Comparison of Isotherm Models for Hydrocarbon Adsorption on Activated Carbon

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A number of equilibrium isotherm models can be utilized for correlating experimental equilibrium results. Seven different isotherm models are studied using equilibrium data of methane, ethane and propane in activated carbon. Besides comparing the goodness of data fit, the limiting behaviors as well as the pressure and temperature derivatives of the equilibrium isotherm models are also investigated. Performance of multicomponent extensions of these isotherm models and their combinations with the ideal adsorbed solution theory are also compared with experimental data. This systematic evaluation of the more important equilibrium isotherm models provides the general basis for making a preliminary selection of an effective model for a given application. Although an accurate and thermodynamically consistent model is desirable, these requirements may often be compromised for computational simplicity in dynamic process modeling studies.

Introduction

Numerous equilibrium isotherm models have been introduced over the years. Some of these models have gained more importance than others due to their simplicity and, in some cases, due to their ubiquitous applicability. Accuracy of an isotherm model is generally a function of the number of independent parameters in the model, while its popularity in relation to process application is generally a function of its mathematical simplicity. The linear isotherm model (Henry's law), for instance, has only two independent parameters, and hence is applicable to only a limited class of adsorption systems. However, due to its unparalleled mathematical simplicity, it has been used in many adsorption process modeling studies, including early pressure swing adsorption research.

The literature on both single- and multicomponent adsorption isotherm models is replete with isolated claims of improved accuracy either by addressing new physics of adsorption or through empirical modification of preexisting models. Some of these developments are also shown to give improved computational efficiency. However, a systematic and detailed comparative evaluation of these isotherm models on a common basis is somewhat lacking. Such a study can provide a general guideline for selecting an effective isotherm model for a given application.

In this work, a number of the more important isotherm models are reviewed in the context of modeling experimental equilibrium data for methane, ethane, and propane in activated carbon. The main emphasis of the study is to compare the characteristics of these equilibrium isotherm models with regard to their applicability in adsorption process modeling. Equilibrium data used in this study were obtained by the dynamic column-breakthrough method. The experimental procedure as well as the equilibrium data obtained are detailed in two recent publications (Malek et al., 1995; Malek and Farooq, 1996). In addition, multicomponent adsorption data of methane–ethane–propane mixtures onto activated carbon at various compositions and pressures were obtained from constant-volume experiments. These results are used to compare the prediction characteristics of the various multicomponent isotherm models.

The ultimate goal of the research work undertaken is to develop a multibed, multicomponent PSA simulation model for hydrogen purification from refinery fuel gas. In this regard, determining the effectiveness of various equilibrium isotherm models in terms of both model adequacy and computational load is evidently crucial.

Nonlinear Isotherm Models

Isotherm model formulation can generally be classified in terms of three fundamental approaches. The first approach is based on kinetic considerations. Here, adsorption equilibrium is considered as being a state of dynamic equilibrium, with both the adsorption and desorption rates equal (Langmuir, 1918). The second approach is based on thermodynam-

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ics, which provides a framework of deriving many forms of adsorption isotherm models. Three of the more important results from thermodynamics are the Gibbs adsorption isotherm equation (deBoer, 1928; Myers and Prausnitz, 1965), the vacancy solution model (Suwanayuen and Danner, 1980; Cochran et al., 1985), and statistical thermodynamic models (Fowler and Guggenheim, 1939; Hill, 1960; Ruthven, 1984). The third approach is based on potential theory (Dubinin, 1960). The main idea behind this theory is the generation of the characteristic curve. It is interesting to note that some isotherm models, like the Langmuir isotherm model and the Fowler and Guggenheim equation, can be derived using more than one approach, thus leading to a difference in the physical interpretation of the model parameters. In some cases, one approach can lead to a physically more meaningful model than the others (Ruthven, 1984).

A notable trend in the progression of isotherm modeling is the increasing number of independent parameters being utilized. This is an indication of the growing emphasis on very accurate single-component isotherm models. A higher number of parameters enhances the usefulness of the model in fitting equilibrium data that are not linear. However, it also generally increases the numerical complexity, particularly in extending the model to multicomponent systems and incorporating it in real process models.

The minimum number of parameters required to fit a nonlinear isotherm is three, as in the elementary Langmuir isotherm model. In this model, the independent parameters are the saturation solid loading, q_s^*, the heat of adsorption, ΔH_A, and the adsorption equilibrium constant, b_o. The Langmuir isotherm model is applicable for monolayer adsorption on a homogeneous adsorbent surface with negligible intermolecular forces. Discernibly, this is an ideal model. In many cases, the Langmuir model is not applicable, particularly at high sorbate concentrations as the intermolecular forces become appreciable. Table 1 introduces a number of other nonlinear isotherm models that take into account system nonidealities and have been used in adsorption process modeling. The Langmuir–Freundlich and Toth isotherms are empirical equations and are generally popular because of their ability to model a wide variety of equilibrium data. As shown in Table 1, these models possess four independent parameters, thereby providing an additional degree of freedom as compared to the Langmuir isotherm. There are also a number of other modified forms of the Langmuir isotherm. Yang and Doong (1985) and Tsai et al. (1983) used a form that allows a temperature-dependent saturation coverage. This is generally thought to account for thermal expansion of the adsorbed phase, which results in a decrease in the monolayer coverage at high temperatures. However, the exact form of the temperature dependence of saturated surface coverage is not well validated. Tsai et al. (1983) used a linear ratio to account for the reduction of saturation capacity, while von Gemmingen (1993) used a liquid-like linear dependence as follows:

$$q_s^* = q_{so}^*[1 - \alpha_T(T - T_o)], \tag{1}$$

where

α_T = thermal expansion coefficient
T_o = reference temperature.

Doong and Yang (1986) and Mutasim and Bowen (1992) also used different modifications of the Langmuir or Langmuir–Freundlich isotherms. However, these empirical modifications were introduced mainly to improve model agreement with experimental equilibrium data. Another isotherm model worth mentioning is that derived by von Gemmingen (1993). This isotherm model exhibits a mixed statistical and potential-type behavior. However, the model has a form very similar to the Langmuir–Freundlich equation, except that the exponent can be temperature dependent. Hence, this model, as well as those of Doong and Yang (1986) and Mutassim and Bowen (1992) would be excellent candidates if the Langmuir–Freundlich isotherm fails to fit experimental data.

One of the main reasons for isotherm nonideality stems from adsorbent surface heterogeneity. This is generally the case for activated carbon (Jaroneic et al., 1990; Kuro-Oka et al., 1984; Nitta et al., 1991). Surface heterogeneity invariably depends on the relative sizes of the adsorbate and the active sites, and can be quantified through a plot of the derivative of the characteristic curve obtained using the potential theory (Jaroniec et al., 1990). The general approach to account for surface heterogeneity is to assume that the surface exhibits a distribution of adsorption potential. In this way, the adsorbed amount can be calculated from an integral over the entire distribution, with an appropriate local isotherm model, as follows:

$$q_{\text{het}}^* = \int_0^\infty q_{\text{hom}}^* F(-\Delta H_A) d(-\Delta H_A), \tag{2}$$

where

$$\int_0^\infty F(-\Delta H_A) d(-\Delta H_A) = 1.0.$$

Application of this approach together with an appropriate distribution function can give various forms of isotherm equations for heterogeneous surfaces (Seidel and Carl, 1989). Of significance is the observation that the energy distribution function is more critical in affecting the overall equilibrium profile than is the local isotherm model (Hines et al., 1990). Hines et al. (1990) and Hassan et al. (1992) introduced new isotherm models using this approach. Both models used the Jovanovich equation for the local isotherm. These isotherm models appear very promising, although very complex. Unfortunately, the temperature dependence of the model parameters are not yet well correlated. A further modification to the Langmuir isotherm that takes into account surface heterogeneity was given by O'Brien and Myers (1984). As shown in Table 1, this introduces a first-order correction term to the Langmuir isotherm.

Nitta et al. (1984) derived an isotherm model based on statistical thermodynamics, which is also studied here. In fact, two types of multisite isotherm models were derived by them, one for a homogeneous surface and the other for a heterogeneous surface. The former model has five parameters, but can be simplified by ignoring molecular interaction. The latter is, however, somewhat complicated and is not considered in this study. The last isotherm model considered is the Flory–Huggins form of the vacancy solution model (Cochran et al., 1985; Huang and Fair, 1988). This model possesses five

Table 1. Isotherm Models Studied

Isotherm Model	Model Equation	Direct Multicomponent Extension	No. of Independent Parameters	Numerical Solution	$\left(\frac{\partial q^*}{\partial P}\bigg\vert_T\right)$ as $P \to 0$
Langmuir	$\theta^* = \frac{b_1 P}{1+b_1 P}$ $b_1 = b_{o1}\exp\left(\frac{-\Delta H_A}{RT}\right)$	$\theta_1^* = \frac{b_{1i}P_i}{1+\Sigma_j b_{1j}P_j}$ $j = 1,2,\ldots,N$	3	Explicit	Constant
Modified Langmuir 1 (Yang and Doong, 1985)	$\theta^* = \frac{b_1 T^{-n} P}{1+b_1 P}$ $b_1 = b_{o1}\exp\left(\frac{-\Delta H_A}{RT}\right)$	$\theta_i^* = \frac{b_{1i}T^{n_i}P_i}{1+\Sigma_j b_{1j}P_j}$ $j = 1,2,\ldots,N$	4	Explicit	Constant
Modified Langmuir 2 (O'Brien and Myers, 1984)	$\theta^* = \frac{b_1 P}{1+b_1 P}\left(1+\frac{\sigma^2(1-b_1 P)}{2(1+b_1 P)^2}\right)$ $b_1 = b_{o1}\exp\left(\frac{-\Delta H_A}{RT}\right)$	Not applicable	4	Explicit	Constant
Langmuir-Freundlich	$\theta^* = \frac{b_1 P^n}{1+b_1 P^n}$ $b_1 = b_{o1}\exp\left(\frac{-\Delta H_A}{RT}\right)$	$\theta_i^* = \frac{b_{1i}P_i^{n_i}}{1+\Sigma_j b_{1j}P_j^{n_j}}$ $j = 1,2,\ldots,N$	4	Explicit	Varying
Toth	$\theta^* = \frac{(b_1)^{1/n}P}{(1+b_1 P^n)^{1/n}}$ $b_1 = b_{o1}\exp\left(\frac{-\Delta H_A}{RT}\right)$	Not applicable	4	Explicit	Constant
Nitta (Nitta et al., 1984)	$\theta^* = n(1-\theta^*)^n \frac{b_1}{T}P$ $b_1 = b_{o1}\exp\left(\frac{-\Delta H_A}{RT}\right)$	$n_i b_{1i} P_i = \frac{\theta_i^*}{(1-\Sigma_j \theta_j^*)^{n_i}}$ $j = 1,2,\ldots,N$	4	Implicit	Constant
FH-VSM (Cochran et al. 1985; Huang and Fair, 1988)	$P = \left(\frac{q^*}{b_{\upsilon sm1}(1-\theta^*)}\right)\exp\left(\frac{\alpha_{1\upsilon}^2\theta^*}{1+\alpha_{1\upsilon}\theta^*}\right)$ $\theta^* = \frac{q^*}{q_{so}^*\exp\left(\frac{-h}{T}\right)}$ $b_{\upsilon sm1} = b_{\upsilon smo1}\exp\left(\frac{-\Delta H_A}{RT}\right)$ $\alpha_{1\upsilon} = b_{\upsilon smo2}q_{so}^*\exp\left(\frac{-h}{T}\right)-1$	$x_i\phi_i P = \gamma_i^s y_i \frac{q_m^*\exp(\alpha_{i\upsilon})}{b_i 1+\alpha_{i\upsilon}}$ $\times\exp\left(\left(\frac{q_{si}^*-q_{sm}^*}{q_m^*}-1\right)\ln(\gamma_\upsilon^s y_\upsilon^s)\right)$	5	Implicit	Constant

independent parameters, with the saturated solid loading, q_s^*, being temperature dependent. Cochran et al. (1985) suggested the following relationship for the temperature dependence

$$q_s^* = q_{so}^*\exp\left(\frac{-h}{T}\right). \tag{3}$$

The FH-VSM model was introduced in order to correct the original VSM-Wilson equation (Suwanayuen and Danner, 1980), which fails to explicitly account for temperature effects. The potential theory is not considered here for two reasons. First, some parameters, like the adsorbed phase molar volume, are not well defined, although there seems to be a general consensus in the definitions now (Yang, 1987). Secondly, the results of Reich et al. (1980) indicate that, although the pure gas equilibrium data could be satisfactorily correlated by either the "linear" equation of Lewis et al. (1950) or the Dubinin–Radushkevic equation (Dubinin, 1960), the multicomponent results were poorly correlated. Their results are significant since their experimental data, as well as those of Szepesy and Illes (1963), cover a wide range of pressures and of various light hydrocarbons. In most cases, these equations are not capable of correlating data at extreme pressures. The "linear" equation is generally inaccurate at low pressures, while the Dubinin–Radushkevic equation is inaccurate at very low as well as high pressures (Reich et al., 1980). Saunders et al. (1985), however, obtained better results, but these authors only considered the adsorption of methane and hydrogen at very high pressures. Under these conditions, the "linear" equation provides accurate fits of experimental data.

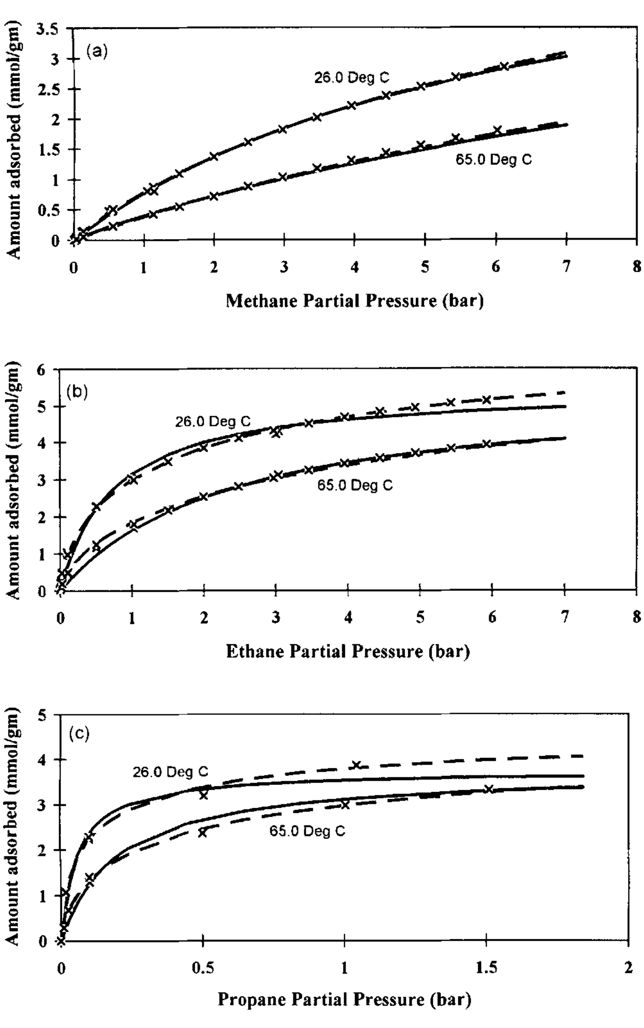

Figure 1. Adsorption isotherms.

(a) Methane, (b) ethane, and (c) propane in activated carbon; symbols, experimental; solid line, Langmuir; dashed line, Langmuir–Freundlich.

Solution of Isotherm Models

The different models studied here were used to correlate experimental equilibrium data of light hydrocarbon adsorption in activated carbon. Representative experimental data for methane, ethane, and propane at two different temperatures, along with their Langmuir and Langmuir–Freundlich model fits, are as shown in Figure 1. Complete equilibrium data for these systems at three different temperatures are given elsewhere (Malek and Farooq, 1996). A clear trend in the equilibrium results is the increasing nonlinearity of the isotherms with increasing molecular weight of the hydrocarbon. This trend is pertinent in comparing the equilibrium isotherm models, since the performance of a model would be judged by its ability to fit isotherms of different degrees of nonlinearity.

The isotherm parameters for each model were determined simultaneously at all three temperatures using multivariable, nonlinear regression. In this regard, a modified Levenberg–Marquardt algorithm was used (IMSL routine DUNLSF). The goodness-of-fit was calculated for each regression by comparing the square of residuals (SOR), defined as follows:

$$\mathrm{SOR} = \frac{1}{2}\Sigma(q^*_{\mathrm{exp}} - q^*_{\mathrm{cal}})^2. \tag{4}$$

Note that as just defined, the SOR is an absolute value, the magnitude of which is dependent on the goodness-of-fit as well as the number of experimental points. The model parameters as well as the SOR are shown in Table 2. Figure 2 also shows plots of the local residual, $\mathcal{R}$ ($= q^*_{\mathrm{exp}} - q^*_{\mathrm{cal}}$), along the entire isotherm curve. From the plots, it is apparent that the fits for the more nonlinear isotherms are less accurate. This is also observable in Figure 1. Since the plots indicate similar residual values throughout the isotherm curve, the percentage of deviations is higher at low pressures. For all the three hydrocarbons, the Langmuir isotherm provides a somewhat less satisfactory fit compared to the other isotherms. The modified Langmuir 2, which have an additional independent parameter, provide a considerable improvement as compared to the Langmuir isotherm. However, the modified Langmuir 1 does not provide any significant improvement in terms of the sum of residuals. The Langmuir–Freundlich, Toth, Nitta, and FH-VSM equations all provide a very close fit of the experimental data. On a finer distinction, the Langmuir–Freundlich isotherm is perhaps marginally superior, as it provides equally good fits for all three hydrocarbon isotherms over the entire experimental pressure range. This indicates its versatility in fitting isotherms of various degrees of nonlinearity, which is important in multicomponent equilibrium prediction.

Table 1 gives the solution method for each isotherm equation. Except, for the Nitta and FH-VSM models, all the other models considered here can be solved explicitly for the equilibrium solid loading. The Nitta and FH-VSM models are implicit and must be solved using a nonlinear equation solver. The additional computation introduces a significant disadvantage in dynamic adsorption process simulations. As will be discussed later, this computational load is more significant in multicomponent solutions. For the purpose of comparison, the computation times of the Nitta and FH-VSM equations were studied by solving for the ethane equilibrium data at various gas pressures. The nonlinear equations were solved using the Ridders algorithm (Press et al., 1992). It generally took twice as much time to solve the FH-VSM equation as the Nitta equation.

Thermodynamic Consistency and Heat of Adsorption, ΔH_A

Apart from its numerical aspect, the question of thermodynamic consistency of the model should also be addressed. The following list gives the more pertinent characteristics of the isotherm models:

$$\left.\frac{\partial q^*}{\partial P}\right|_T \rightarrow \text{constant} \quad \text{as } P \rightarrow 0 \tag{5a}$$

$$q^* \rightarrow 0 \quad \text{as } P \rightarrow 0 \tag{5b}$$

$$q^* \rightarrow q^*_s \quad \text{as } P \rightarrow \infty. \tag{5c}$$

Table 2. Parameter Values and Sum of Residuals for the Different Isotherm Models

Isotherm Model	Methane		Ethane		Propane	
	Isotherm parameters	SOR (NE = 64)	Isotherm parameters	SOR (NE = 56)	Isotherm parameters	SOR (NE = 17)
Langmuir	$q_s^* = 5.8243$ $-\Delta H_A = 16.6330\times10^3$ $b_{o1} = 1.9178\times10^{-4}$	0.0296	$q_s^* = 5.4738$ $-\Delta H_A = 25.1015\times10^3$ $b_{o1} = 5.6113\times10^{-5}$	0.6592	$q_s^* = 3.7348$ $-\Delta H_A = 26.4418\times10^3$ $b_{o1} = 4.1051\times10^{-4}$	0.2148
Langmuir–Freundlich	$q_s^* = 7.3304$ $-\Delta H_A = 15.9562\times10^3$ $b_{o1} = 1.9953\times10^{-4}$ $n = 0.9169$	0.0301	$q_s^* = 7.6364$ $-\Delta H_A = 15.1720\times10^3$ $b_{o1} = 1.4403\times10^{-3}$ $n = 0.6590$	0.0561	$q_s^* = 4.8416$ $-\Delta H_A = 17.4536\times10^3$ $b_{o1} = 3.2151\times10^{-3}$ $n = 0.6285$	0.0399
Toth	$q_s^* = 6.3367$ $-\Delta H_A = 15.2795\times10^3$ $b_{o1} = 3.6898\times10^{-4}$ $n = 0.9221$	0.0299	$q_s^* = 10.84$ $-\Delta H_A = 8.7796\times10^3$ $b_{o1} = 4.5645\times10^{-2}$ $n = 0.3838$	0.0679	$q_s^* = 6.720$ $-\Delta H_A = 10.0865\times10^3$ $b_{o1} = 7.7488\times10^{-2}$ $n = 0.3752$	0.0547
Modified Langmuir 1	$q_s^* = 476.0$ $-\Delta H_A = 19.1239\times10^3$ $b_{o1} = 1.250\times10^{-4}$ $n = 0.821$	0.0307	$q_s^* = 428.63$ $-\Delta H_A = 19.7083\times10^3$ $b_{o1} = 4.6122\times10^{-4}$ $n = 0.7613$	0.6257	$q_s^* = 1278.0$ $-\Delta H_A = 23.9343\times10^3$ $b_{o1} = 1.0447\times10^{-3}$ $n = 1.0114$	0.2309
Modified Langmuir 2	$q_s^* = 6.7791$ $-\Delta H_A = 16.4293\times10^3$ $b_{o1} = 1.5490\times10^{-4}$ $\sigma^2 = 0.3485$	0.0285	$q_s^* = 6.2008$ $-\Delta H_A = 25.4949\times10^3$ $b_{o1} = 3.7224\times10^{-5}$ $\sigma^2 = 1.3082$	0.3404	$q_s^* = 4.6790$ $-\Delta H_A = 28.3275\times10^3$ $b_{o1} = 1.0261\times10^{-4}$ $\sigma^2 = 1.8570$	0.0685
Nitta	$q_s^* = 17.896$ $-\Delta H_A = 13.3598\times10^3$ $b_{o1} = 1.8244\times10^{-2}$ $n = 4.0208$	0.0298	$q_s^* = 18.441$ $-\Delta H_A = 19.9611\times10^3$ $b_{o1} = 8.15\times10^{-3}$ $n = 8.0213$	0.1360	$q_s^* = 20.412$ $-\Delta H_A = 23.0672\times10^3$ $b_{o1} = 1.0381\times10^{-2}$ $n = 15.538$	0.0873
FH-VSM	$q_{so}^* = 5.7371$ $-\Delta H_A = 15.7475\times10^3$ $b_{vsmo1} = 1.61\times10^{-3}$ $-h = 77.76$ $b_{vsmo2} = 0.23657$	0.0251	$q_{so}^* = 3.7688$ $-\Delta H_A = 22.4370\times10^3$ $b_{vsmo1} = 1.96\times10^{-3}$ $-h = 174.29$ $b_{vsmo2} = 0.4933$	0.1144	$q_{so}^* = 2.9731$ $-\Delta H_A = 30.1125\times10^3$ $b_{vsmo1} = 5.41\times10^{-3}$ $-h = 166.98$ $b_{vsmo2} = 1.1621$	0.0514

Requirements 5b and 5c are generally not a problem. Table 1 displays the form of the isotherm equation at low coverage. Except for the Langmuir–Freundlich and FH-VSM equations, all the other isotherm models considered here reduce to the Henry's law at low coverage (i.e., as $P \rightarrow 0$, $(\partial q^*/\partial P)|_T \rightarrow$ constant). It is worth mentioning that the isotherms proposed by Hines et al. (1990) and Hassan et al. (1992) also reduce to Henry's law, while the von Gemmingen equation does not, since it is of a form similar to the Langmuir–Freundlich equation. One may therefore question the reliability of these isotherm models in the low concentration region. However, the impact of this limitation on a process application should be assessed in relation to the overall effectiveness of alternative isotherm models.

Table 2 also shows the heat of adsorption, ΔH_A, derived from the various models for the three hydrocarbon gases. The Langmuir isotherm, as well as its other modified versions, the Nitta isotherm, and the FH-VSM isotherm all seem to portray the correct trend in heat of adsorption, which is an increase with hydrocarbon molecular weight. It is important to note that the value of ΔH_A found for each isotherm has a strong effect on the predicted temperature profile, and hence on the heat-transfer parameter if it is extracted from nonisothermal adsorption experiments.

Pressure and Temperature Derivatives

The other characteristics of the various isotherm models that are considered here are the pressure and temperature derivatives. These functions are important in studies on adsorption kinetics, the temperature derivative being particularly important in nonisothermal simulations. Figure 3 shows plots of the derivative of solid loading with respect to pressure, $(\partial q^*/\partial P)|_T$, for all the models. The plots are for the ethane equilibrium isotherm at a temperature of 299.15 K. All the isotherms that reduce to Henry's law have a finite gradient in the limit $P \rightarrow 0$. The Langmuir–Freundlich isotherm, however, has a very large gradient at low coverage, which eventually reduces to zero at zero coverage. The next largest gradient is that from the Toth equation. Indeed, both these isotherms have very close gradient profiles at low coverage. As expected, the Langmuir isotherm and its modifications all have similar gradient profiles at low coverage. Interestingly, the Nitta isotherm has a gradient profile closer to that of the Langmuir isotherm, while the FH-VSM model has a gradient profile closer to that of Langmuir–Freundlich and Toth models.

Figure 4 shows the temperature derivative plots for the various isotherms, including experimental data (shown as points). The plots indicate that the Langmuir–Freundlich, Toth, Nitta, and FH-VSM models show similar gradient profiles and correlate experimental temperature derivatives at both high and low pressures reasonably well. In contrast, for the Langmuir isotherm and its modified forms, the agreement between the predicted temperature derivative profiles and experimental data is rather poor, particularly at high pressure and extrapolated temperatures. Indeed, the Langmuir model exhibits an erroneous gradient profile at high

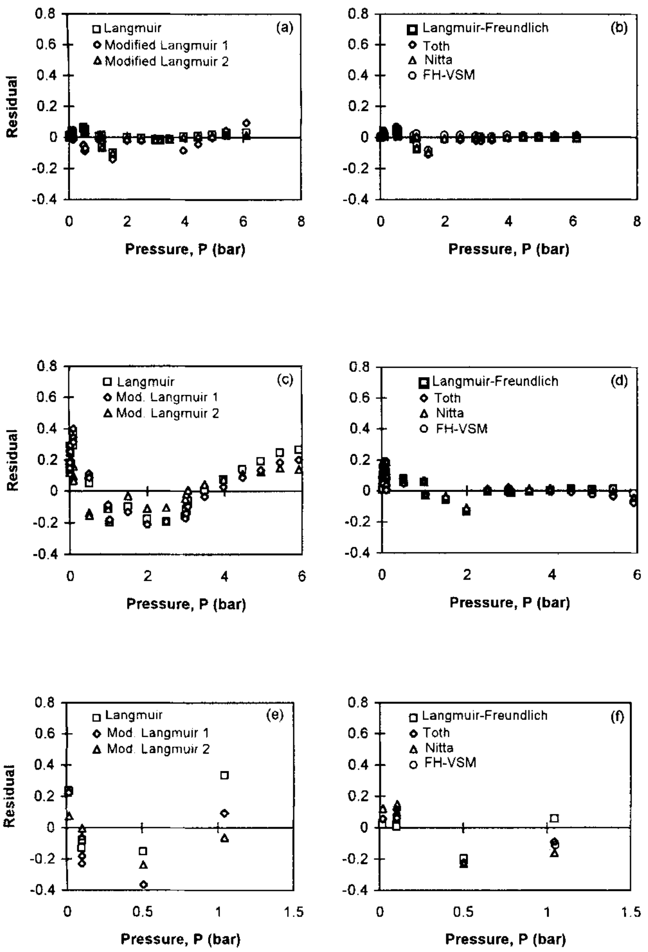

Figure 2. Residual of regression.

(a) and (b) Methane, (c) and (d) ethane, and (e) and (f) propane.

pressure. The main reason for the seemingly inaccurate derivative profiles obtained from these models is the less satisfactory equilibrium data fit of these models at high pressures. The temperature derivative plots shown here are crucial in the study of nonisothermal adsorption processes. The temperature derivative indicates the suitability of the isotherm model in simulating the shape and movement of the heat front in an adsorption process.

Multicomponent Equilibria

There are basically four different techniques of calculating multicomponent equilibria (Huang and Fair, 1988). Only two of these—namely, the direct extension of a single-component isotherm and the ideal adsorbed solution theory (IAST)—are considered in this study. In dynamic adsorption process studies, using an explicit multicomponent equilibrium model allows a significant savings in terms of computational workload. As may be seen from Table 1, among the isotherm models studied here, only the Toth and the modified Langmuir 2 do not possess direct multicomponent extensions. For the modified Langmuir 1, an extension similar to that for Langmuir can be adopted as a simple approximation (Yang and Doong, 1985). As with their single-component models, the extended Nitta and FH-VSM models are also implicit and hence require iterations. In particular, the computational load for multicomponent FH-VSM model is higher compared to the Nitta isotherm due to the highly nonlinear multicomponent equations in the former model. However, the FH-VSM

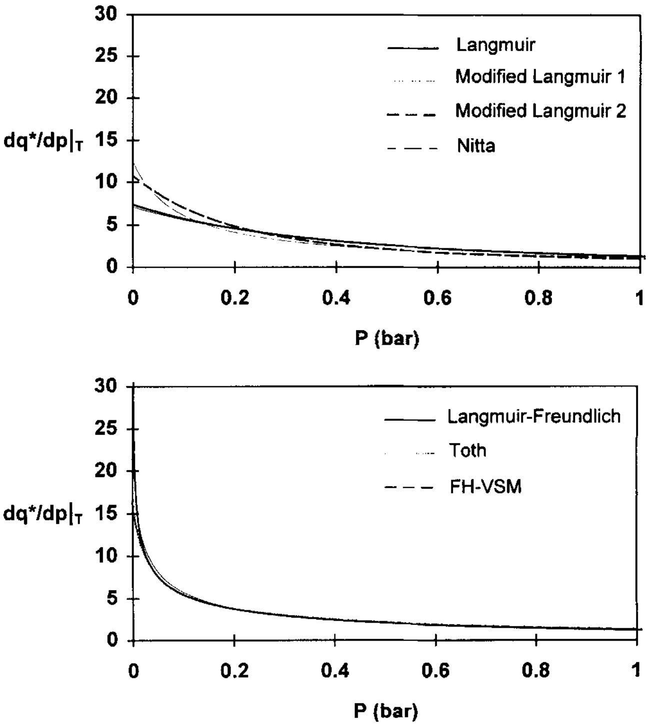

Figure 3. Pressure derivative of ethane equilibrium isotherms at 299.15 K.

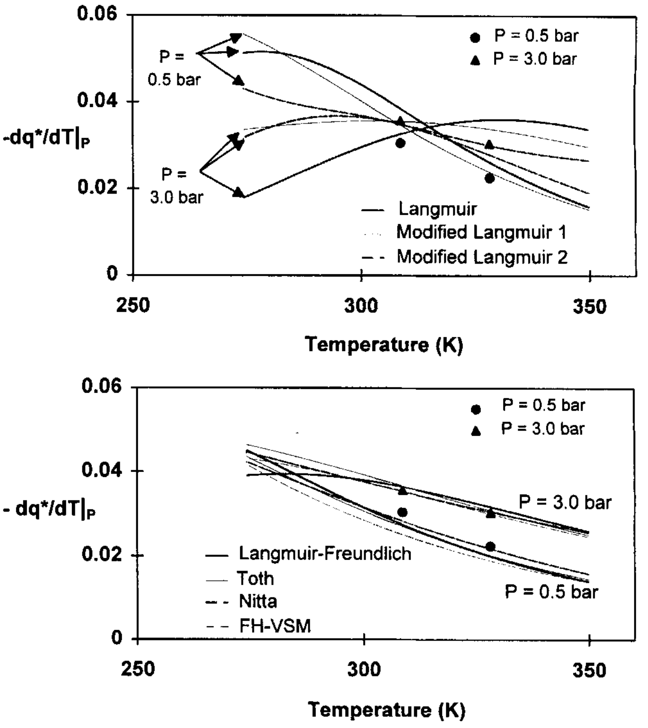

Figure 4. Temperature derivative of ethane equilibrium isotherms.

Symbols are experimental data.

is known to provide excellent multicomponent predictions using pure gas model parameters (Cochran et al., 1985).

One of the most notable multicomponent equilibrium model follows from the IAST (Myers and Prausnitz, 1965). The IAST is a general theory that attempts to predict multicomponent adsorption from any functional form of the pure component isotherm model. The relevant equations for computing multicomponent equilibria from the IAS theory, as well as the solution algorithm as used here, are given in the Appendix. The main drawback of this approach, however, is the excessive computational requirements compared to direct extensions of single-component isotherms (O'Brien and Myers, 1985). This is particularly so for isotherm models like Langmuir–Freundlich and Toth, since the Gibbs equations for spreading pressure using these isotherms cannot be integrated analytically. In contrast, due to the model simplicity, the Langmuir isotherm allows an analytical solution to the Gibbs integral, thereby reducing computational requirements considerably. This integral is given by

$$\frac{\Pi_i A}{RT} = q_{si}^* \ln(1 + b_i P_i^o). \tag{6}$$

However, as shown in previous sections, the Langmuir isotherm is generally not accurate in fitting the hydrocarbon-activated carbon system. Considering this factor, it is interesting to study the accuracy and speed of computation using the IAST together with the modified Langmuir 2 isotherm model, as proposed by O'Brien and Myers (1985), since this model gives an improved data fit and allows an analytical integration of the Gibbs equation. The corresponding solution to the Gibbs integral is

$$\frac{\Pi_i A}{RT} = q_{si}^* \left[\ln(1 + b_i P_i^o) + \frac{\sigma^2 b_i P_i^o}{2(1 + b_i P_i^o)^2} \right]. \tag{7}$$

Thus, in this study, the IAS theory is used together with the Langmuir (IAS-L), Langmuir–Freundlich (IAS-LF), Toth (IAS–T), and modified Langmuir 2 (IAS–ML2) isotherm models. A relatively efficient way of calculating multicomponent equilibria for cases where an analytical solution to the Gibb's integral can be derived was described by O'Brien and Myers (1985). The original FASTIAS method proposed by O'Brien and Myers (1985), its improved version known as IFASTIAS (O'Brien and Myers, 1985), as well as a modified version known as the MFASTIAS proposed by Moon and Tien (1987), are also studied here. The detailed solution algorithm for each of these quick IAS computational methods can be found in the references mentioned.

There are two other factors that are worth mentioning at this point. The first involves the method of deriving single-component isotherm parameters. The most ideal way of obtaining model parameters is through multivariable, nonlinear regression, as was done in this study. In this regard, the Levenberg–Marquardt algorithm (Marquardt, 1963) is perhaps the most effective. The advantage of using this method is that the model parameters can be derived simultaneously, covering the entire experimental pressure and temperature ranges, without the need for reformulating the model equation. However, in using the IAS theory to predict multicomponent equilibria, it generally turns out that the greatest errors are incurred at low pressure points, since the Gibbs adsorption isotherm equation involves the ratio q_i^*/P_i. One way of resolving this problem is to reformulate the model equation in order to give more "weight" to the low-pressure data during regression (Richter et al., 1989). However, Richter et al. have also shown that if too much weight is accorded to the low-pressure data, the high-pressure data would be grossly inaccurate. Hence, some trade-off in overall accuracy would be inevitable. This is, of course, not a problem if the isotherm model accurately represents the experimental data over the entire pressure range. The second issue that needs to be mentioned is the modification of the IAS theory to include nonidealities. Here, the two important approaches are the real adsorbed solution theory (RAST) (Costa et al., 1981; Talu and Zweibel, 1986) and the heterogeneous ideal adsorbed solution theory (HIAST) (Hoory and Prausnitz, 1967; Valenzuela et al., 1988). The RAST generally requires multicomponent experimental results in order to quantify the model nonidealities, and hence is not particularly attractive. The HIAST, on the other hand, does not require additional multicomponent experiments, but instead incorporates an energy-distribution function, which is similar to the heterogeneous isotherm models for single components. An excellent comparison of the various forms of IAST and HIAST applications in a multicomponent equilibria study was performed by Hu and Do (1995). Their study indicated the advantage of using the HIAST in terms of prediction accuracy. As in the single-component case, the energy-distribution function was also found to be very important in affecting multicomponent equilibria predictions. Unfortunately, no information on the magnitude of the computation times were given.

Ternary multicomponent adsorption equilibrium data of methane–ethane–propane of varying compositions and pressures were obtained using a constant-volume experiment. Figure 5 shows a diagram of the experimental setup. The experimental procedure entails first introducing the gas mixture into the dose chamber. By rapidly opening and closing the solenoid feed valve, varying amounts of the gas can be fed to the sorption vessel. The gas compositions in both chambers were analyzed before feeding and upon equilibration by collecting a small amount (1 mL) of the gas in a sy-

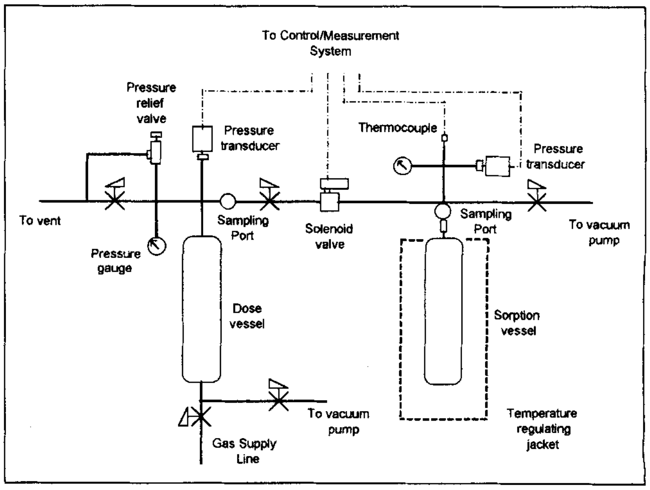

Figure 5. Constant volume apparatus.

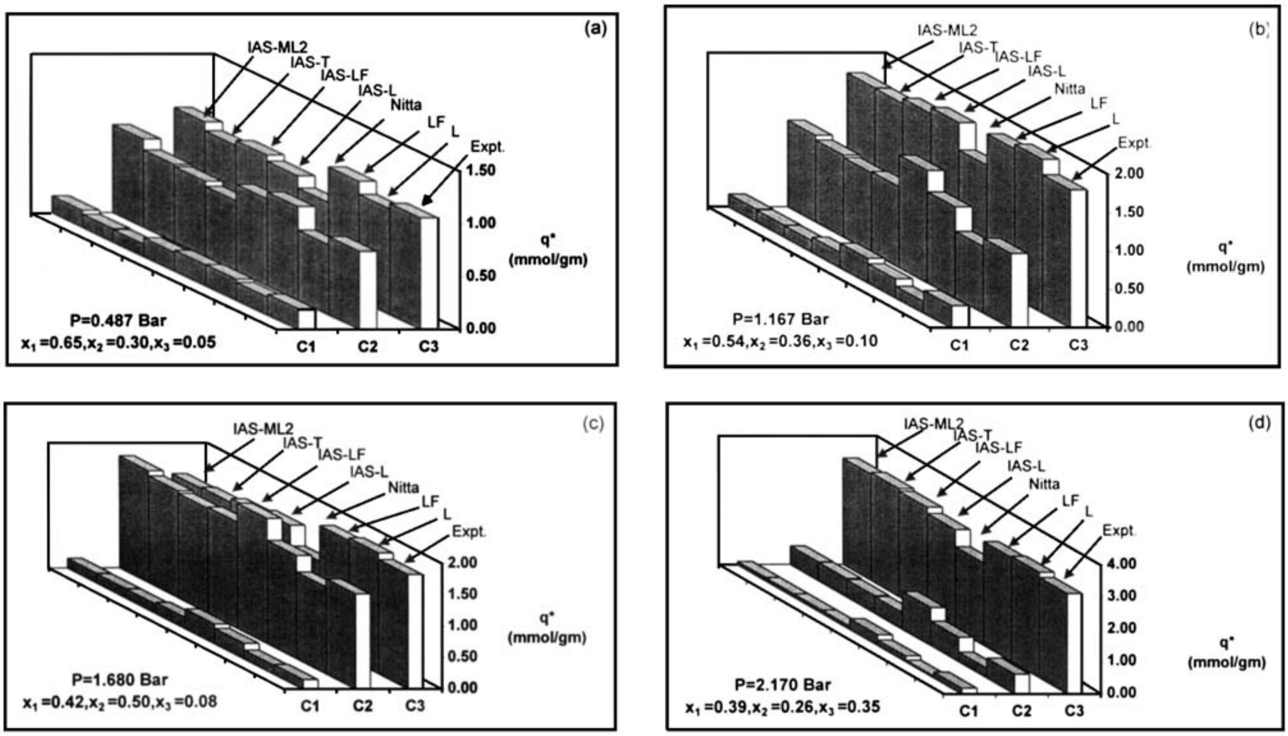

Figure 6. Experimental multicomponent adsorption data vs. model predictions.

$T = 298.15$ K; $C1$: methane; $C2$: ethane; $C3$: propane.

ringe. The compositions of the gases were determined using a Perkin-Elmer Autosystem GC fitted with a TCD and a Supelco Carboxen-1004 Micropacked Column. The pressures in both chambers were measured using precalibrated pressure transducers. The composition and pressure change in the dose tank upon feed charging gave the individual amounts of the species introduced as a mixture to the sorption tank. The difference between the initial and final pressure and composition in the sorption tank provided the equilibrium gas and solid-phase concentrations through simple material balance.

Figure 6a–6d show some of the multicomponent equilibrium results obtained, together with the calculated values from the various multicomponent isotherm models. In general, the multicomponent predictions using the various isotherm models give approximately similar results, which are in reasonable agreement with the measured values. In particular, the extended Langmuir–Freundlich isotherm model provides the best overall multicomponent predictions for all the experimental results obtained here. Of significance, however, are the results from the multicomponent Nitta isotherm model. This model generally underpredicts the equilibrium adsorption of propane while it overpredicts the adsorption equilibrium of ethane. Hence, although the form of the equation is accurate for single-component equilibrium modeling, the multicomponent extension used here is inadequate. This inadequacy perhaps indicates the necessity of including the molecular interaction parameter for multicomponent calculations. As in the FH-VSM model, this interaction parameter can either be estimated from pure component adsorption equilibrium or left as an additional degree of freedom, in which case, multicomponent experiments are mandatory (Nitta et al., 1984). It is worth mentioning that the extended Langmuir model, as well as the mixed Langmuir model, require that all the adsorbates have the same saturation capacity (i.e., equal molecular sizes in the adsorbed phase) for thermodynamic consistency.

As a further study on the suitability of the various multicomponent isotherm models, especially for dynamic adsorption process modeling, the computation speed of the more complex IAS models were investigated. In the first set of models (Set 1), the speed of computation of the IAS-L, IAS-LF, and IAS-T were determined. In this set, the models were solved numerically using a combination of the Levenberg–Marquardt algorithm (IMSL routine DUNLSF) and a univariate quadrature routine (IMSL routine DQDAG) to calculate the Gibb's integral. The equations were solved on a DEC 4000 Model 620. In the second set of simulations (Set 2), the IAS-L and IAS-ML2 were solved numerically using the FASTIAS algorithm as proposed by O'Brien and Myers (1985). The analytical solution of the Gibbs integral for spreading pressure for both these models was used (i.e., Eqs. 6 and 7, respectively). However, due to the problems of singularities in the Jacobian matrix in this analysis, the Levenberg–Marquardt algorithm (IMSL routine DNEQNF) was used, instead of the Newton–Raphson method as proposed by O'Brien and Myers (1985), to solve for the set of nonlinear equations. The Levenberg–Marquardt algorithm provided a more robust scheme, albeit at a slightly higher computation cost. In a later publication, O'Brien and Myers (1988) proposed a further improvement to the FASTIAS algorithm which essentially reformulates the nonlinear equations so as to obtain a special structure of the Jacobian matrix, thereby allowing a more efficient solution scheme. The computational improvements obtained using this method, referred to

Table 3. Comparison of CPU Time for Solving Multicomponent Equilibria by Various Methods

Gas-Phase Composition ($P = 1.0$ to 10.0 bar)	Total CPU Time (s) for Computing 500 Pressure Points*						
	Set 1			Set 2			Set 3
	IAS-L	IAS-LF	IAS-T	FASTIAS-L**	FASTIAS-ML2**	IFASTIAS-ML2†	MFASTIAS-ML2†
$x_1 = 0.6$, $x_2 = 0.3$, $x_3 = 0.1$	18.96	454.54	351.96	0.92	0.86	0.17	0.06
$x_1 = 0.4$, $x_2 = 0.2$, $x_3 = 0.4$	26.20	465.40	391.52	1.17	1.04	0.17	0.06
$x_1 = 0.8$, $x_2 = 0.15$, $x_3 = 0.05$	17.69	428.81	366.12	0.85	0.88	0.18	0.06
$x_1 = 0.15$, $x_2 = 0.8$, $x_3 = 0.05$	24.21	471.02	379.67	1.18	1.06	0.11	0.06

*CPU time error ≅ ±10%.
**Computed using Levenberg–Marquardt algorithm instead of Newton–Raphson method.
†Computed using Newton–Raphson method.

as the IFASTIAS, are also shown in Set 2 of Table 3. In the third set of computations (Set 3), the modified FASTIAS (MFASTIAS) scheme, as proposed by Moon and Tien (1987), was used together with the modified Langmuir 2 isotherm model.

In all the calculations, the same initial guess of the relevant parameters was used and the same numerical tolerance (1.0×10^{-8}) was adopted. The computations were performed in a loop by fixing the gas-phase compositions and increasing pressure from 1.0 to 10.0 bar. A total of 500 pressure points were taken. The initial guessed parameters were reset before each new pressure point. The total CPU time for the calculations was then noted. Table 3 shows the total CPU time required by these various schemes. Comparing between the results in Set 1, it is apparent that the computation-time requirements for the IAS-LF and IAS-T are significantly larger than the IAS-L. This is expected due to the greater nonlinearity of the former isotherm equations. Indeed, the CPU time required by both the IAS-LF and IAS-T is prohibitively large for the purpose of dynamic process modeling. Furthermore for gas mixtures with a larger number of adsorbing components, these models would quickly become even more unattractive. Referring to Figure 6a–6d, it is apparent that there is no real advantage, in terms of accuracy, in adopting the IAS-LF models over the direct-extension model in this case.

A significant reduction in computation time is achieved by using FASTIAS, as shown in the results of Set 2. Of interest is the fact that the FASTIAS-ML2 requires about the same computation time as that for the FASTIAS-L model. It should be recalled that the modified Langmuir 2 model generally gives a better fit of single-component isotherms than does the Langmuir isotherm. Hence, this model appears relatively attractive in terms of both accuracy and speed of computation. A further improvement in the computation time for multicomponent adsorption equilibria calculations can be achieved using the IFASTIAS-ML2. Interestingly, the MFASTIAS allowed a further reduction in the required computation times for the same calculation tolerance. It is also interesting to note that in using the MFASTIAS, the computation time is sufficiently small such that it is practically independent of the gas-phase compositions, which is a significant advantage in dynamic adsorption process modeling. As a basis for reference, for the same gas-phase compositions, using the extended Langmuir model, which is an explicit model, allowed computations of about 800,000 pressure points (between 1.0 and 10.0 bar) in the same time it took for the MFASTIAS-ML2 scheme to calculate 500 pressure points.

It is evident from this systematic evaluation of the more important equilibrium isotherm models that greater quantitative accuracy has been the focus of fundamental development in adsorption equilibrium models, and this has generally been achieved at the expense of increasing mathematical complexity. On the other hand, the engineering application of equilibrium calculation is mainly associated with large-scale process modeling, which requires that numerically simple isotherm models are chosen in order to restrict the already heavy computational load from being unrealistic. These more practical engineering aspects of equilibrium isotherm model selection will become clearer when the effectiveness of the various isotherm models studied here are examined by integrating with dynamic process modeling studies in the next phase of our research work.

Conclusions

Only when the equilibrium isotherm model is thermodynamically consistent and the system to which the model is applied agrees closely with the model assumptions is it possible to assign any physical meaning to the model parameters with certainty. The second requirement is only loosely satisfied in most engineering applications, and the models are in effect gauged by their performance as a regression model for experimentally derived equilibrium data. From this point of view, the seven single-component equilibrium isotherm models studied here have, in general, performed reasonably well; but the Langmuir–Freundlich model is certainly superior compared to the others.

On the other hand, for multicomponent equilibria, the simpler extended versions of the single-component models provide adequate and numerically convenient means of predictions. A general superiority of any particular model is, however, not evident. Among the various versions of the multicomponent prediction based on IAS theory, the IAS–Langmuir–Freundlich and IAS–Toth require considerably higher computational load without actually offering any significant improvement over the other models in terms of accuracy. Among the implicit multicomponent models, the use of the modified FASTIAS scheme together with the modified Langmuir 2 isotherm, which includes a first-order correction, offers a computationally more attractive means of solving multicomponent equilibria.

Therefore, the main distinguishing feature for selecting an equilibrium model in our process application is likely to come from the extent to which the multicomponent model will affect the computational intensity of the dynamic process simulation.

Notation

A = adsorption surface area as defined in the ideal adsorbed solution theory
b_1, b_{o1}, b_{o2} = constant in isotherm equations, bar^{-n}
$b_{\upsilon sm1}, b_{\upsilon smo1}, b_{\upsilon smo2}$ = constant in FH-VSM equation, mmol/g·bar
h = constant in FH-VSM equation, K^{-1}
n = exponent in isotherm model equations
n_i = exponent for component i
NC = number of components in mixture
NE = number of experimental points
P = total pressure, bar
P_i = partial pressure of component i, bar
q^* = equilibrium solid loading, mmol/g
q^*_{hom} = local patch isotherm equation as used in Eq. 2, mmol/g
q^*_i = equilibrium solid loading of component i, mmol/g
$q^*_{i\,\text{exp}}$ = experimental equilibrium solid loading of component i, mmol/g
$q^*_{i\,\text{cal}}$ = calculated equilibrium solid loading of component i, mmol/g
q^*_m = amount of mixture adsorbed, mmol/g
q^*_{sm} = saturated amount of mixture adsorbed, mmol/g
q^*_{si} = saturated equilibrium solid loading of component i, mmol/g
q^*_{so} = constant in isotherm equations, mmol/g
R = universal gas constant
x_i = gas-phase mole fraction of component i
y_i = adsorbed-phase mole fraction of component i
y_υ = adsorbed-phase mole fraction of vacancy

Greek letters

$F(-\Delta H_A)$ = energy distribution function as used in Eq. 2
$\alpha_{1\upsilon}$ = constant in FH-VSM equation
$\alpha_{i\upsilon}$ = constant in FH-VSM equation for component i
ϕ_i = fugacity of component i
γ_i^s = activity coefficient of component i
γ_υ^s = activity coefficient of component of vacancy
σ^2 = constant in modified Langmuir 2 equation
$\theta^* = q^*/q^*_s$
$\theta^*_i = q^*_i/q^*_{si}$

Literature Cited

Cochran, T. W., R. L. Kabel, and R. P. Danner, "Vacancy Solution Theory of Adsorption Using Flory-Huggins Activity Coefficient Equations," *AIChE J.*, **31**(2), 268 (1985).

Costa, E., J. L. Sotelo, G. Calleja, and C. Marron, "Adsorption of Binary and Ternary Hydrocarbon Gas Mixtures on Activated Carbon: Experimental Determination and Theoretical Prediction of the Ternary Equilibrium Data," *AIChE J.*, **27**(1), 5 (1981).

DeBoer, J. H., *The Dynamical Character of Adsorption*, 2nd ed., Oxford Univ. Press, London (1968).

Doong, S. J., and R. T. Yang, "Bulk Separation of Multicomponent Gas Mixtures by Pressure Swing Adsorption: Pore/Surface Diffusion and Equilibrium Models," *AIChE J.*, **32**(3), 397 (1986).

Dubinin, M. M., "The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Non-uniform Surfaces," *Chem. Rev.*, **60**, 235 (1960).

Fowler, R. H., and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge Univ. Press, Cambridge, England (1939).

Hassan, N. M., T. K. Ghosh, A. L. Hines, and S. K. Loyalka, "An Isotherm Model for Adsorption of Gases and Vapours on Heterogeneous Adsorbents," *Gas Sep. Purif.*, **6**(4), 229 (1992).

Hill, T. L., *Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA (1960).

Hines, A. L., S. L. Kuo, and N. H. Dural, "A New Analytical Isotherm Equation for Adsorption on Heterogeneous Adsorbents," *Sep. Sci. Technol.*, **25**(7), 869 (1990).

Hoory, S. E., and J. M. Prausnitz, "Monolayer Adsorption of F/Gas Mixtures on Homogeneous and Heterogeneous Solids," *Chem. Eng. Sci.*, **22**, 1025 (1967).

Hu, X., and D. D. Do, "Comparing Various Multicomponent Adsorption Equilibrium Models," *AIChE J.*, **41**(6), 1585 (1995).

Huang, C. C., and J. R. Fair, "Study of the Adsorption and Desorption of Multiple Adsorbates in a Fixed Bed," *AIChE J.*, **34**(11), 1861 (1988).

Jaroneic, M., X. C. Lu, and R. Madey, "Use of Polynomial Equation for Analyzing Low Concentration Adsorption Measurements of Ethane on Activated Carbon," *Sep. Sci. Tech.*, **24**(15), 1355 (1990).

Kuro-Oka, M., T. Suzuki, T. Nitta, and T. Katayama, "Adsorption Isotherms of Hydrocarbon and Carbon Dioxide on Activated Carbon," *J. Chem. Eng. Japan*, **17**(6), 588 (1984).

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *J. Chem. Soc.*, **40**, 1361 (1918).

Lewis, W. K., E. R. Gilliland, B. Chertow, and W. P. Cadogen, "Adsorption Equilibria: Hydrocarbon Gas Mixtures," *Ind. Eng. Chem.*, **42**(7), 1326 (1950).

Malek, A., S. Farooq, M. N. Rathor, and K. Hidajat, "Effect of Velocity Variation Due to Adsorption-Desorption on Equilibrium Data from Breakthrough Experiments," *Chem. Eng. Sci.*, **50**, 737 (1995).

Malek, A., and S. Farooq, "Determination of Equilibrium Isotherms Using Dynamic Column Breakthrough and Constant Flow Equilibrium Desorption," *J. Chem. Eng. Data*, **41**, 25 (1996).

Marquardt, D. W., "An Algorithm for Least Squares Estimation of Nonlinear Parameters," *J. Soc. Ind. Appl. Math.*, **11**(2), 431 (1963).

Moon, H., and C. Tien, "Further Work on Multicomponent Adsorption Equilibria Calculations Based on the Ideal Adsorbed Solution Theory," *Ind. Eng. Chem. Res.*, **26**, 2042 (1987).

Mutassim, Z. Z., and J. H. Bowen, "Multicomponent Pressure Swing Adsorption for Non-Isothermal, Non-Equilibrium Conditions," *Trans. Inst. Chem. Eng.* **70**, Part A, 346 (1992).

Myers, A. L., and J. M. Prausnitz, "Thermodynamics of Mixed Gas Adsorption," *AIChE J.*, **11**(1), 121 (1965).

Nitta, T., T. Shigetomi, M. Kuro-Oka, and T. Katayama, "An Adsorption Isotherm of Multi-Site Occupancy Model for Homogeneous Surface," *J. Chem. Eng. Japan*, **17**(1), 39 (1984).

Nitta, T., A. Yamaguchi, N. Tokunaga, and T. Katayama, "A Practical Isotherm Equation for Adsorption on a Heterogeneous Surface and its Applications to Single and Mixed Gas Adsorption on an Activated Carbon Fibre," *J. Chem. Eng. Japan*, **24**(3), 312 (1991).

O'Brien, J. A., and A. L. Myers, "A Comprehensive Technique for Equilibrium Calculations in Adsorbed Mixtures: The Generalized FASTIAS Method," *Ind. Eng. Chem. Process Des. Dev.*, **27**, 2085 (1988).

O'Brien, J. A., and A. L. Myers, "Physical Adsorption of Gases on Heterogeneous Surfaces-Series Expansion of Isotherms Using Central Moments of the Adsorption Energy Distribution," *J. Chem. Soc., Faraday Trans. 1*, **80**, 1467 (1984).

O'Brien, J. A., and A. L. Myers, "Rapid Calculations of Multicomponent Adsorption Equilibria from Pure Isotherm Data," *Ind. Eng. Chem. Process Des. Dev.*, **24**, 1188 (1985).

Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in FORTRAN*, 2nd ed., Cambridge Univ. Press, Cambridge, England (1992).

Reich, R., W. T. Ziegler, and K. A. Rogers, "Adsorption of Methane, Ethane, and Ethylene Gases and Their Binary and Ternary Mixtures and Carbon Dioxide on Activated Carbon at 212-301 K and Pressures to 35 Atmospheres," *Ind. Eng. Chem. Process Des. Dev.*, **19**, 336 (1980).

Richter, E., W. Schultz, and A. L. Myers, "Effect of Adsorption

Equation on Prediction of Multicomponent Adsorption Equilibria by the Ideal Adsorbed Solution Theory," *Chem. Eng. Sci.*, **44**(8), 1609 (1989).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York (1984).

Saunders, J. T., B. M. C. Tsai, and R. T. Yang, "Adsorption of Gases on Coals and Heat-treated Coals at Elevated Temperature and Pressure," *Fuel*, **64**, 621 (1985).

Seidel, A., and P. S. Carl, "The Concentration Dependence of Surface Diffusion for Adsorption on Energetically Heterogeneous Adsorbents," *Chem. Eng. Sci.*, **44**(1), 189 (1989).

Suwanayuen, S., and R. P. Danner, "A Gas Adsorption Isotherm Equation Based on Vacancy Solution Theory," *AIChE J.*, **26**, 68 (1980).

Szepesy, L., and V. Illes, "Adsorption of Gases and Gas Mixtures: I. Measurement of the Adsorption Isotherms of Gases on Activated Carbon up to Pressures of 1000 torr," *Acta Chim. Hung.*, **35**, 37 (1963).

Talu, O., and I. Zweibel, "Multicomponent Adsorption Equilibria of Nonideal Mixtures," *AIChE J.*, **32**(8), 1263 (1986).

Tsai, M. C., S. S. Wang, and R. T. Yang, "Pore-Diffusion Model for Cyclic Separation: Temperature Swing Separation of Hydrogen and Methane at Elevated Pressures," *AIChE J.*, **29**(6), 966 (1983).

Valenzuela, D. P., A. L. Myers, O. Talu, and I. Zweibel, "Adsorption of Gas Mixtures: Effect of Energetic Heterogeneity," *AIChE J.*, **34**(3), 397 (1988).

von Gemmingen, U., "A New Approach to Adsorption Isotherms," *Gas Sep. Purif.*, **7**(3), 175 (1993).

Yang, R. T., and S. J. Doong, "Gas Separation by Pressure Swing Adsorption: A Pore-Diffusion Model for Bulk Separation," *AIChE J.*, **31**(11), 1829 (1985).

Yang, R. T., *Gas Separation by Adsorption Processes*, Butterworths, Boston (1987).

Appendix: Multicomponent Equilibria Calculations using the IAS Theory

The fundamental equations in the IAS theory are:

$$\frac{\Pi A}{RT} = \int_0^{p_i^o} \frac{q_i^*(p_i)}{p_i} dp_i \quad i = 1,2,\ldots,\mathrm{NC} \qquad \text{(A1)}$$

$$Px_i = p_i^o y_i \qquad i = 1,2,\ldots,\mathrm{NC} \qquad \text{(A2)}$$

$$\sum_{i=1}^{\mathrm{NC}} y_i = 1.0 \qquad i = 1,2,\ldots,\mathrm{NC}. \qquad \text{(A3)}$$

In the preceding equations, Π is the spreading pressure while p_i^o are the hypothetical partial pressures of each component that yield the spreading pressure. Equation A1 is the Gibbs adsorption equation. Equations A1 and A3 form a set of (NC + 1) equations in (NC + 1) unknowns, namely the NC p_i^o values and ΠA. These can be solved simultaneously for the unknowns using a nonlinear equation solver, such as the Newton-Raphson method. Here, a quadrature for the Gibbs integral is also required. The final solution in terms of the p_i^o is then used to calculate the amount adsorbed for each component using the following set of equations:

$$q_t = \left(\sum \frac{y_i}{q_i^*(p_i^o)} \right)^{-1} \qquad i = 1,2,\ldots,\mathrm{NC} \qquad \text{(A4)}$$

$$q_i^*(Px_i) = y_i q_t \qquad i = 1,2,\ldots,\mathrm{NC}. \qquad \text{(A5)}$$

In the case of FASTIAS, the two modifications to the algorithm are as follows:

1. No quadrature is required, since the integral can be solved analytically, and
2. ΠA is eliminated from Eq. A1 to give NC − 1 equations. Hence, a set of NC equations (including Eq. A3) are solved for NC unknowns.

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