model and experimental data, as expected, is very good for 0.01 $<Re'_{po} < 40$. Unfortunately, no other experimental data set is available to assess the range of validity of the proposed model. The Carberry model for Newtonian fluids is valid to about $Re = 1{,}000$. It is particularly important to realize that our Eq. 12 does not contain any adjustable parameters. It may, therefore, be concluded that the present model yields a satisfactory representation of non-Newtonian fluid-particle mass transfer in granular beds.

NOTATION

$A_1(n)$ = function of flow index defined by Eq. 6
$A_2(n,\epsilon)$ = function of flow index and void fraction defined by Eq. 14
c = *concentration at any point in the fluid*
c_w = concentration at surface
c_∞ = bulk concentration
D_p = particle diameter
$\mathcal{D}$ = diffusivity coefficient
J'_{po} = $\dfrac{\bar{k}}{u_o} Sc'_{po}{}^{2/3}$, mass transfer factor
K = consistency index in power-law model
K' = $K\left(\dfrac{3n+1}{4n}\right)^n$, modified consistency index
$\bar{k}$ = average mass transfer coefficient
n = flow index in power-law model
Re = xu/ν, Reynolds number
Re^* = $x^n u^{2-n} \rho / K$, Reynolds number
Re'_{po} = $D_p^n u_o^{2-n} \rho / K' \left\{12 \dfrac{(1-\epsilon)}{\epsilon^2}\right\}^{n-1}$, Reynolds number
Sc = $\nu / \mathcal{D}$, Schmidt number
Sc^* = $K x^{1-n} / u^{1-n} \rho \mathcal{D}$, Schmidt number
Sc'_{po} = $K' \left\{12 \dfrac{(1-\epsilon)}{\epsilon^2}\right\}^{n-1} D_p^{1-n} / u_o^{1-n} \rho \mathcal{D}$, Schmidt number
$\overline{Sh}$ = $\bar{k}x/\mathcal{D}$, average Sherwood number
u = velocity component along x
u_a = average velocity
u_o = superficial velocity
u_∞ = velocity at boundary layer edge
x = distance along the surface
y = distance normal to the surface

Greek Letters

δ = hydrodynamic boundary layer thickness
ϵ = void fraction
ν = kinematic viscosity
ρ = density
τ_{xy} = shear stress

Subscripts

a = based on u_a
p = based on D_p

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Activity Coefficients of Mixtures Adsorbed on Heterogeneous Surfaces

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Negative deviations from Raoult's law have been reported for the adsorption of mixtures on heterogeneous surfaces like activated carbon and silica gel (Minka and Myers, 1973; Peisen and Tiren, 1979; Costa, Sotelo, Calleja and Marrón, 1981). In such cases it is impossible to make accurate predictions of mixed gas adsorption equilibria using the method of ideal adsorbed solutions (IAS) (Myers and Prausnitz, 1965; Sircar and Myers, 1973).

The nature of these adsorbed-phase nonidealities is very interesting. For mixtures of aliphatic and aromatic hydrocarbons, the adsorbed solutions exhibit strong negative deviations from Raoult's law. Activity coefficients at infinite dilution are about 0.5 to 0.7, and the curves for activity coefficients are asymmetric about the equimolar composition as shown on Figure 1. This solution behavior is surprising because liquid mixtures of these hydrocarbons have moderate positive deviations from Raoult's law, and the activity coefficients are nearly symmetric about $x_1 = 1/2$.

One explanation of this anomalous behavior is that the surface perturbs the interactions of the adsorbed molecules to such an extent that there is no correlation between the excess free energies of adsorbed solutions and bulk liquid solutions. If this were the case, one would expect some mixtures to show positive deviations from Raoult's law and others to show negative deviations. Since all of the excess free energies are negative and uncorrelated with bulk liquid properties, it is possible that the phenomenon is not explained by

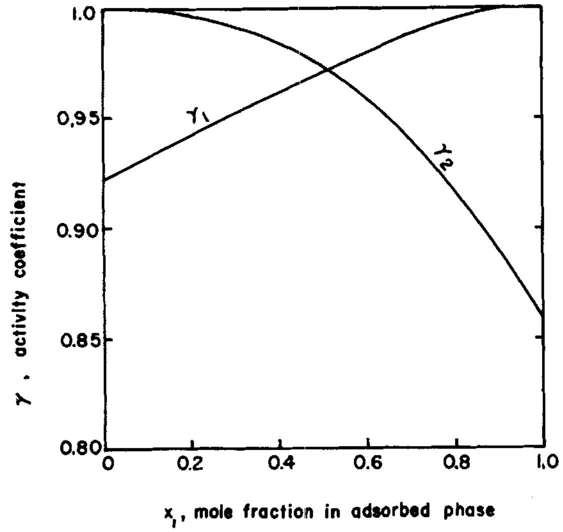

Figure 1. Activity coefficients of adsorbed solutions at constant pressure, calculated from Eq. 17 using the constants given in Table 1. The heterogeneity of the surface and the local variation in composition are ignored.

nonideal adsorbate interactions, but by something else. It is proposed that the apparent negative deviations from Raoult's law are due to the heterogeneity of the surface.

TWO-SITE HETEROGENEOUS SURFACE MODEL

The Langmuir equation (Langmuir, 1918) is selected to construct a two-site model of a heterogeneous surface. For the pure gases adsorbed on a non-heterogeneous surface:

$$n_i = \frac{m_i C_i P}{1 + C_i P} \tag{1}$$

For the postulated two-site surface consisting of A sites and B sites, the pure gas isotherm is:

$$n_i = \frac{m_{iA} C_{iA} P}{1 + C_{iA} P} + \frac{m_{iB} C_{iB} P}{1 + C_{iB} P} \tag{2}$$

The additivity for adsorption on different sites implies that the sites A and B are independent of one another. For a mixture of gases 1 and 2 adsorbed on the composite surface, the Langmuir equation is:

$$n_1 = \frac{m_{1A} C_{1A} p_1}{1 + C_{1A} p_1 + C_{2A} p_2} + \frac{m_{1B} C_{1B} p_1}{1 + C_{1B} p_1 + C_{2B} p_2} \tag{3}$$

$$n_2 = \frac{m_{2A} C_{2A} p_2}{1 + C_{1A} p_1 + C_{2A} p_2} + \frac{m_{2B} C_{2B} p_2}{1 + C_{1B} p_1 + C_{2B} p_2} \tag{4}$$

These equations are not thermodynamically consistent unless the monolayer coverage (m) is the same for both gases, so these are set equal to one another:

$$m_{1A} = m_{2A} \tag{5}$$

$$m_{1B} = m_{2B} \tag{6}$$

Equations 2 through 6 constitute a thermodynamically consistent model of binary, heterogeneous adsorption.

The mixture Eqs. 3 and 4 are based on Raoult's law and can be predicted using IAS from the adsorption isotherms of the pure gases on sites A and B, respectively. From Eq. 2 for site A alone, equality of spreading pressure for each pure gas in the standard state requires that:

$$\left[\frac{\Pi A}{RT}\right]_A = m_{1A} ln(1 + C_{1A} \overset{\circ}{P}_{1A}) = m_{2A} ln(1 + C_{2A} \overset{\circ}{P}_{2A}) \tag{7}$$

It follows that:

$$\frac{\overset{\circ}{P}_{2A}}{\overset{\circ}{P}_{1A}} = \frac{C_{1A}}{C_{2A}} = \frac{x_1/y_1}{x_2/y_2} = s_{1,2} \tag{8}$$

TABLE 1. VALUES OF HENRY'S CONSTANT FOR TWO-SITE MODEL OF HETEROGENEOUS SURFACE

	C, Units of P^{-1}	
	Site A (High Energy)	Site B (Low Energy)
Component No. 1 (Strongly Adsorbed)	2.0	0.3
Component No. 2 (Weakly Adsorbed)	0.2	0.1
Selectivity, $s_{1,2}$	10	3

In addition, for site A, the total amount adsorbed (n_A) is equal to the amount of either component adsorbed at the standard state defined by equality of spreading pressures:

$$n_A = \overset{\circ}{n}_{1A} = \overset{\circ}{n}_{2A} \tag{9}$$

so that the amount of component number 1 adsorbed on site A is:

$$n_{1A} = n_A x_1 = \frac{m_{1A} C_{1A} p_1}{1 + C_{1A} p_1 + C_{2A} p_2} \tag{10}$$

A similar equation for site B gives n_{1B}. The sum $n_1 = (n_{1A} + n_{1B})$ is identical to Eq. 3. Thus it has been shown that the two-site model is based on Raoult's law, and the purpose of this development is to examine the apparent nonidealities which arise when the heterogeneity of the surface is either unknown or ignored.

ACTIVITY COEFFICIENTS ON A HETEROGENEOUS SURFACE

Suppose that the adsorbed mixture obeys Eqs. 3 and 4 and the single gas isotherms are given by Eq. 2. The heterogeneity of the surface will be neglected by determining activity coefficients for the total adsorption represented by the sum of both terms in Eqs. 2, 3 and 4. Even for the simple two-site model under consideration, it is not possible to derive a simple expression for the activity coefficients so a calculation will be made for a specific case. Let component number 1 be the more strongly adsorbed species so that $s_{1,2} > 1$. It is reasonable to suppose that the ratio of energies for the pair of sites A and B is the same for both gases. However, the Henry's constant C in Eq. 1 varies exponentially with energy. Therefore, the preference of the surface for component number 1 should increase with the energy of the site. Specifically, Henry's constants for different gases adsorbed on different sites should show the trend in Table 1 of decreasing selectivity with decreasing site energies (Eq. 8). This hypothetical two-site heterogeneous surface has a selectivity between 10 and 3 which decreases with increasing surface coverage.

Suppose that both sites have equal surface area and the total coverage for the mixture and for each pure gas is unity:

$$m_{1A} = m_{1B} = m_{2A} = m_{2B} = m = \frac{1}{2} \tag{11}$$

Instead of applying IAS to each site, we assume (incorrectly) that the adsorbed solution is homogeneous and calculate activity coefficients at the overall composition of the composite surface layer in the conventional manner (Minka and Myers, 1973). From Eq. 2, the spreading pressure for the single-gas isotherm is:

$$\left[\frac{\Pi A}{mRT}\right]_i = ln[(1 + C_{iA} \overset{\circ}{P}_i)(1 + C_{iB} \overset{\circ}{P}_i)] \tag{12}$$

From Eqs. 3 and 4, the spreading pressure of the adsorbed mixture is:

$$\frac{\Pi A}{mRT} = ln \{[1 + (C_{1A} y_1 + C_{2A} y_2)P][1 + (C_{1B} y_1 + C_{2B} y_2)P]\} \tag{13}$$

The adsorbate vapor pressure at the standard state ($\overset{\circ}{P}_i$) is defined by equality of spreading pressures (Π) of the mixture and the standard state. From Eqs. 12 and 13, it is found that:

$$P_i^\circ = \frac{\sqrt{(C_{iA} - C_{iB})^2 + 4C_{iA}C_{iB}e^{\Pi A/mRT}} - (C_{iA} + C_{iB})}{2C_{iA}C_{iB}} \tag{14}$$

Mole fractions in the adsorbed phase are found from Eqs. 3 and 4:

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{15}$$

$$x_2 = 1 - x_1 \tag{16}$$

The adsorbed phase activity coefficient is:

$$\gamma_i = \frac{Py_i}{P_i^\circ x_i} \tag{17}$$

In summary, the apparent activity coefficient is calculated at a given value of P and y_1 as follows. First the spreading pressure is found from Eq. 13, which permits the calculation of the vapor pressures at the standard state by Eq. 14. n_1 and n_2 are given by Eqs. 3 and 4, from which the mole fractions in the adsorbed phase follow from Eqs. 15 and 16. Finally the value of the activity coefficient γ_i is determined by Eq. 17. The result is plotted on Figure 1 for a constant pressure of 10 (units of P consistent with the values of C in Table 1). At this pressure, the total surface coverage is about 80% of the saturation value of unity.

There are two important conclusions to be made from Figure 1. First, the deviations from Raoult's law are negative. Second, the curves for the activity coefficients are somewhat asymmetric like those found experimentally (Minka and Myers, 1973).

As an aside, it is noted that the activity coefficients at constant pressure are not constrained to obey the restricted form of the Gibbs-Duhem equation:

$$x_1 d\ ln\ \gamma_1 + x_2 d\ ln\ \gamma_2 = 0 \tag{18}$$

even though the pressure and temperature are fixed. Equation 18 is satisfied for adsorbed solutions under the conditions of constant temperature and spreading pressure. Thus it is not possible to fit activity coefficients measured at constant pressure with the van Laar, Wilson and UNIQUAC equations used for isothermal VLE. Furthermore, adsorbed phase activity coefficients are a strong function of spreading pressure, approaching the limit of unity (Raoult's law) at the limit of zero surface coverage.

There is a physical explanation of the apparent negative deviations from Raoult's law on a heterogeneous surface. The relative separation factor in Eq. 8 is given by:

$$s_{1,2} = \frac{x_1/y_1}{x_2/y_2} = \frac{P_2^*\gamma_2}{P_1^*\gamma_1} \tag{19}$$

for nonideal adsorbates. At constant pressure, IAS predicts a nearly constant value of selectivity because the activity coefficients are equal to unity and the ratio of adsorbate vapor pressures (P_2^*/P_1^*) is nearly constant. For adsorption on a heterogeneous surface, it is observed experimentally that $s_{1,2}$ decreases rapidly with x_1. At low values of x_1, most of the more strongly adsorbed component 1 appears on the high energy sites where the local value of $s_{1,2}$ is highest (Table 1). As x_1 increases, less high energy sites are available and increasing amounts of component 1 are displaced to sites of lower energy, resulting in a decrease in the overall value of $s_{1,2}$. If the heterogeneity is ignored, then the strong decrease in $s_{1,2}$ with x_1 must be artificially described by the ratio of activity coefficients γ_2/γ_1. As x_1 approaches zero, γ_2 approaches unity and the average value of $s_{1,2}$ must be multiplied by a value of $\gamma_1^\infty < 1$ (Figure 1) to explain the observed maximum of $s_{1,2}$. Similarly as x_1 and γ_1 approach unity, the average value of $s_{1,2}$ must be multiplied by a value of $\gamma_2^\infty < 1$ in order to reproduce the observed minimum in $s_{1,2}$. In this way the ratio γ_2/γ_1 (Figure 1) reproduces the strong monotonic decrease in $s_{1,2}$ with x_1 which is due to surface heterogeneity. Clearly the effect will always correspond to negative deviations from Raoult's law.

These results indicate that adsorbed phase activity coefficients calculated for heterogeneous surfaces such as activated carbon may be deceptive, in the sense that they are not due to nonideal molecular interactions between the unlike components of the adsorbed mixture. If the surface is properly treated as a collection of sites of different energies, then the apparent nonidealities will decrease or even vanish. This cannot be proved for experimental data until a suitable model of a heterogeneous surface (the two-site model is too simplistic) can be verified for the pure gases and then extended to adsorption of mixtures. However, we have studied more realistic continuous energy distributions and the results are qualitatively the same as for the two-site model. We are working now on a new, heterogeneous version of IAS which is intended to allow the prediction of mixed-gas equilibria in terms of the adsorption of the single gases.

NOTATION

A = specific surface area
$C_{i\alpha}$ = Henry's constant for ith component on site α, units of P^{-1}
$m_{i\alpha}$ = monolayer coverage of ith component on site α
$n_{i\alpha}$ = moles of ith component adsorbed on site α, per unit mass of adsorbent
$n_{i\alpha}^\circ$ = moles of ith component adsorbed on site α, per unit mass of adsorbent at standard state
P = pressure
$P_{i\alpha}^\circ$ = pressure of ith component on site α at std. state
p_i = partial pressure (fugacity) of ith component in gas phase
R = gas constant
$s_{1,2}$ = selectivity, $\frac{x_1/y_1}{x_2/y_2}$
T = absolute temperature
x_i = mole fraction of component i in adsorbed phase
y_i = mole fraction of component i in gas phase

Greek Letters

γ_i = activity coefficient of ith component in adsorbed phase
Π = spreading pressure

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