Influence of Adsorbate Size and Adsorbent Heterogeneity on IAST

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The ideal adsorbed solution theory (IAST) can introduce serious errors in the calculation of multicomponent gas adsorption equilibria from the corresponding pure gas adsorption isotherms when the adsorbate sizes and the degree of adsorbent heterogeneity for adsorption of the components differ substantially. The multisite Langmuir and heterogeneous Langmuir models were used to evaluate the extent of these errors. It is shown that large differences in adsorbate sizes and degrees of heterogeneity of adsorption of the components of a mixture can cause the formation of an adsorption azeotrope that cannot be described by IAST.

Introduction

The ideal adsorbed solution theory (IAST) of Myers and Prausnitz (1965) has become the benchmark for calculating mixed gas adsorption equilibria from the corresponding pure gas adsorption equilibrium isotherms. This theory is frequently used to obtain first-pass prediction of multicomponent gas adsorption equilibria for design purposes as well as for comparing the predictions by other adsorption models. It is thermodynamically consistent and is based on the elegant concept of creating the multicomponent ideal adsorbed phase by mixing pure gas adsorbed phases at constant surface potential and temperature. The mathematical framework for the theory for an N-component system is reproduced below:

$$-\frac{\phi_i^*}{RT} = \int_o^{P_i^*} \frac{n_i^*(P)}{P}\, dP \quad \text{constant } T, \quad i = 1,2,\ldots,N \qquad (1)$$

$$\phi_i^*(P_i^*,T) = \text{constant} = \phi(P,T,y_i) \qquad i = 1,2,\ldots,N \qquad (2)$$

$$x_i = Py_i/P_i^* \qquad i = 1,2,\ldots,N \qquad (3)$$

$$(1/n) = \sum_i x_i/[n_i^*(P_i^*)] \qquad i = 1,2,\ldots,N \qquad (4)$$

where ϕ_i^* (a negative quantity) is the surface potential for adsorption of pure gas i at a pressure of P_i^* and temperature T; $n_i^*(P)$ is the specific amount adsorbed (mol/kg) of pure gas i at pressure P and temperature T; R is the gas constant; y_i is the equilibrium gas phase mole fraction of component i of a mixed gas system at a total gas pressure of P and temperature T; x_i is the corresponding equilibrium adsorbed phase mole fraction of component i; n is the specific total amount (mol/kg) of all components adsorbed at P, T, and y_i; $n_i^*(P_i^*)$ is the specific amount adsorbed of pure component i at pressure P_i^* and T; and ϕ is the surface potential (a negative quantity) of the mixed adsorbed phase in equilibrium with a gas phase at P, T, and y_i.

Equation 1 provides the thermodynamic relationship for calculating $\phi_i^*(P_i^*, T)$ from the pure gas adsorption isotherm of component i [$n_i^*(P)$ at constant T]. Equation 2 provides the relationship between P_i^* for all components of the adsorption system when $\phi_i^* = \phi$ (condition of mixing in the IAST). Equations 3 and 4 relate x_i and n with P, y_i, n_i^*, and P_i^* at constant T. For a given set of P, T, and y_i, and the pure gas adsorption isotherms, there are $(3N+1)$ unknowns (x_i, n, P_i^*, ϕ_i^*) for the system. Equations 1–4 and the constraint [$\Sigma x_i = 1$] provide $(3N+1)$ independent equations relating them. Thus, a unique solution can be obtained for n and x_i as functions of P, T, and y_i if the pure gas adsorption isotherms are known. The specific amount of component i adsorbed, $n_i (= nx_i)$ at P, T, and y_i can then be easily calculated.

The concept of a nonideal adsorbed phase can be incorporated into the framework of IAST by modifying Eq. 3 as (Myers and Prausnitz, 1965):

$$x_i = Py_i/P_i^*\gamma_i \qquad (5)$$

where γ_i is the activity coefficient of component i in the nonideal adsorbed phase. Coefficients γ_i can be calculated as

functions of P, T, and y_i or x_i and T, and they are not known *a priori*. Consequently, the nonideal adsorbed phase concept is not a predictive model. It is used to calculate γ_i from experimental mixed gas adsorption data when IAST fails to predict the mixture equilibrium. It has been suggested that γ_i can be correlated as a function of x_i at a constant T (binary system only) by measuring a few data points for the binary gas adsorption isotherm and then using one of the conventional activity coefficient–composition relationships developed for describing nonideal vapor–liquid equilibrium data. The correlation can then be used in Eqs. 1, 2, 4 and 5 to calculate the complete binary adsorption isotherm from pure component adsorption isotherms. This approach, however, has found limited success.

Many workers have used and tested the IAST in the past 25 years for predicting (correlating) mixed gas adsorption equilibria from pure gas adsorption data. Most published results, however, are restricted to binary adsorption systems. The theory often predicts the binary adsorption equilibria very well when pure gas adsorption isotherms are accurately known over a large range of pressures, particularly at the limit of $P \to 0$ for accurate estimation of ϕ_i^* using Eq. 1. At other times, the theory fails to predict the binary adsorption data by a large margin. A recent systematic evaluation of IAST using many different published pure and binary gas adsorption data (Valenzuela and Myers, 1984) indicated that the average error in calculating the selectivity (S) of adsorption of component 1 over component 2 for a binary system ($S = n_1 y_2 / n_2 y_1$) may be $\pm 40.0\%$ or more.

A very common observation from the analysis of the published binary adsorption data is that the values of γ_i at the limit of infinite dilution ($x_i \to 0$) of component i ($\gamma_i \to \gamma_i^\infty$) are less than unity. This is often the case even when the gas mixture is a condensable vapor and the corresponding equilibrium binary liquid phase shows activity coefficients greater than unity at the limits of infinite dilution of the components. Energetic heterogeneity of the adsorbent is generally believed to cause $\gamma_i^\infty < 1$ for adsorption from gas or vapor mixtures.

The purpose of this article is to demonstrate, by using simple thermodynamically consistent models of pure and binary gas adsorption isotherms, that IAST can introduce serious errors in calculation of n_i as a function of y_i for a given P and T. The two key factors causing this behavior are unequal sizes of the adsorbates and the adsorbent heterogeneity.

Role of Unequal Adsorbate Sizes

The multisite Langmuir (MSL) model (Nitta et al., 1984) is used to evaluate the effect of the difference in adsorbate sizes on multicomponent adsorption. The model assumes that a_i number of sites (equivalent space) is occupied by component i in the adsorbed phase. The governing adsorption isotherm equations are

$$\textit{Pure gas:} \quad \theta_i^* = K_i^* P [1 - \theta_i^*]^{ai} \quad \text{constant } T, \quad i = 1,2,\ldots,\mathrm{N} \tag{6}$$

$$\textit{Mixed gas:} \quad \theta_i = K_i^* P y_i \left[1 - \sum_i \theta_i\right]^{ai} \quad \text{constant } T, \quad i = 1,2,\ldots,\mathrm{N} \tag{7}$$

where $\theta_i (= n_i/m_i)$ is the fractional amount of component i adsorbed; m_i is the specific saturation adsorption capacity (mol/kg) of pure component i on the adsorbent; m_i and a_i are independent of T. The superscript asterisk represents pure gas adsorption on the adsorbent. A site or space balance of the adsorbed phase gives

$$a_i m_i = \text{constant}. \tag{8}$$

Equation 8 is a requirement for thermodynamic consistency of the MSL model; K_i^* is the Henry's law constant (atm^{-1}) for adsorption of pure gas i in the $\theta_i^* - P$ domain $[(\partial\theta_i^*/\partial P)_T = K_i^*$ at $P \to 0]$. The Henry's law constant (K_i^H) for adsorption of pure gas i (mol/kg/atm) in the $n_i^* - P$ domain $[(\partial n_i^*/\partial P)_T = K_i^H$ at $P \to 0]$ is related to K_i^* by ($K_i^H = m_i K_i^*$); K_i^* and K_i^H are both functions of temperature only:

$$\frac{d \ln K_i^*}{dT} = \frac{d \ln K_i^H}{dT} = -\frac{q_i^0}{RT^2} \tag{9}$$

where q_i^0 is the isosteric heat of adsorption of pure gas i at the limit of $P \to 0$.

It can be shown from Eqs. 6–9 that

$$q_i^*(\theta_i^*) = -RT^2 \cdot \left[\frac{\partial \ln P}{\partial T}\right]_{\theta_i^*} = q_i^0 \tag{10}$$

$$q_i(\theta_i) = -RT^2 \cdot \left[\frac{\partial \ln (Py_i)}{\partial T}\right]_{\theta_i} = q_i^0 \tag{11}$$

where q_i^* is the isosteric heat of adsorption of pure gas i at a fractional coverage of θ_i^* for that component; q_i is the isosteric heat of adsorption of component i from a mixture at a fractional coverage of θ_i for component i (Sircar, 1985). Equations 10 and 11 show that both q_i^* and q_i are independent of adsorbate loadings, and equal q_i^0. Thus, the MSL model represents an energetically homogeneous adsorbent characterized by the heat (q_i^0) for pure gas i.

Equation 9 can be integrated to get

$$K_i^* = K_i^0 \exp[+ q_i^0/RT] \tag{12}$$

where K_i^0 is the value of K_i^* at the limit of $T \to \infty$.

According to the MSL model, the selectivity of adsorption $(S)^{\mathrm{MSL}}$ for a binary system is

$$\frac{S^{\mathrm{MSL}}}{S^H} = (1 - \theta)^{(a_1 - a_2)}; \qquad \theta = \Sigma\theta_i \tag{13}$$

$$S^H = (K_1^H/K_2^H) = (a_2 K_1^*/a_1 K_2^*) \tag{14}$$

where S^H is the Henry's law selectivity of component 1 over component 2 for the binary system at the limit of $P \to 0$ ($\theta i \to 0$). Equation 13 shows that S^{MSL} is a function of θ_i or P and y_i when $a_1 \neq a_2$. This is a very interesting property of the MSL model that makes it extremely flexible: S^{MSL} can increase ($a_2 > a_1$) or decrease ($a_1 > a_2$) with increasing θ because of the unequal adsorbate sizes; and it is independent of

θ only when $a_1 = a_2$. The MSL model reduces to the well-known Langmuir adsorption equation when $a_i = 1$ (one molecule adsorbed per site).

The pure gas MSL model (Eq. 6) has three parameters [m_i, a_i, and $K_i^*(T)$]. It can be used to describe the pure gas adsorption isotherms of the components of a gas mixture using the constraint of Eq. 8. The mixed gas adsorption of the components can then be calculated using Eq. 7 and the pure gas model parameters.

Equation 7 can be rearranged to get

$$Z + \sum K_i^*(Py_i)Z^{ai} = 1; \qquad Z = (1-\theta). \tag{15}$$

Equation 15 can be used to calculate Z for a given P and y_i and then obtain θ_i using Eq. 7.

One interesting characteristic of the MSL mixed gas model is that it can describe binary adsorption azeotropy ($x_i = y_i$). It follows from Eqs. 13 and 14 that ($S^{\mathrm{MSL}} \to 1$) when Z equals $[1/(S^H)]^{[1/(a_1-a_2)]}$. The corresponding gas phase mole fraction (y_i^a) of component i ($y_1^a + y_2^a = 1$) can then be calculated using Eq. 15 for a given P. Azeotropy exists for a given value of P and T if y_i^a lies between zero and unity. Obviously, no azetrope can be formed if the adsorbates have equal sizes ($a_1 = a_2$).

Equations 6 and 7 satisfy the key thermodynamic tests between pure and mixed gas (binary) isotherms (Sircar, 1985) when constraint (Eq. 8) is obeyed:

$$\frac{(\phi_2^* - \phi_1^*)}{RT} = \int_0^1 \left(\frac{n_1}{y_1} - \frac{n_2}{y_2}\right) dy_1 \quad \text{constant } T, P \tag{16}$$

$$n_2^*(P) = n(P,y_1) - P\cdot\frac{\partial}{\partial P}\left[\int_0^{y_1}\left(\frac{n_1}{y_1} - \frac{n_2}{y_2}\right) dy_1\right] \quad \text{constant } T. \tag{17}$$

Equations 16 and 17, respectively, represent the integral isothermal–isobaric and the isothermal differential thermodynamic consistency tests for adsorption of a binary system. The quantities on the righthand side of these equations can be evaluated from isothermal binary adsorption data (Eq. 7), while the quantities on the lefthand side can be calculated from pure component adsorption data (Eq. 6).

The MSL model therefore represents a simple, analytical, flexible, as well as thermodynamically and physically consistent framework for describing pure and mixed gas adsorption from adsorbates of different sizes on an energetically homogeneous adsorbent. The model has been successfully used to describe several pure and binary gas adsorption isotherms (Nitta et al., 1984; Golden and Sircar, 1994a). It will be shown later that the model can describe pure gas adsorption isotherms for adsorbates of substantially different sizes on the same adsorbent over a large range of P and T.

The MSL model was recently derived by Nitta and coworkers (1984) by using a statistical thermodynamic argument. It, however, can be very simply derived by using the classic Langmuirian kinetic argument (Henry, 1922). Thus, one molecule of gaseous component i reacts with a_i number of empty sites available on the adsorbent to form one molecule of adsorbed component i. Using the mass action law for the reversible multicomponent adsorption process, the net rate of uptake (change of θ_i with time, t) of component i may be written as

$$\frac{d\theta_i}{dt} = k_i^a P_i(1-\Sigma\theta_i)^{ai} - k_i^d\theta_i \quad i = 1,2\ldots \tag{18}$$

where k_i^a and k_i^d are, respectively, specific reaction rate constants for the adsorption and desorption processes. The instantaneous adsorption rate is determined by gas phase partial pressure ($P_i = Py_i$) of component i and the total number of empty sites ($1-\Sigma\theta_i$) available, while the instantaneous desorption rate of component i is determined by its adsorbed phase composition (θ_i). For a dynamic equilibrium ($d\theta_i/dt = 0$), Eq. 18 reduces to Eq. 7 for a gas mixture, or to Eq. 6 for a pure gas adsorption with $K_i^* = (k_i^a/k_i^d)$.

It should be emphasized, however, that the MSL model does not include the effect of adsorbent heterogeneity and lateral interactions in the adsorbed phase. Thus, its general application for describing pure and multicomponent adsorption equilibria may be limited. The model is being used here only to demonstrate the role of adsorbate size differences on mixed gas equilibria.

IAST and MSL Model

The IAST can be used to calculate mixed gas adsorption equilibria for a system where the pure gas adsorption isotherms are given by the MSL model (Eq. 6). We restrict our analysis to a binary adsorption system ($i = 1, 2$) for the sake of simplicity. Surface potential ϕ_i^* can be calculated by combining Eqs. 1 and 6 as

$$+(\phi_i^*/RT) = m_i[(a_i - 1)\theta_i^* + a_i\ln(1-\theta_i^*)] \quad \text{constant } T. \tag{19}$$

For a binary system, Eqs. 2 and 8 yield

$$a_2(a_1-1)\theta_1^0 + a_1a_2\ln(1-\theta_1^0) = a_1(a_2-1)\theta_2^0 + a_1a_2\ln(1-\theta_2^0) \tag{20}$$

where θ_i^0 in Eq. 20 is fractional coverage of pure gas i at T when ϕ_i^* is equal to ϕ for a mixture at P, T, and y_i; and P_i^0 is the corresponding equilibrium gas pressure for pure component i

$$\theta_i^0 = K_i^*P_i^0(1-\theta_i^0)^{ai}. \tag{21}$$

Equations 3 and 4 can then be used ($\dot{n} = \Sigma m_i\theta_i$, $\theta = \Sigma\theta_i$) to get

$$\theta_1^{\mathrm{IAST}} = \frac{a_1K_1^*Py_1\theta_1^0(\theta_2^0)^2(1-\theta_1^0)^{a1}}{\left[a_1K_1^*Py_1(\theta_2^0)^2(1-\theta_1^0)^{a1} + a_2K_2^*Py_2(\theta_1^0)^2(1-\theta_2^0)^{a2}\right]} \tag{22}$$

$$\theta_2^{\text{IAST}} = \frac{a_2 K_2^* P y_2 \theta_2^0 (\theta_1^0)^2 (1-\theta_2^0)^{a2}}{\left[a_1 K_1^* P y_1 (\theta_2^0)^2 (1-\theta_1^0)^{a1} + a_2 K_2^* P y_2 (\theta_1^0)^2 (1-\theta_2^0)^{a2}\right]} \tag{23}$$

$$K_1^* P y_1 \frac{(1-\theta_1^0)^{a1}}{\theta_1^0} + K_2^* P y_2 \frac{(1-\theta_2^0)^{a2}}{\theta_2^0} = 1. \tag{24}$$

Equations 20 and 24 can be used to calculate θ_1^0 and θ_2^0 for a given P, T, and y_1. Equations 22 and 23 can then be used to calculate θ_i^{IAST}.

The binary selectivity of adsorption (S^{IAST}) by the IAST for a given P, T, and y_i is

$$\frac{S^{\text{IAST}}}{S^H} = \frac{a_1}{a_2} \cdot \frac{\theta_2^0}{\theta_1^0} \frac{(1-\theta_1^0)^{a1}}{(1-\theta_2^0)^{a2}} \tag{25}$$

where S^H is given by Eq. 14.

It can be easily shown that Eqs. 22 and 23 reduce to Eq. 7 when $a1 = a2$ ($\theta 1^0 = \theta 2^0$). Thus, the IAST prediction of multicomponent adsorption equilibria for MSL pure gas isotherms is identical to those by the MSL mixed gas model when the adsorbate sizes are equal. Otherwise, the IAST predictions will be different and a nonideal adsorbed phase needs to be invoked to describe the mixed gas adsorption data.

The adsorbed phase mole fractions of the components (x_i) of a binary system may be calculated by using the fractional coverages (θ_i) as

$$x_1 = \frac{a_2 \theta_1}{a_2 \theta_1 + a_1 \theta_2}; \quad x_2 = (1 - x_1). \tag{26}$$

The activity coefficient of component i for the nonideal adsorbed phase (IAST framework) is given by

$$\gamma_i = \frac{(x_i)^{\text{IAST}}}{x_i} \qquad i = 1,2,\ldots, \tag{27}$$

$$\text{Binary System} \quad \gamma_1^\infty = \left[\frac{S^{\text{IAST}}}{S}\right]_{y_1 \to 0}; \quad \gamma_2^\infty = \left[\frac{S}{S^{\text{IAST}}}\right]_{y_1 \to 1} \tag{28}$$

where x_i^{IAST} is the adsorbed phase mole fraction of component i calculated by the IAST; x_i and S are, respectively, the actual adsorbed phase mole fraction of component i and the binary adsorption selectivity.

The activity coefficients defined by Eqs. 27 and 28 are defined to show the difference between the calculated values of x_i by IAST and the actual value of x_i given by MSL. They are not thermodynamic activity coefficients for the MSL model, which could be calculated to describe the difference between the x_i given by the MSL model and the actual experimental data for a binary system.

Numerical calculation of errors exhibited by the use of IAST in predicting binary MSL mixed gas adsorption equilibria will be given later.

Role of Adsorbent Heterogeneity

The heterogeneous Langmuir (HL) model (Sircar, 1991) is used to evaluate the effect of adsorbent heterogeneity on multicomponent adsorption. The adsorbates have equal sizes ($m_i = m$). The model assumes that the heterogeneous adsorbent consists of a patchwise distribution of Langmuirian sites. A uniform distribution of site Henry's law constants characterizes the heterogenity. It is further assumed that the cumulative distribution of the Henry's law constants for each component coalesce. The adsorbed phase is ideal. Thus, Eqs. 6 and 7 (with $a_i = 1$) describe the pure and multicomponent gas adsorption isotherms on a homogeneous patch of the HL model. The overall adsorption isotherm equations are

$$\text{Pure gas} \quad \theta_i^* = \theta_{iH}^* \left[1 - \frac{(\psi_i - z_i^*)}{z_i^*} \oint(z_i^*)\right], \quad i = 1,2,\ldots \tag{29}$$

$$\theta_{iH}^* = \frac{K_i^* P}{1 + K_i^* P} \tag{30}$$

$$z_i^* = \psi_i \theta_{iH}^* \tag{31}$$

$$\oint(z_i^*) = \frac{1}{2z_i^*} \ln\left[\frac{1+z_i^*}{1-z_i^*}\right] - 1. \tag{32}$$

$$\text{Mixed gas} \quad \theta_i = \theta_{iH}\left[1 - \frac{(\psi_i - z)}{z} \oint(z)\right] \tag{33}$$

$$\theta_{iH} = \frac{K_i^* P y_i}{1 + \Sigma K_i^* P y_i} \tag{34}$$

$$z = \Sigma \psi_i \theta_{iH} \tag{35}$$

$$\oint(z) = \frac{1}{2z} \ln\left[\frac{1+z}{1-z}\right] - 1. \tag{36}$$

The temperature dependence of K_i^* is given by Eq. 12; ψ_i is the degree of heterogeneity of component i. It is proportional to the ratio of dispersion to the mean of the distribution of the Henry's law constants for that component; $\psi_i = 0$ represents a homogeneous adsorbent; and $\psi_i = 1$ represents the maximum heterogeneity by the HL model.

The model parameters for the pure gas isotherm are [m, ψ_i, and $K_i^*(T)$]. Equations 33–36 can be used to calculate mixed gas adsorption isotherm for a given set of P, T, and y_i in conjunction with pure gas model parameters.

According to the HL model, the selectivity of adsorption (S^{HL}) for a binary system is

$$\frac{S^{\text{HL}}}{S^H} = \frac{\left[1 - \frac{(\psi_1 - z)}{z} \oint(z)\right]}{\left[1 - \frac{(\psi_2 - z)}{z} \oint(z)\right]} \tag{37}$$

where S^H is defined by Eq. 14. It has been shown (Sircar, 1991) that S^{HL} decreases with increasing θ when $\psi_1 \neq \psi_2$. Also S^{HL} is independent of θ when $\psi_1 = \psi_2$, including the

case where the adsorbent is homogeneous toward both adsorbates ($\psi_1 = \psi_2 = 0$).

The HL model can also describe adsorption azeotropy. It can be shown (Sircar, 1991) that S^{HL} can go through a value of unity at a constant P and T if

$$S^{HL}\left[\frac{1-\psi_1}{1-\psi_2}\right] < 1. \tag{38}$$

The HL model provides a simple, analytical, and very flexible framework for describing the effect of adsorbent heterogeneity on multicomponent adsorption of equal-sized adsorbates. It is also thermodynamically consistent (satisfies Eqs. 16 and 17). The model has been tested for several binary adsorption systems (Sircar, 1991). The model, however, does not account for adsorbed phase lateral interactions.

IAST and HL Model

The IAST can be used to calculate binary gas adsorption isotherms from the pure gas isotherms given by the HL model (Eqs. 29–32). Equations 1–3 for a binary system are now given by (Sircar, 1991):

$$\left(\frac{\phi_i^*}{RT}\right) = -m\ln\left[\left(\frac{\psi_i}{\psi_i - z_i^0}\right)\left(e^{\phi(z_i^0)}\right)\left\{1-(z_i^0)^2\right\}^{0.5}\right] = \left(\frac{\phi}{RT}\right) \tag{39}$$

$$\sum \frac{\psi_i \theta_{iH}}{z_i^0} = 1, \qquad i = 1,2 \tag{40}$$

$$P_i^0 = \frac{z_i^0}{K_i^*(\psi_i - z_i^0)}, \quad i = 1,2. \tag{41}$$

Equations 39 and 40 relate z_i^0 $(i = 1,2)$ for a given P and y_i at constant T so that $(\phi_i^* = \phi)$. Equation 41 gives the corresponding values of P_i^0; x_i and $\theta(= \theta_1 + \theta_2)$ for the binary mixture can then be calculated by

$$x_i = \frac{Py_i}{P_i^0} \quad i = 1,2 \tag{42}$$

$$\frac{1}{\theta} = \sum \frac{PK_i^*\psi_i(\psi_i - z_i^0)}{(z_i^0)^2\left[1 - \frac{(\psi_i - z_i^0)}{z_i^0}\phi(z_i^0)\right]} \tag{43}$$

The selectivity of adsorption by the IAST (S^{IAST}) in this case is given by

$$\frac{S^{IAST}}{S^H} = \left[\frac{z_2^0}{(\psi_2 - z_2^0)}\right]\left[\frac{(\psi_1 - z_1^0)}{z_1^0}\right] \tag{44}$$

where S^H is again given by Eq. 14.

It can be easily shown analytically that $\theta_i(= x_i\theta)$ estimated by Eqs. 42 and 43 are equal to those given by Eq. 33 only when $\psi_1 = \psi_2(z_1^0 = z_2^0)$. It follows that the selectivity of adsorption is independent of adsorbate loading ($S^{HL} = S^{IAST} = S^H$) for that case. Thus, the binary gas adsorption isotherms calculated by IAST for the pure gas HL isotherms are identical to those by the HL model when the degrees of heterogeneity exhibited by the adsorbent for both adsorbates (ψ_i) are equal. Otherwise, the IAST will calculate different mixed gas isotherms, and a nonideal adsorbed phase has to be postulated to describe the discrepancy. A numerical example of the extent of this error will be given later.

The just described analytical comparison between actual mixed gas adsorption isotherms by MSL and HL models and those calculated by IAST using pure gas MSL and HL models provides the following important conclusions.

(a) IAST will give incorrect predictions of multicomponent adsorption equilibria when the adsorbate sizes of the components are different, even when the adsorbent is energetically homogeneous and the lateral interactions in the adsorbed phase are absent.

(b) IAST will give incorrect predictions of multicomponent adsorption equilibria on a heterogeneous adsorbent when the degrees of adsorbent heterogeneity for the adsorbates differ even when the adsorbate sizes are identical and the lateral interactions in the adsorbed phase are absent. In other words, the prediction by IAST will be erroneous if there is a distribution of binary adsorption selectivities from site to site on a heterogeneous adsorbent.

It is emphasized here that MSL and HL models are simplistic frameworks for describing the effects of adsorbate size difference and adsorbent heterogeneity, respectively. They must be rigorously tested before they are used for calculation of multicomponent equilibria.

Characteristics of Errors by IAST

Effect of adsorbate size differences

Ammonia, carbon dioxide, and dichlorodifluoro methane (Freon-12) are three adsorbates whose molecular sizes differ substantially as indicated by their molar volumes at normal boiling points reported in Table 1. We measured the adsorption isotherms of these gases on the BPL-activated carbon produced by Calgon Corporation (Calgon, 1983). The adsorption isotherms for NH_3 (30.0 and 45.5°C) and CO_2 (30.0 and 70.5°C) were measured in the pressure ranges of 0.2–8.0 and 0.2–50.0 atm, respectively, using a conventional volumetric adsorption apparatus. The adsorption isotherm of CF_2Cl_2 (37.8°C) in the pressure range of 0.0006–1.0 atm was measured in a gravimetric adsorption apparatus. The experimental isotherms (circles) are shown in Figures 1–3. The data represent both adsorption and desorption points indicating that the isotherms were reversible. The isotherms are plotted as $ln(\theta^*)$ vs. lnP to cover three decades of pressure range. The saturation capacities (m) for the gases are given in the figures.

The MSL pure gas model (Eq. 6) was used to fit these isotherms. The solid lines in the Figures 1–3 show the results. The model can describe very well these isotherms over the entire pressure and temperature ranges of the data. The model parameters are given in Table 1. The a_i values of NH_3, CO_2, and CF_2Cl_2 were, respectively, 1.53, 3.0, and 6.92, while the quantities ($a_i m_i$) were practically constant as required by Eq. 8. Thus, the binary mixtures of these gases provide good

Table 1. Pure Gas Adsorption Model Parameters

Adsorbate		Molar Vol* (cm^3/mol)	MSL Parameters for BPL Carbon				HL Parameters for 5A-Zeolite		
			K^* (atm^{-1})	m (mol/kg)	a	q^0 (kcal/mol)	m (mol/kg)	Ψ	K^* (atm^{-1})
NH_3	30.0°C		0.212	28.0	1.53				
	45.5°C	25.0	0.115	28.0	1.53	7.572			
	37.8°C		0.155†	28.0	1.53				
CO_2	30.0°C		0.192	15.0	3.0				
	70.5°C	40.0	0.082	15.0	3.0	4.347			
	37.8°C		0.160†	15.0	3.0				
CF_2Cl_2	37.8°C	80.0	97.0	6.5	6.92				
CO	−128.9°C	32.9					5.14	0.975	600.0
O_2	−128.9°C	25.7					5.14	0.0	15.0

*At normal boiling point.
†Estimated by Eq. 12.

cases for testing IAST predictions of binary isotherms against the binary MSL model. The MSL model can also describe the binary adsorption of CF_2Cl_2 from CO_2 on the BPL carbon (Golden and Sircar, 1994b) at the infinite dilution of CF_2Cl_2 fairly well. The affinity of adsorption of these gases on the carbon decreased in the order $CF_2CL_2 > NH_3 > CO_2$. The Henry's law constants (K^H) for CF_2Cl_2, NH_3, and CO_2 at 37.8°C were, respectively, 630.5, 4.34, and 2.40 mol/kg/atm. CF_2Cl_2 was extremely strongly adsorbed on the carbon and its high a (low m) value caused its isotherm to intersect the isotherms for the other two gases at some intermediate pressure, as shown by Figure 4. The isotherms for NH_3 and CO_2 on the carbon at 37.8°C were calculated using Eq. 6 and the model parameters of Table 1.

$CF_2Cl_2(1) + NH_3(2)$ binary mixture

The fractional amounts adsorbed (θ_i^{MSL}) of both components were calculated as functions of equilibrium gas-phase mole fraction (y_1) of component 1 at total gas pressures of 1.0 and 5.0 atm using the binary MSL model (Eq. 7) and the pure gas MSL model parameters of Table 1 at 37.8°C. The corresponding fractional amounts adsorbed of each component (θ_i^{IAST}) were also calculated using the IAST (Eqs. 20–24). Figure 5 shows the comparative results. It plots the ratio ($\theta_i^{IAST}/\theta_i^{MSL}$) as a function of y_1 at constant P. It may be seen from the figure that IAST severely underestimates the amount adsorbed of more strongly adsorbed component (CF_2Cl_2) when its composition is low ($y_1 < 0.2$). The ratio is slightly higher than unity at higher compositions. On the other hand, the IAST underpredicts the amount adsorbed for the less strongly adsorbed component (NH_3) at all values of $y_1 > 0.1$. The degree of underprediction increases substantially as y_1 increases. The errors of IAST predictions are also strong functions of the total gas pressure. The underprediction of CF_2Cl_2 adsorption from NH_3 at low y_1 is more pronounced at higher pressures. The situation is reversed for NH_3. Figure 5 also gives the γ_i^∞ values for both components. They are less than unity at both pressures. In particular, γ_1^∞ can be very low when the pressure is high.

Figure 6 shows the plots of the adsorbed phase mole fraction of CF_2Cl_2 (x_1) as a function of y_1 at a constant P. The binary mixture exhibits an adsorption azeotrope (solid line) at $y_1 = 0.60$ when the total gas pressure is 5.0 atm. The IAST (dashed lines) fails to predict the azeotrope. It generally predicts a larger value of x_1 at all values of y_1 except for the low y_1 region at the higher pressure.

Figure 7 compares the selectivity of adsorption (S) of Freon-12 over NH_3 as a function of y_1 at two pressures. The Henry's law limiting selectivity (S^H) for the mixture at 37.8°C

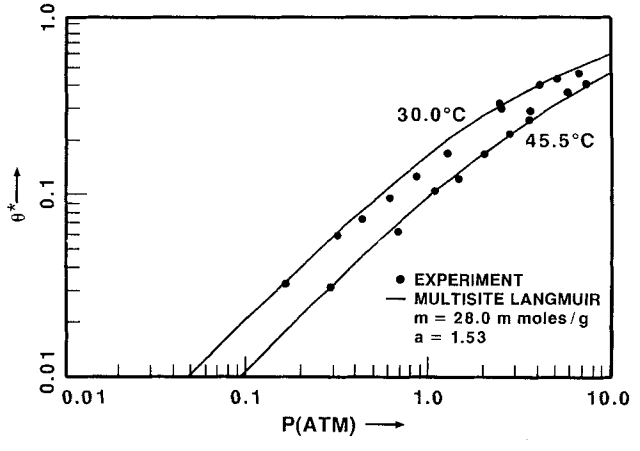

Figure 1. Adsorption of pure ammonia on BPL carbon.

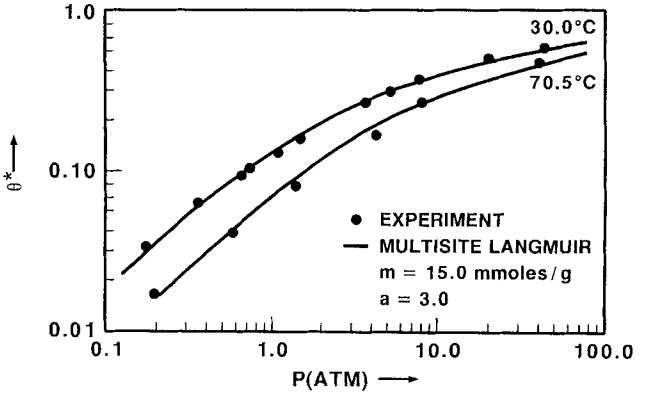

Figure 2. Adsorption of pure carbon dioxide on BPL carbon.

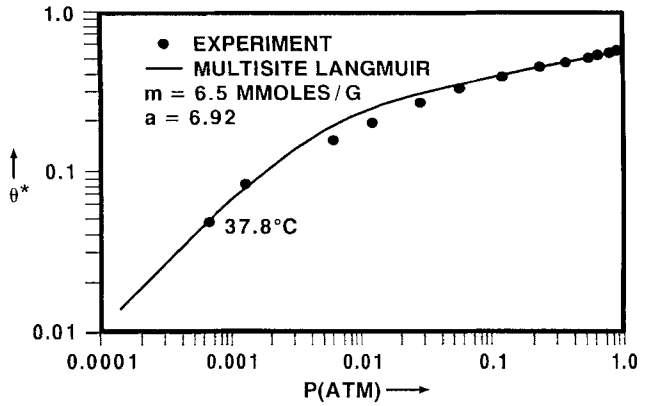

Figure 3. Adsorption of pure freon-12 on BPL carbon.

is 138.4. The selectivity rapidly decreases with increasing y_1 at constant P for this system. The IAST also predicts such a decrease, but at a much less pronounced rate. Furthermore, IAST predicts a smaller than actual selectivity at lower values of y_1 and a larger than actual selectivity at higher concentrations of component 1. The actual differences in the MSL and IAST selectivities are significant.

Clearly, a nonideal adsorbed phase needs to be postulated in order to describe the CF_2Cl_2–NH_3 binary isotherms described earlier in the framework of IAST. Equations 27 and 28 were used to calculate the adsorbed phase activity coefficients for this system. Figure 8 shows the results. It plots γ_i as a function of y_1 at constant P. It may be seen that γ_1 is less than unity at low values of y_1, and then it goes above unity at higher concentrations of Freon. It approaches unity at the limit of $y_1 \to 1$ after going through a maximum. On the other hand, γ_2 is slightly above unity at lower values of y_1, and then it becomes less than unity and decreases steadily as y_1 increases. This behavior is exhibited at both 1.0 and 5.0 atmospheric pressure, even though there is an adsorption azeotrope at the higher pressure for the system and no such azeotropy is exhibited at the lower pressure.

The activity coefficients of Figure 8 are therefore artifacts created by the failure of IAST to describe the binary adsorption isotherm from adsorbates of different sizes on a homogeneous adsorbent. Furthermore, this exercise demonstrates that the concept of experimentally measuring a few points of the binary adsorption isotherm and correlating the adsorbed phase activity coefficients using a conventional nonideal vapor–liquid equilibrium model of activity coefficient may not succeed in prediction of the entire binary adsorption isotherm because the adsorbed phase nonidealities may not be real.

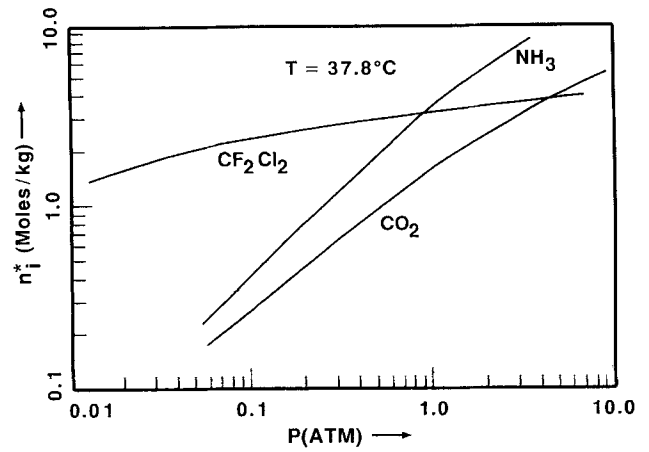

Figure 4. Adsorption of pure CF_2Cl_2, NH_3, and CO_2 on BPL carbon at 37.8°C.

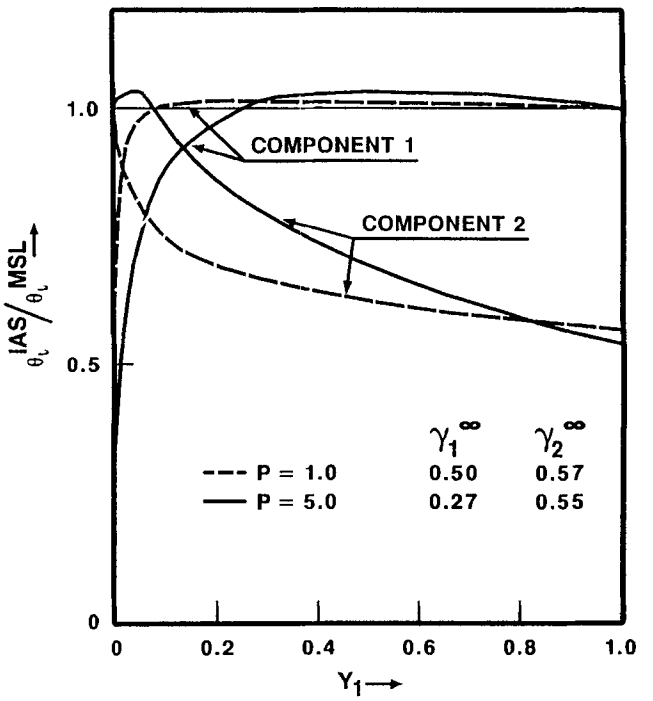

Figure 5. Comparison of calculated binary CF_2Cl_2-NH_3 isotherm on BPL carbon by MSL and IAST models.

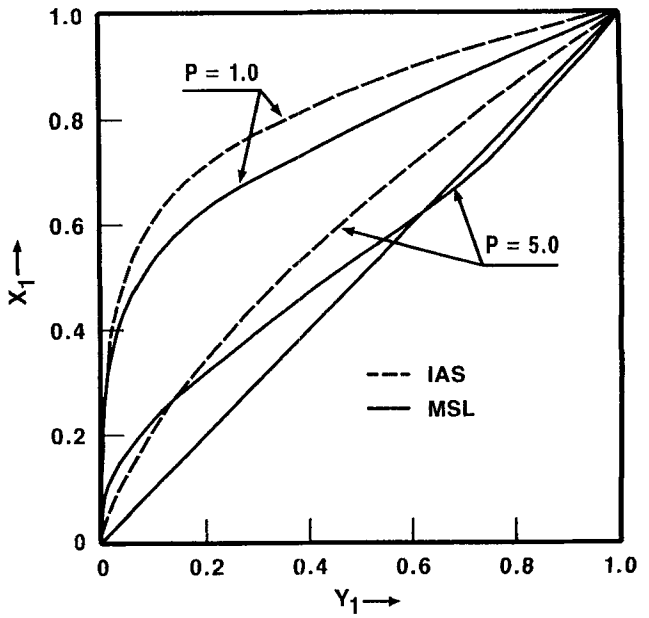

Figure 6. Calculated x-y plot for adsorption of CF_2Cl_2-NH_3 binary mixture on BPL carbon.

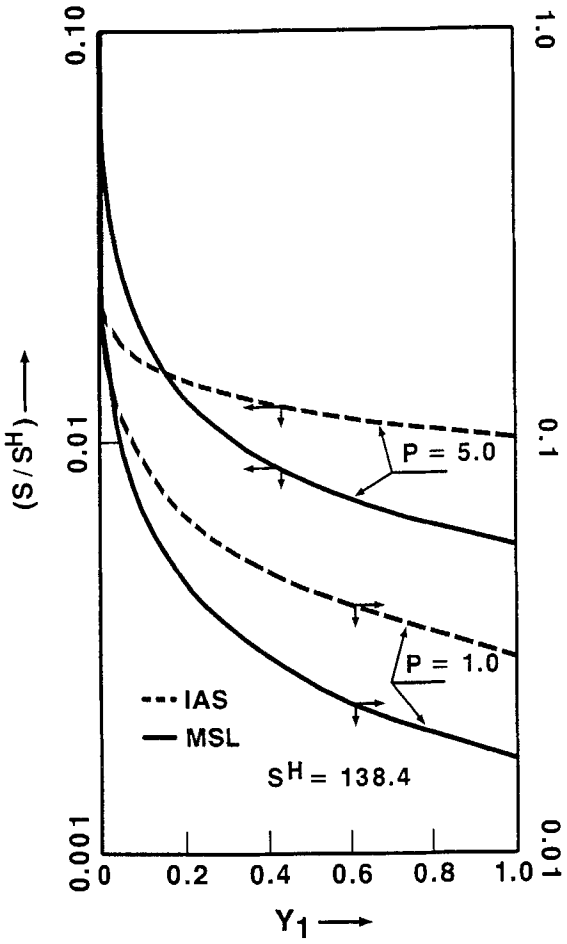

Figure 7. Selectivity of adsorption of CF_2Cl_2 over NH_3 on BPL carbon.

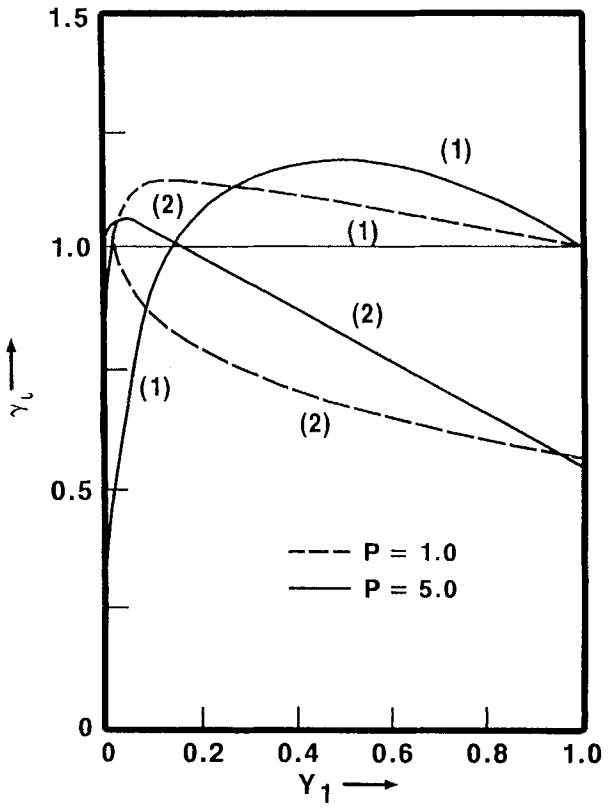

Figure 8. Adsorbed phase activity coefficients for adsorption of CF_2Cl_2 and NH_3 on BPL carbon calculated by IAST.

$NH_3(1) + CO_2(2)$ binary mixture

The pure gas adsorption characteristics of the components of this binary mixture indicate that NH_3 is preferably adsorbed over CO_2 on the carbon because of its higher K^H and q^0 values. However, a_1 is smaller than a_2. Thus, the selectivity of NH_3 should increase with increasing y_1 (or θ) at a constant P and T as indicated by Eq. 13. The limiting Henry's law selectivity for this system is 1.9.

Figure 9 shows the plots of S vs. y_1 for this system at 37.8°C and a total gas pressure of 5.0 atm. The solid line in the figure shows the increase in S with increasing y_1 by the MSL model. Interestingly, S is greater than S^H over the entire composition range at this pressure. The dashed line in Figure 9 shows the S vs. y_1 plot predicted by IAST for this system. It correctly predicts the increase in S with increasing y_1, but it underpredicts the actual S value at the low y_1 region and overpredicts the S value at higher values of y_1.

Figure 10 shows the $\theta_i^{\text{IAST}}/\theta_i^{\text{MSL}}$ for this system as a function of y_1. In this case, θ_1 is slightly underpredicted at the lower value of y_1, while θ_2 is underpredicted at all values of $y_1 > 0$. The magnitude of underprediction, however, is relatively small in this case. The limiting values of γ_1^∞ and γ_2^∞ are, respectively, 0.92 and 0.85, which are again less than unity. The smaller differences of adsorbate sizes and the relatively small values of S^H are responsible for the smaller errors in the predictions of binary adsorption isotherms by the IAST for this system.

The apparent adsorbed phase nonideality exhibited by the use of IAST in calculating mixed gas equilibria for adsorbates

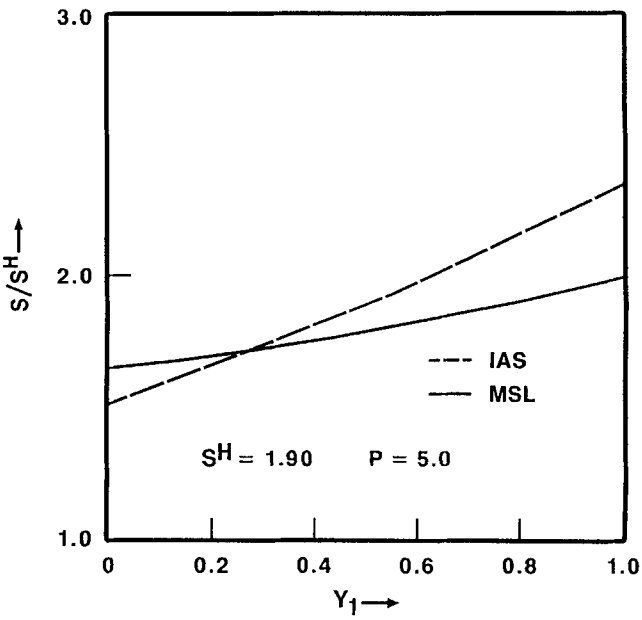

Figure 9. Selectivity of adsorption of NH_3 over CO_2 on BPL carbon.

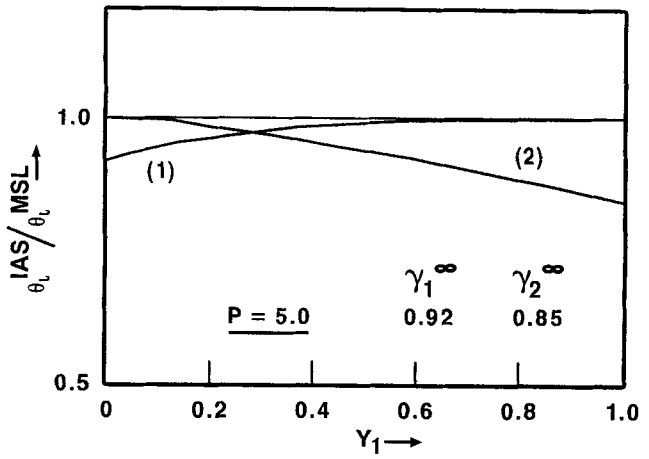

Figure 10. Comparison of calculated binary NH_3–CO_2 isotherm on BPL carbon by MSL and IAST models.

with large size differences has recently been experimentally demonstrated (Joseph et al., 1993; Golden and Sircar 1994a).

Effect of adsorbent heterogeneity

The adsorption of pure carbon monoxide (1) and oxygen (2) and their binary mixtures on 5A zeolite at -128.9°C can be described very well by the pure gas HL model (Eq. 29) using the same values of saturation capacities (Sircar, 1991). Figure 11 shows the best fit of the pure gas isotherms by the HL model. The experimental data were measured by Danner and Wenzel (1969). CO is much more strongly and selectively adsorbed over O_2. The adsorbent exhibits a very high degree of heterogeneity for CO adsorption ($\Psi_1 = 0.975$) while it behaves like a homogeneous adsorbent for O_2 adsorption ($\Psi_2 = 0$). The other pure gas model parameters for this system are given in Table 1.

Equations 39–44 were used to evaluate the IAST predictions of the binary adsorption isotherm for this system at a total gas pressure of 1.0 atm. Figure 12 shows the plots of $(\theta_i^{IAST}/\theta_i^{HL})$ as a function of y_1. It may be seen that IAST underpredicts the adsorption of CO when its gas phase concentration is low. Otherwise, θ_1 calculated by IAST is very

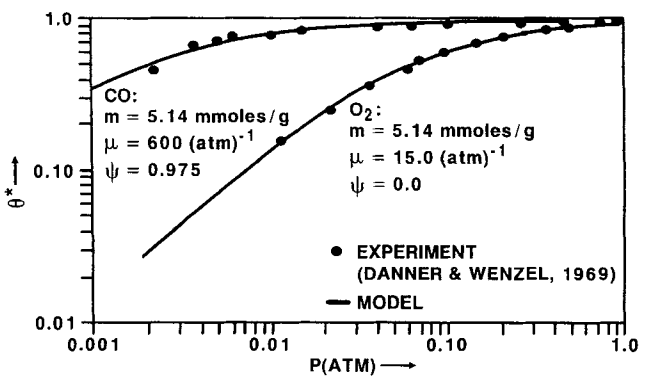

Figure 11. Pure gas adsorption isotherms of carbon monoxide and oxygen on 5A zeolite.

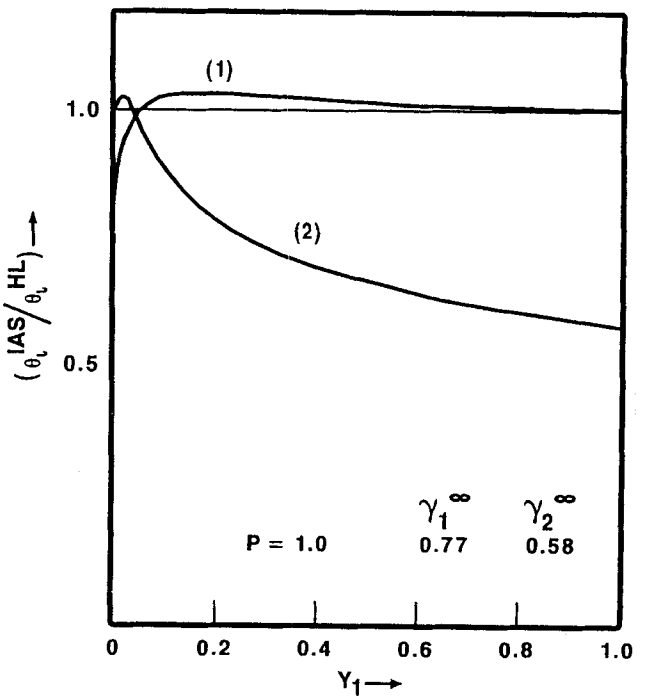

Figure 12. Comparison of calculated binary isotherm for adsorption of CO–O_2 mixture on 5A zeolite by HL and IAST models.

close to that obtained by the HL model. The amount of O_2 adsorption, on the other hand, is substantially underpredicted by the IAST except at the very low values of y_1. The limiting values of γ_1^∞ and γ_2^∞ for this system are, respectively, 0.77 and 0.58. Thus, they are again less than unity.

The Henry's law selectivity of adsorption (S^H) of CO over O_2 at -128.9°C is 40.0. Figure 13 shows that the selectivity (S) is a rapidly decreasing function of y_1 for this system. The ratio (S/S^H) decreases from unity at $y_1 = 0$ to 0.45 at $y_1 = 1.0$. The IAST fails to predict this variation of selectivity with concentration. A practically constant value of ($S/S^H = 0.78$) is given by the IAST for the entire concentration range except at $y_1 \to 0$ where (S/S^H) changes from 0.78 to 1.0.

Consequently, a nonideal adsorbed phase must be postulated to describe the binary adsorption isotherm for this system using the framework of IAST. The calculated adsorbed phase activity coefficients, however, will be artifacts created by the failure of the IAST to account for the effects of adsorbent heterogeneity. This role of adsorbent heterogeneity is well recognized (Myers, 1984; O'Brien and Myers, 1987). The present work is an attempt to quantify the effect.

Parametric study of the error

A convenient method to size the error introduced by IAST in estimating binary adsorption isotherm is to calculate the values of γ_i^∞ required to match IAST predictions with actual isotherm data. It is a relative measure of the actual or artificial nonideality of the adsorbed phase under the framework of IAST.

Figure 14a gives the results of a parametric study conducted to evaluate the error introduced by IAST in interpret-

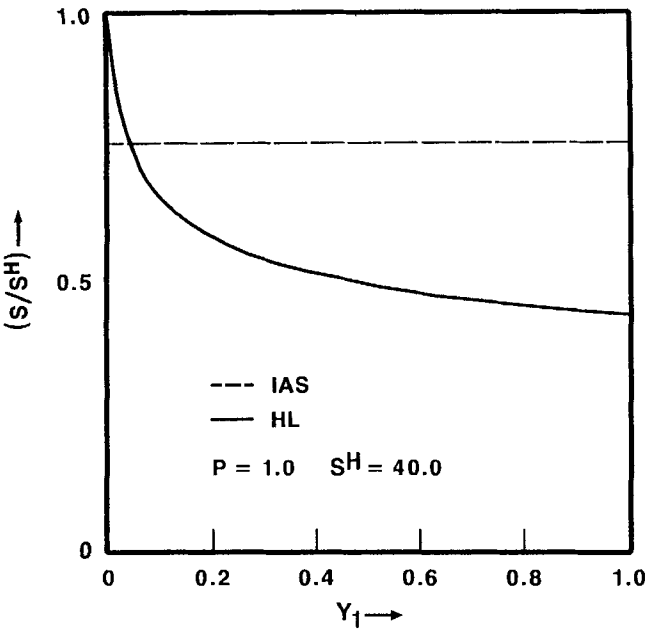

Figure 13. Selectivity of adsorption of CO over O_2 on 5A zeolite.

ing binary MSL isotherms. It plots the values of γ_1^∞ for binary mixtures obeying mixed gas MSL adsorption isotherms, where component 2 occupies one site per molecule ($a_2 = 1$), and component 1 has different a_1 values. The calculations were carried out at two different total gas pressure conditions at which the pure component 2 had fractional coverages (θ_2^*) of 0.2 and 0.8. It may be seen that γ_1^∞ is equal to unity only when $a_1 = 1$. Otherwise $\gamma_1^\infty < 1$, and the value of γ_1^∞ decreases as the ratio of a_1/a_2 decreases or increases. The decrease in the value of γ_1^∞ is much larger for the same value of a_1 when θ_2^* is larger. This indicates that the error in the prediction of binary adsorption isotherm by IAST will be more pronounced when the difference in the sizes of the adsorbates are large and the adsorption pressure is high.

Figure 14b gives the results of a parametric study to evaluate the error introduced by IAST in interpreting binary HL isotherms. It plots the values of γ_1^∞ as functions of θ_2^* for binary mixtures obeying mixed gas HL isotherms, where the degree of heterogeneity for component 1 is large ($\Psi_1 = 0.975$), and that for component 2 is low ($\Psi_2 = 0,0.5$). Variable θ_2^* is the fractional amount adsorbed of pure component 2 at the total gas pressure of the system. The figure shows that γ_1^∞ decreases as θ_2^* increases for any given Ψ_2. Furthermore, γ_1^∞ also decreases for any given θ_2^* when the difference between

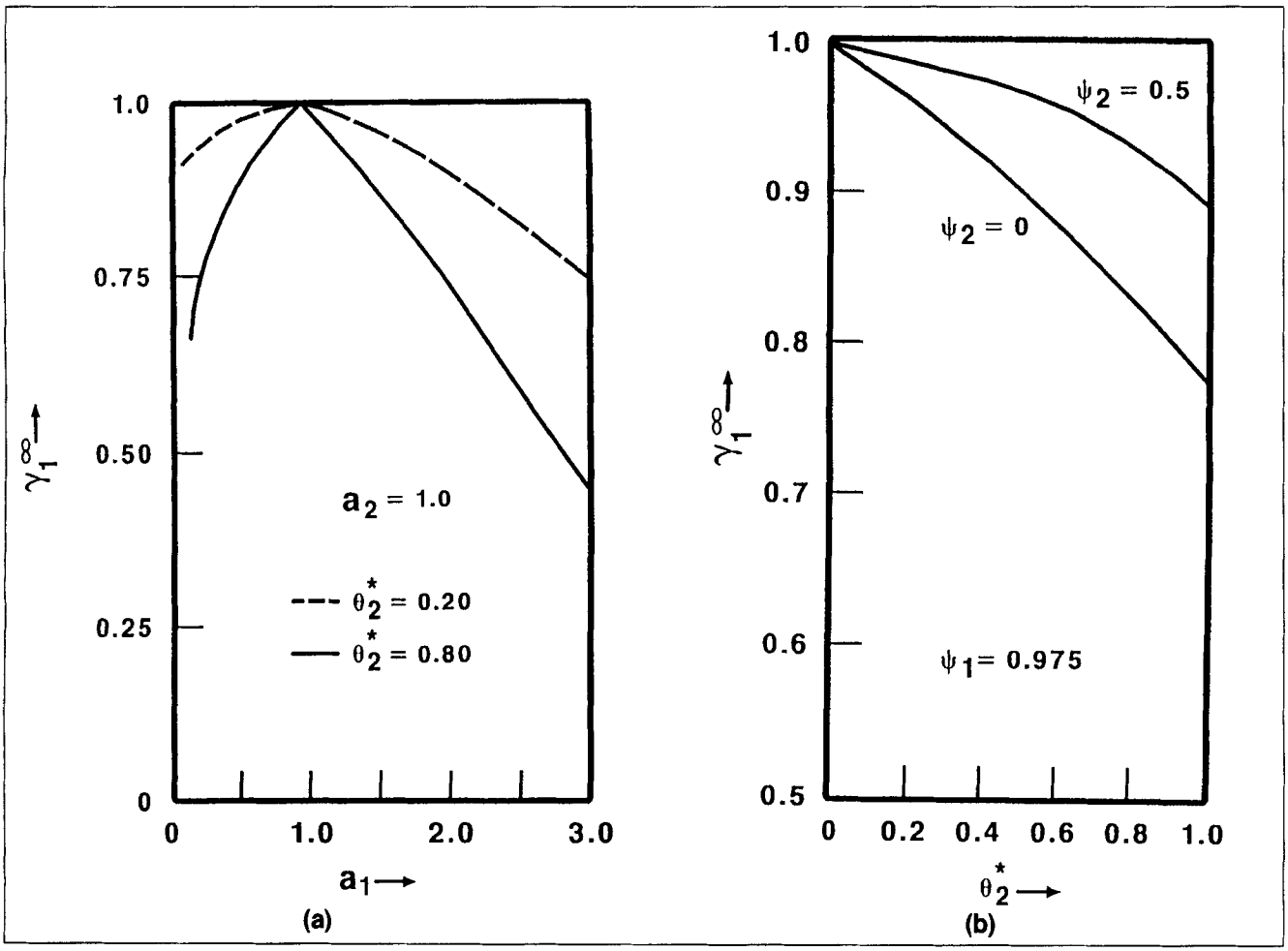

Figure 14. Parametric study of errors involved in the use of IAST in representing binary MSL and HL isotherms.

Ψ_1 and Ψ_2 increases. This indicates that the error in the prediction of binary adsorption isotherm by IAST will be more pronounced when the difference in the degree of heterogeneity of the adsorbates is large and the adsorption pressure is high.

Conclusions

The adsorption of the components of a gas mixture on an energetically homogeneous or heterogeneous adsorbent is significantly influenced by the differences in the sizes of the components and their degrees of heterogeneity for adsorption. The prediction of the multicomponent adsorption equilibria from the corresponding pure gas adsorption isotherms by the IAST can be substantially erroneous when these differences are large. Consequently, an artificial nonideality may be introduced by the IAST framework for interpretation of mixed gas adsorption isotherms for these cases. It was found by model studies that these nonidealities are manifested by a negative deviation from Raoult's law (activity coefficients less than unity at infinite dilution of the components). This deviation can be caused by (a) size differences of adsorbates, or (b) different energetic heterogeneity of the adsorbent for the components, or both. These differences can also create adsorption azeotropy in the binary adsorption isotherm that cannot be described by the IAST framework. The IAST predictions may be reasonable when these differences are small, but the quality of prediction cannot be judged *a priori*.

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