Multimodel Approach to Mixed-Gas Adsorption Equilibria Prediction

Richard T. Maurer
UOP, Tarrytown R&D Center, Tarrytown, NY 10591

A thermodynamically consistent, multimodel approach for the prediction of mixture adsorption equilibria from pure-component adsorption isotherms is described. The ideal adsorbed solution (IAS) model is employed at low surface coverage, where potential attractive forces tend to govern adsorption behavior. An energetically quasi-homogeneous version of the Langmuir-Freundlich (LF) model is proposed at high coverage, where lateral adsorbate interactions and finite-adsorbent geometric constraints tend to homogenize such attractive forces. The classical LF model is used for intermediate coverage, where both energetic attractive and geometric constraining forces contribute significantly to mixed-gas adsorption behavior. A major benefit of this three-regime modeling method is that physically realistic adsorptive selectivities can be adhered to at both extremes of coverage, a property not generally shared by either the IAS or LF models taken singly. This three-regime approach yields better multicomponent equilibria predictions than IAS-only modeling approaches for many relatively nonideal adsorption systems.

Introduction

Mixed-gas adsorption equilibria prediction from pure component data based on ideal adsorbed solution (IAS) concepts (Myers and Prausnitz, 1965) has demonstrated better success than many earlier-proposed prediction methods. However, many relatively simple gas-phase adsorption systems, especially those exhibiting energetic heterogeneity of the adsorbent sites or significant size differences in the adsorbing molecules, are rather poorly predicted by IAS theory (Ruthven, 1984). Direct predictive enhancements, such as spreading pressure dependent (SPD) (Talu and Zwiebel, 1986) or heterogeneous ideal adsorbed solution models (Valenzuela et al., 1988), often result in only minor improvements for such systems.

A well-known limitation to the IAS concept lies in its inability to work in a physically realistic way with mixtures involving adsorbates of different molecular size or limiting adsorption capacity (Myers and Prausnitz, 1965). Another limitation arises for cases involving heterogeneous adsorption behavior. Both limitations are discussed in greater detail by Sircar (1995). Such limitations may explain many of the prediction errors that occur using IAS-based models. Furthermore, attempts to correct such problems directly within the IAS model, for example, using adsorbed-phase activity coefficient prediction methods, can sometimes yield problematic results in circumstances approaching the loading at saturation, for reasons discussed in the next section.

As an alternative to such IAS model refinements, a new multimodel approach for mixed-gas adsorption equilibria prediction from pure component data is proposed. In this approach, adsorption conditions for which the IAS prediction method is expected to be valid are identified. When such conditions are inadequately met, mixture equilibria predictions are based instead on one of two variants of the pure-component Langmuir-Freundlich (LF) model (Sips, 1948) and its extension to mixture equilibria prediction (Yon and Turnock, 1971). Three special features of the new multimodel approach are

- *Thermodynamic Consistency:* Unlike the classical LF model, the new approach does not violate Henry law constraints at low coverage conditions.
- *Physically Consistent Framework:* Unlike IAS, the new method approaches more reasonable adsorbate selectivity limits at ultimate coverage for mixtures with unequal adsorbate sizes.

Correspondence concerning this article should be addressed to R. T. Maurer who is currently with PractiChem, Inc., 263 Treetop Circle, Nanuet, NY 10954.

- *Inclusion of Energetic Heterogeneity Effects.*

The new multimodel approach employs three separate (though continuous) prediction models for cases of low, moderate or high surface coverage and will thus be referred to as the three-regime (or TR) adsorption model. Such an approach results in the successful prediction of many mixture equilibria often considered unassailable using current single-model approaches, including mixtures exhibiting unequal size or azeotropic behavior.

IAS Difficulties for Cases with Unequal Saturation Capacity

Almost all theories of physical adsorption, including IAS theory, assume that the adsorbent possesses a temperature-invariant area that is the same for all adsorbates (Myers and Prausnitz, 1965). For the many systems failing to adhere to this assumption, the resulting deviations from the "ideal" system state are generally accounted for by means of adsorbed-phase activity coefficients in the same manner as methods developed for vapor-liquid equilibria. However, when the potential for adsorption becomes constrained by finite adsorbent geometry, such strategies can lead to physically implausible results at conditions approaching the adsorbent's ultimate capacity, that is, at high system pressure or surface coverage. For example, for bulk-phase equimolar binary mixtures in which both species exhibit virtually identical pure-component Langmuir adsorption isotherms, IAS theory predicts that differences (even infinitesimal ones) in saturation capacity between the two adsorbing species should produce infinite separability between such species in the limit of total surface coverage. While concepts of selectivity tend to lose their meaning at or near this limit (as pressure approaches infinity, the mixture loading isotherm goes through a maximum coinciding with equality of densities in the adsorbed and bulk gas phases), the implication for real systems below such a limit is that the species having the infinitesimally greater adsorption capacity can be purified to any extent desired by an appropriate increase in system pressure. In reality, the two species' loading under such circumstances might more reasonably be expected to rise in virtual tandem with one another as pressure is increased, resulting in essentially no mixture separability at any system pressure level.

From the example just discussed, it should also be clear that *correlative* equilibrium models based on IAS (so-called real adsorbed solution or RAS models), at the limit of high surface coverage, experience the same difficulties as IAS theory for cases of unequal adsorbate size. That is, such models possess no mathematical corrector (such as adsorbed-phase activity coefficients) capable of transforming an essentially infinite IAS-predicted selectivity to a finite one. Such violations of physical expectations at high surface coverage can affect the accuracy of equilibria predictions at intermediate surface coverage as well, in much the same way as can thermodynamic inconsistencies at low surface coverage (so-called Henry law violations).

TR Model Approach to MCAE Prediction

Despite its various shortcomings for predicting multicomponent adsorption equilibria (MCAE), IAS theory is known to be completely rigorous, from a statistical mechanical viewpoint, for the special case of low surface coverage (Myers and Prausnitz, 1965). Here, the theory's inherent assumption of a single MCAE driving force (presumed to be proportional to the adsorbate's chemical potential) is quite valid. For situations in which such an assumption is invalid, a hybrid three-regime (TR) model for MCAE prediction is presently proposed, wherein the *single driving-force* IAS model at low coverage is supplemented by a *dual driving-force* model for predictions at higher coverage. The TR model assumes that the dual driving forces chiefly responsible for deviations from IAS predictions are

- Adsorbate-adsorbent energetic effects due to differences in potential attractive forces
- Adsorbate-adsorbent geometry effects which may be correlated to the limiting capacity of the adsorbent for the various adsorbing species.

In the TR model framework, therefore, IAS theory is expected to deviate from real equilibria whenever the influence of adsorbate-adsorbent energetic (or *driving*) forces is significantly different from that due to system geometric (or *constraining*) forces. Rather than attempting to solve for the effects of both forces directly, the TR model makes predictions at two extremes of adsorption behavior, where such behavior is determined by only one of these two forces. In cases where both forces play a significant role, a third prediction model is invoked to estimate the simultaneous effect of both forces on mixed-gas adsorption. These three regimes of adsorption behavior are described briefly below:

- At low coverage (Henry law region), geometric confinement effects are minimal, and lateral interactions are few and far apart. Differences in the potential attractive forces between the two adsorbing species thus become the sole determinants of the selectivity on the adsorbent. In terms of the previously-described dual driving-force paradigm, such IAS-valid adsorption conditions might be usefully referred to as a *geometrically quasi-homogeneous adsorption regime*. By this, we mean a regime in which supposed adsorbent heterogeneities of a geometric nature affect multicomponent adsorption behavior in an identical manner as that for pure-component adsorption of the same species contained in the mixture.
- At high coverage, the existence of a complementary *energetically quasi-homogeneous adsorption regime* is assumed. Here, energetic effects of attractive (driving) force differences become minimized in the face of increasingly large constraining-force effects imposed by the finite geometry of the adsorbent and adsorbing molecules.
- At moderate coverage, a *transitional adsorption regime* is assumed, wherein neither of the above quasi-homogeneity assumptions is expected to apply. In this regime, both energetic *and* geometric factors significantly influence adsorptive loading and selectivity for the mixture.

For systems exhibiting Type I single-component isotherms (i.e., convex toward the loading axis), the present work will show that various modifications of the classical LF adsorption model often prove helpful in the task of translating single-component energetic vs. geometric (i.e., driving vs. constraining force) effects to those for mixtures.

TCLF Model for the Geometrically Quasi-Homogeneous (IAS-valid) Adsorption Regime

Sips (1948) derived the first statistical mechanical interpretation of the familiar Langmuir-Freundlich (LF) model for

Type I adsorption isotherms. By this interpretation, the LF model represents energetic heterogeneities as a nearly Gaussian distribution of Langmuir-like adsorption sites with increasing attractive force constants. The classical LF model takes the following form

$$q(LF) = q_s \frac{\phi}{1+\phi} \tag{1}$$

where

$$\phi = (bP)^{\frac{1}{n}} \tag{2}$$

ϕ is the LF isotherm equation variable. The classical LF model is known to fit a wide variety of adsorbents exhibiting Type I adsorption behavior (Yon and Turnock, 1971) and also retains the relative theoretical clarity of the Langmuir adsorption model, which is derivable from either an adsorption kinetics (Langmuir, 1918) or a statistical mechanical standpoint (Ruthven, 1984). Unfortunately, because the LF model is thermodynamically inconsistent, it predicts infinite adsorption isotherm slopes at zero coverage (and thus undefined Henry constants). The presently proposed multimodel approach corrects this important deficiency in the classical LF model by defining a crossover pressure P_c and a new form of the LF model for adsorption occurring below such a reference pressure

$$q(\text{TCLF}) = q_s \frac{\phi'}{1+\phi'} \tag{3}$$

where

$$\phi' = (bP_c)^{\frac{1}{n}} \left(\frac{P}{P_c} \right)^{\frac{1/n - \ln(P/P_c)}{1 - \ln(P/P_c)}} \quad \text{when } P \le P_c \tag{4a}$$

and

$$\phi' = (bP)^{\frac{1}{n}} \quad \text{when } P \ge P_c \tag{4b}$$

ϕ' is the modified LF isotherm equation variable. Subscript c is the crossover pressure level below which the LF isotherm equation is forced to thermodynamic consistency by a gradual shift toward pure Langmuir isotherm behavior as represented by Eqs. 4a and 4b. This modification of the classical LF model is referred to as the thermodynamically consistent LF (or TCLF) model. This pure-component adsorption model yields a mathematically smooth transition from pure Langmuir behavior to LF behavior as system pressure varies from zero to P_c and retains both continuous isotherm slope (dq/dP) and Type I adsorption curvature ($d^2q/dP^2 < 0$) throughout its operative range. Pure-component TCLF model isotherm properties are illustrated in Figure 1 for various values of b and n, assuming (arbitrarily) 1 kPa as the presumed TCLF crossover pressure. b is the homogeneous attractive force constant in Langmuir or LF isotherm equation, kPa^{-1}. Physically, the TCLF model implies that below P_c, the statistical distribution of adsorbate molecules on adsorption sites of varying attractive potentials progressively narrows as pressure approaches zero. The result at zero system pressure is a delta function, meaning that only one particular type of site will always be the first to undergo adsorption on an initially clean surface (this same type of site being also the last to undergo the reverse process of desorption). The Henry constant for the new TCLF model is finite (as thermodynamic consistency requires) and equal to the following value:

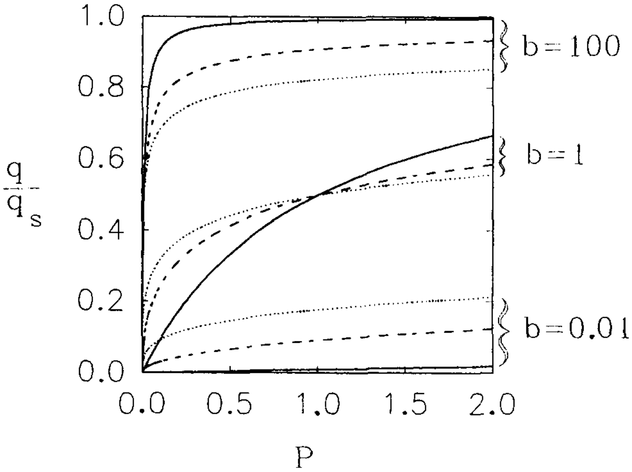

Figure 1. Thermodynamically consistent Langmuir-Freundlich (TCLF) adsorption isotherms.

Parameter range shown: $b = 0.01$, 1 and 100 (as marked on plots), $n = 1$ (—— = Langmuir), 2 (---------) and 3 (··········), $P_c = 1$.

$$K_H(\text{TCLF}) = q_s b^{\frac{1}{n}} \left(\frac{P_c}{e} \right)^{\frac{1}{n} - 1} \tag{5}$$

The cost for the thermodynamic consistency afforded by the new TCLF model is the introduction of a fourth fitting parameter P_c into the pure component LF isotherm model (the other three being b, n and q_s). Such an apparent tradeoff becomes minimal in practice, however, because any real, positive value of P_c will yield the desired thermodynamic consistency. At present, no special significance should be accorded the value of the crossover pressure. Its function in the new TR prediction model is merely to permit thermodynamically consistent IAS predictions using LF-type pure-component adsorption isotherms. Thus, the best choice of P_c is simply the one that best fits the pure-component isotherm data of interest. Figure 2 compares the fitting power of the classical LF and TCLF models using isotherm data for propane on H mordenite (Talu and Zwiebel, 1986). The TCLF model gives a much better fit of the data than the classical LF model even at pressures far above the P_c value (= 1.2 kPa) used to correlate these data to the model. The (four-parameter) TCLF fit is also significantly better than those using various other three-parameter isotherm models, for example, more than fiftyfold reductions in the (loading-weighted mean-square) residuals as compared to Toth or UNILAN model fits of the data shown in Figure 2 (Valenzuela and Myers, 1989). (e is the Euler number (= 2.7182818...); k_H is the

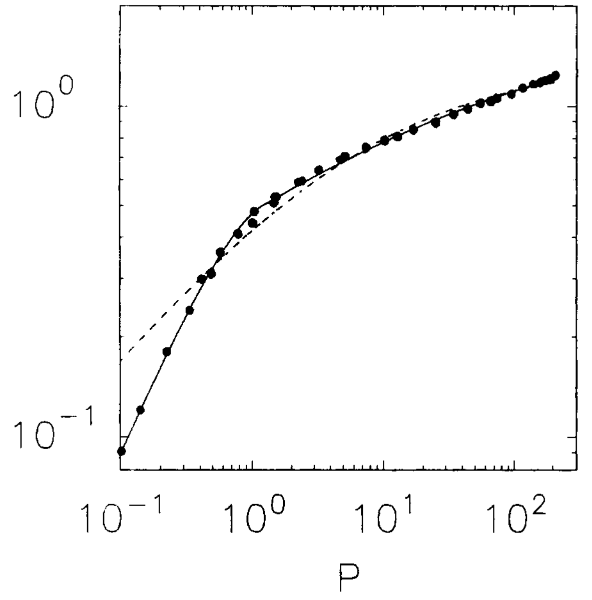

Figure 2. Comparison of classical LF and TCLF model fits for propane adsorption on H-mordenite at 30°C (data of Talu and Zwiebel, 1986).

Isotherm Model	Symbol	Best Fit Parameters b	n	q_s	P_c
Classical LF	– – –	0.188	2.02	1.38	-
TCLF	——	0.036	3.15	1.86	1.2

Henry constant = slope of pure component adsorption isotherm at zero pressure, mol·kg^{-1} kPa^{-1}.)

The TCLF model for single-component adsorption thus provides a reasonable basis for IAS predictions of MCAE within the presumed geometrically quasi-homogeneous adsorption regime. The increased fitting power afforded by this model can be crucial to predictional success in this regime, because the IAS method is known to be quite sensitive to the precision of the isotherm model for fitting the single-component data of interest (Richter et al., 1989).

Classical LF Model for the Transitional Adsorption Regime

At system pressures or surface coverage beyond the Henry region, the accuracy of the MCAE predictions appears to be less dependent on the precision of the single-component isotherm fits but more sensitive to the choice of the MCAE mixing-rule employed to estimate the relative contributions of the various adsorption driving forces responsible for single-component adsorption. In the transitional adsorption regime, the simpler (three-parameter) classical LF model appears, for the cases studied here, to adequately represent the relative effect of such contributions.

By the method of Markham and Benton (1931), the classical LF isotherm equation can be extended to multicomponent adsorption (Yon and Turnock, 1971), leading to the following predictions for the multicomponent loadings of a species i

$$q_i(\text{LF}) = q_{si}\frac{\phi_i}{1+\sum_j \phi_j} \qquad (6)$$

where the ϕ_i values are defined by Eq. 2, except that P in Eq. 2 (total system pressure) is replaced by the appropriate p_i (species partial pressure, kPa) value for each species in the mixture. i and j are components. The summation indicated in Eq. 6 is performed over all components in the mixture. (Note: Eq. 6 is thermodynamically inconsistent when the saturation capacities q_{si} (mol·kg^{-1}) are unequal. Its use in the TR modeling approach is strictly limited to selectivity predictions (*not* total loading predictions) within the so-called transitional adsorption regime, however. A subsequent section of this article will address the thermodynamic consistency of the TR model in greater detail. (q is the adsorbed concentration (mol·kg^{-1}).)

Equation 6 expresses alternative estimates of species by species multicomponent loadings to those assumed by IAS theory. Its predictions of adsorptive selectivity for a binary mixture are also different and given by

$$S_{ij}(\text{LF}) = \frac{x_i/y_i}{x_j/y_j} = \frac{y_j q_{si}\phi_i}{y_i q_{sj}\phi_j} \qquad (7)$$

where p_i replaces P in the definition of ϕ (Eq. 2), as for Eq. 6 above. y is the mole fraction in gas phase. S_{ij} is the adsorbed phase selectivity of species i relative to species $j = (x_i/y_i)(x_j/y_j)$. For nonideal gases or vapors, Eqs. 6 and 7 (as well as Eq. 8 below) might more preferably use fugacities in place of partial pressures. Such vapor-phase corrections are often small compared to the effect of nonidealities in the adsorbed phase, however (Talu and Myers, 1988). In the present work, only partial pressures are employed in the TR model calculations.

Equation 7 implies that within the transitional (or dual driving-force dominated) adsorption regime, the loading of any given component will be directly proportional to the product of its energetics-derived driving force (represented by ϕ, the attractive potential) times its geometry-based constraining force (represented by q_s, the saturation capacity). Of course, the assumption of such a simple, uncoupled relationship between such energetic and geometric effects could tend to be overly simplistic if applied to sufficiently nonideal systems. However, because such energetic and geometric factors are fundamental to the concept of Type I adsorption behavior, such behavior might still be more reasonably represented (for moderate-coverage "transitional" regime conditions, at least) by a simple dual driving-force model than by one presuming a single mechanism to underlie all aspects of adsorption behavior, as when using IAS theory alone. Simple as it is, the multicomponent LF model nonetheless includes abilities to predict azeotropic behavior and either increasing (when $n_i > n_j$), constant (when $n_i = n_j$), or decreasing (when $n_i < n_j$) adsorbate selectivity S_{ij} with increasing system pressure or site coverage.

Although the LF model's dual driving-force paradigm might be more reasonable than the IAS model's single-force paradigm for moderate-coverage situations, high-coverage situations would appear to require yet another approach. One possible approach, proposed in the following section, forms an approximate complement at high coverage to the single-force paradigm of the IAS model for low-coverage situations. This approach de-emphasizes the contribution of relative attractive force potentials to adsorptive selectivity for the mixture, thereby increasing the relative importance of finite adsorption capacity to such selectivity. This situation is the reverse of that for IAS theory and one somewhat reasonable to expect in situations approaching the limiting capacity of the adsorbent for the adsorbing species.

Modified LF Model for Energetically Quasi-Homogeneous Adsorption Regime

For many adsorption systems, either the IAS or the LF prediction model appears to characterize the mixture selectivities at equilibrium fairly well. However, for many others, especially those involving polar adsorbates at relatively high coverages, neither model performs adequately. For this reason, a third adsorption regime and its associated prediction model are proposed. This *energetically quasi-homogeneous LF* adsorption model approaches physically reasonable selectivity values at the limit of total surface coverage in many cases where the IAS model does not. It also compensates for the observed tendency of the classical LF model to underpredict adsorptive selectivity at high surface coverage. Such selectivity underpredictions may be due to the LF model's rather simplistic representation of adsorbent heterogeneities through the use of the so-called Freundlich heterogeneity parameter n.

The new energetically quasi-homogeneous LF model effectively limits the extent to which such heterogeneities can influence an adsorbent's selectivity performance at high surface coverage (where the classical LF adsorption model appears frequently to overemphasize such an influence). It does so by introducing a *heterogeneity-normalizing parameter* n_{ij} into the formula for binary selectivity prediction using the LF model (Eq. 7), in the following manner

$$S_{ij}(\text{Energetically Quasi-Homogeneous LF}) = \frac{y_j q_{si}}{y_i q_{sj}}\left(\frac{\phi_i}{\phi_j}\right)^{n_{ij}} \tag{8}$$

where

$$n_{ij} = \frac{y_i n_j + y_j n_i}{y_i + y_j} \tag{9}$$

From the definition of ϕ_i (Eq. 2, with p_i replacing P for mixtures, as in Eqs. 6 and 7) and inspection of Eq. 8, observe that another way to state the difference between Eq. 8 and the classical LF method for selectivity estimation (Eq. 7) is that wherever Eq. 7 uses n, Eq. 8 uses n/n_{ij} instead; hence the characterization of n_{ij} as a heterogeneity-normalizing parameter in the statement immediately above.

For cases of isoheterogeneous ($n_i = n_j$) binary adsorption, Eq. 8 reduces to

$$S_{ij}(\text{Energetically Quasi-Homogeneous LF for } n_i = n_j) = \frac{q_{si} b_i}{q_{sj} b_j} \tag{10}$$

which is identical to the selectivity predicted by the Markham and Benton extension of the Langmuir adsorption model and, unlike IAS theory, predicts finite *i-j* selectivity for all extremes of system pressure, even when the adsorbate saturation capacities are unequal. As shown by both Eqs. 9 and 10, when the gas-phase mole fraction of either component i or j approaches zero, the binary parameter n_{ij} in the quasi-homogeneous LF model also causes binary selectivities to approach finite values. This property is important when establishing the overall thermodynamic consistency of the TR model, as will be demonstrated in a later section. Physically, the energetically quasi-homogeneous LF model implies that above a certain coverage level, a progressive narrowing occurs in the statistical distribution of adsorbate molecules on adsorption sites of varying attractive potentials with increased coverage. This situation is the reverse of that encountered at extremely low coverage when employing the TCLF model described above (Eqs. 3, 4a and 4b).

Matching the TR Adsorption Model to the Appropriate Adsorption Regimes

The concepts discussed for predicting adsorptive selectivity using three separate adsorption models have limited usefulness unless the conditions for which each submodel is most appropriate can also be delineated. For adsorption from binary gas mixtures, an investigation of how these submodels apply for a variety of adsorbate-adsorbent systems under a variety of adsorption conditions has led to the following heuristic guidelines:

- The single-driving-force based (as discussed previously) IAS model, which recognizes no specifically geometric component of pure-species adsorption behavior (such components tending more generally to *reduce* the contribution of differential adsorbent attractive forces to the adsorptive selectivity values), generally predicts the *maximum*-possible selectivity values for the mixture under consideration. [The validity of this assumption is tested in a subsequent section for a wide variety of adsorbents and adsorbing species. An even better upper bound might be provided by the MSL or HL adsorption models recently analyzed by Sircar (1995). Such an approach would require fitting each pure-component adsorption isotherm to three separate adsorption models (MSL, HL, LF), however, in contrast to the more unified modeling approach attempted in the present study.]
- The energetically quasi-homogeneous LF model, which assumes that (generally selectivity-*limiting*) geometric constraining-forces, rather than (generally selectivity-*enhancing*) attractive forces, dominate the adsorption picture at very high surface coverage, generally predicts the *minimum* possible selectivity values for the mixture under consideration.
- When the selectivity prediction using the classical LF model recommended for the transitional adsorption regime falls between that predicted by the IAS and by the energetically quasi-homogeneous LF models, the classical LF model is considered the appropriate choice for binary selectivity prediction.

These guidelines assume that the selectivity values predicted by the three adsorption models yield sufficient information to identify the appropriate adsorption regime for any given *i-j* adsorbate pair. The most appropriate mathematical statement of these guidelines is then

For cases where $K_{Hi} > K_{Hj}$

$$S_{ij} = \mathrm{Min}[S_{\mathrm{IAS}}, \mathrm{Max}(S_{\mathrm{LF}}, S_{\mathrm{EQHLF}})]_{ij} \qquad (11a)$$

For cases where $K_{Hi} < K_{Hj}$,

$$S_{ij} = \mathrm{Max}[S_{\mathrm{IAS}}, \mathrm{Min}(S_{\mathrm{LF}}, S_{\mathrm{EQHLF}})]_{ij} \qquad (11b)$$

where LF and EQHLF refer to the classical LF and energetically quasi-homogeneous LF models, respectively.

For a binary mixture, the definition of selectivity and the fact that $x_1 + x_2 = 1$ lead easily to the calculation of adsorbed phase mole fraction as

$$x_i(\text{Binary Mixture}) = \frac{y_1 S_{12}/y_2}{1 + y_1 S_{12}/y_2} \qquad (12)$$

The TR model selectivity prediction method is internally consistent when applied to binary mixtures (see the section "Thermodynamic Consistency of the TR Model" for more discussion on this point). For ternary or higher-order mixtures, however, the method can sometimes exhibit internal inconsistencies. For example, if we treat a binary mixture of i and j as a ternary mixture in which two of the adsorbing species are identical and sum to the same concentration as for the equivalent binary, resultant predictions of S_{ij} may differ from those assuming a binary mixture. A rigorous extension of the TR adsorption model to ternary and higher-order mixtures appears possible, although a detailed discussion is beyond the scope of this article. One approach involves correlating loading predictions based on the TR model for all binary pairs in the mixture to a thermodynamically consistent adsorbed-phase activity coefficient model, such as the SPD model of Talu and Zwiebel (1986). Such an approach ensures that the resulting MCAE predictions will satisfy the Gibbs-Duhem relation as dictated by thermodynamics and also incorporate the dual driving-force (energetics vs. geometry) interpretation of Type I single-component adsorption behavior, at least for binary interactions. Higher-order effects are then assumed to be related to a single driving force only (for example, surface attractive potential using the SPD modeling approach). Reverting to such a simplistic assumption in the treatment of ternary and higher-order systems may, however, limit the predictive success of the TR model when applied to such mixtures.

Estimation of Total Adsorbed Phase Loading Using the TR Adsorption Model

The adsorbed-phase mole fraction and selectivity predictions using the TR adsorption model are continuous in all parameter space. That is, no "jumps" are encountered in such predictions when variations of system pressure, system temperature, or component mole fraction cause the system to cross over from one adsorption regime to another. However, the continuity of adsorbed mixture total loading is not assured between the IAS model and the various LF model forms described in this article. To ensure such continuity, a single-model prediction approach is followed when estimating this parameter. Fortunately, whereas the accuracy of MCAE selectivity predictions can be quite sensitive to assumptions underlying the chosen prediction methods, total mixture loading prediction methods are often much less sensitive to such underlying assumptions (Valenzuela and Myers, 1984).

In the TR modeling approach, IAS theory serves as the starting point for estimation of the mixture's total adsorbed-phase loading. For binary mixtures, the basic IAS loading prediction model of Myers and Prausnitz (1965) is modified to reflect selectivity predictions based on the new TR model and optionally to reflect also the potential for more efficient adsorbed-phase packing densities for mixtures whose adsorbing molecules differ greatly in size (and by extension, in ultimate adsorption capacity as well). Although the latter assumption might be expected to be strictly valid only for systems that are energetically homogeneous (such as when both adsorbates exhibit solely nonpolar interactions with the adsorbent), such effects appear to be observed even in energetically heterogeneous adsorption systems (see data comparisons to follow).

The prediction of total loading by the TR model for binary mixtures requires first finding the pressure P_i^o associated with each species of the binary mixture yielding the same spreading pressure for the pure component as for the mixture, as computed by the IAS theory (Myers and Prausnitz, 1965)

$$P_i^o = y_i \frac{P}{x_i} \qquad (13)$$

The difference is that the x_i values are now predicted from the TR rather than the IAS model. The total mixture loading is then estimated as

$$q_{\mathrm{Total}} = C_T \left[\sum_i \frac{x_i}{q_i^o(P_i^o)} \right]^{-1} \qquad (14)$$

q_{Total} is the total adsorbed concentration of all mixture species, mol kg^{-1}. Superscript o is a variable evaluated at the standard state for a component, defined as the state when only that component is present, which corresponds to the spreading pressure of the mixture under consideration. Equation 14 is identical to that proposed by Myers and Prausnitz (1965) except for the addition of the multiplicative correction factor C_T. An empirical relation for C_T derived from the total loading deviations observed for the systems investigated here is

$$C_T = \mathrm{Min}[\exp(8.4D^{4.2}), 1.5] \qquad (15)$$

where

$$D = \frac{N\left[\sum_i x_i \left(\frac{1}{q_{si}} - \sum_j \frac{x_j}{q_{sj}}\right)^2\right]^{\frac{1}{2}}}{\sum_i \frac{1}{q_{si}}} \qquad (16)$$

N is the number of components in the mixture. The parameter D represents a normalized measure of the standard deviation of the size distribution of molecules in the adsorbed-phase region of the mixture. It can vary between zero (for pure species or mixtures with equal-sized adsorbate molecules) and unity (for a hypothetical mixture exhibiting infinite differences in molecular size). To avoid adding any new parameters to the prediction method, however, Eq. 16 employs the inverse of species saturation (or monolayer) capacity as an approximately proportional measure of adsorbate size. Equation 15 limits the correction factor C_T to a maximum of 1.5, this being the highest value observed (for H_2S-C_3H_8-H mordenite) in the systems investigated for this article as well as the maximum theoretically attainable value in going from a monodisperse ($D = 0$), maximally packed assemblage of hard-shelled, spherical molecules (maximum void fraction of 0.32–0.33 (Leva, 1959)) to an infinitely disperse one ($D = 1$), where the void fraction is zero as a result of perfect molecular "nesting."

Loading predictions for ternary and higher-order mixtures using the TR model presently require the intermediate use of activity coefficients, as discussed in the previous section. Equations 13–16 are then applied only to binary mixture behavior, that is, for the generation of binary activity coefficients.

TR Prediction Method for Binary Equilibria

It is useful at this point to summarize the computational steps required for prediction of binary adsorption equilibria using the three-regime adsorption model. Such predictions may be obtained in the following manner, given knowledge of the system pressure and gas-phase mole fractions of the adsorbing species:

(1) Determine S_{IAS} by classical IAS methods (Myers and Prausnitz, 1965). Due to its apparent superiority over three-parameter models for the system investigated here, the four-parameter TCLF pure-component adsorption isotherm model is recommended for use in such calculations. If a three-parameter model (such as Toth or UNILAN) is found to yield comparable isotherm fits for the system of choice, the latter may be employed instead in the IAS selectivity calculations, leading perhaps to faster computation times overall.

(2) Derive the LF isotherm model (Eqs. 1 and 2) fitting parameters b, n and q_s for each of the adsorbing species.

(3) Given the LF fitting parameters from step 2, determine S_{LF} (Eq. 7) and S_{EQHLF} (Eqs. 8 and 9).

(4) Given S_{IAS} (step 1), S_{LF} and S_{EQHLF} (step 3), determine the TR model adsorptive selectivity (via the rule of Eqs. 11a or 11b, as appropriate) and the adsorbed phase mole fraction (x_i) corresponding to such a selectivity prediction (Eq. 12).

(5) Determine the total mixture loading (q_{Total}) via Eqs. 13–16.

(6) Compute the loading of the ith species as $q_i = x_i q_{\text{Total}}$.

Thermodynamic Consistency of the TR Model

Ideal adsorbed solution theory, while thermodynamically consistent when applied to systems with equal-sized adsorbate molecules, has limited physical consistency where mixtures of variously sized adsorbate molecules are concerned. The TR modeling approach attempts to improve such physical consistency and maintains both internal and thermodynamic consistency for the overall adsorption paradigm of multiple adsorption regimes under different conditions of multicomponent adsorption. Internal consistency requires that all mixture approaches toward single-component conditions yield adsorption behavior identical to that for the pure-component species whose mole fraction is approaching unity. Thermodynamic consistency requires a similar approach to single-component adsorption behavior as the system pressure of the mixture (and thus surface coverage) approaches zero.

Internal consistency of the TR model is assured through the use of the modified IAS method for the total mixture loading prediction previously described (Eqs. 13–16). The correction factor C_T approaches unity as the mixture mole fraction of any given component species approaches unity (leading to $D = 0$ in Eqs. 15 and 16), leading to purely ideal adsorbed solution behavior for such conditions.

The TR model meets the thermodynamic consistency requirements (mixture behavior approaching single-component Henry law behavior as zero-coverage conditions are approached) so long as, at zero surface coverage, either the classical LF or the energetically quasi-homogeneous LF (EQHLF) model predicts at least the same *qualitative* preference for a given species in each mixture binary pair as demanded by thermodynamic considerations, that is, a preference (however great) for the species having the larger Henry constant in a single-component adsorption. In such cases, when the fitting parameter n in the TR model differs among mixture species, its effect in the exponent of Eq. 2 is to cause the LF and EQHLF selectivity estimations (Eqs. 7, 8 and 9) to go to infinity (or zero from the less preferred component's standpoint). The result is that the (thermodynamically consistent) IAS model is chosen for such selectivity predictions, as set forth by the TR model's "selectivity-bounding" paradigm of Eqs. 11a and 11b. For cases of purely Langmuir adsorption (where $n = 1$ for all mixture species), all three (IAS, LF and EQHLF) submodels of the TR adsorption model devolve to the same selectivity predictions (being then identical to the right side of Eq. 10). Thus, thermodynamic consistency at zero coverage conditions is ensured.

An important exception to thermodynamic consistency of the TR adsorption model can occur for cases involving isoheterogeneous mixtures of a non-Langmuir type (wherein separate species n values are identical but do not equal one). In such cases, the zero-coverage LF and EQHLF model selectivity predictions are *not* unbounded, leading to the possibility of finite but thermodynamically inconsistent selectivity predictions. This difficulty can be easily overcome, however, by assigning an infinitesimally different n value to each species' single-component isotherm-fitting equation in a way that satisfies the thermodynamic consistency criteria stated at the beginning of the previous paragraph. These constraints, which are needed to retain the thermodynamic consistency of the TR model, are fairly easy to implement in actual practice.

The selectivity-bounding paradigm of the TR model (Eqs. 11a and 11b) serves also to constrain the model's selectivity predictions to take only finite (and positive, naturally) values. This property is not shared by the classical LF model (when not so bounded by other models as it is here) except for cases of Langmuir isotherms ($n = 1$ for all species in the mixture). Because both the IAS-TCLF and (as discussed in a previous section) EQHLF models give finite (and positive) selectivity predictions throughout the y- or x-plane, these models serve as upper and lower bounds on the TR model selectivity predictions. Though finite selectivity predictions are not demanded by thermodynamics, the concept of potentially infinite separability (selectivity) at infinite dilution of a given mixture species would seem to be physically attainable only under very special circumstances of adsorption site (or pore) geometry. As such, the TR model treats such predictions as an unfortunate artifact of the LF model's mathematical functionality, which is essentially the same one (the $1/n$ exponentiation operation of Eq. 2) responsible for the LF model's thermodynamically incorrect limiting behavior at zero surface coverage.

With the above constraints on its use which are generally easily met, the TR adsorption model gives results that are internally and thermodynamically consistent. The model also satisfies important physical constraints at high surface coverage (such latter benefits having been discussed in a previous section).

Comparison of IAS and TR Models for Prediction of Mixed-Gas Adsorption Equilibria

Figure 3 compares actual binary selectivity data with IAS model predictions for a wide variety of gas-solid adsorption systems at equilibrium (209 data points in all, comprising 12 adsorbates and 7 adsorbent types). The data derive both from work internal to UOP and from the academic literature. The UOP-generated data were obtained using a volumetric-type adsorption apparatus similar to that of Kaul (1987). The literature-derived data include those tabulated by Valenzuela and Myers (1984) as well as other data for which the IAS model is known to yield poor selectivity predictions (Hyun and Danner, 1982; Talu and Zwiebel, 1986).

Two points to note concerning the results shown in Figure 3. First, the IAS predictions are widely scattered about the true selectivity values. Thus, for many of the systems shown, IAS theory by itself appears inadequate. Second, 71% of the IAS predictions are greater than or equal to the actual selectivity values. Note also that for this and subsequent plots, selectivities below the value of unity imply azeotropic adsorption behavior; that is, the binary selectivities are plotted in terms of the selectivity of component 1 relative to component 2 and the limiting zero-system pressure (Henry ratio predicted) selectivity of the adsorbent at the temperature of interest is for component 1 over component 2. Assuming the existence of random errors (whether in the binary data or the pure-component fits used in the IAS prediction method) that are possibly confounding the comparisons shown in Figure 3, a statistical test leads this researcher, with better than 99% confidence, to reject the null hypothesis that the true IAS-predicted selectivity is always lower than the true system selectivity. The nonparametric sign test (Rickmers and Todd, 1967) is the statistical test used here, since such errors appear from Figure 3 to be non-normally distributed. This analysis appears to validate heuristic guideline number 1 previously discussed, from a statistical standpoint though not necessarily the general standpoint. That is, IAS prediction deviations below the observed selectivities might or might *not* be attributable to random errors although such is the assumption used to make the statistical test.

Figure 4 compares actual binary selectivity data with IAS model predictions for a more restricted data set than that shown in Figure 3 (66 data points in all, comprising 9 adsorbates and 6 adsorbent types). Sufficient pure-component information exists for these data to generate selectivity predictions based on both the IAS and TR models. The restricted data set behaves much like the more general data set of Figure 3: 77% of the IAS predictions are equal to or greater than the observed selectivity data. Three adsorption systems manifesting particularly large deviations in the IAS-predicted selectivities are highlighted in Figure 4. Azeotropic adsorption behavior is exhibited for two of these systems: isobutane-ethylene-13X and hydrogen sulfide-propane-H mordenite.

Figure 5 compares the same selected data set with the selectivity predictions based on the TR model. The distribution

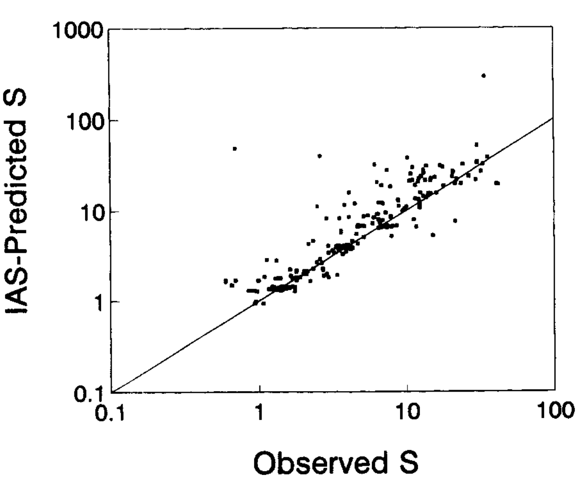

Figure 3. Observed vs. IAS-predicted selectivity.

Adsorbents: Activated carbon, silica gel, various zeolites (5A, 10X, 13X, CaNaX, H-Mordenite); components: O_2, N_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, H_2S.

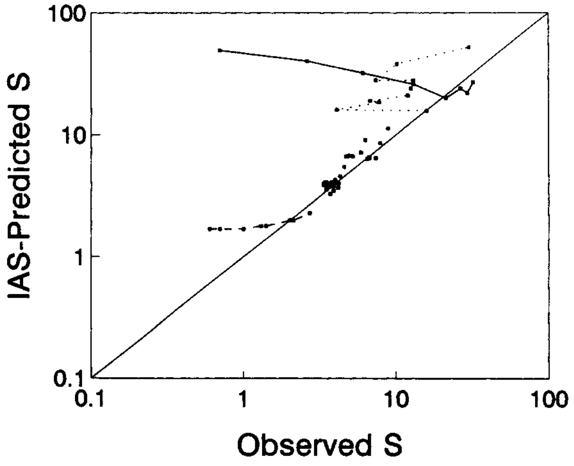

Figure 4. Observed vs. IAS-predicted selectivity.

Adsorbents: Activated carbon and various zeolites (5A, 10X, 13X, CaNaX, H-Mordenite); components: O_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, iC_4H_{10}, H_2S. Selected literature data: —— H_2S-C_3H_8-H-Mordenite (Talu and Zwiebel, 1986); -------- iC_4H_{10}-C_2H_4-13X (Hyun and Danner, 1982); ········· iC_4H_{10}-C_2H_6-13X (Hyun and Danner, 1982).

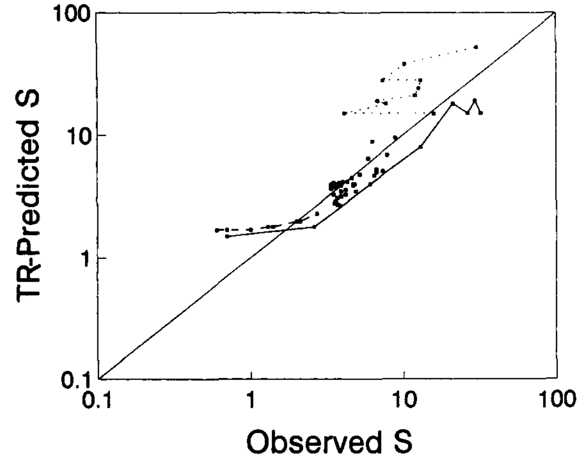

Figure 5. Observed vs. TR-predicted selectivity.

Adsorbents: Activated carbon and various zeolites (5A, 10X, 13X, CaNaX, H-Mordenite); components: O_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, iC_4H_{10}, H_2S. Selected literature data: —— H_2S-C_3H_8-H-Mordenite (Talu and Zwiebel, 1986); -------- iC_4H_{10}-C_2H_4-13X (Hyun and Danner, 1982); ········· iC_4H_{10}-C_2H_6-13X (Hyun and Danner, 1982).

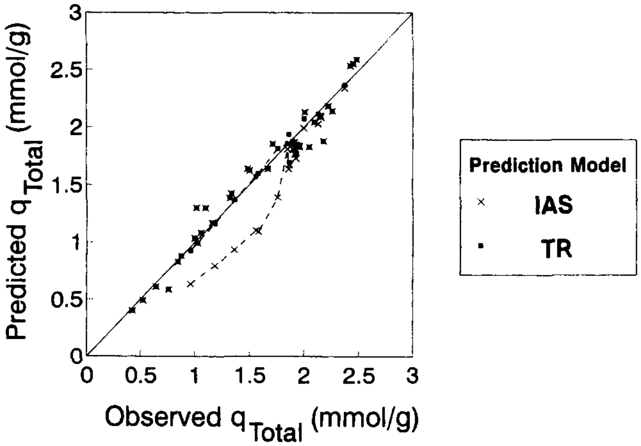

Figure 6. Observed vs. predicted total loading.

Adsorbents: Activated carbon and various zeolites (5A, 10X, 13X, H-Mordenite); components: O_2, N_2, CH_4, C_2H_4, C_2H_6, C_3H_8, iC_4H_{10}, H_2S. ········· Data for H_2S-C_3H_8-H-Mordenite (Talu and Zwiebel, 1986).

of the TR model predictions about the observed = predicted selectivity line is much more uniform than that for the IAS based predictions: essentially half the TR model predictions lie above this line, the other half below it (vs. a split of 77% above and 23% below the line for IAS, as observed in Figure 4). Thus, the TR model yields better selectivity predictions on average than IAS for these adsorption systems.

For the azeotropically inclined hydrogen sulfide-propane-H mordenite system (Talu and Zwiebel, 1986), the TR model improves the selectivity predictions enormously relative to using IAS theory alone: 35% average error using the TR model vs. 1,140% average error for IAS. For the other azeotrope shown (isobutane-ethylene-13X system of Hyun and Danner, 1982), both models give identical selectivity predictions, which, though unpredictive of the azeotrope, are at least on the approximate order of the observed selectivity values (60% average error for both models).

For the isobutane-ethane-13X system shown (Hyun and Danner, 1982), the TR model (150% average error) does little to improve the selectivity predictions (compare with 153% average error for the IAS model). For this particular case, however, there are certain aspects of the experimentally measured data that raise questions as to the accuracy of at least a portion of these data. Specifically, these (constant-pressure, constant-temperature) data indicate a selectivity dependence on species mole fraction that changes in direction five separate times over the range of measurement. Given the relative simplicity of the adsorbing molecules (nonpolar, moderately low molecular weight and configurational complexity) and the relatively large pore size associated with 13X adsorbent, the observed selectivity dependence on species mole fraction seems considerably more complex than underlying adsorption processes would suggest is likely for this case.

Total mixture loadings for some of the more nonideal systems investigated here are compared in Figure 6 for both IAS-model and TR-model predictions (the latter employing the correction factor based on adsorbate size-distribution as defined by Eqs. 15 and 16). The IAS and TR model predictions are similar for all but the hydrogen sulfide-propane-H mordenite system, where the IAS model tends to severely underpredict the total mixture loading. The TR model substantially corrects such deviations and only minimally influences the relatively accurate IAS-based loading predictions for the other systems shown.

Conclusions

The thermodynamically consistent TR adsorption model shows early promise as a tool for predicting multicomponent equilibria from pure component data alone. It appears to be more successful than pure IAS theory in this regard and also fulfills more reasonable expectations of relative mixture loadings at high surface coverage, especially when the saturation capacities of the adsorbing molecules are unequal. Moreover, relying as it does on insights derived from two fairly simple and familiar adsorption theories (ideal adsorbed solution theory and Langmuir adsorption theory), the new model offers the eventual hope of improved adsorbent design through a more detailed understanding of the mechanisms responsible for adsorption.

Notwithstanding the predictive abilities of the three-regime adsorption for the systems investigated here, further testing is recommended to determine if such concepts may be extended to other nonideal adsorption systems, including others exhibiting azeotropic adsorption behavior or strong adsorbed phase lateral interactions. The "heterogeneity-normalizing"parameter invoked in the selectivity prediction (Eqs. 8 and 9) and the "molecular-nesting" concepts invoked in the prediction of total loading (Eqs. 13–16) also require further validation and possible modification to improve the predictional accuracy of the proposed method. Past adsorption research experience indicates that prediction of total mixture loading is generally far less sensitive to the limitations of the particular prediction method employed than is the prediction of mixture selectivity behavior. In regard to the latter, substituting for the IAS method, other, possibly superior selectivity prediction models (the MSL or HL adsorption models cited above, for example) within the so-called IAS-valid adsorption regime of the TR model paradigm could conceivably yield further improvements to such selectivity prediction. Finally, a less onerous method for extending the TR adsorption model to ternary and higher-order mixed-gas equilibria prediction should be sought if the method is to enjoy any enduring success beyond the realm of academia.

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