Thermodynamically Consistent Equilibrium Adsorption Isotherms for Mixtures of Different-Size Molecules

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Simple and general differential criteria are derived for testing equilibrium adsorption isotherms for consistency with the laws of thermodynamics. The generalized Langmuir isotherm (L-model) for binary solutes of different sizes or adsorption capacities fails the test, as previously noted. A consistent isotherm is derived for the first time, by using the framework of the ideal adsorbed solution (IAS) theory of Myers and Prausnitz (*AIChE J.* **1965,** *11,* 121). The scaled particle theory isotherms for circular disks are shown to be thermodynamically consistent and to lead to almost identical predictions as an IAS model based on a modified Langmuir isotherm. All models with ideal mixing in the adsorbed solution predict that at high coverages the larger molecules (those with smaller adsorption capacity) are substantially depleted from the surface for steric and entropic reasons. With increasing concentration, the models predict selectivity reversals in cases where the larger molecules are not much more surface active than the smaller molecules.

1. Introduction

Binary and multicomponent adsorption at air/water, oil/water, gas/solid, and liquid/solid interfaces is an important practical problem in foams, emulsions, detergency, catalysis, and certain separation methods.[1-7] One normally determines the adsorption equilibria of the individual components and then describes the adsorption of the mixtures.[8-24] The Langmuir equilibrium isotherm is the simplest and most popular among the adsorption isotherms, for noninteracting molecules on a lattice. Improvements include modified forms of the Langmuir isotherm, the Frumkin isotherm, and others.[24-27] The simplest isotherm for mixtures is a generalization of the single-component isotherm, without introducing additional mixing parameters. This is the point of reference for introducing intermolecular adsorbate—adsorbate interactions in classical thermodynamic or in molecular thermodynamic theories.

A set of adsorption equations are the generalized Langmuir isotherms (see section 2.2.1), which are still cited in recent books and monographs and are still used by researchers in adsorption, chromatography, and other areas.[3,21-23,28,29] These equations have been reported, however, by various authors, to be thermodynamically inconsistent if the molecular sizes or adsorption capacities of the components are different.[15,30,31] This has given the impetus for developing improved isotherms, such as the scaled-particle theory isotherm[25] or the ideal adsorbed solution theory.[8]

In this article, we develop (i) simple and quite general criteria for testing isotherms for necessary conditions for thermodynamic consistency and (ii) guidelines for developing thermodynamically consistent isotherms. We derive the thermodynamically rigorous form of the Langmuir isotherm for mixtures of different-size molecules, using the ideas of the ideal adsorbed solution model of Myers and Prausnitz.[8] The predictions of the consistent and the inconsistent Langmuir isotherms for mixtures differ substantially, both quantitatively and qualitatively. Differences between the consistent form and experimental data may still exist, of course, if there are significant adsorption features or intermolecular interactions which are not incorporated in the model.

Using the same approach, we also prove that the Scaled-Particle Theory (SPT) isotherms of hard disks are indeed thermodynamically consistent and essentially equivalent to the ideal adsorbed solution model of a modified version of the Langmuir isotherm. These models account explicitly for steric effects of adsorbed molecules in dense packings at high area coverages.[25]

2. Theory

2.1. General Criteria. For a dilute solution of two components 1 and 2 and a solvent, the Gibbs adsorption

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isotherm relates the surface tension γ with Γ_1, Γ_2, c_1, and c_2 as follows:

$$-\frac{d\gamma}{RT} = \Gamma_1\, d\ln c_1 + \Gamma_2\, d\ln c_2 = \frac{\Gamma_1}{c_1}\, dc_1 + \frac{\Gamma_2}{c_2}dc_2 \quad (1)$$

where $\Gamma_i(c_1,c_2)$, $i = 1, 2$, is the adsorbed solute density at equilibrium with bulk concentrations c_1 and c_2, or more precisely the Gibbs surface excess densities relative to the solvent. Here, the solution is assumed to be ideal.[3] For nonideal solutions, eq 1 should be modified, and the subsequently derived criteria should be rederived. This equation is generally valid for air/water and oil/water interfaces and also for gas/solid and liquid/solid interfaces, where the surface tension or the spreading pressure, $\Pi \equiv \gamma_o - \gamma$, are defined but cannot be directly measured. This equation rests on the foundations of classical surface thermodynamics and is of course consistent with the Gibbs–Duhem equation.[32] If $\Gamma_1(c_1,c_2)$ and $\Gamma_2(c_1,c_2)$ are known or postulated via a model, then one can integrate eq 1 to obtain the function $\gamma(c_1,c_2)$, and then the surface equation of state $\gamma(\Gamma_1,\Gamma_2)$.

The functions $\Gamma_1(c_1,c_2)$ and $\Gamma_2(c_1,c_2)$ are not independent, however, since the sum $\Gamma_1/c_1\, dc_1 + \Gamma_2/c_2\, dc_2$ must be an exact (or total) differential of the function $-\gamma/RT$, which is a state function. In order for the above differential to be exact, the following condition must be satisfied, namely that the mixed second partial derivatives of any differentiable function must be equal:

$$\frac{\partial^2\gamma}{\partial c_2\partial c_1} = \frac{\partial^2\gamma}{\partial c_1\partial c_2} \quad (2)$$

From eqs 1 and 2 it follows that

$$\frac{\partial}{\partial c_2}\left[\frac{\Gamma_1(c_1,c_2)}{c_1}\right] = \frac{\partial}{\partial c_1}\left[\frac{\Gamma_2(c_1,c_2)}{c_2}\right] \quad (3)$$

If the functions Γ_1 and Γ_2 do not satisfy condition 3, then the expression $-d\gamma/RT$ is an inexact differential. This would mean that γ is not a state function, or that γ depends on the integration path (or physically on the sequence of adding the solutes in the solutions), which of course is false. Consequently, if eq 3 is not satisfied, then Γ_1 and Γ_2 violate the combined first and second law of thermodynamics (from which eq 1 was derived), which means that they are thermodynamically inconsistent.

This criterion should be heeded when formulating or postulating adsorption equilibrium isotherms based on molecular theory or kinetic considerations. Before some specific examples are considered, eq 1 will be formulated in a different form, since certain adsorption equilibrium equations are given in the following functional form:

$$c_i = f_i(\theta_1,\theta_2) = \frac{\theta_i}{K_i\phi_i(\theta_1,\theta_2)} \qquad i = 1,2 \quad (4)$$

where $\theta_i \equiv \Gamma_i/\Gamma_{m_i}$ is the fractional area coverage, Γ_{m_1} and Γ_{m_2} are the maximum (close-packed) surface densities of the individual components 1 and 2, K_1 and K_2 are adsorption equilibrium constants, and ϕ_1 and ϕ_2 are known functions, in certain cases being called "available surface" functions. The criterion for thermodynamic consistency is derived from eqs 1 and 4 as follows:

$$\Gamma_{m_1}\frac{\partial\ln\phi_1}{\partial\theta_2} = \Gamma_{m_2}\frac{\partial\ln\phi_2}{\partial\theta_1} \quad (5)$$

If, in turn, $\phi_1(\theta_1,\theta_2)$ and $\phi_2(\theta_1,\theta_2)$ are of the form

$$\phi_1(\theta_1,\theta_2) = (1 - \theta_1 - \theta_2)\exp[-A(\theta_1,\theta_2)] \quad (6)$$

$$\phi_2(\theta_1,\theta_2) = (1 - \theta_1 - \theta_2)\exp[-B(\theta_1,\theta_2)] \quad (7)$$

where A and B are functions determined from the molecular mixture model used, then criterion 5 simplifies to

$$\left(\frac{\Gamma_{m_1}}{\Gamma_{m_2}} - 1\right)\frac{1}{1 - \theta_1 - \theta_2} = \frac{\partial B}{\partial\theta_1} - \frac{\Gamma_{m_1}}{\Gamma_{m_2}}\frac{\partial A}{\partial\theta_2} \quad (8)$$

These criteria are quite general and simple, allowing testing of complex isotherms, and will be applied to certain important examples of binary isotherms. For systems of three or more solutes or for nonideal solutions, the criteria 3, 5, and 8 can be generalized on the basis of the same ideas.

2.2. Examples. *2.2.1. Generalized Langmuir Isotherm.* Here, Γ_1 and Γ_2 are given as explicit functions of c_1 and c_2

$$\Gamma_1 = \Gamma_{m_1}\frac{K_{L_1}c_1}{1 + K_{L_1}c_1 + K_{L_2}c_2} \quad (9)$$

$$\Gamma_2 = \Gamma_{m_2}\frac{K_{L_2}c_2}{1 + K_{L_1}c_1 + K_{L_2}c_2} \quad (10)$$

This isotherm has been derived on the basis of kinetic considerations, by generalizing the Langmuir–Hinshelwood kinetic equation.[3,22] Using eqs 17 and 18 in criterion 3, one gets the following condition for thermodynamic consistency:

$$\Gamma_{m_1}\frac{K_{L_1}K_{L_2}}{(1 + K_{L_1}c_1 + K_{L_2}c_2)^2} = \Gamma_{m_2}\frac{K_{L_1}K_{L_2}}{(1 + K_{L_1}c_1 + K_{L_2}c_2)^2} \quad (11)$$

This equation is valid only if $\Gamma_{m_1} = \Gamma_{m_2}$. Hence, for molecules of different size or adsorption capacities, $\Gamma_{m_1} \neq \Gamma_{m_2}$, the generalized Langmuir eqs 9 and 10 are thermodynamically inconsistent. This has been pointed out previously by several authors, most clearly by LeVan and Vermeulen.[15] They used an equivalent integral criterion, namely that if $\Gamma_{m_1} \neq \Gamma_{m_2}$, then γ depended on the integration path.

For adsorption of surfactants at the air/water interface, several sets of data have been fit well with the Langmuir isotherm. The values of K_L range from ca. 10^{-2} to 10^4 m^3/mol. The values of Γ_m range from 1.5×10^{-6} to 10×10^{-6} mol/m^2.[33]

2.2.2. Scaled Particle Theory Isotherms. The following eqs 13 and 14 were derived based on kinetic and molecular theory considerations, using the scaled-particle theory for two-component mixtures of hard circular disks of diameters σ_1 and σ_2, where 2 is the larger disk and

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$$R_\sigma \equiv \frac{\sigma_2}{\sigma_1} \quad (12)$$

$$c_1 = y_1 c_T = \frac{\theta_1 \exp A}{K_1(1 - \theta_1 - \theta_2)} \quad (13)$$

$$c_2 = y_2 c_T = \frac{\theta_2 \exp B}{K_2(1 - \theta_1 - \theta_2)} \quad (14)$$

These equations are of the form of eq 4. $A(\theta_1,\theta_2)$ and $B(\theta_1,\theta_2)$ in eqs 6 and 7 are given by the following equations:

$$A(\theta_1,\theta_2) \equiv \frac{3\theta_1 + \frac{1}{R_\sigma}\left(\frac{1}{R_\sigma} + 2\right)\theta_2}{1 - \theta_1 - \theta_2} + \frac{\left(\theta_1 + \frac{1}{R_\sigma}\theta_2\right)^2}{(1 - \theta_1 - \theta_2)^2} \quad (15)$$

$$B(\theta_1,\theta_2) \equiv \frac{3\theta_2 + R_\sigma(R_\sigma + 2)\theta_1}{1 - \theta_1 - \theta_2} + \frac{(\theta_2 + R_\sigma\theta_1)^2}{(1 - \theta_1 - \theta_2)^2} \quad (16)$$

The term γ, which is used in ref 25, was changed here to R_σ, to avoid confusion with the surface tension γ. These equations account kinetically and molecularly for available areas for disks of different sizes, especially at large packing densities. For one-component systems, they reduce to a modified form of the Langmuir isotherm (see section 2.3.2). The extra term aims at accounting better for the steric effects, at high coverages.[25] For disks,

$$\frac{\Gamma_{m_1}}{\Gamma_{m_2}} = \left(\frac{\sigma_2}{\sigma_1}\right)^2 = R_\sigma^2 \quad (17)$$

Equations 13–16 do satisfy eq 8 exactly (the simple derivation is omitted). Hence, the scaled-particle theory isotherms are thermodynamically consistent with the Gibbs adsorption equation.

2.2.3. Other Isotherm Functions. Other isotherms, containing the same ϕ_1 and ϕ_2 functions but different functional forms, are also thermodynamically consistent. For example, the set

$$f_1(\theta_1,\theta_2) = \frac{\theta_1^n}{K_1\phi_1(\theta_1,\theta_2)} \quad (18)$$

$$f_2(\theta_1,\theta_2) = \frac{\theta_2^n}{K_2\phi_2(\theta_1,\theta_2)} \quad (19)$$

is also thermodynamically consistent for values of n other than 1. Hence, for desorption being not linear with θ_1, the scaled particle theory isotherms yield thermodynamically consistent equations.

Using criterion 3, one can show easily that the binary Freundlich isotherm[13,15]

$$\Gamma_i(c_1,c_2) = K_i^{1/n_i} c_i (K_1^{1/n_1} c_1 + K_2^{1/n_2} c_2)^{n_i - 1} \qquad i = 1, 2 \quad (20)$$

is valid only when $n_1 = n_2$. This result was also obtained with the integral method.[15] Hence, this isotherm is thermodynamically inconsistent when $n_1 \neq n_2$. Moreover, the following binary Langmuir–Freundlich empirical isotherms are used in several chromatography calculations:[11,14]

$$\Gamma_1 = \frac{a_1 c_1^{n_1}}{1 + b_1 c_1^{n_1} + b_2 c_2^{n_2}} \quad (21)$$

$$\Gamma_2 = \frac{a_2 c_2^{n_2}}{1 + b_1 c_1^{n_1} + b_2 c_2^{n_2}} \quad (22)$$

Using criterion 3, one finds that these equations are consistent with thermodynamics only if

$$\frac{a_1}{a_2} = \frac{n_1 b_1}{n_2 b_2} \quad (23)$$

and inconsistent otherwise. The same criterion is derived if the constant term 1 is not present in the denominators of eqs 21 and 22 (then one obtains the Freundlich–Fritz–Schluender isotherms[14]). Moreover, if the denominator terms were of the form $b_1 c_1 n_1^*$ and $b_2 c_2 n_1^*$, where $n_1^* \neq n_1$ and $n_2^* \neq n_2$, then application of the criterion 3 would require that $n_1^* = n_1$ and $n_2^* = n_2$, as a simple derivation shows.

The Freundlich and, to an extent, the Langmuir isotherm are empirical or semiempirical. If one decides to use them as a basis for building mixture isotherms, one should still use thermodynamically consistent mixture isotherms. This is particularly important if one makes use of such isotherms for predicting dynamic separation effects.

2.3. Methods for Obtaining Thermodynamically Consistent Models. *2.3.1. Ideal Adsorbed Solution Model for Langmuir Isotherms.* One may wish to use these individual component isotherms as a point of departure for deriving the mixture isotherm and then use information on thermodynamic or molecular interactions to describe adsorbed mixtures. For ideal adsorbed solutions, the framework which satisfies the thermodynamic consistency criteria, reduces to the single component isotherms, and requires no additional mixture parameters is the ideal adsorbed solution theory of Myers and Prausnitz.[8] It can be used with the Langmuir, modified Langmuir, Freundlich, Langmuir–Freundlich, or other isotherms for the individual components. It is applied here to the first two cases. Even though some of these equations have been presented before, the application to this system and the final result (eqs 31 and 32) are new.

For two components with surface densities Γ_1 and Γ_2, one defines

$$\Gamma_t \equiv \Gamma_1 + \Gamma_2 \quad (24)$$

$$x_i \equiv \frac{\Gamma_i}{\Gamma_t} \qquad i = 1, 2 \quad (25)$$

Equality of the chemical potentials of component 1 in the bulk and in the adsorbed solution yields[8]

$$c_i(\Pi) = c_i^0(\Pi_i^0)x_i \quad (26)$$

where $c_i^0(\Pi_i^0)$ is the concentration of pure component 1 at the same surface pressure $\Pi_1^0 = \Pi_2^0 = \Pi$ as the mixed solution. The surface pressure defines the reference state chemical potential of the individual components.[34] Moreover, the Langmuir isotherm is used for the reference state of each individual component,

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$$\Gamma_i^0 = \Gamma_{m_i}\left(\frac{K_{L_i}c_i^0}{1 + K_{L_i}c_i^0}\right) \qquad i = 1,2 \qquad (27)$$

where Γ_i^0 and Γ_{m_i} are the reference state surface densities, also at the same surface pressure. For this isotherm for nonionic solutes, the Szyszkowski equation relates Γ_i^0 to c_i^0:[3]

$$\Pi_i^0 = RT\,\Gamma_{m_i}\ln(1 + K_{L_i}c_i^0) \qquad i = 1,2 \qquad (28)$$

Finally, the specific surface area $\bar{a}$ of an adsorbed solution from mixing x_1 mols of 1 at a density of Γ_1^0 with x_2 mols of 2 at density of Γ_2^0 is (since the molar area $\bar{a} = 1/\Gamma_t$)

$$\frac{1}{\Gamma_t} = \frac{x_1}{\Gamma_1^0} + \frac{x_2}{\Gamma_2^0} \qquad (29)$$

This equation is valid when there is no area change upon mixing, and it is consistent with the ideal adsorbed solution assumption.[8] Equations 24–29 (along with $\Pi = \Pi_1^0 = \Pi_2^0$) are solved for Γ_1, Γ_2, Γ_t, x_1, x_2, c_1^0, c_2^0, Γ_1^0, Γ_2^0, Π_1^0, Π_2^0, and Π. Solution of this system will yield Γ, how Γ_1 and Γ_2 depend on c_1 and c_2, as well as the function $\gamma(c_1,c_2)$ and the surface equation of state, $\gamma(\Gamma_1,\Gamma_2)$. These solutions cannot be put in an explicit analytical form.

Equations 24, 25, and 29 yield

$$\frac{\Gamma_1}{\Gamma_1^0} + \frac{\Gamma_2}{\Gamma_2^0} = 1 \qquad (30)$$

By using eqs 26–28, one obtains

$$\frac{\Gamma_1[\Gamma_1 + K_{L_1}c_1(\Gamma_1 + \Gamma_2)]}{\Gamma_{m_1}K_{L_1}c_1} + \frac{\Gamma_2[\Gamma_2 + K_{L_2}c_2(\Gamma_1 + \Gamma_2)]}{\Gamma_{m_2}K_{L_2}c_2} = \Gamma_1 + \Gamma_2 \quad (31)$$

and

$$1 + K_{L_2}c_2\left(\frac{\Gamma_1 + \Gamma_2}{\Gamma_2}\right) = \left[1 + K_{L_1}c_1\left(\frac{\Gamma_1 + \Gamma_2}{\Gamma_1}\right)\right]^{R_\Gamma} \quad (32)$$

where

$$R_\Gamma \equiv \frac{\Gamma_{m_1}}{\Gamma_{m_2}} \qquad (33)$$

The above eqs 31 and 32 provide in an implicit and compact form how Γ_1 and Γ_2 depend on c_1, c_2, and the parameters Γ_{m_1}, Γ_{m_2}, K_{L_1}, and K_{L_2}. These equations can be generalized to nonideal adsorbed solutions and to ionic adsorbates. These equations are solved simultaneously by iterative methods. For

$$\theta_1 \equiv \frac{\Gamma_1}{\Gamma_{m_1}}, \quad \theta_2 \equiv \frac{\Gamma_2}{\Gamma_{m_2}}, \quad K_{L_1}c_1 \equiv C_1, \quad K_{L_2}c_2 \equiv C_2 \quad (34)$$

they reduce to their dimensionless forms,

$$\frac{\theta_1\left[\theta_1 + C_1\left(\theta_1 + \dfrac{\theta_2}{R_\Gamma}\right)\right]}{C_1} + \frac{\theta_2\left[\dfrac{\theta_2}{R_\Gamma} + C_2\left(\theta_1 + \dfrac{\theta_2}{R_\Gamma}\right)\right]}{C_2} = \\ \theta_1 + \frac{\theta_2}{R_\Gamma} \quad (35)$$

and

$$1 + C_2\left(\frac{\theta_1 + \dfrac{\theta_2}{R_\Gamma}}{\dfrac{\theta_2}{R_\Gamma}}\right) = \left[1 + C_1\left(\frac{\theta_1 + \dfrac{\theta_2}{R_\Gamma}}{\theta_1}\right)\right]^{R_\Gamma} \quad (36)$$

The same equations also can be solved for the inverse problem, namely for finding C_1 and C_2 given θ_1 and θ_2. The inverse problem is important for finding the equation of state $\gamma(\theta_1,\theta_2)$, and in the solution of the adsorption dynamics problem, in which one needs to calculate $\gamma(t)$ given $\Gamma_1(t)$ and $\Gamma_2(t)$.[33]

To avoid solving numerically the system of eqs 31 and 32, one can rearrange eqs 26 and 28 to obtain a single equation for x_1:

$$1 + \left(\frac{K_{L_2}c_2}{1 - x_1}\right) = \left[1 + \left(\frac{K_{L_1}c_1}{x_1}\right)\right]^{R_\Gamma} \quad (37)$$

Once x_1 is found, one finds successively the other parameters from the above system of equations. A minor disadvantage of this algorithm, compared to solving eqs 31 and 32, is that one needs to calculate the above reference parameters (c_i^0, Γ_i^0).

The problem of generalizing the Langmuir isotherm without other parameters or interactions does have a thermodynamically consistent solution which corresponds to an ideal adsorbed solution. The Myers–Prausnitz (M-P) theory is crucial for finding this solution. It is recommended that eqs 9 and 10 be avoided and that eqs 31 and 32 be used instead.

These equations are valid for an ideal solution reference state in which the molar entropy of mixing is $\Delta S^{mix} = R(x_1 \ln x_1 + x_2 \ln x_2)$ and $\Delta H^{mix} = 0$. It is possible for molecules differing greatly in size to have $\Delta H^{mix} = 0$ but ΔS^{mix} different from above, or to have "nonideal" entropy of mixing. In other words, if a different reference state is considered, then the "ideal" mixing condition may be different and the consistent Langmuir isotherm for the mixtures will be different from eqs 31 and 32.

A series expansion/approximation of the M-P ideal adsorbed solution theory was obtained by LeVan and Vermeulen[15] and will be used in section 3.1 for comparison. In this approximation,

$$\gamma = \gamma_o - RT\bar{\Gamma}_m \ln(1 + K_{L_1}c_1 + K_{L_2}c_2) \quad (38)$$

The two-term LeVan–Vermeulen expansion yields a set of thermodynamically consistent equations, which do reduce properly to the single-component limits where[15]

$$\bar{\Gamma}_m \equiv \frac{\Gamma_{m_1}K_{L_1}c_1 + \Gamma_{m_2}K_{L_2}c_2}{K_{L_1}c_1 + K_{L_2}c_2} \quad (39)$$

This approximation works when $R_\Gamma \leq 1.5$, as sample calculations (section 3) show: at sufficiently high concentrations, θ_2 (or θ_1) can become negative, and θ_1 (or θ_2) can exceed the limit of pure component 1.[15]

2.3.2. Ideal Adsorbed Solution Model for Modified Langmuir Isotherm. Using the isotherm represented by

eqs 13–16 for one component, or $\theta_2 = 0$, yields[25]

$$Kc = \left(\frac{\theta}{1-\theta}\right)\exp\left[\frac{3\theta}{1-\theta} + \frac{\theta^2}{(1-\theta)^2}\right] \quad (40)$$

This isotherm, where $\theta \equiv \Gamma/\Gamma_m^*$, is consistent with the SPT theory for hard disks (see section 2.2.2). Since the maximum packing density Γ_m^* is generally different from Γ_m of the Langmuir isotherm, the area fractions can be different in the two models for the same set of data. We will refer to it as the modified Langmuir isotherm (ML). Using this equation along with the Gibbs adsorption (eq 1) for one solute yields the following equation of state:

$$\Pi(\theta) = RT\Gamma_m\left[\frac{\theta}{(1-\theta)^2}\right] \quad (41)$$

From eqs 40 and 41 one obtains implicitly the relation $\Pi(c)$. No analytical form seems possible.

Equations 24–26 and 29 are the same as in the Langmuir isotherm case. Then, for

$$\theta_i \equiv \frac{\Gamma_i}{\Gamma_{m_i}^*} \quad \text{and} \quad \theta_i^o \equiv \frac{\Gamma_i^o}{\Gamma_{m_i}^*} \quad i = 1,2 \quad (42)$$

one gets

$$K_i c_i^o = \frac{\theta_i^o}{1-\theta_i^o}\exp\left[\frac{3\theta_i^o}{1-\theta_i^o} + \frac{\theta_i^{o2}}{(1-\theta_i^o)^2}\right] \quad (43)$$

and

$$\Pi_i^o = RT\Gamma_{m_i}^*\left[\frac{\theta_i^o}{(1-\theta_i^o)^2}\right] \quad (44)$$

By defining

$$t_i^o \equiv \frac{\theta_i^o}{1-\theta_i^o} \quad (45)$$

one obtains, after some algebra

$$t_2^o = \frac{1}{2}\{[1 + 4R_\Gamma t_1^o(1 + t_1^o)]^{1/2} - 1\} \quad (46)$$

and

$$\frac{K_1 c_1}{t_1^o\exp[3t_1^o + (t_1^o)^2]} + \frac{K_2 c_2}{t_2^o\exp[3t_2^o + (t_2^o)^2]} = 1 \quad (47)$$

3. Sample Calculations and Discussion of the Models

3.1. Results for the L-IAS, L-V, and L Models.

The L-IAS and the L-V model predictions for θ_1 and θ_2 are reasonably close, as expected. The predictions of both are quite different from those of the L-model, which cannot account for size effects. For $y_1 = y_2 = 0.5$ and $\Gamma_{m_1} > \Gamma_{m_2}$ (molecules of 2 are larger) both models predict $\theta_1 > \theta_2$, i.e. that the smaller molecules occupy a larger fraction of the surface than their share, even for equally surface active molecules. For both $y_1 = 0.50$ and $y_1 = 0.25$ (figures are omitted), θ_2 shows a maximum. This phenomenon is a lot more pronounced for values of $R_\Gamma = 3$ (Figure 1) or higher. For large values of R_Γ, the second-order L-V approximation is no longer valid, predicting $\theta_2 < 0$ and $\theta_1 > 1$ at high concentrations. The L-V equations are a good approxi-
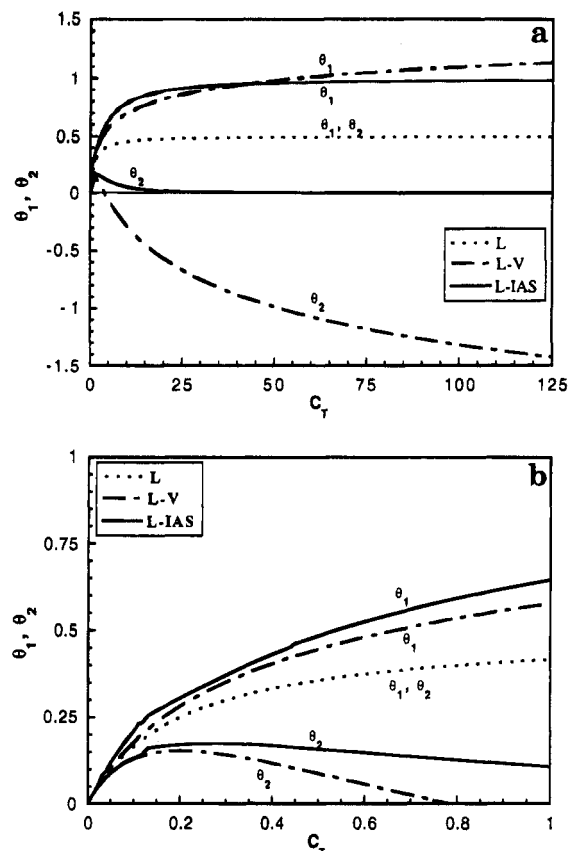

Figure 1. Equilibrium fractional area coverages of components 1 and 2 for the L-IAS model vs the generalized Langmuir equations (L) and the L-V approximation; $y_1 = c_1/(c_1 + c_2) = 0.50$, $R_K \equiv K_{L_1}/K_{L_2} = 1$, and $R_\Gamma \equiv \Gamma_{m_1}/\Gamma_{m_2} = 3.0$; lower figure: enlargement of the range $0 < C_T < 1$.

mation up to about $C_T \cong 2$ in this example. At large surface coverages θ of the larger molecules (at $C_T \cong 1$), apparently for steric and entropic reasons, it is more favorable for the smaller molecules to adsorb and expel the larger molecules. These predictions may change, if there are significant energetic interactions between the adsorbates. Energetic interactions between the adsorbates and the surface are accounted for by the equilibrium constants K_{L_1} and K_{L_2}. These interactions are assumed to remain unchanged after mixing in the monolayer.

The previous generalized Langmuir model (eqs 9 and 10) cannot account for size effects and cannot predict the equilibrium tension in a unique way (see section 2.2.1). If eq 38 is used, the L-model tension predictions overlap with those of the L-V model (Figure 2). If the larger molecules ($R_\Gamma = 3$) are at a higher concentration ($y_1 = 0.25$, or $y_2 = 0.75$), but with the same surface activity (same value of K_L), then at low concentrations they have larger area fraction in the adsorbed layer ($\theta_2 > \theta_1$) until medium to high coverages. At higher concentrations, there is a maximum, followed by a pronounced selectivity reversal ($\theta_2 < \theta_1$).[18] At the higher total coverages, the smaller molecules crowd out the larger ones. This occurs, but to a lesser extent, even when the larger molecules are more surface active ($K_{L_2} = 10K_{L_1}$, or $R_K = 0.1$, Figure 4). The surface tensions predictions (Figure 4) vary less strongly with concentration than the adsorbed densities, because the contribution to the tension of the larger molecules is compensated by the contribution of the smaller molecules. Data on adsorbed densities may provide a stronger test of the model than data on surface or interfacial tensions. If $K_{L_2} \gg K_{L_1}$, then the energetic adsorption effects may overcome the size effects.
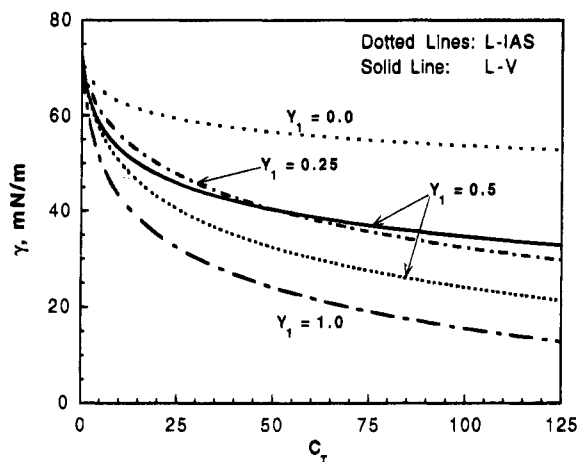
Figure 2. Surface tensions for the L-IAS and L-V models for $R_K = 1$, $R_\Gamma = 3$, $\Gamma_{m_1} = 5 \times 10^{-6}$ mol/m^2, $T = 298$ K, and $y_1 = 0.0$, 0.25, 0.50, and 1.0. Predictions for the L model are not unique (see text), but if eq 38 is used, they essentially overlap with the L-V model predictions.
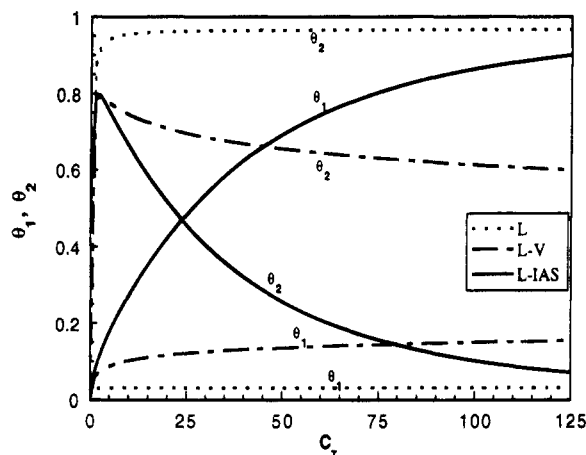

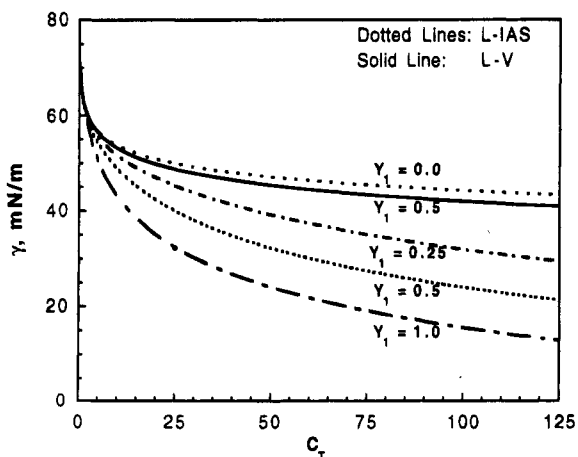**Figure 3.** Same as Figure 1a but for $R_K = 0.1$, i.e. when the larger molecules (2) are more surface active.

Figure 4. Same as Figure 2 but for $R_K = 0.1$.

3.2. Results for the ML-IAS Model and the SPT Theory.

The SPT system of the two implicit equations 13 and 14 for c_1 and c_2 as a function of θ_1 and θ_2 was solved with the Newton–Raphson method (in which for improving convergence the Jacobians were reorganized to avoid large numbers which may introduce numerical instabilities). For $R_\Gamma = 1.2$ no maximum is predicted for θ_2 vs C_T in the this model, unlike the case of the L-IAS model under similar conditions. For larger values of R_Γ, however,
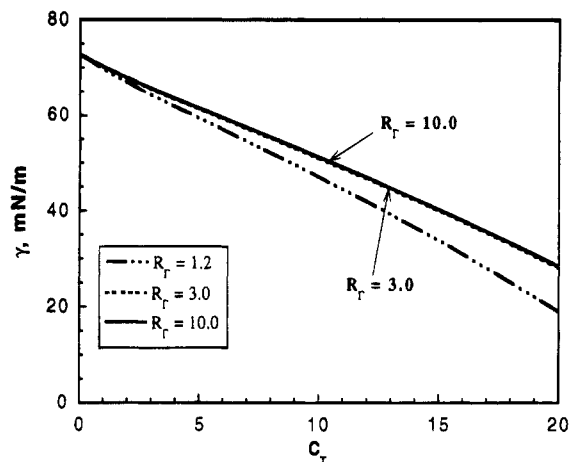

Figure 5. Tension predictions for the ML-IAS model with $R_K = 0.1$, $y_1 = 0.25$, $\Gamma_{m_1} = 5 \times 10^{-6}$ mol/m^2, and $T = 298$ K.
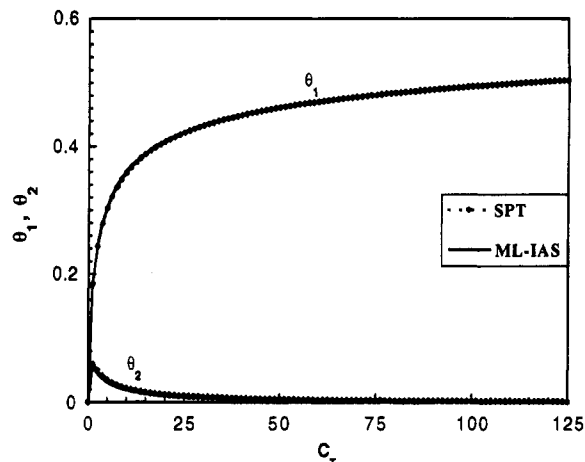

Figure 6. Comparison of the ML-IAS to the SPT model, for $y_1 = 0.50$, $R_K = 0.1$, and $R_\Gamma = 3$.

strong maxima are observed, and at high concentrations C_T, the small molecules again dominate the adsorption layer. The tension is almost linear with C_T for these examples (Figure 5), in clear contrast to the Langmuir–IAS model (Figure 1) and to many experimental results for the air/water interface.[33] The effect of the relative adsorption equilibrium constants (R_K) in the ML-IAS model is as expected, and qualitatively quite similar to the L-IAS model. Predictions of the SPT-model are nearly identical (to 1% or better) to the predictions of the ML-IAS model (Figure 6), even though the equations look quite different (section 2.3.2).

The two models yield essentially the same results, because they rely on the same individual component isotherms and because they do not consider adsorbate–adsorbate interactions. The latter model in essence considers the same entropy of mixing as in the standard ideal solution model based on mole fractions. The SPT model is simpler to formulate, involving only two equations, without the reference parameters (c_i^0, Γ_i^0) of the L-IAS model.

4. Conclusions

This article presents general criteria for testing equilibrium adsorption isotherms for binary mixtures of different sizes adsorbing from an ideal bulk solution. The criteria can be generalized to nonideal bulk solutions, nonideal adsorbed solutions, and multicomponent mixtures. Using these criteria, one can show that the generalized Langmuir, Freundlich, and certain other

empirical isotherms for mixtures are inconsistent with the laws of thermodynamics and that the scaled-particle theory isotherms are indeed consistent.

The rigorous form of the Langmuir isotherms for binary solutes has been derived analytically, but in implicit form, based on the ideal adsorbed solution theory of Myers and Prausnitz.[8] This theory was also used for formulating another model based on a modified Langmuir isotherm for the individual components. Both models predict that the larger molecules may adsorb more than their bulk mole fraction at low concentrations, if they have a larger adsorption equilibrium constant (K_L). As the total concentration increases, however, and for steric and entropic reasons, the larger molecules can be replaced by the smaller molecules, which can eventually dominate the adsorption, provided that their size advantage is not overwhelmed by a K_L disadvantage. This prediction of possible selectivity reversal due to size differences may be important for adsorptive separations and calls for further theoretical evaluation and experimental testing in future work.

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