Explicit Calculation of Multicomponent Equilibria for Ideal Adsorbed Solutions

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Precise multicomponent isotherms are usually required to properly analyze the dynamic behavior of adsorption separation processes (for example, Frey, 1992). Among the most accurate and versatile isotherms for this purpose are those resulting from ideal adsorbed solution (IAS) theory (Myers and Prausnitz, 1965; Valenzuela and Myers, 1989). In most cases, however, the equations resulting from IAS theory must be solved iteratively, which makes it inconvenient to incorporate those equations into numerical simulations of column dynamics.

In this study, two formulations for IAS theory are developed which yield explicit relations for the adsorbed concentrations for arbitrary numbers of components. The first method involves fitting the relation between the spreading pressure and the gas-phase pressure for each individual component to a three-parameter Padé approximation which is the ratio of first- and second-order polynomials. This method can be applied to a variety of single-component isotherms, including those which deviate significantly from Langmuir isotherms. The second method is an extension to any number of adsorbates of the Taylor series solution for two adsorbates developed by LeVan and Vermeulen (1981). The second method applies when the single-component isotherms correspond closely to Langmuir isotherms and when the maximum adsorption capacities for the various adsorbates are not too dissimilar.

Although this study considers only the use of IAS theory on a homogeneous surface, the methods discussed here can also be employed in certain types of heterogeneous IAS theories, such as those in which the adsorbent surface is postulated to consist of several types of uniform surface patches, and IAS theory is used to determine the amounts adsorbed on each type of surface patch (Myers, 1987).

IAS Theory

The basic equation for IAS theory can be written (Myers and Prausnitz, 1965):

$$P_i = x_i P_i^o(\Pi) \tag{1}$$

where P_i and x_i are the gas-phase partial pressure and adsorbed-phase mole fraction of component i, and Π is the spreading pressure of the mixture. The standard state pressure P_i^o is defined to be the gas pressure when only component i is present which corresponds to the spreading pressure of the mixture. The quantity P_i^o is given by the Gibbs adsorption equation as:

$$\Pi(P_i^o) = \int_0^{P_i^o} \frac{q_i^o(P_i^o)}{P_i^o}\, dP_i^o \tag{2}$$

where $q_i^o(P_i^o)$ is the single-component isotherm. Since there is no area change on mixing for an ideal adsorbed mixture, it follows that:

$$\frac{1}{q_{\text{total}}} = \sum_i \frac{x_i}{q_i^o(P_i^o)} \tag{3}$$

Finally, the sum of the adsorbed-phase mole fractions must be unity, which can be expressed as:

$$1 = \sum_i x_i = \sum_i \frac{P_i}{P_i^o(\Pi)} \tag{4}$$

Equations 1-4 employ the component partial pressures and can therefore be applied directly to the calculation of gas-phase adsorption equilibrium. These equations can also be used to calculate liquid-phase adsorption equilibrium if the partial pressures are replaced by molar concentrations.

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Equations 1-4 can be solved numerically for any type of single-component isotherm. An explicit solution of these equations, however, is generally not possible since Eq. 2 often cannot be integrated analytically and, even when it can, it is generally not possible to find the inverse of $\Pi(P_i^o)$ needed in Eq. 4. Finally, even if $P_i^o(\Pi)$ is known, it is usually not possible to solve Eq. 4 to find $\Pi(P_1,P_2,\ldots)$. Nevertheless, if the function $\Pi(P_1,P_2,\ldots)$ is known explicitly, then the multicomponent isotherms $q_i(P_1,P_2,\ldots)$ can also be determined explicitly either by using Eqs. 1 and 3 and the relation $q_i=x_i q_{\text{total}}$ or by noting that the Gibbs adsorption equation for a mixture,

$$d\Pi=\sum_i \frac{q_i}{P_i}\,dP_i \tag{5}$$

implies that

$$q_i=P_i\frac{\partial \Pi}{\partial P_i} \tag{6}$$

Method Based on Fitting $P_i^o(\Pi)$ to a Padé Approximation

The function $P_i^o(\Pi)$ always exhibits linear behavior for small Π and, if a maximum adsorption capacity exists, $P_i^o(\Pi)$ has exponential behavior for large Π. Functions of this type can usually be represented accurately by a Padé approximation (Press et al., 1986). Furthermore, if a Padé approximation which is centered at $P_i^o=\Pi=0$ and which is the ratio of first- and second-order polynomials (that is, a 1/2 approximation) is used to represent $P_i^o(\Pi)$, an analytical result for $\Pi(P_1,P_2,\ldots)$ can be obtained from Eq. 4 from which the multicomponent isotherms can be determined explicitly. Note that the use of Padé approximations centered at $P_i^o=\Pi=0$ ensures that the multicomponent isotherms resulting from these approximations reduce to linear isotherms at low pressure.

These observations suggest the following method for determining the multicomponent isotherms.

Step 1. Determine (either analytically or numerically) the functions $\Pi(P_i^o)$ and $P_i^o(\Pi)$ for each component from the known single-component isotherms.

Step 2. Fit the function $P_i^o(\Pi)$ to a three-parameter 1/2 Padé approximation having the following form:

$$P_i^o=\frac{\Pi}{a_i+f_i\Pi+c_i\Pi^2} \tag{7}$$

Step 3. Substitute Eq. 7 written for each component into Eq. 4 to yield the following equation that can be solved for Π using the quadratic formula:

$$0=\Pi^2\sum_i c_iP_i+\Pi\sum_i f_iP_i-\Pi+\sum_i a_iP_i \tag{8}$$

Step 4. Determine explicit multicomponent isotherms using the relation for $\Pi(P_1,P_2,\ldots)$ from Eq. 8 together with Eq. 6 or by using the relation for $\Pi(P_1,P_2,\ldots)$ together with Eqs. 1 and 3 and the relation $q_i=x_iq_{\text{total}}$. Note that since Eq. 8 is a quadratic equation, it yields two solutions for the function Π. The proper solution can be selected using the criterion that at low partial pressures for all the components, the multicomponent isotherms derived from the correct solution yield the same Henry's law constants as the starting single-component isotherms.

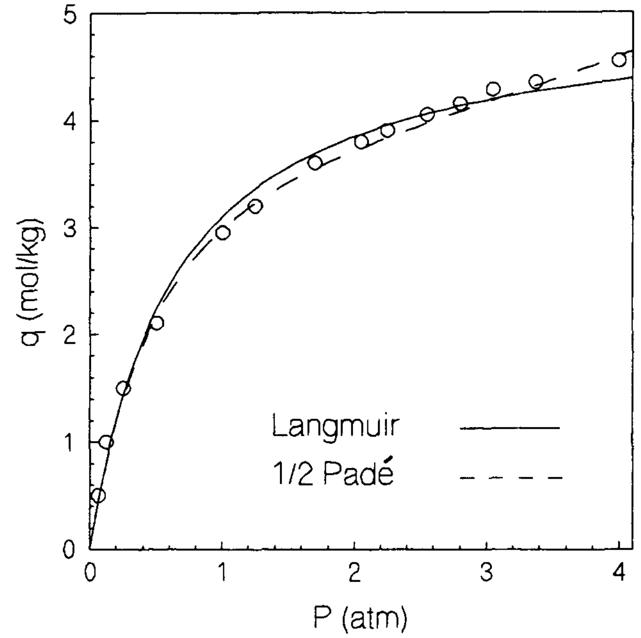

Figure 1. Langmuir isotherm (Eq. 10) and isotherm from Padé approximation (Eq. 9) used to fit experimental data for ethane adsorption on attrition-resistant activated carbon at 311 K as reported by Kaul (1987) and Valenzuela and Myers (1989).

Parameters for Eq. 10: $q_{i,m}=5.06$, $b_i=1.58$; parameters for Eq. 9: $a_i=8.0$, $f_i=-0.835$, $c_i=0.02777$ (units are given in the Notation section).

Although the procedure just described involves fitting the function $P_i^o(\Pi)$ to a Padé approximation, it is generally simpler to fit the experimentally determined single-component isotherm $q_i^o(P_i^o)$ to the appropriate form. In particular, if Eq. 7 applies, then Eq. 6 yields the following single-component isotherm for each component:

$$q_i^o=\left(\frac{1-f_iP_i^o}{\sqrt{(f_i^2-4a_ic_i)(P_i^o)^2-2f_iP_i^o+1}}-1\right)\Big/(2c_iP_i^o) \tag{9}$$

Even though Eq. 9 may yield a complex number for q_i^o when P_i^o is large, this equation can fit a wide variety of experimental data at moderate values of P_i^o, often more accurately than a Langmuir isotherm. This is illustrated in Figure 1, which shows both Eq. 9 and the single-component Langmuir isotherm given by:

$$q_i^o=\frac{q_{i,m}b_iP_i^o}{1+b_iP_i^o} \tag{10}$$

fitted to experimental data for ethane adsorption on activated carbon at 311 K. In each case, the calculated isotherms in

Figure 1 were fitted exactly to the data in the Henry's law region (the data at low pressures corresponding to the linear portion of the isotherm) and all the other adjustable parameters where chosen to yield the best fit with the remainder of the experimental data.

When Eq. 9 is fitted to experimental data using standard regression methods (Press et al., 1986), it is necessary to provide initial estimates for the parameters a_i, c_i, and f_i in that equation. This can be accomplished by fitting the experimental data $[q_i^o(P_i^o)]$ to a single-component Langmuir isotherm and then examining the 1/2 Padé approximation for the function $P_i^o(\Pi)$ which fits that Langmuir isotherm (see Eq. 18). The parameters a_i, c_i and f_i corresponding to that Padé approximation are given in terms of the Langmuir isotherm parameters $q_{i,m}$ and b_i by the relations $a_i = q_{i,m}b_i$, $f_i = -b_i/2$ and $c_i = b_i/(12\ q_{i,m})$, which provide the required initial estimates.

Extension of the Series Solution of LeVan and Vermeulen to Arbitrary Numbers of Components

Consider the case where the Langmuir isotherm applies to the individual components. If $q_{1,m}$ is used as a reference saturation capacity, a series expansion parameter ϵ_i can be defined for each component as:

$$\epsilon_i = q_{i,m} - q_{1,m} \tag{11}$$

where by definition $\epsilon_1 = 0$. If the spreading pressure is considered to be a function of ϵ_i, then the following first term in a Taylor series approximation applies for small ϵ_i:

$$\Pi(\epsilon_2,\epsilon_3, \ldots) = \Pi(0,0, \ldots) + \sum_{i=2}^{n} \epsilon_i \left(\frac{\partial \Pi}{\partial \epsilon_i} \bigg|_{\epsilon_2=\epsilon_3=\ldots=0} \right) \tag{12}$$

The partial derivatives in Eq. 12 can be determined as follows. Combine Eqs. 2, 10 and 11 to determine the function $\Pi(P_i^o,\epsilon_i)$. Rearrange that result to yield the function $P_i^o(\Pi,\epsilon_i)$. Substitute the function $P_i^o(\Pi,\epsilon_i)$ for each component into Eq. 4 and take the derivative of each side of the resulting equation with respect to one of expansion parameters ϵ_i. Set all of the expansion parameters ϵ_i equal to zero in the equation that results from the previous step and then solve for the derivative of the spreading pressure. For any number of components, this procedure yields the result:

$$\frac{\partial \Pi}{\partial \epsilon_i} \bigg|_{\epsilon_2=\epsilon_3=\ldots=0} = \frac{b_iP_i\Pi(0,0, \ldots)}{q_{1,m}\sum_i b_iP_i} \tag{13}$$

When the single-component isotherms are Langmuir isotherms and $\epsilon_i = 0$, Eqs. 2 and 4 yield the following relation for $\Pi(0,0, \ldots)$:

$$\Pi(0,0, \ldots) = q_{1,m} \ln\left(1 + \sum_i b_iP_i\right) \tag{14}$$

Combining Eqs. 6 and 12–14 yields the following multicomponent isotherms:

$$q_i = \frac{b_iP_i \sum_i b_iP_iq_{i,m}}{\left(\sum_i b_iP_i\right)\left(1 + \sum_i b_iP_i\right)} + \frac{\left[\sum_j b_jP_j(q_{i,m} - q_{j,m})\right] b_iP_i \ln\left(1 + \sum_i b_iP_i\right)}{\left(\sum_i b_iP_i\right)^2} \tag{15}$$

Note that when all of the $q_{i,m}$ are equal, Eq. 15 reduces to the extended Langmuir isotherm (see Eq. 20) and that, for the case of only two adsorbates, Eq. 15 reduces to the two-term Taylor series approximation described by LeVan and Vermeulen (1981).

A procedure similar to that just described can be used to develop higher-order terms in the Taylor series expansion. These higher-order terms, however, are algebraically complex and will not be reported here.

Example Involving Single-Component Langmuir Isotherms

Although the procedures described in the preceding sections apply to any number of adsorbates, for illustrative purposes this section considers the case of two adsorbates whose single-component isotherms are described by Langmuir isotherms. For single-component Langmuir isotherms, the functions $\Pi(P_i^o)$ and $P_i^o(\Pi)$ can both be found analytically and are given by:

$$P_i^o = [\exp(\Pi/q_{i,m})]/b_i - 1/b_i \tag{16}$$

$$\Pi = q_{i,m} \ln(b_iP_i^o + 1) \tag{17}$$

The 1/2 Padé approximation centered at $P_i^o = \Pi = 0$ for the function $P_i^o(\Pi)$ given by Eq. 16 can be written as:

$$P_i^o = \frac{12q_{i,m}\Pi}{b_i(12q_{i,m}^2 - 6q_{i,m}\Pi + \Pi^2)} \tag{18}$$

For the 1/2 Padé approximation given by Eq. 18, Eq. 8 yields the following equation which can be solved for Π using the quadratic formula:

$$0 = \Pi^2 \sum_i \left(b_iP_i \prod_{j \neq i} q_{j,m} \right) - 6\Pi \left(2 + \sum_i b_iP_i \right) \prod_i q_{i,m} + 12 \left(\prod_i q_{i,m} \right) \sum_i b_iq_{i,m}P_i \tag{19}$$

In Eq. 19 the symbol $j \neq i$ indicates that the product is over all components except for component i.

For the case of two adsorbates, Table 1 compares results from the method based on the 1/2 Padé approximation, from the methods based on the two- and three-term Taylor series approximations, and from the following extended Langmuir isotherm:

Table 1. Prediction Methods for Adsorbed Concentrations*

	Extended Langmuir (Eq. 20)	Exact IAS	2-term Taylor Series	3-term Taylor Series	1/2 Padé Approx.
q_1	1.333	1.449	1.441	1.448	1.446
q_2	1.000	0.899	0.892	0.899	0.901

*Conditions correspond to single-component Langmuir isotherms with $P_1 = P_2 = 1$; $b_1 = b_2 = 1$; $q_{1,m} = 4$; $q_{2,m} = 3$ (units are given in the Notation section).

$$q_i = \frac{q_{i,m} b_i P_i}{1 + \sum_i b_i P_i} \tag{20}$$

Conditions in the table are identical to the example problem considered by LeVan and Vermeulen (1981). As shown in Table 1, the 1/2 Padé approximation yields results that are somewhat less accurate than the three-term Taylor series approximation. Table 1 also indicates that the 1/2 Padé approximation is more accurate than the two-term Taylor series approximation, even though in both cases the calculations are based on single-component Langmuir isotherms. This is because there is a significant difference in the maximum adsorption capacities for the two components in Table 1 so that, although the Taylor series approximations explicitly assume single-component Langmuir isotherms, more than two series terms are needed to achieve accuracies better than the 1/2 Padé approximation.

Figure 2 compares the exact function $P_i^o(\Pi)$ given by Eq. 16 and the Padé approximation given by Eq. 18 for component 1 in Table 1. The figure indicates that the 1/2 Padé approximation yields good agreement with the exact result well into the region where $P_i^o(\Pi)$ exhibits exponential behavior. Nevertheless, since Padé approximations fail to fit exponential functions accurately for large values of the function argument, the use of this approximation for predicting adsorbed concentrations eventually fails to yield accurate results for large amounts of adsorption whenever a well-defined maximum adsorption capacity exists. For example, in Figure 2 the 1/2 Padé approximation yields better than 5% accuracy for the function $P_i^o(\Pi)$ provided that $P_i^o < 6$ atm, which corresponds to $q_i/q_{i,m} < 0.85$. This implies that the method based on the Padé approximation should be used with caution when it is employed to predict the adsorbed phase composition for very high levels of adsorbate loading if single-component Langmuir isotherms apply. Fortunately, the case of low to moderate amounts of adsorbate loading normally applies to most industrial processes involving gas adsorption separations (Yang, 1987).

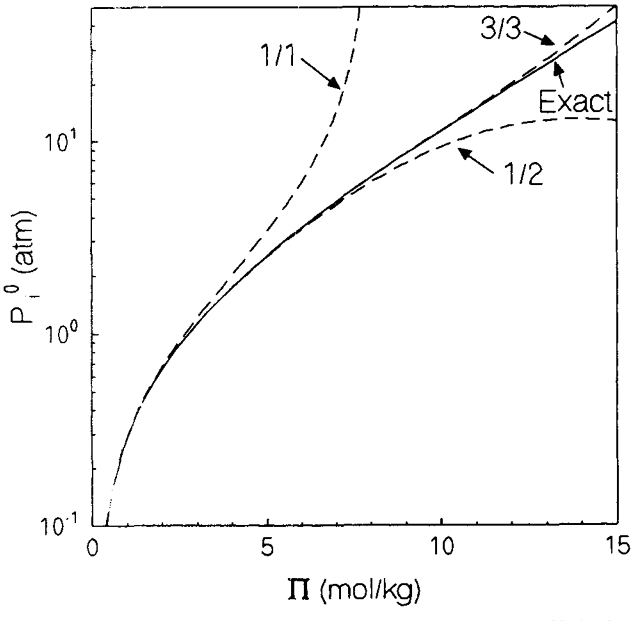

Figure 2. Padé approximations for function $P_i^o(\Pi)$ derived for a single-component Langmuir isotherm with $b_i = 1$ and $q_{i,m} = 4$.

Units are given in the Notation section.

Figure 2 also shows the 1/1 Padé approximation given by deleting the Π^2 term in Eq. 18 and the 3/3 Padé approximation given by:

$$P_i^o = \frac{3\Pi(60 q_{i,m} + \Pi^2)}{b_i(120 q_{i,m}^3 - 60 q_{i,m}^2 \Pi + 12 q_{i,m} \Pi^2 - \Pi^3)} \tag{21}$$

As shown, the 1/1 Padé approximation yields acceptable accuracy only at very low pressures, while the 3/3 Padé approximation fits the exact function for $P_i^o(\Pi)$ over an extended pressure range.

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Notation

a_i = constant in Eq. 7, mol·kg^{-1}
b_i = constant in the Langmuir isotherm equation, atm^{-1}
c_i = constant in Eq. 7, mol·kg^{-1}
f_i = constant in Eq. 7
P_i = partial pressure in gas phase, atm
q_i = adsorbed concentration, mol·kg^{-1}
$q_{i,m}$ = monolayer capacity in Langmuir isotherm equation, mol·kg^{-1}
x_i = mole fraction in adsorbed phase

Greek letters

ϵ_i = series expansion parameter, mol·kg^{-1}
Π = spreading pressure, mol·kg^{-1}

Subscripts

i, j = components i and j

Superscript

o = variable evaluated at the standard state for a component, defined to be the state when only that component is present which corresponds to the spreading pressure of the mixture under consideration

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