectivity reversal occurs, even though the single gas adsorption isotherms at  $P = 5$  atm suggest that the selectivity should be favorable for component 2. In this situation, the attractions are between dissimilar components; therefore, at high  $y_2$  component 2 significantly enhances the adsorption of component 1 and vice versa at high  $y_1$ . This suggests that azeotropic behavior cannot be so simply predicted by observing that the single gas isotherms cross at some pressure.

The adsorption selectivity toward component 1 also increases with both increasing  $y_1$  at positive  $k_{12}$  and with decreasing  $y_1$  at negative  $k_{12}$ . This phenomenon is again explained by the fact that  $k_{12}$  reflects the type of interactions between similar and dissimilar components. Therefore,  $k_{12}$ , a correlative interaction parameter, is capable of describing all minor nonidealities that are not accounted for by surface heterogeneity and simple lateral interactions in binary mixtures, such as pore exclusion effects, which have been shown to cause azeotropic behavior.<sup>4,5</sup>

**Effect of Lateral Interactions (Cases 3 and 4).** The parameters for the effect of lateral interactions are given in cases 3 and 4 of Table 1. For these cases, the pressure is held constant, and component 1 is slightly more strongly adsorbed than component 2 in case 3 and much more strongly adsorbed than component 2 in case 4. Three different situations are considered where the heterogeneity and lateral interactions of both components are varied. In the first situation (case 3), component 1 is at its maximum heterogeneity, whereas component 2 is at its minimum heterogeneity (so it experiences a homogeneous surface), and the lateral interactions of both components are varied. In the second and third situations (case 4), the heterogeneities and lateral interactions of both components are varied systematically. The results for case 3 are shown in Figure 3, and those for case 4 are shown in Figure 4.

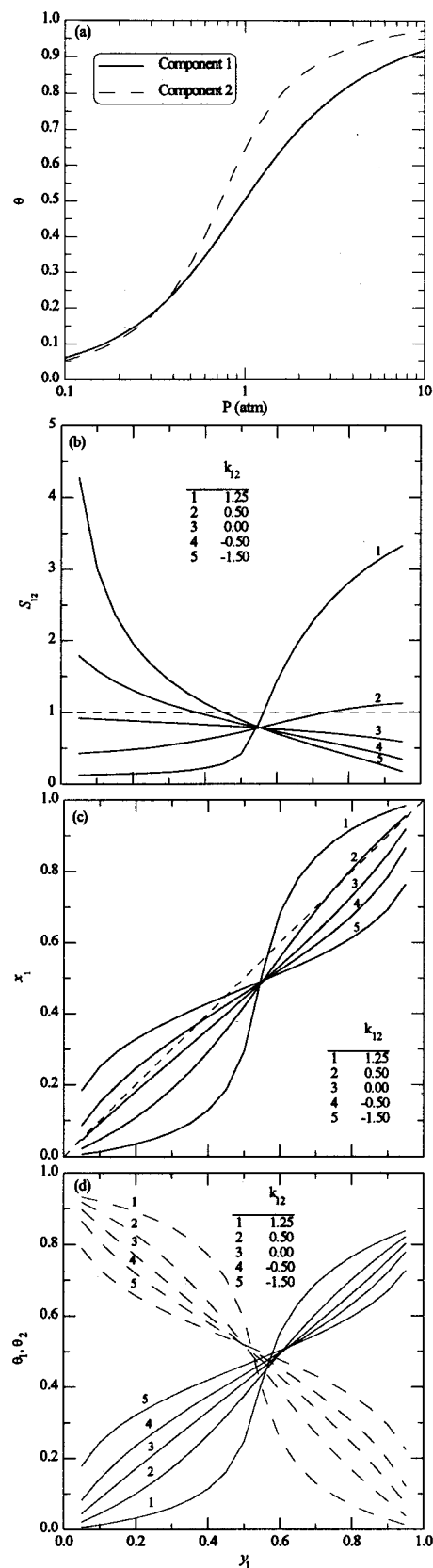
Figure 3a shows that the single-component isotherms cross each other only when equal lateral interactions are exhibited by components 1 and 2, i.e.,  $\alpha_1 = \alpha_2$ . Moreover, the increasing lateral interactions are clearly participating in the increases in surface coverage of both components. However, the increase in surface coverage of component 2 becomes slightly less than that of component 1 at high pressures because of the different adsorption affinities between them. Parts b and c of Figure 3 show that, for a binary mixture described by case 3, the azeotrope again occurs at equal lateral interactions and above where the single-component isotherms cross each other. When the lateral interactions of one of the components deviate from the other, the adsorption affinity tends to be higher for the component with higher lateral interactions, regardless of the mixture composition. Therefore, the variation of the



**Figure 1.** Effect of pressure on (a) single-component isotherms, (b) selectivities, (c)  $x$ - $y$  diagrams, and (d) fractional surface coverages (dashed lines correspond to component 2).

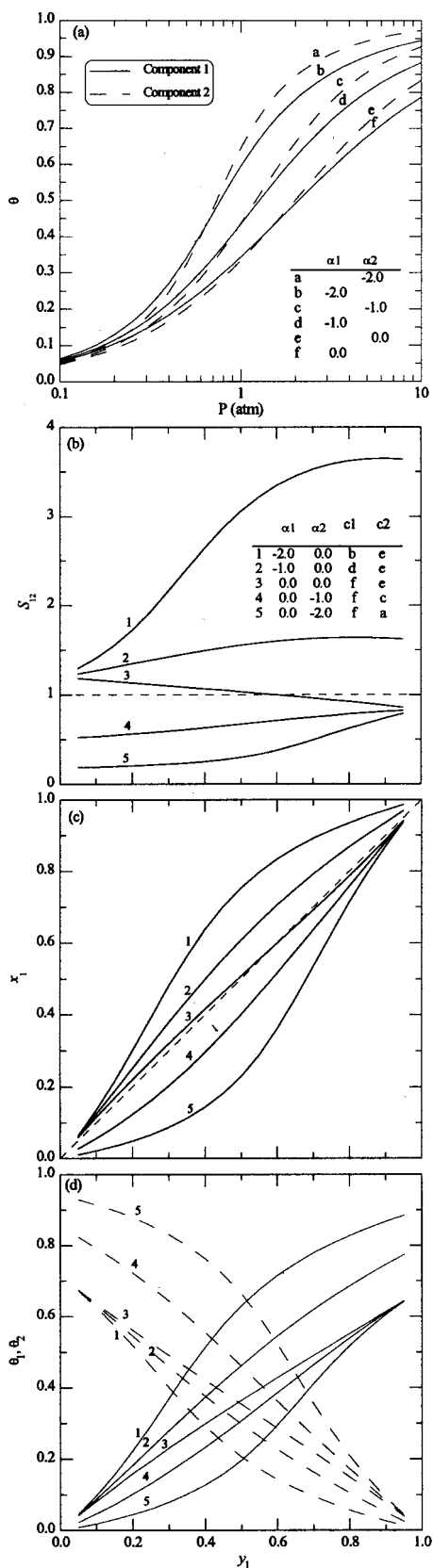
relative magnitude of lateral interactions of the two components is responsible for how much the equilibrium line deviates from equality.

Moreover, except at the azeotropic composition, if the lateral interactions are equal, higher lateral interactions



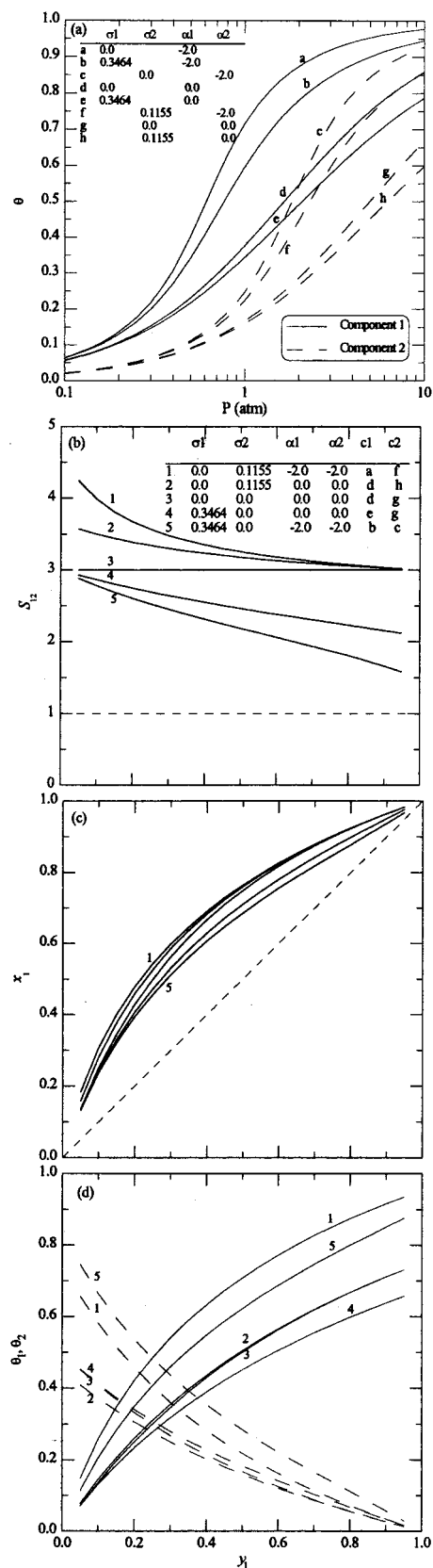
**Figure 2.** (a) Single component isotherms and effect of  $k_{12}$  on (b) selectivities, (c)  $x$ - $y$  diagrams, and (d) fractional surface coverages (dashed lines correspond to component 2).

foster a higher tendency for the dominant component to be more heavily adsorbed. This implies that sigmoidal-shaped mixed gas adsorption isotherms are more likely to be observed at high, but equal, lateral interactions of both components. This same phenomenon is observed in



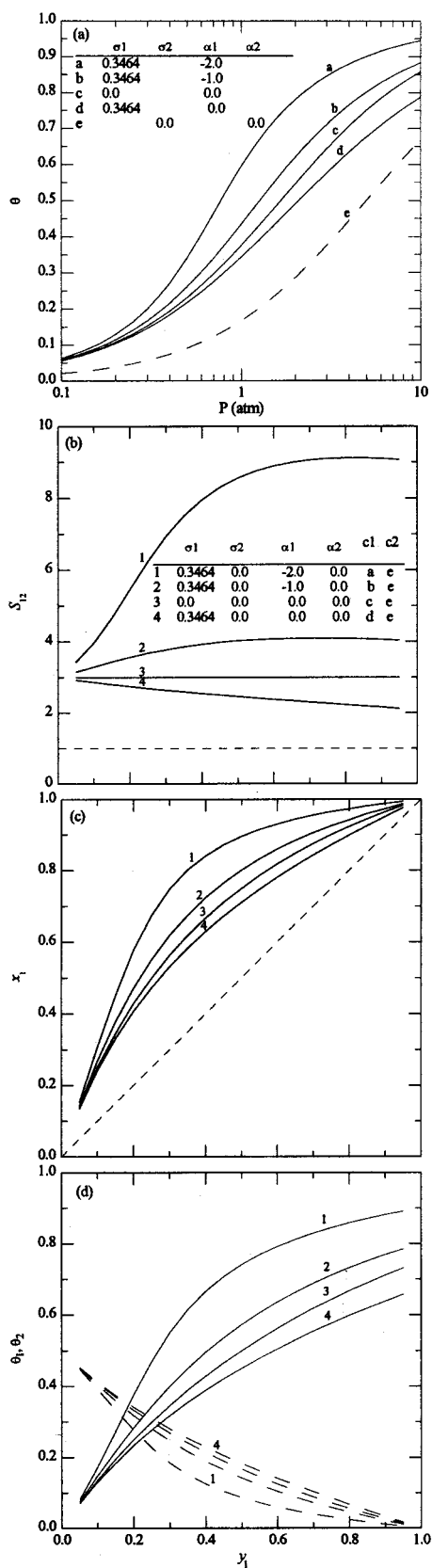
**Figure 3.** Effect of lateral interactions of two components with close adsorption affinities on (a) single-component isotherms, (b) selectivities, (c)  $x$ - $y$  diagrams, and (d) fractional surface coverages (dashed lines correspond to component 2).  $c_1$  and  $c_2$  indicate the single-component isotherm pairs corresponding to the binary results.

Figure 3b where, again, an azeotropic mixture is predicted but only at equal lateral interactions; unequal lateral



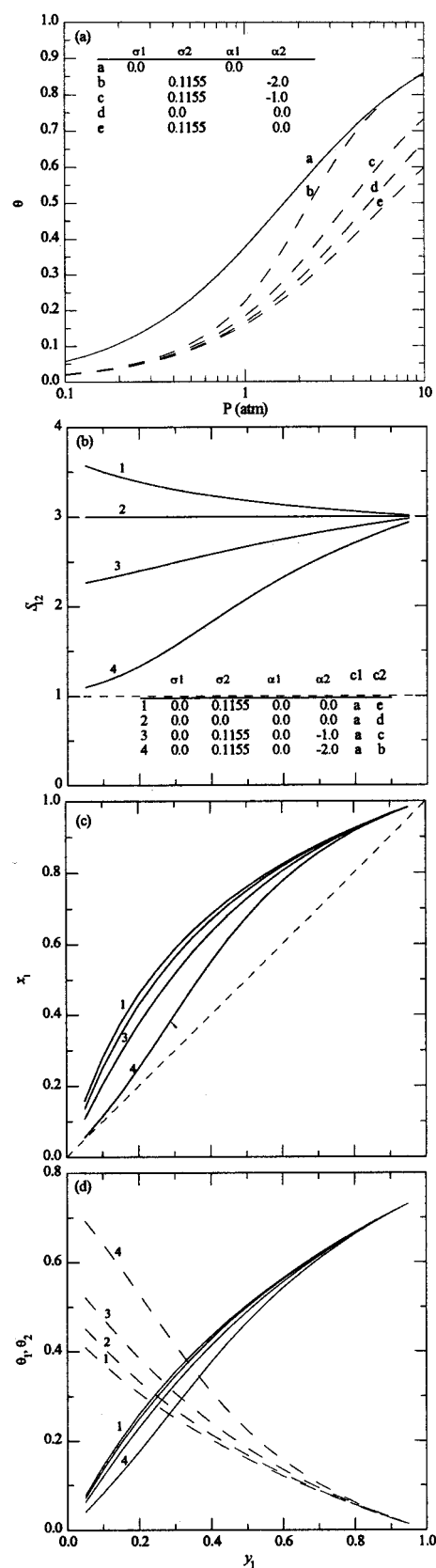
**Figure 4.** Effect of lateral interactions of two components with distinctly different adsorption affinities on (a) single-component isotherms, (b) selectivities, (c)  $x$ - $y$  diagrams, and (d) fractional surface coverages (dashed lines correspond to component 2).  $c_1$  and  $c_2$  indicate the single-component isotherm pairs corresponding to the binary results.

interactions cause the selectivity to deviate increasingly from unity as the mixture is more concentrated with the



**Figure 5.** Effect of heavy component nonidealities on (a) single-component isotherms, (b) selectivities, (c)  $x$ - $y$  diagrams, and (d) fractional surface coverages (dashed lines correspond to component 2).  $c_1$  and  $c_2$  indicate the single-component isotherm pairs corresponding to the binary results.

component with the higher lateral interactions. However, because component 1 in this case is slightly more strongly adsorbed than component 2, the effect of lateral interac-



**Figure 6.** Effect of light component nonidealities on (a) single-component isotherms, (b) selectivities, (c)  $x$ - $y$  diagrams, and (d) fractional surface coverages (dashed lines correspond to component 2).  $c_1$  and  $c_2$  indicate the single-component isotherm pairs corresponding to the binary results.

tions of component 1 are more marked. Figure 3d also indicates that varying the lateral interactions of only one component changes the mixed-gas adsorption isotherms



of both components significantly, but only when that component is in the mixture at high concentrations.

The last point made about case 3 is that an azeotrope occurs when  $\alpha_1 = \alpha_2 = 0$ , i.e., when no lateral interactions between either of the components exist. Figure 3b shows that for the ideal situation,  $S_{12} = 1.2$ . However, for a very heterogeneous component 1 and a homogeneous component 2, both with no lateral interactions,  $S_{12}$  decreases from a nearly ideal value at  $y_1 = 0$  to smaller values with increasing  $y_1$  to the point where selectivity reversal (azeotropic behavior) occurs at  $y_1 \approx 0.6$ . This azeotropic behavior is caused solely by the effect of surface heterogeneity, as first shown by Sircar.<sup>6</sup> Since component 1 is more strongly adsorbed and heterogeneous than component 2, the adsorption isotherms (curves e and f in Figure 3a) necessarily cross each other at  $P \approx 1.5$  atm. However, the effect of surface heterogeneity on the formation of an azeotrope is rather weak according to this particular model. In fact it is very difficult to find the conditions to produce such a behavior. Moreover, the effect of slight lateral interactions between either of the components essentially overwhelms the effect of surface heterogeneity and the azeotropic behavior. For example, when component 1 lateral interactions are included,  $S_{12}$  increases substantially with  $y_1$ ; conversely, when component 2 lateral interactions are included,  $S_{12}$  decreases with increasing  $y_2$ .

In contrast, the results for case 4, shown in Figure 4, illustrate the capability of surface heterogeneity to overcome lateral interactions. Figure 4a shows that the single-component isotherms of two components with distinctly different adsorption affinities are more spread apart than those of case 3. However, they again cross only at equal lateral interactions. This is also noticed in parts b and c of Figure 4 which show that varying  $\alpha$  or  $\sigma$  of either of the two components only causes very slight shifts in the equilibrium curves; and in all cases, no azeotropic behavior is predicted for a mixture characterized with these sets of parameters (see case 4 in Table 1). These results imply that the crossing of single-component isotherms is a necessary but not sufficient condition for formation of azeotropic mixtures. As a result of this behavior, Figure 4d shows that at the same lateral interactions and surface heterogeneity, the fractional surface coverage of component 1 at  $y_1 = 1$  is always higher than that of component 2 at  $y_1 = 0$ . Nevertheless, this trend is overcome with stronger lateral interactions for component 2 and much higher surface heterogeneity toward component 1.

Figure 4b also shows that for the ideal situation,  $S_{12} = 3$ . However, for a very heterogeneous component 1,  $S_{12}$  decreases from a nearly ideal value at  $y_1 = 0$  to smaller values with increasing  $y_1$ ; and by allowing both components to have significant lateral interactions,  $S_{12}$  decreases even more with increasing  $y_1$ . A similar behavior is seen for component 2. These results imply that the lateral interactions may augment the effect of heterogeneity.

**Effect of Partial Nonidealities in the Mixture (Cases 5 and 6).** The effect of partial nonidealities (heterogeneity and lateral interactions) of only one component in the binary mixture is studied to account for the effect of partial nonidealities of the strongly adsorbed component independently of the weakly adsorbed component (case 5) and vice versa (case 6). For these cases, component 1 is much more strongly adsorbed than component 2. The parameters for each of these two cases are shown in Table 1, and the results are plotted in Figures 5 and 6 for cases 5 and 6, respectively.

Again, as noticed in case 4, for two components with distinctly different adsorption affinities, Figure 5a shows that varying the lateral interactions and surface heterogeneity of the more strongly adsorbed component does not result in any crossing of the single-component isotherms; this implies that the formation of an azeotropic mixture at these conditions is impossible. However, the surface coverage of component 1 is markedly affected by each of the lateral interactions and also the heterogeneity of the surface toward this component, but in opposite directions. This is clearly seen in Figure 5a by the increasing surface coverage of component 1 with both increasing lateral interactions and decreasing surface heterogeneity.

Figure 5b shows a case where component 2 is ideal and component 1 varies from being ideal to nonideal. Again, significant heterogeneity for component 1 causes  $S_{12}$  to decrease from the ideal value ( $S_{12} = 3$ ) with increasing  $y_1$ . This is also seen in Figure 5c where the mixture does not exhibit any azeotropic behavior. Therefore, the surface heterogeneity has a negative effect on the adsorption affinities. However, increasing the lateral interactions of component 1 counteracts the effects of heterogeneity to the extent that  $S_{12}$  starts increasing with  $y_1$ .

Figure 6 shows the case where component 1 is ideal and component 2 varies from being ideal to nonideal. Figure 6a shows that increasing the lateral interactions of the more weakly adsorbed component causes it to cross the ideal single-component isotherm of the strongly adsorbed component at  $P \approx 5$  atm. However, increasing the surface heterogeneity toward the weak component with no lateral interactions causes a decreasing adsorption affinity.

Figure 6b shows a behavior similar to that shown in Figure 5b. For example, significant heterogeneity for component 2 causes  $S_{12}$  to decrease toward the ideal  $S_{12} = 3$  with increasing  $y_1$ . However, increasing the lateral interactions of component 2 counteracts the effect of heterogeneity to the extent that  $S_{12}$  starts increasing with  $y_1$ . In this case (case 6), ideality is approached as  $y_1 \rightarrow 1.0$ , with significant deviation from ideality as  $y_2 \rightarrow 1.0$ . Just the opposite behavior results in case 5, which is understandable by the way the partial nonidealities are imparted to each of the components in the specific cases. It is interesting that the results in Figures 5b and 6b are in contrast to those shown in Figure 4b, as a result of including similar lateral interactions for both components in case 4. In both scenarios in case 4, the lateral interactions of the opposite component augment the effects of heterogeneity of the opposing component.

Figure 6c also shows that increasing the lateral interactions of the light component tends to cause azeotropic behavior at high  $y_2$ . However, this mixture does not actually exhibit an azeotrope, as the equilibrium curve becomes parallel to the equality line when  $y_2 \rightarrow 1.0$ . Figure 6d shows that the partial nonidealities of the light component also affect the adsorption affinities of both components, especially when component 2 is in the mixture at high concentrations. However, as also noticed in Figure 5d, the dependence of the adsorption affinity of component 1 on the partial adsorption nonidealities of each of the two components is considerably higher than that of component 2. This result is due to the already much higher adsorption affinity of component 1, which makes the surface coverage more sensitive to variations in composition.

**Correlation with Literature Data.** The practical use of the new single-component adsorption isotherm model (eq 10) is demonstrated by correlating the single-component adsorption isotherms for methane, ethane,

ethylene, and carbon dioxide on Nuxite-AL activated carbon.<sup>24,25</sup> The objective function is presented in eq 27 and the average relative error (ARE) is defined by eq 28.

$$F = \left[ \sum_{i=1}^N (n_{R,i}^{\text{exp}} - n_{R,i}^{\text{calc}})^2 \right]_{\text{minimum}} \quad (27)$$

$$\text{ARE} = \frac{100\%}{N} \sum_{i=1}^N \frac{|n_{R,i}^{\text{exp}} - n_{R,i}^{\text{calc}}|}{n_{R,i}^{\text{exp}}} \quad (28)$$

$N$  is the number of experimental points and the superscripts exp and calc denote experimental and calculated number of moles (see eq 10b), respectively. Figure 7 shows sample comparisons between the experimental and correlated single-component adsorption data. The optimized fitting parameters and the ARE values are presented in Table 2. This four-parameter model does fairly well in correlating the data, with the worst fit giving rise to only about 9% ARE. These results are very encouraging, especially since the single-component adsorption isotherm data presented in Figure 7 are simultaneously fitted to all of the data at all of the temperatures. These correlations would necessarily be more accurate when independently fitted to each adsorption isotherm at the different temperatures, which is typically done in the literature. However, it is more desirable to include the temperature effects within the fitted parameters whenever it is required to use the correlations at different temperatures, for example, when modeling nonisothermal adsorption processes.

The corresponding binary adsorption isotherm data are correlated by optimizing the  $k_{ij}$  values directly with the binary experimental data using the objective function presented in eq 29, and the average relative error (ARE) is calculated according to eq 30,

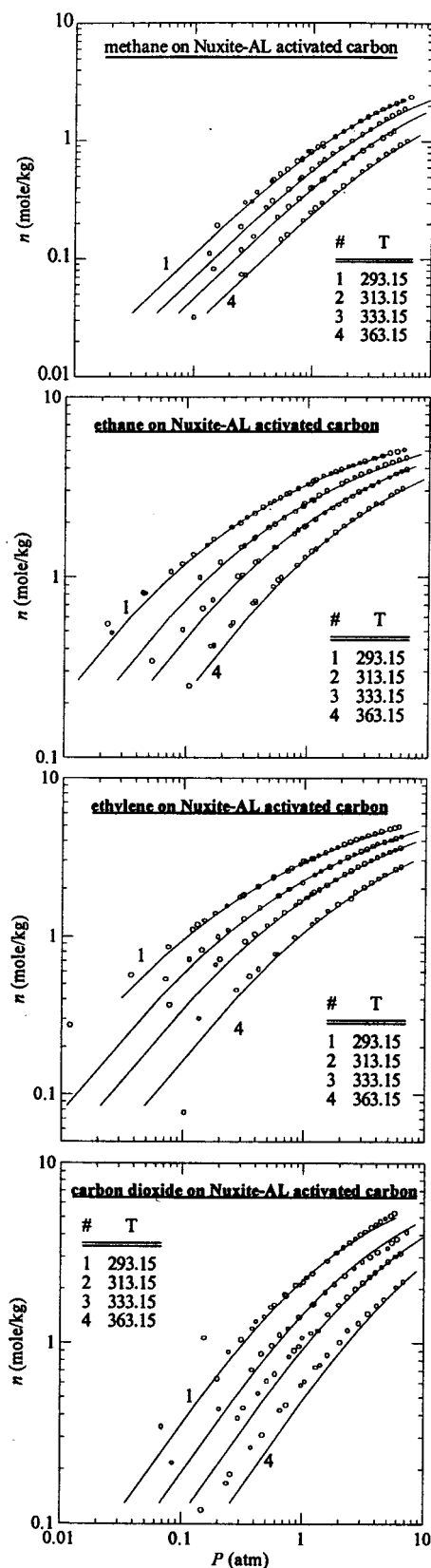
$$F = \left[ \sum_{j=1}^2 \sum_{i=1}^N \left| \frac{n_j^{\text{exp}}}{m_j} - \theta_{R,j}^{\text{calc}} \right| \right]_{\text{minimum}} \quad (29)$$

$$\text{ARE} = \frac{100\%}{2N} \sum_{j=1}^2 \sum_{i=1}^N \left[ \frac{|n_{R,j}^{\text{exp}} - n_{R,j}^{\text{calc}}|}{n_{R,j}^{\text{exp}}} \right]_i \quad (30)$$

where  $j$  is the component counter,  $m_j$  is the single-component saturation limit as optimized from eq 27 and  $\theta_{R,j}^{\text{calc}}$  is the calculated fractional surface coverage of component  $j$  as obtained from eq 26. Figure 8 shows sample comparisons between experimental and correlated binary adsorption isotherm data on Nuxite-AL activated carbon.<sup>26</sup> The optimized  $k_{ij}$  values and the corresponding ARE values are also displayed in Figure 8. The ARE values are quite reasonable, ranging from about 4 to 9%, and the new model is fully capable of correlating not only the binary loadings but also the selectivities, as shown very convincingly in the  $x$ - $y$  diagrams. The ability and flexibility of this model are manifest in the single binary fitting parameter ( $k_{ij} = k_{ji}$ ), which also allows it to account for very nonideal phase behavior, as demonstrated in the parametric study.

## Conclusions

Analytical expressions for the adsorption of a binary gas mixture that laterally interacts on a random hetero-



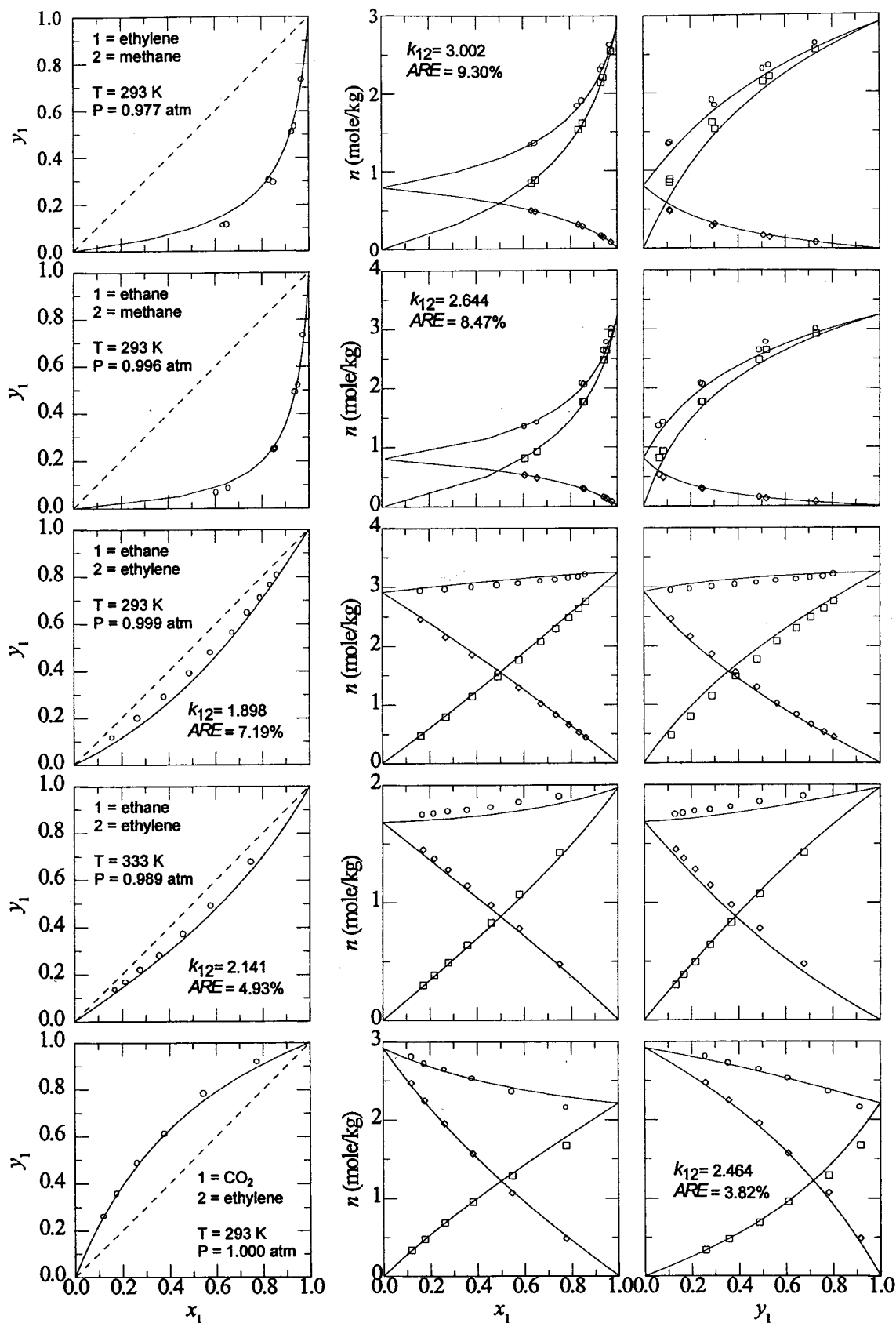
**Figure 7.** Correlated (lines) and experimental (symbols) single-component adsorption isotherms on Nuxite-AL activated carbon.<sup>24,25</sup>

geneous surface are developed. A parametric study is performed using this model to investigate subtle nonidealities associated with laterally interacting mixtures on random heterogeneous surfaces. The results show that, for most cases, the adsorption affinities tend to increase

(24) Szepeszy, L.; Illés, V. *Acta Chim. Hung. Tomus.* **1963**, 35, 37.

(25) Szepeszy, L.; Illés, V. *Acta Chim. Hung. Tomus.* **1963**, 35, 53.

(26) Szepeszy, L.; Illés, V. *Acta Chim. Hung. Tomus.* **1963**, 35, 245.



**Figure 8.** Correlated (lines) and experimental binary adsorption data (symbols) on Nuxite-AL activated carbon.<sup>26</sup> Each row in this figure represents one binary system plotted in different coordinates.

with increasing lateral interactions and/or decreasing surface heterogeneity. However, the effect of lateral interactions is stronger, in most cases, than that of surface heterogeneity; and they are capable of overwhelming the usually opposing effects exhibited by heterogeneous

surfaces. Nevertheless, the model shows that lateral interactions may in some cases enhance but in other cases counteract the effects of heterogeneity, depending on the strength of the lateral interactions and which components are interacting.

**Table 2. Fitted Isotherm Parameters and ARE Values for the Single Component Adsorption Isotherms on Nuxite-AL Activated Carbon<sup>24,25</sup>**

adsorbate	$m$ (mol/kg)	$10^5 b_0$ (atm <sup>-1</sup> )	$10^{-3} \epsilon_k/k$ (K <sup>-1</sup> )	$\sigma\sqrt{3}$ (atm <sup>-1</sup> )	$10^{-3} z\omega/k$ (K <sup>-1</sup> )	ARE (%)
methane	4.610	14.784	2.179	0.081	0.260	3.10
ethane	7.458	2.462	3.453	0.002	0.965	3.90
ethylene	9.596	1.841	3.353	0.151	1.314	4.85
CO <sub>2</sub>	7.949	1.560	3.033	$1.44 \times 10^{-5}$	0.250	9.00

This model is also capable of predicting nonideal adsorption behavior, including adsorption azeotropes and sigmoidal-shaped mixed gas adsorption isotherms. Azeotropic mixtures are predicted but only when the single-component isotherms cross each other, which is a necessary but not sufficient condition to cause azeotropic behavior. Azeotropic behavior and sigmoidal-shaped mixed gas adsorption isotherms are also caused by high values of  $k_{12}$ , which controls the strength of interactions between like and unlike components to the extent that  $k_{12}$  can account qualitatively for pore exclusion phenomenon. Sigmoidal-shaped adsorption isotherms are also predicted at high positive (or negative) lateral interactions between similar components, even when  $k_{12} = 0$ .

The practical application of this model is demonstrated by correlation with single-component and binary data from the literature. The results are quite satisfactory, when considering the simplicity of this model, which has only

one binary fitting parameter, and when considering that it requires few iterations to simultaneously solve the implicit set of coupled algebraic expressions. This model should thus find considerable use in modeling adsorption processes that exhibit complex phase behavior. Part 2 will further demonstrate the utility of this new model in correlating complex binary adsorption isotherms and predicting multicomponent adsorption equilibria from correlated single and binary data.

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