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MULTICOMPONENT ADSORPTION CALCULATIONS BASED ON ADSORBED SOLUTION THEORY

Jeong Ho Yun, Heung Chul Park and Hee Moon†

Department of Chemical Technology, Chonnam National University, Kwangju 500-757, Korea
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Abstract – A new calculation method for multicomponent adsorption equilibria was proposed based on the real adsorbed solution theory (RAST) and the concept of arbitrary isotherm. According to the latter, we assigned a respective isotherm, which gave the best fit to single-component equlibrium data, to each component, instead of using a specific type of isotherm for all adsorbates as in most previous works. This enabled us to evaluate the spreading pressure for pure components more accurately, which will be used in multicomponent adsorption calculations later. The usefulness of the proposed method is verified by carrying out sample calculations for ternary data reported in literature.

Key words: Adsorbed Solution Theory, Concept of Arbitrary Isotherm, Multicomponent Adsorption, Nonideality

INTRODUCTION

The use of adsorption as an efficient method for separating multicomponent mixtures is becoming common. To design and operate adsorption-based separation and purification systems, multicomponent adsorption equilibrium data must be known over a broad range of mole fraction and pressure (or concentration) [Ruthven, 1984; Yang, 1987; Wilson and Danner, 1983]. In principle, equilibrium data should be obtained by a large number of experiments for a particular adsorbent and a given mixture of interest, but it is quite tedious or sometimes impossible that such a large number of experiments are carried out. That is why theoretically or empirically derived theories for predicting multicomponent adsorption equilibria have been used [Tien, 1993]. One of widely used thermodynamic models to predict multicomponent adsorption equilibrium data is the adsorbed solution theory (AST), developed by Myers and Prausnitz [1965], which has been extended to the real adsorbed solution theory (RAST) when dealing with the adsorbed phase nonideality.

However, in most calculation schemes based on AST, there is a fixed idea that a specific type of isotherm should be employed for all adsorbates regardless of different adsorption characteristics [Fritz and Schlunder, 1981; Myers, 1986; Moon and Tien, 1987; Moon and Tien, 1988; Richter et al., 1989; Valenzuela et al., 1988]. Such an idea cannot be justified because the equilibrium relationship for each adsorbate is not always expressed by a single isotherm equation. When individual components in a mixture have quite different physical or chemical properties, the conventional method will surely give large discrepancies between experimental and predicted results. This fundamental problem can be conceptually solved by obtaining the relationship between spreading pressure and fluid-phase pressure (or concentration) from experimental data directly without specifying an isotherm equation. However, this direct method is not convenient in incorporating the relationship into most adsorption calculations such as the simulation of breakthrough curves for fixed-bed adsorption. As an alternative, some workers [Fritz and Schlunder, 1981; Kim et al., 1985] have employed a set of piecewise isotherms which can fit isotherm data for a wide concentration range accurately but they assigned a specific type of isotherm to all components. Furthermore, the calculation itself was somewhat complex.

Generally speaking, there is no restriction for the type of single-component isotherm for prediction of multicomponent adsorption equilibrium data. Thus, the isotherm that gives the best fit to the experimental data over the whole pressure range of an adsorbate must be recommended for application [Richter et al., 1989; Kim, 1993]. The choice of the isotherm equation for predicting multicomponent equilibrium data leads to very different arguments about the suitability of AST. Applying suitable single-component isotherms in calculations sometimes can give good results without introducing activity coefficients. The successful application of AST depends on not only the introduction of nonideality but also the use of a proper isotherm for each component.

In this paper, a new method for multicomponent equilibrium calculations is proposed based on the best-fitted isotherm for each component. First, we assess some generally used isotherms to fit the single-component equilibrium data accurately and decide the most proper combination of isotherms for a given mixture. The usefulness of the proposed method will be rigorously tested by sample calculations later.

ADSORBED SOLUTION THEORY

The basic concept of AST for adsorption equilibria is analogous to Raoult's law for the vapor-liquid equilibria (VLE). The essential difference between adsorption equilibria and VLE is that the presence of the solid adsorbent introduces an additional degree of freedom, i.e. the adsorbent imposes the potential field upon the solid surface, which behaves like a two-dimensional gas at high density and like a bulk liquid at low density. In AST, the standard state is defined as the pure com-

†To whom all correspondences should be addressed.

ponent at the same spreading pressure and temperature as the mixture. Utilizing the equilibrium criteria of equal chemical potentials for each species in the gas and the adsorbed phases, Myers and Prausnitz [1965] derived the following relation at a constant temperature:

$$Py_i = \gamma_i x_i P_i^0(\pi) \tag{1}$$

where $P_i^0(\pi)$ is the standard state gas pressure which can be determined from the single-component adsorption data. In AST, the prediction of multicomponent adsorption equilibria is greatly dependent on the accuracy of the spreading pressure for pure components. Generally, the spreading pressures for pure components can be evaluated numerically from experimental data or analytically from theoretical isotherms. Therefore the most important part in multicomponent adsorption equilibrium calculations based on AST is how to express the spreading pressure in terms of the corresponding pressure, which will be used for the mixture calculations.

In the case of an ideal solution, the activity coefficients in Eq. (1) are equal to unity. For RAST, these activity coefficients may be determined from binary equilibrium data experimentally or from theoretical correlations. In VLE, liquid-phase activity coefficients are functions of temperature and composition, whereas the adsorbed phase activity coefficients are functions of spreading pressure, temperature, and composition [Myers and Prausnitz, 1965]. According to Talu and Zweibel [1986] who suggested a spreading pressure dependence (SPD) model, it has been noted that most previous works based on RAST were thermodynamically inconsistent because the theoretical activity coefficients can be used to describe an adsorbed phase in equilibrium with a gas phase only if the spreading pressure is constant [Talu and Zweibel, 1986]. Talu and Zwiebel also stated that it is practically impossible to keep the spreading pressure constant during adsorption.

From the classical thermodynamic concept, the modified spreading pressure is given by

$$\Pi = \frac{\pi A}{RT} = \int_0^{P_i^0} \frac{Q_i^0(P_i^0)}{P_i^0} dP_i^0 \tag{2}$$

where $Q_i^0(P_i^0)$ is the adsorption equilibrium amount at pure state. Eqs. (1) and (2) can be used to compute multicomponent equilibrium data, together with the stoichiometric constraint:

$$\sum_i^N x_i = 1.0 \tag{3}$$

where N is the number of components.

The adsorbed amount for each component may be calculated as follows;

$$Q_i = Q_T x_i \tag{4}$$

and

$$\frac{1}{Q_T} = \sum_i^N \frac{x_i}{Q_i^0(P_i^0)} + \sum_i^N x_i \left(\frac{\partial \ln \gamma_i}{\partial \Pi} \right) \tag{5}$$

Q_T is the total amount adsorbed and Q_i is the amount of component i adsorbed at equilibrium state. The ideal adsorbed solution theory (IAST) only requires knowledge of single-component adsorption isotherms. However, the RAST needs binary equilibrium data to estimate the adjustable binary interaction parameters such as the activity coefficients. In adsorption, no such information about the intermolecular interaction between two different components can be extracted from single-component equilibrium data [Gamba et al., 1989]. Eq. (5) illustrates that the activity coefficient is a function of the spreading pressure. It should be noted that if the spreading pressure dependence of the activity coefficient is neglected, the excess load due to the nonideality of the adsorbed phase disappears. Talu and Zwiebel [1986] suggested that strongly nonideal gaseous systems need this correction, or errors as high as 30% can be introduced. However, Gamba et al. [1990] reported that, for the compounds considered in their work, the maximum percentage excess of the total adsorbed amount never exceeds 6% of the average saturation load even for highly nonideal cases. The correction of the total adsorbed amount which depends on the spreading pressure is not easy and sometimes impossible because of the lack of experimental data.

CALCULATION OF NONIDEALITY

To calculate the activity coefficients in Eq. (1), one needs the following binary experimental data: the total pressure of the gas phase mixture, the composition x_i of the adsorbed phase, the composition y_i of the gas phase, the spreading pressure π for the adsorbed mixture, and the pure component isotherms for each adsorbate [Myers and Prausnitz, 1965]. Most of all, the spreading pressure π for the experimental binary data must be known to calculate the activity coefficients from Eq. (1). Thus the Gibbs adsorption isotherm equation has to be integrated and several different integration paths are available, since the spreading pressure is a point function [Talu and Zwiebel, 1986]. The partial derivatives of the Gibbs adsorption isotherm for two independent variables, P and y_1, are:

$$\left[\frac{\partial \Pi}{\partial y_1} \right]_P = Q_T \left[\frac{x_1}{y_1} - \frac{x_2}{y_2} \right] \tag{6}$$

$$\left[\frac{\partial \Pi}{\partial P} \right]_{y_1} = \frac{Q_T}{P} \tag{7}$$

In the case of the integration path along a constant gas pressure, the spreading pressure of a binary mixture, Π_B, could be evaluated as follows;

$$\Pi_B = \Pi_2^0 + \Delta\Pi \tag{8}$$

$$\Delta\Pi = \int_0^{y_1} Q_T \left(\frac{x_1}{y_1} - \frac{x_2}{y_2} \right) dy_1 \tag{9}$$

where Π_2^0 is the spreading pressure of component 2 at pure state.

Once the experimental activity coefficients are calculated, these activity coefficients must be represented by a theoretical model [Costa et al., 1981; Kemeny and Manczinger, 1978; Myers, 1983; Prausnitz et al., 1986]. In this case, the well-known Wilson, UNIQUAC, and SPD equations are generally used.

$$\text{Wilson: } \ln \gamma_k = 1 - \ln \left(1 - \sum_j^N x_j \Lambda_{kj} \right) - \sum_i^N \frac{x_i \Lambda_{ik}}{1 - \sum_j^N x_j \Lambda_{ij}} \tag{10}$$

where, Λ_{ij} is the binary interaction parameter between components i and j.

UNIQUAC:

$$\ln\gamma_i = \ln\frac{\Phi_i}{x_1} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + \Phi_j\left(l_i - \frac{r_i}{r_j} l_j\right) - q_i \ln(\theta_i + \theta_j\tau_{ji}) + \theta_j q_i\left(\frac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right) \quad (11)$$

where, τ_{ij} is the binary interaction parameter and others are defined as

$$\Phi_i = \frac{r_i x_i}{\sum_j^m r_j x_j},\quad \theta_i = \frac{q_i x_i}{\sum_j^m q_j x_j},\quad l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

$$r_i = \sum_k \nu_k^{(i)} R_k,\quad q_i = \sum_k \nu_k^{(i)} Q_k,$$

z, r_i and q_i are the coordination number and the pure component molecular-structure constants depending on molecular size and external surface area.

SPD model for Wilson equation [Myers, 1986]:

$$\ln\gamma_k = [1 - e^{-C\Pi}]\left\{1 - \ln\left(1 - \sum_j^N x_j \Lambda_{kj}\right) - \sum_i^N \frac{x_i \Lambda_{ik}}{1 - \sum_j^N x_j \Lambda_{ij}}\right\} \quad (12)$$

where, C is an adjustable parameter.

Although Eq. (12) is empirical but it satisfies the limiting value: the activity coefficient becomes unity as the spreading pressure approaches zero. However it can be used only for binary mixtures. Thus we modified this equation slightly for multicomponent systems by replacing the parameter, C, with an average value as follows;

$$C = \sum_j x_j C_{kj} \quad (13)$$

Here, $C_{kj}=C_{jk}$ and $C_{jj}=1.0$. In Eq. (13), C_{kj}, is the parameter for the binary mixture of components k and j. The SPD models above are thermodynamically consistent and it can be expected that three constants for a binary system provide sufficient flexibility to describe a very complicated phase behavior.

The binary interaction and adjustable parameters of the given function can be estimated by minimizing the sum of squared deviations between measured and calculated mole fractions. In this work, the following objective function is used [Edgar and Himmelblau, 1988].

$$\min = \sum_i^N \left(\frac{y_{1i}^{exp} - y_{1i}^{cal}}{y_{1i}^{exp}}\right)^2 + \left(\frac{y_{2i}^{exp} - y_{2i}^{cal}}{y_{2i}^{exp}}\right)^2 \quad (14)$$

NUMERICAL CALCULATION PROCEDURES

Let the adsorption isotherm for a pure component be represented by a theoretical equation:

$$Q_i^0 = f(P_i^0) \quad (15)$$

In Eq. (15), the function f is arbitrary; for many systems, Sips (Langmuir-Freundlich), Toth, and Dubinin-Astakov equations are adequate because they include three parameters. Whatever the choice, it is most important that the isotherm for a pure component provides an accurate representation of the experimental data down to low surface coverage approaching the Henry's law region. The reason is that the spreading pressure function should be integrated from low coverage to high coverage. From Eq. (2), the spreading pressure can be evaluated analytically or numerically using a selected isotherm for each component.

From Eqs. (2) and (15), the following relations can be obtained:

$$P_i^0 = g(\Pi) \quad (16)$$

$$\Pi = g^{-1}(P_i^0) \quad (17)$$

$$Q_i^0(P_i^0) = h(\Pi) \quad (18)$$

From Eqs. (1) and (3), and given P and y_i, a set of N nonlinear equations is given as follows;

$$\begin{aligned}
&\frac{Py_1}{\gamma_1(x_1)P_1^0(\Pi)} - x_1 = 0\\
&\frac{Py_2}{\gamma_2(x_2)P_2^0(\Pi)} - x_2 = 0\\
&\vdots\\
&\frac{Py_{N-1}}{\gamma_{N-1}(x_{N-1})P_{N-1}^0(\Pi)} - x_{N-1} = 0\\
&\frac{Py_N}{\gamma_N(x_N)P_N^0(\Pi)} + \cdots + \frac{Py_2}{\gamma_2(x_2)P_2^0(\Pi)} + \frac{Py_1}{\gamma_1(x_1)P_1^0(\Pi)} - 1 = 0
\end{aligned} \quad (19)$$

This set of nonlinear equations should be solved simultaneously for x_1-x_{N-1} and Π using Newton's method with numerically evaluated Jacobians for direction vectors. In order to do this calculation, initial estimations of the spreading pressure, Π, and the adsorbed mole fractions, x_i, should be given. In this study, the initial estimations are given by

$$\Pi_{ini} = \sum_i^N y_i \Pi_i(P) \quad (20)$$

$$P_{i,ini}^0 = g(\Pi_{ini}) \quad (21)$$

$$x_{i,ini} = \frac{Py_i}{P_{i,ini}^0(\Pi_{ini})} \quad (22)$$

This method, that was proposed by Myers [1986], did not make any trouble during calculations for many sets of binary and ternary equilibrium data. In addition, it also has a stable convergence property.

SAMPLE CALCULATIONS

In order to investigate the reliability of the proposed approach, sample calculations with selected isotherm equations for individual components have been performed. Prior to sample calculations, it will be worthwhile to get the relationships between the spreading pressure and the fluid-phase pressure. These relationships for generally used isotherms are as follows;

$$\text{Langmuir: } Q_i = \frac{q_{mi} b_i P}{1 + b_i P} \rightarrow \Pi = q_{mi} \ln(1 + b_i P_i^0) \quad (23)$$

Freundlich: $Q_i = K_i P^{1/n_i} \rightarrow \Pi = n_i K_i P_i^0$ (24)

Sips: $Q_i = \frac{q_{mi} b_i P^{1/n_i}}{1 + b_i P^{1/n_i}} \rightarrow \Pi = n_i q_{mi} \ln(1 + b_i P_i^{0(1/n_i)})$ (25)

From the thermodynamic definition, these pure component isotherms should be reduced to Henry's law at the limit of zero pressure as follow;

$$\lim_{P \to 0} \frac{dQ}{dP} = \lim_{P \to 0} \frac{Q}{P} = \Omega \quad (26)$$

The limiting slope, Ω, must be positive and finite. However, some generally used isotherms violate this limiting condition except the Langmuir equation. Thus, the Freundlich and the Sips isotherms cannot be used to fit the experimental data at low pressure or to calculate the spreading pressure in the strict sense. However although thermodynamic inconsistency occurs as mentioned above, these equations have been widely used for fitting experimental data for many years. In order to verify the applicability of the proposed calculation procedures, several reported mixture's data are selected from literature [Talu and Zwiebel, 1986; Costa et al., 1981; Reich et al., 1980].

1. Talu and Zwiebel [1986]

1-1. adsorption of CO_2-H_2S-C_3H_8 on H-mordenite at 303 K

The corresponding parameters for Eqs. (23)-(25) obtained by fitting the experimental data and the average percent deviations are listed in Table 1. The comparison of the isotherms with the experimental data is also shown in Fig. 1. In this figure, we do not show the Langmuir isotherm since it does not fit the equilibrium data for all individual components properly. The Sips isotherm fits all of the data satisfactorily while the Freundlich does moderately. Especially in the case of hydrogen sulfide, the difference between the Sips and Freundlich isotherms is considerable especially in the extended pressure range. This difference greatly influences the spreading pressure in terms of pressure as shown in Fig. 2. This result will also affect on the prediction of multicomponent equilibrium data. It will be discussed in detail later.

Equilibrium data for binary mixtures of CO_2-H_2S, C_3H_8-H_2S and C_3H_8-CO_2 are fitted using the proposed algorithm. A typical result for the C_3H_8-H_2S system is shown in Fig. 3, and comparisons with the experimental data are listed in Tables 2-4. From the results, the case of the Sips isotherm employed for all

Table 1. Estimated parameter values of single-component isotherm equations for equilibrium data (303 K) reported by Talu and Zweibel [1986]

Equation	Parameters (mean error, %)	Species CO_2	H_2S	C_3H_8
Langmuir	q_m	1.4231	1.9727	0.9475
	b	0.4558	1.5028	1.0429
	%	22.5413	6.7097	9.9737
Freundlich	K	0.3946	1.1280	0.3653
	n	2.6054	4.4632	3.7607
	%	5.2349	2.2735	19.9179
Sips	q_m	4.7105	4.0675	1.2845
	b	0.0872	0.3819	0.4430
	n	2.0024	2.7452	1.6113
	%	1.0457	1.0244	7.8867

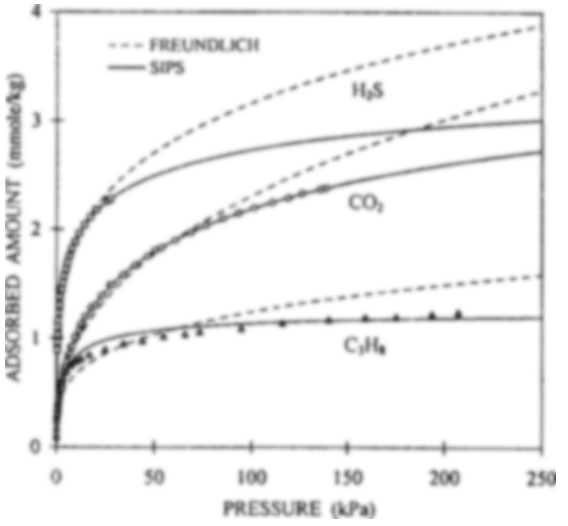

Fig. 1. Experimental and predicted equilibrium isotherms at 303 K [Data reported by Talu and Zweibel, 1986].

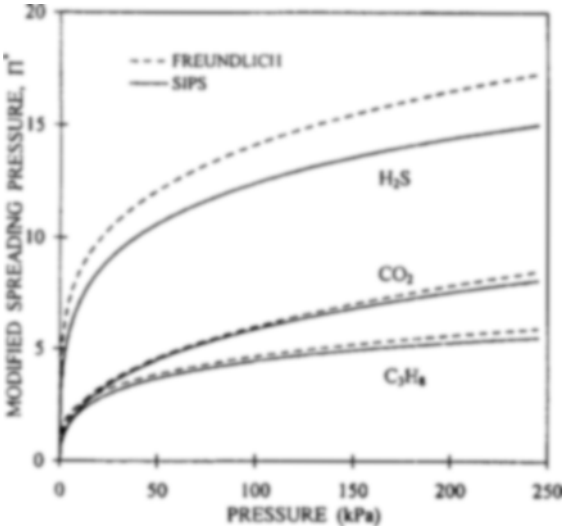

Fig. 2. Evaluated spreading pressures for pure components at 303 K [Data reported by Talu and Zweibel, 1986].

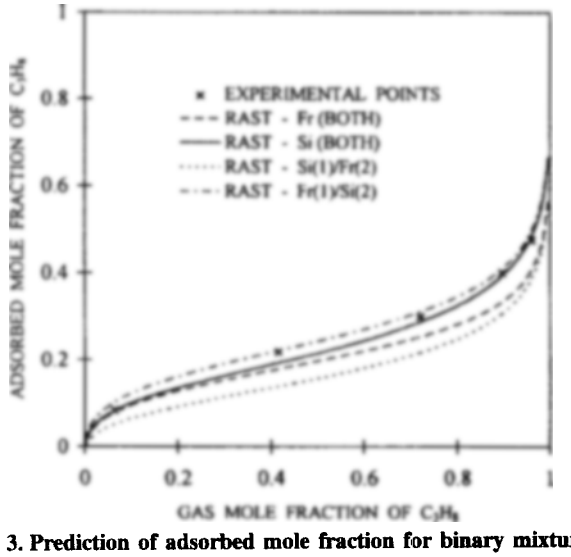

Fig. 3. Prediction of adsorbed mole fraction for binary mixtures, Propane(1)-Hydrogen Sulfide(2), at 303 K and 8.13 kPa [Data reported by Talu and Zweibel, 1986].

Table 2. Comparison results between experimental and predicted of CO_2(1)-H_2S(2) binary mixture on H-modernite at 303 K and 15.55 kPa [Talu and Zweibel, 1986]

Experimental			Real adsorbed solution theory							
			Fr(both)		Si(both)		Si(1)/Fr(2)		Fr(1)/Si(2)	
$y_{CO_2}^{exp}$	$x_{CO_2}^{exp}$	Q_T^{exp}	$x_{CO_2}^{cal}$	Q_T^{cal}	$x_{CO_2}^{cal}$	Q_T^{cal}	$x_{CO_2}^{cal}$	Q_T^{cal}	$x_{CO_2}^{cal}$	Q_T^{cal}
0.819	0.265	1.614	0.198	1.638	0.282	1.705	0.188	1.612	0.290	1.721
0.160	0.032	1.945	0.022	1.999	0.030	2.003	0.018	1.991	0.033	2.011
0.362	0.078	1.886	0.055	1.938	0.076	1.955	0.048	1.920	0.082	1.971
0.536	0.128	1.826	0.093	1.873	0.130	1.904	0.084	1.848	0.137	1.926
0.934	0.462	1.436	0.315	1.451	0.441	1.536	0.307	1.433	0.450	1.533
Ave. error (%)			29.491	2.128	4.366	4.703	35.594	1.141	5.117	5.352

Table 3. Comparison results between experimental and predicted of C_3H_8(1)-H_2S(2) binary mixture on H-modernite at 303 K and 8.13 kPa [Talu and Zweibel, 1986]

Experimental			Real adsorbed solution theory							
			Fr(both)		Si(both)		Si(1)/Fr(2)		Fr(1)/Si(2)	
$y_{C_3H_8}^{exp}$	$y_{C_3H_8}^{exp}$	Q_T^{exp}	$x_{C_3H_8}^{cal}$	Q_T^{cal}	$x_{C_3H_8}^{cal}$	Q_T^{cal}	$x_{C_3H_8}^{cal}$	Q_T^{cal}	$x_{C_3H_8}^{cal}$	Q_T^{cal}
0.064	0.084	1.851	0.078	1.857	0.083	1.788	0.052	1.770	0.103	1.878
0.416	0.218	1.863	0.180	1.812	0.193	1.658	0.139	1.629	0.222	1.833
0.721	0.299	1.762	0.254	1.656	0.287	1.508	0.217	1.464	0.311	1.679
0.897	0.400	1.558	0.334	1.430	0.395	1.339	0.308	1.285	0.410	1.445
0.960	0.476	1.357	0.407	1.269	0.486	1.226	0.388	1.170	0.498	1.272
Ave. error (%)			14.051	4.756	3.836	10.507	28.667	13.030	7.148	4.259

Table 4. Comparison results between experimental and predicted of C_3H_8(1)-CO_2(2) binary mixture on H-modernite at 303 K and 40.93 kPa [Talu and Zweibel, 1986]

Experimental			Real adsorbed solution theory							
			Fr(both)		Si(both)		Si(1)/Fr(2)		Fr(1)/Si(2)	
$y_{C_3H_8}^{exp}$	$y_{C_3H_8}^{exp}$	Q_T^{exp}	$x_{C_3H_8}^{cal}$	Q_T^{cal}	$x_{C_3H_8}^{cal}$	Q_T^{cal}	$x_{C_3H_8}^{cal}$	Q_T^{cal}	$x_{C_3H_8}^{cal}$	Q_T^{cal}
0.042	0.198	1.670	0.212	1.724	0.204	1.663	0.199	1.662	0.217	1.719
0.367	0.423	1.705	0.425	1.824	0.411	1.583	0.405	1.603	0.431	1.788
0.662	0.510	1.611	0.539	1.720	0.527	1.475	0.522	1.486	0.543	1.696
0.833	0.594	1.475	0.621	1.591	0.613	1.389	0.608	1.392	0.625	1.579
0.965	0.727	1.271	0.745	1.360	0.741	1.260	0.738	1.256	0.748	1.360
Ave. error (%)			4.024	6.369	2.879	4.543	2.180	4.206	5.199	5.426

species, Si(both), and the case of the Sips isotherm employed for hydrogen sulfide and the Freundlich isotherm for carbon dioxide and propane, Fr(1)/Si(2), show good agreement with the experimental data. The suitable isotherm for hydrogen sulfide is only the Sips equation while both the Sips and the Freundlich equations are suitable for carbon dioxide and propane.

Even in ternary mixtures, it was also proven that the choice of suitable single-component isotherms is also important. Equilibrium data for ternary mixtures of CO_2-H_2S-C_3H_8 are predicted using both IAST and RAST with the spreading pressure shown in Fig. 2. A typical result is shown in Fig. 4 and comparisons with the experimental data are listed in Table 5. It should be noted that in the case of carbon dioxide and propane the Freundlich isotherm gave more accurate results than the Sips isotherm in the binary prediction. Consequently the combination of the Sips isotherm for hydrogen sulfide and the Freundlich isotherm for carbon dioxide and propane, Fr(1)/Si(2)/Fr(3), in the ternary system shows good agreement with the experimental data. This result implies that a special care should be placed on the choice of individual single-component iso-

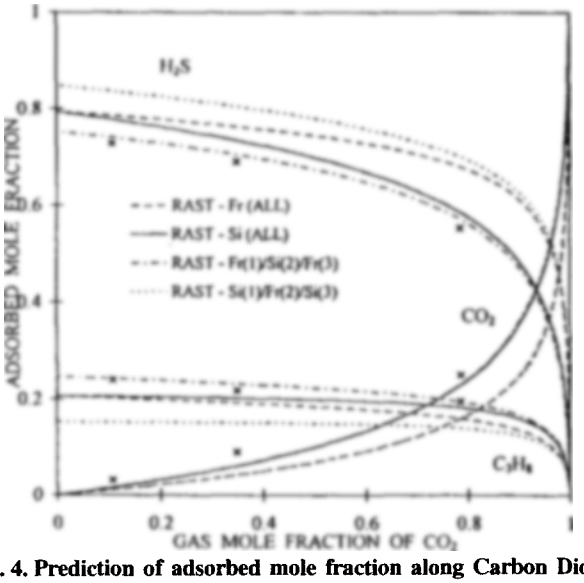

Fig. 4. Prediction of adsorbed mole fraction along Carbon Dioxide for ternary mixtures, Carbon Dioxide(1)-Hydrogen Sulfide(2)-Propane(3), at 303 K and 13.35 kPa [Data reported by Talu and Zweibel, 1986].

Table 5. Comparison results between experimental and predicted of CO_2(1)-H_2S(2)-C_3H_8(3) ternary mixture on H-modernite at 303 K and 13.35 kPa [Talu and Zweibel, 1986]

Experimental					Real adsorbed solution theory											
					Fr(all)			Si(all)			Fr(1)/Si(2)/Fr(3)			Si(1)/Fr(2)/Si(3)		
$y^{exp}_{CO_2}$	$y^{exp}_{H_2S}$	$x^{exp}_{CO_2}$	$x^{exp}_{H_2S}$	Q_T^{exp}	$x^{cal}_{CO_2}$	$x^{cal}_{H_2S}$	Q_T^{cal}	$x^{cal}_{CO_2}$	$x^{cal}_{H_2S}$	Q_T^{cal}	$x^{cal}_{CO_2}$	$x^{cal}_{H_2S}$	Q_T^{cal}	$x^{cal}_{CO_2}$	$x^{cal}_{H_2S}$	Q_T^{cal}
0.097	0.814	0.022	0.868	1.99	0.009	0.895	2.050	0.013	0.896	1.909	0.013	0.867	2.049	0.009	0.933	1.914
0.102	0.091	0.069	0.560	1.69	0.021	0.644	1.603	0.032	0.591	1.441	0.032	0.568	1.628	0.021	0.680	1.388
0.108	0.431	0.031	0.729	1.95	0.012	0.785	1.951	0.017	0.777	1.723	0.016	0.740	1.964	0.011	0.836	1.703
0.349	0.326	0.091	0.690	1.87	0.043	0.767	1.860	0.062	0.740	1.689	0.061	0.710	1.890	0.042	0.810	1.650
0.443	0.098	0.161	0.532	1.72	0.085	0.644	1.600	0.126	0.570	1.490	0.126	0.551	1.642	0.085	0.675	1.423
0.445	0.449	0.100	0.763	1.90	0.053	0.830	1.886	0.075	0.804	1.779	0.075	0.780	1.920	0.052	0.864	1.743
0.785	0.101	0.251	0.553	1.65	0.161	0.676	1.545	0.232	0.581	1.524	0.234	0.567	1.603	0.160	0.697	1.442
Ave. error (%)					53.29	12.73	3.26	32.31	5.75	9.64	32.37	2.05	2.41	53.79	18.15	12.04

Table 6. Estimated parameter values of single-component isotherm equations for equilibrium data (293 K) reported by Costa et al. [1981]

Equation	Parameters (mean error, %)	Species		
		CO_4	C_2H_4	C_2H_6
Langmuir	q_m	0.0752	0.0681	0.0652
	b	0.0009	0.0250	0.0521
	%	1.9660	11.2250	25.9910
Freundlich	K	0.0001	0.0035	0.0049
	n	1.1918	1.9494	2.0722
	%	1.6700	4.6366	5.5340
Sips	q_m	0.1604	0.2622	0.2492
	b	0.0006	0.0113	0.0173
	n	1.0918	1.6701	1.7325
	%	0.7971	1.3536	1.1376

therms to predict multicomponent equilibrium data accurately using AST.

2. Costa et al. [1981]

2-1. Adsorption of CH_4-C_2H_4-C_2H_6 on Activated Carbon at 293 K

The isotherm parameters obtained by fitting the experimental data and the average percent deviations are listed in Table 6. Generally, most researchers have usually employed the Freundlich equation for activated carbon systems so far. While the Sips equation fits all of the data satisfactorily, the Freundlich equation does moderately. The Langmuir equation can fit only the equilibrium data for methane well.

To check the validity of the concept of arbitrary isotherm, we employed the Langmuir isotherm to fit the equilibrium data for methane here since it gave comparable fits to single-component data for methane. The spreading pressures calculated from the single-component isotherms are shown in Fig. 5. Equilibrium data for a binary mixture of CH_4-C_2H_4 are predicted using both IAST and RAST and are shown in Fig. 6. Their comparisons with the experimental data are listed in Tables 7 and 8. In this case, the SPD model is employed for activity coefficients. As shown in Fig. 6, RAST-SPD-La(1)/Si(2) gives the best fit to the experimental data. However, it is worthwhile to see that, when employing the Langmuir isotherm for methane, IAST can predict the binary data more accurately than RAST which employs the Freundlich isotherm for two components. We do not contain the comparisons for C_2H_4-C_2H_6 binary mixtures which show a nearly perfect ideal behavior here.

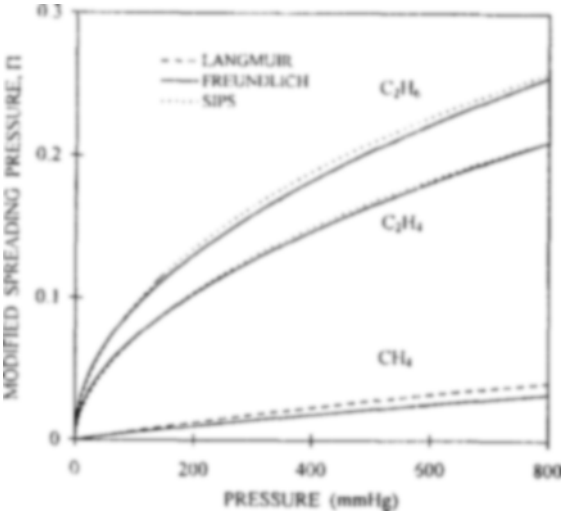

Fig. 5. Evaluated spreading pressures for pure components at 293 K [Data reported by Costa et al., 1981].

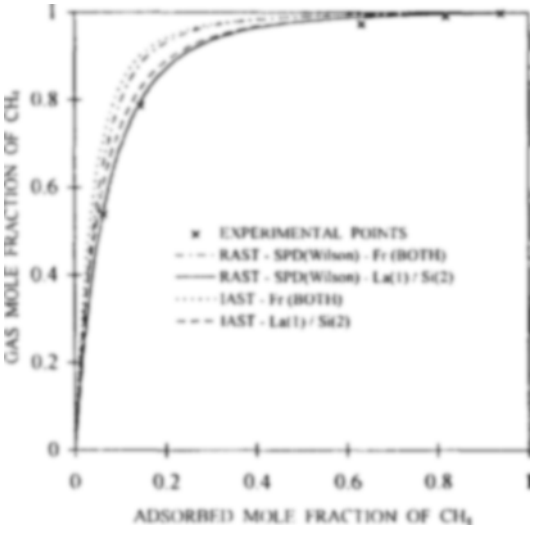

Fig. 6. Prediction of adsorbed mole fraction for binary mixtures, Methane(1)-Ethylene(2), at 293 K and 75 mmHg [Data reported by Costa et al., 1981].

As expected, the positive effect of suitable single-component isotherms on the prediction of adsorption equilibrium data was observed consistently even for ternary mixtures. Equilibrium

Table 7. Comparison results between experimental and predicted of $CH_4(1)$-$C_2H_4(2)$ binary mixture on Activated Carbon at 293 K and 75 mmHg [Costa et al., 1981]

Experimental		Ideal adsorbed solution theory		Real adsorbed solution theory (SPD)	
		Fr(both)	La(1)/Si(2)	Fr(both)	La(1)/Si(2)
$y^{exp}_{CH_4}$	$x^{exp}_{CH_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{CH_4}$
0.998	0.939	0.774	0.878	0.770	0.873
0.991	0.818	0.498	0.654	0.504	0.653
0.974	0.632	0.311	0.445	0.324	0.454
0.787	0.144	0.083	0.122	0.097	0.139
0.539	0.063	0.036	0.051	0.045	0.062
Ave, error(%)		38.46	18.23	33.18	11.95

Table 8. Comparison results between experimental and predicted of $CH_4(1)$-$C_2H_6(2)$ binary mixture on Activated Carbon at 293 K and 75 mmHg [Costa et al., 1981]

Experimental		Ideal adsorbed solution theory		Real adsorbed solution theory (SPD)	
		Fr(both)	La(1)/Si(2)	Fr(both)	La(1)/Si(2)
$y^{exp}_{CH_4}$	$x^{exp}_{CH_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{CH_4}$
0.998	0.848	0.630	0.792	0.628	0.789
0.996	0.728	0.501	0.678	0.502	0.676
0.987	0.546	0.305	0.453	0.312	0.457
0.975	0.380	0.221	0.337	0.231	0.345
0.790	0.116	0.059	0.084	0.070	0.098
0.580	0.051	0.029	0.039	0.037	0.048
Ave. error(%)		39.12	15.58	34.28	10.19

data of ternary mixtures, $CH_4(1)$-$C_2H_4(2)$-$C_2H_6(3)$, are also predicted using both IAST and RAST and their comparisons with the experimental data are listed in Table 9. Table 9 shows that, when employing the Langmuir isotherm for methane, the IAST can give comparable results to the case of RAST which employs the Freundlich isotherm for all components. In particular, the combination of the Langmuir isotherm for methane and the Sips isotherm for others gives the best result as in the corresponding binary system. This result comes from the fact that the Freundlich isotherm is not suitable for methane. It implies that, if one fails to choose proper isotherms for single components, good results can not be expected. Consquently it may be concluded that the success of AST in multicomponent adsorption calculations will be surely dependent on the accurate individual isotherms.

3. Reich et al. [1980]

3-1. adsorption of CH_4-C_2H_6-C_2H_4 on Activated Carbon at 301 K and 212 K

For another hydrocarbons-activated carbon system, the corresponding parameters obtained by fitting the experimental data and the average percent deviations are listed in Table 10. In this case, equilibrium data of ternary mixtures, $CH_4(1)$-$C_2H_6(2)$-$C_2H_4(3)$, are predicted only by IAST using the concept of arbitrary isotherm. The results are shown in Figs. 7 and 8. For this case, we could not apply RAST because their data are not suitable to calculate experimental activity coefficients.

As shown in Table 10, the Sips isotherm gives the best fits for all single components. However, in Figs. 7 and 8, the most accurate results are obtained by a combination of Fr(1)/Si(2)/Si(3) at 301 K and Fr(all) at 212 K. This unexpected result

Table 9. Comparison results between experimental and predicted of $CH_4(1)$-$C_2H_4(2)$-$C_2H_6(3)$ ternary mixture on Activated Carbon at 293 K and 75 mmHg [Costa et al., 1981]

Experimental				I.A.S.T.				R.A.S.T.			
				Fr(all)		La(1)/Si(2)/Si(2)		Fr(all)		La(1)/Si(2)/Si(2)	
$y^{exp}_{CH_4}$	$y^{exp}_{C_2H_4}$	$x^{exp}_{CH_4}$	$x^{exp}_{C_2H_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{C_2H_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{C_2H_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{C_2H_4}$	$x^{cal}_{CH_4}$	$x^{cal}_{C_2H_4}$
0.950	0.035	0.376	0.309	0.190	0.315	0.287	0.393	0.246	0.396	0.336	0.358
0.921	0.033	0.276	0.239	0.131	0.485	0.199	0.223	0.182	0.225	0.253	0.214
0.899	0.085	0.275	0.480	0.132	0.245	0.199	0.593	0.180	0.585	0.251	0.540
0.790	0.113	0.161	0.417	0.069	0.422	0.100	0.352	0.107	0.344	0.146	0.335
0.685	0.250	0.113	0.582	0.052	0.305	0.075	0.631	0.081	0.614	0.111	0.597
0.710	0.138	0.113	0.293	0.051	0.594	0.072	0.313	0.082	0.308	0.110	0.302
0.633	0.230	0.091	0.445	0.042	0.464	0.058	0.457	0.068	0.446	0.091	0.439
Ave. error(%)				53.48	15.70	31.93	12.98	31.19	12.02	5.96	9.36

Table 10. Estimated parameter values of single-component isotherm equations for equilibrium data reported by Reich et al. [1980]

Equation	Parameters (mean error, %)	Species					
		CH_4		C_2H_6		C_2H_4	
		301.4K	212.7K	301.4K	212.7K	301.4K	212.7K
Langmuir	q_m	4.4498	6.1022	4.6168	6.2367	4.7115	6.0121
	b	0.0111	0.1260	0.1474	4.2152	0.0960	3.9799
	%	4.4103	10.4974	8.7031	8.4100	8.2318	17.7035
Freundlich	K	0.1731	1.3294	1.0840	3.6332	0.8709	3.3611
	n	1.8617	3.2637	3.2183	4.8660	2.8815	4.6981
	%	8.1360	9.5132	8.9263	11.1835	7.8157	8.3968
Sips	q_m	5.8710	8.5370	6.0980	7.6900	6.5020	10.3640
	b	0.0117	0.1125	0.1331	1.2601	0.0929	0.5355
	n	1.1587	1.5500	1.4565	1.6841	1.4560	2.5080
	%	0.5213	0.9020	0.5511	3.5119	0.5210	3.2101

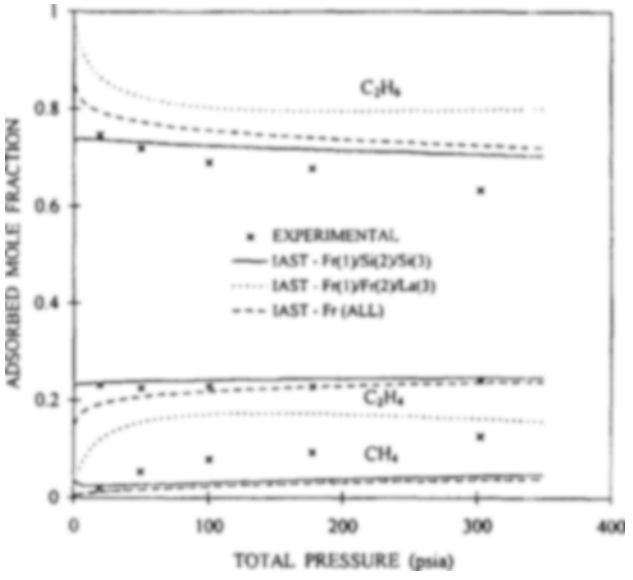

Fig. 7. Prediction of adsorbed mole fraction along total pressure for ternary mixtures, Methane(1)-Ethane(2)-Ethylene(3), at 301.4 K [Data reported by Reich et al., 1980].

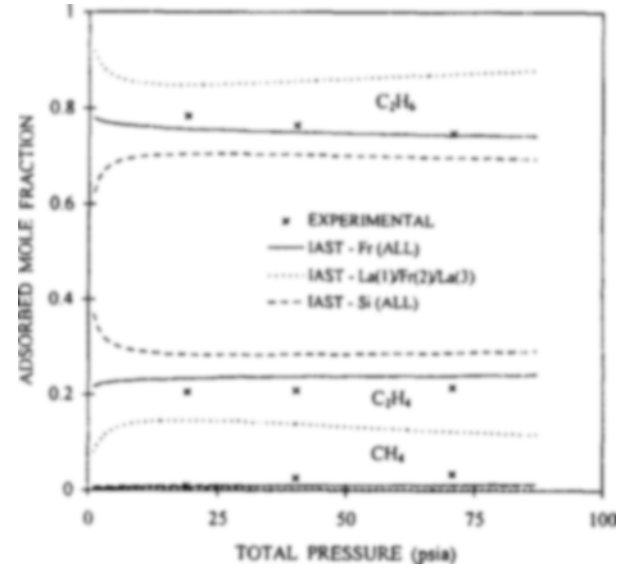

Fig. 8. Prediction of adsorbed mole fraction along total pressure for ternary mixtures, Methane(1)-Ethane(2)-Ethylene(3), at 212.7 K [Data reported by Reich et al., 1980].

maybe comes from the nonideal character of the mixture. It seems that there exists the adsorbed phase nonideality which cannot be ignored and this nonideality effect dominates over the dependence of isotherms.

DISCUSSION AND RECOMMENDATIONS

The success of AST in predicting multicomponent adsorption equilibrium data greatly depends on the accuracy of single-component isotherms as well as the adsorbed-phase nonideality. As shown in the sample calculations, the suitable combination of isotherm equations, which give the best fit for the single-component adsorption data, is useful for predicting the binary and ternary equilibrium data for corresponding mixtures, comparing with other cases. In the case of a hydrocarbons-activated carbon system reported by Costa et al. [1981], IAST which employs the optimum combination of isotherms can give more accurate results than RAST which employs the Freundlich isotherm for all components. This result implies that the use of suitable single-component isotherms is one of the major factors in predicting multicomponent equilibrium data successfully using AST. The concept of arbitrary isotherm proposed here will be very useful in the case that individual components in a given mixture have different physical and chemical properties. Furthermore the concept of arbitrary isotherm can be more generalized by evaluating the spreading pressure in terms of pressure from single-component experimental data themselves directly. To do this, one needs a good correlation to represent the spreading pressure rather than an isotherm.

In the case of Reich et al.'s data, the combination of isotherms, which gave the best fits to single-component adsorption data, do not give the best predictions for their ternary data. Such a result implies that the other effect, namely the adsorbed phase nonideality, can dominate the mutual interaction between adsorbates. Therefore it may be concluded that one should account for the nonideality as well as the concept of arbitrary isotherm to apply AST to multicomponent adsorption calculations successfully.

The calculation procedures presented here have a good convergence property and can be easily implemented in more complex systems. Thus, it can be utilized for the analyses of batch and adsorption column dynamics in the future.

NOMENCLATURE

A : specific area of adsorbent
bi : isotherm parameter of component i in Langmuir and Sips equations
C : adjustable parameter in SPD model for binary mixture
C_{ij} : adjustable parameter in SPD model for multiple mixture
f : arbitrary function of isotherm equation
g : arbitrary function of spreading pressure
h : arbitrary function of adsorbed amount
K_i : isotherm parameter of component i in Freundlich equation
N : number of component
n_i : isotherm parameter of component i in Freundlich and Sips equations
P : total gas pressure
$P_i^0(\pi)$: equilibrium pressure of component i corresponding to π
$P_{i,ini}^0$: initial guessed equilibrium pressure of component i
Q_i^0 : adsorbed amount of component i at pure state
Q_i : adsorbed amount of component i at equilibrium
Q_T : total adsorbed amount
Q_k : van der Waals surface area for group k in UNIQUAC equation
q_{mi} : isotherm parameter of component i in Langmuir and Sips equation
q_i : molecular-structure constants of component i for pure component in UNIQUAC equation
R_k : van der Waals volumn for group k in UNIQUAC equation

R : gas constant
r_i : molecular-structure constants of component i for pure component in UNIQUAC equation
T : absolute temperature
x_i : mole fraction of component i in adsorbed phase
$x_{i,ini}$: initial guessed mole fraction of component i
y_i : mole fraction of component i in gas phase
y_{ij}^{exp} : j th experimental gas mole fraction of component i
y_{ij}^{cal} : j th calculated gas mole fraction of component i
z : coordination number in UNIQUAC equation

Abbreviations

Fr : Freundlich isotherm equation
IAST : ideal adsorbed solution theory
La : Langmuir isotherm equation
RAST : real adsorbed solution theory
Si : Sips isotherm equation
SPD : spreading pressure dependence
not-SPD : spreading pressure not dependence

Greek Letters

Δ : increment
γ_i : activity coefficient of component i
Φ_i : segment fraction of component i in UNIQUAC equation
π : spreading pressure
Π : modified spreading pressure defined in Eq. (2)
Π_B : modified spreading pressure of the binary mixture
Π_i^0 : modified spreading pressure of component i at equilibrium
Π_{ini} : initial guessed modified spreading pressure
Λ_{ij} : interaction parameter between component i and j in Wilson equation
$\nu_k^{(i)}$: number of groups of type k in molecule i in UNIQUAC equation
θ_i : area fraction of component i in UNIQUAC equation
τ_{ij} : interaction parameter between component i and j in UNIQUAC equation
Ω : limiting slope at the limit of zero pressure

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