Sung, C. Y., J. Estrin, and G. R. Youngquist, "Secondary Nucleation of Magnesium Sulfate by Fluid Shear," *AIChE J.*, **19**, 957 (1973).

Van Hook, A., *Principles of Sugar Technology*, Elsevier, Amsterdam (1959).

Wey, J. S., and J. P. Terwilliger, "Effect of Temperature on Suspension Crystallization Processes," *Chem. Eng. Comm.*, **4**, 297 (1980).

Wojciechowski, B., "Structure of Water and Saturated Aqueous Solutions According to Recent Investigations," *Industrial Crystallization '81*, S. J. Jančić and E. J. deJong, Eds., North-Holland Publ. Co., Amsterdam (1982).

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Vacancy Solution Theory of Adsorption Using Flory-Huggins Activity Coefficient Equations

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New equations for the physical adsorption of gases on solids have been developed based on the vacancy solution model of adsorption in conjunction with the Flory-Huggins activity coefficient equations. The isotherm equation contains three regression parameters: a Henry's law constant, the limiting amount of adsorption, and a gas-solid interaction term. Pure-gas data over a range of temperature can be correlated using only five parameters. Gas-mixture equilibria can be predicted using only the parameters obtained from the pure-gas data. Pure-component, binary, and ternary adsorption equilibrium data on activated carbons, silica, and zeolites over a wide range of conditions have been used to evaluate the model. The results show that, except for a few systems, this model predicts gas-mixture equilibria better than any other model.

SCOPE

In order to exploit the physical adsorption of gases in separation processes, quantitative characterization of the multicomponent adsorption equilibria are needed as functions of temperature and pressure. Experimental multicomponent adsorption data are difficult and time-consuming to obtain; therefore, a reliable method of predicting multicomponent equilibria at various temperatures and pressures from pure-component adsorption data, and if necessary binary mixture data, would be preferred. Suwanayuen and Danner (1980a, b) proposed a vacancy solution model using the Wilson model for the activity coefficients. Although this approach has been successful for the prediction of isothermal multicomponent equilibria from single-gas isotherms alone, it fails to explicitly include the effect of temperature. Also, the equations in the Suwanayuen and Danner (S&D) model are complex, and it is often difficult to obtain physically significant parameters from the regression of limited isothermal data sets.

The objective of this work was to develop a new gas adsorption model based on vacancy solution theory which corrects the deficiencies inherent in the S&D model and surpasses it in accuracy. Any new model should account for nonideal behavior in the adsorbed phase including the adsorbate-adsorbate interactions and should predict the temperature dependency of the equilibria as well as the pressure and compositional dependencies. The model should be flexible enough to allow the use of binary data to characterize the adsorbate-adsorbate interactions if such data are available and if such binary parameters are needed. Preferably the model should include a method of estimating these adsorbate-adsorbate parameters, thus eliminating the need for the binary data which are seldom available and difficult to obtain experimentally. The model presented in this paper meets these criteria.

CONCLUSIONS AND SIGNIFICANCE

A new model for pure- and multicomponent gas adsorption is developed based on the vacancy solution theory as presented by Suwanayuen and Danner (1980a, b). Activity coefficients based on a Flory-Huggins type expression have been introduced to account for the nonideality in the adsorbed phase. By regressing five temperature-independent parameters for each component from isotherms at various temperatures, multicomponent adsorption equilibria can be predicted over an extended temperature range. The method incorporates a means of estimating the adsorbate-adsorbate interaction parameters using only pure-gas data. In most cases use of estimated parameters gives binary predictions which are just as good as using parameters extracted from the binary data.

The new Flory-Huggins based, pure-component adsorption model accurately correlated with temperature the adsorption equilibria of H_2, CO, CO_2, and light hydrocarbons on three types

of activated carbon (273.2 to 363.2 K); light hydrocarbons on silica (273.2 to 313.2 K); O_2, N_2, and CO on zeolite 10X (144.3 to 273.2 K); and CO_2, C_2H_4, C_2H_6, and i-C_4H_{10} on zeolite 13X (273.2 to 373.2 K). Using only the parameters regressed from the pure-gas data, binary and ternary adsorption equilibria over a wide range of conditions were predicted with an accuracy which surpasses the accuracy of any of the preceding methods.

INTRODUCTION

Of the various multicomponent gas adsorption models available, Suwanayuen and Danner (1980b) and Kaul (1982) showed that the vacancy solution theory using the Wilson activity coefficient model provides the most accurate predictions of adsorption equilibria. A particularly appealing aspect of the vacancy solution model (VSM) is its ability to predict highly nonideal equilibria, such as adsorption azeotropes. In addition, the model is simple to use, and can be applied to adsorption on any substrate.

The VSM of Suwanayuen and Danner (S&D; 1980a, b) is limited to treating adsorption data isothermally, as opposed to correlating the data with temperature. Furthermore, the parameters extracted from isothermal pure-component adsorption data at various temperatures sometimes exhibit erratic behavior with temperature.

Through repeated use of the VSM of S&D it was discovered that the two pure-component parameters used to describe the nonideality in the adsorbed phase are highly correlated. This indicates that the number of parameters in the model can be reduced without sacrificing accuracy. A reduction in the number of parameters enhances the significance of the parameters that remain.

Another drawback in the VSM of S&D is in the manner of accounting for the interactions between unlike adsorbates during gas-mixture adsorption. Generally, such interactions were assumed to be negligible, although a method of estimating the magnitude of the interactions was presented. Hyun and Danner (1982), studying hydrocarbon-CO_2-zeolite systems, found that estimating these interaction parameters as suggested by S&D gave poorer predictions than assuming that they had their ideal values of unity.

To alleviate the problems described above, a new vacancy solution model has been developed which accounts for the nonidealities in the adsorbed phase using a simpler, yet theoretically based approach. Also, temperature functions have been developed for each parameter in the new model to allow correlation of pure-component adsorption data with temperature and then prediction of pure-component adsorption isotherms and multicomponent adsorption equilibria over an extended temperature range.

VACANCY SOLUTION THEORY

Suwanayuen and Danner (1980a, b) combined the vacancy idea of Bering and Serpinskii (1973, 1974) and Dubinin (1977) with the thermodynamic concepts of Lucassen-Reynders (1972, 1973, 1976) to develop their vacancy solution model. The vacancy is an imaginary entity that is defined as the vacuum space which acts as the solvent for the system. Thus, the VSM treats pure-component adsorption as a phase equilibrium between two binary vacancy solutions of different compositions. By equating the chemical potentials of the adsorbed and gas phases, an equation of state for the adsorbed phase is formed. The chemical potential of the adsorbed phase contains an activity coefficient which accounts for the composition dependence of the nonideality in the adsorbed phase. The equation of state is combined with the Gibbs adsorption equation to derive the adsorption isotherm equation. In a form which is general with respect to the activity coefficient, the isotherm equation is

$$P = \left[\frac{n_1^\infty}{b_1}\frac{\theta}{1-\theta}\right]\left[\exp - \int \frac{d \ln \gamma_v^s}{\theta}\right]\left[\lim_{\theta \to 0} \exp \int \frac{d \ln \gamma_v^s}{\theta}\right] \tag{1}$$

The activity coefficient of the vacancy in the adsorbed phase, γ_v^s, is a function of the composition of the adsorbed vacancy solution. For pure-component adsorption, the composition can be specified either by the mole fractions of the adsorbed vacancy solution, x_1^s and x_v^s, or by the fraction of the limiting amount adsorbed, θ. The two terms are related to each other and to the amount of gas adsorbed, n_1, as follows.

$$x_1^s = \theta = \frac{n_1}{n_1^\infty} \tag{2}$$

$$x_v^s = 1 - \theta = 1 - \frac{n_1}{n_1^\infty} \tag{3}$$

Although Eq. 1 contains θ, the actual experimental variable is the amount of gas adsorbed.

Two important parameters that characterize pure-component adsorption appear in Eq. 1. The Henry's law constant, b_1, relates to the adsorbate-adsorbent interaction at infinite dilution, while the limiting amount adsorbed, n_1^∞, refers to the amount of gas adsorbed at saturation of the adsorbent.

As with pure-component adsorption, the vacancy solution theory treats gas-mixture adsorption as an equilibrium between two vacancy solutions of different compositions. By equating the chemical potentials of an adsorbate in the gas and adsorbed phases, an equation for the distribution of that adsorbate between the two phases can be obtained (See Cochran, 1982). This equation is given below in a form which is general with respect to the activity coefficient.

$$y_i\phi_i P = \gamma_i^s x_i \frac{n_m}{n_m^\infty}\frac{n_i^\infty}{b_i}\left[\lim_{n_m \to 0}\frac{1}{\gamma_i^s}\right]\left[\left(\frac{n_i^\infty - n_m^\infty}{n_m}\right) - 1\right] \ln \gamma_v^s x_v^s \tag{4}$$

The activity coefficient of a component in the adsorbed phase, γ_i^s, during gas-mixture adsorption is a function of the mole fractions of the adsorbed vacancy solution, x_i^s and x_v^s. The experimental mole fraction, x_i, however, is on a vacancy-free basis. The relationships between the two mole fractions are:

$$x_i^s = \frac{n_m x_i}{n_m^\infty} \tag{5}$$

and

$$x_v^s = 1 - \frac{n_m}{n_m^\infty} \tag{6}$$

By specification of the appropriate dividing surface, the limiting amount adsorbed of the gas mixture, n_m^∞, is given by:

$$n_m^\infty = \sum_{i=1}^{i=N} x_i n_i^\infty \tag{7}$$

ADSORBED PHASE NONIDEALITY AND THE NEW VACANCY SOLUTION MODEL

The VSM uses activity coefficients to describe the composition dependence of the nonideal solute-solvent interactions during pure and multicomponent adsorption and solute-solute interactions during multicomponent adsorption. Since the vacancy solvent is an abstract entity, the nonidealities accounted for by the activity coefficients are actually caused by concentration-dependent effects at the gas-solid interface. Such effects include adsorbate-adsorbate and adsorbate-adsorbent interactions. As the concentration of the adsorbed phase increases, the adsorbate molecules are closer together, causing an increase in the adsorbate-adsorbate interactions. As for adsorbate-adsorbent interactions, since highly active adsorption areas are filled in preference to slightly active areas, the heterogeneity of the adsorbent leads to weakened adsorbate-adsorbent interactions as the concentration increases. Effects of the above interactions are implicitly coupled in the values of the activity coefficient.

S&D used the Wilson equation, which has been popular for vapor-liquid equilibria, to describe the nonideality in the adsorbed phase. The Wilson equation contains two parameters, Λ_{1v} and Λ_{v1}, that describe the interaction between an adsorbed molecule and an adsorbed vacancy. In the present study, nonlinear regression of the experimental pure-component adsorption data for numerous systems showed that Λ_{1v} and Λ_{v1} were highly correlated. Furthermore, the product of Λ_{1v} and Λ_{v1} was near unity in many cases. When $\Lambda_{1v}\Lambda_{v1} = 1$, the Wilson activity coefficient model reduces to the Flory-Huggins activity coefficient model.

Flory (1942) and Huggins (1942) originally formulated a model for the excess Gibbs energy of a liquid polymer solution by considering the excess enthalpy to be zero. They considered the excess entropy to arise from a change in configurational states on mixing the polymer and solvent. The expression for the excess configurational entropy and, since the excess enthalpy is assumed to be zero, the excess Gibbs energy derived by Flory and Huggins is:

$$\frac{G^E}{RT} = -x_1^l \ln\left(x_1^l + \frac{v_2^l}{v_1^l}x_2^l\right) - x_2^l \ln\left(\frac{v_1^l}{v_2^l}x_1^l + x_2^l\right) \qquad (8)$$

In the present approach, we may imagine that the excess entropy arises from a change in distinguishable configurational states on mixing adsorbed gas molecules and adsorbed vacancies on the limited area of the adsorbent. This can be visualized as first adding gas molecules one by one to sites on the adsorbent and then adding vacancies to the remaining sites while multiplying together factors representing the different ways in which each successively added species can be accommodated by the adsorbent. Assuming that areas in the two-dimensional adsorption case are analogous to volumes in the Flory-Huggins theory, the excess Gibbs energy for a binary vacancy solution can be written as

$$\frac{G^E}{RT} = -x_1^s \ln\left(x_1^s + \frac{a_v}{a_1}x_v^s\right) - x_v^s \ln\left(\frac{a_1}{a_v}x_1^s + x_v^s\right) \qquad (9)$$

The a_v and a_1 terms in Eq. 9 refer to the molar areas of an adsorbed vacancy and an adsorbed gas molecule. For ideal behavior of the adsorbed phase, $a_1 = a_v$.

To simplify the final isotherm equation, a new parameter is defined.

$$\alpha_{1v} = (a_1/a_v) - 1 \qquad (10)$$

Since both a_1 and a_v must attain positive values, α_{1v} must always be greater than -1. By substituting Eqs. 2, 3, and 10 into Eq. 9, a simple one-parameter equation for the excess Gibbs energy is formed.

$$\frac{G^E}{RT} = \theta \ln(1 + \alpha_{1v}) - \ln(1 + \alpha_{1v}\theta) \qquad (11)$$

The equation for the activity coefficient of the vacancy is found from the usual thermodynamic relation to be:

$$\ln \gamma_v^s = \frac{\alpha_{1v}\theta}{1 + \alpha_{1v}\theta} - \ln(1 + \alpha_{1v}\theta) \qquad (12)$$

By substituting Eq. 12 into Eq. 1, the new adsorption isotherm equation is obtained.

$$P = \left(\frac{n_1^\infty}{b_1}\frac{\theta}{1-\theta}\right) \exp\left(\frac{\alpha_{1v}^2\theta}{1 + \alpha_{1v}\theta}\right) \qquad (13)$$

We shall refer to this model as the Flory-Huggins form of the vacancy solution model (F-H VSM). For ideal behavior of the adsorbed phase, $\alpha_{1v} = 0$. In this case the isotherm equation reduces to the form of the familiar Langmuir equation.

For a multicomponent system the Flory-Huggins activity coefficient of a component has successfully been written in terms of only pairwise interactions. By analogy for multicomponent vacancy solutions we obtain:

$$\ln\gamma_i^s = -\ln \sum_{j=1}^{j=M} \frac{x_j^s}{\alpha_{ij} + 1} + \left[1 - \left(\sum_{j=1}^{j=M} \frac{x_j^s}{\alpha_{ij} + 1}\right)^{-1}\right] \qquad (14)$$

where $\alpha_{ij} = (a_i/a_j) - 1$ and $\alpha_{ii} = 0$
The summations in the above equation are over all components, including the vacancy. Since both a_i and a_j must attain positive values, α_{ij} like α_{1v}, must always be greater than -1. Furthermore, from the definition of α_{ij}, an important property emerges.

$$\alpha_{ij} + 1 = \frac{1}{\alpha_{ji} + 1} \qquad (15)$$

By substituting Eq. 14 into Eq. 4, the equation for the distribution of gas species i between the adsorbed and gas phases is obtained:

$$y_i\phi_iP = \gamma_i^s x_i \frac{n_m}{n_m^\infty}\frac{n_i^\infty}{b_i}\left[\frac{\exp \alpha_{iv}}{1 + \alpha_{iv}}\right]\left[\left(\frac{n_i^\infty - n_m^\infty}{n_m}\right) - 1\right] \ln\gamma_v^s x_v^s \qquad (16)$$

Consider the case of binary mixture adsorption. The three activity coefficient equations resulting from Eq. 14 are:

$$\begin{aligned}\ln\gamma_1^s = {} & -\ln\left(x_1^s + \frac{x_2^s}{1 + \alpha_{12}} + \frac{x_v^s}{1 + \alpha_{1v}}\right) \\ & + \left[1 - \left(x_1^s + \frac{x_2^s}{1 + \alpha_{12}} + \frac{x_v^s}{1 + \alpha_{1v}}\right)^{-1}\right] \qquad (17)\end{aligned}$$

$$\begin{aligned}\ln\gamma_2^s = {} & -\ln\left((1 + \alpha_{12})x_1^s + x_2^s + \frac{x_v^s}{1 + \alpha_{2v}}\right) \\ & + \left[1 - \left((1 + \alpha_{12})x_1^s + x_2^s + \frac{x_v^s}{1 + \alpha_{2v}}\right)^{-1}\right] \qquad (18)\end{aligned}$$

$$\begin{aligned}\ln\gamma_v^s = {} & -\ln\left((1 + \alpha_{1v})x_1^s + (1 + \alpha_{2v})x_2^s + x_v^s\right) \\ & + \left[1 - \left((1 + \alpha_{1v})x_1^s + (1 + \alpha_{2v})x_2^s + x_v^s\right)^{-1}\right] \qquad (19)\end{aligned}$$

All the parameters except the binary parameter α_{12} are obtained from regression of the pure-component adsorption data to fit Eq. 13.

An expression for the binary parameter can be obtained by the elimination of a_v from the two equations that are formed when Eq. 10 is applied to gas species i and j.

$$\frac{\alpha_{iv} + 1}{\alpha_{jv} + 1} = \frac{a_i/a_v}{a_j/a_v} = \frac{a_i}{a_j} \qquad (20)$$

Then by using the definition of α_{ij}

$$\alpha_{ij} = \frac{\alpha_{iv} + 1}{\alpha_{jv} + 1} - 1 \qquad (21)$$

Equation 21 expresses the binary parameter in terms of parameters extracted from pure-component adsorption data. Alternatively, these binary parameters can be extracted from experimental binary adsorption data. Both approaches were taken in this study.

Although the functional relationships presented above were developed by analogy with the Flory-Huggins model as used in vapor-liquid equilibria, one should not infer too much physical significance from the regressed parameters. The F-H model provides useful guidelines and invites cautious interpretation of the regression parameters, but it is not to be expected that these parameters can be calculated a priori from fundamental information or, vice versa, that they should reveal significant information regarding the molecular behavior. Ultimately, the value of the model depends on the utility of the final functional relationships to correlate and predict gas adsorption behavior.

TEMPERATURE DEPENDENCE

It is quite desirable to determine the temperature dependency of the parameters contained in the model. The Henry's law constant, b_1, and the isosteric heat of adsorption at infinite dilution, q_1, are related theoretically by the following expression:

$$b_1 = b_{o1} \exp\left(-\frac{q_1}{RT}\right) \tag{22}$$

The parameter b_{o1} is characteristic only of the adsorbate-adsorbent system and thus is independent of temperature.

For lack of an adequate theory, an empirical equation was used to describe the temperature dependence of n_1^∞

$$n_1^\infty = n_{o1}^\infty \exp\left(\frac{r_1}{T}\right) \tag{23}$$

If n_1^∞ is not a function of temperature, a value of $r_1 = 0$ will be obtained. This result would be anticipated if one envisioned the adsorbed phase as a liquidlike or solidlike packing on the surface. For microporous adsorbents, however, the adsorbed phase might better be pictured as a dense gas filling the pores. In this case one would expect n_1^∞ to be a function of temperature. Frequently, however, data are not available at sufficiently high pressures to approach saturation conditions, especially for supercritical adsorbates. In these cases the temperature dependency of n_1^∞ is not well defined and a value of $r_1 = 0$ results from the regression of the experimental pure-gas data.

The temperature dependence of α_{1v} was also determined empirically. It was observed that there was a direct correspondence in many systems between α_{1v} and n_1^∞ which could be expressed by the following equation.

$$\alpha_{1v} = m_1 n_1^\infty - 1 \tag{24}$$

The constant m_1 is assumed to be independent of temperature. Thus, the temperature dependency of α_{1v} is assumed to follow the temperature dependency of n_1^∞. This approach also implies that a_1/a_v is temperature dependent, which is a deviation from the basic concepts of the F-H model. The assumption of zero excess enthalpy is no longer valid.

There is still the potential issue of the temperature dependence of the adsorbate-adsorbate interaction parameter, α_{12}. As discussed below, however, the use of binary parameters regressed from binary mixture adsorption data did not, in general, increase the accuracy of the equilibria predictions (regressions). Thus, these binary parameters, α_{ij}, are calculated directly from the pure-component α_{iv} parameters and the temperature dependency is transmitted implicitly to α_{ij} via those pure-component parameters.

COMPUTATIONAL METHODS

Two methods of extracting pure-component parameters from experimental pure-gas adsorption data were investigated. The first method, which will be referred to as the isothermal method, was to regress individual isotherms to determine the values of n_1^∞, b_1 and α_{1v} that provide the best fit of Eq. 13 to the data. In this case nine parameters would be necessary to describe three specific isotherms. The second method, which will be called the temperature correlation method, was to regress multiple isotherms simultaneously to determine the values of n_{o1}^∞, r_1, b_{o1}, q_1, and m_1 when Eqs. 22, 23, and 24 were substituted into Eq. 13. In this case, for three isotherms, the five parameters will describe these three specific isotherms as well as any other isotherm in the temperature range. A least-squares fitting procedure utilizing the Marquardt algorithm was used to obtain the values of the pure-component parameters. The optimization program is a procedure in the Statistical Analysis System.

The procedure for calculating the adsorption phase diagrams and the total amount adsorbed, n_m, for multicomponent adsorption from only single-component adsorption data is as follows:

1. If isotherms are given at various temperatures, use the temperature correlation regression method to extract values of b_{o1}, q_1, n_{o1}^∞, r_1, and m_1 from pure-gas data. If the pure-component data are given at only one temperature, use the isothermal regression method to obtain values of b_1, n_1^∞, and α_{1v} from the data.
2. Use Eq. 21 to calculate a value for each of the binary parameters, α_{ij}.
3. Select the composition of the adsorbed phase, x_1.
4. Use Eq. 7 to calculate n_m^∞.
5. Use Eq. 14 for the activity coefficients. There is one activity coefficient for each component in the adsorbed vacancy solution, including the vacancy.
6. Solve the equilibrium equations as expressed by Eq. 16 simultaneously for the gas phase mole fractions, y_i and n_m, using an iterative procedure. One equilibrium equation is formed for each adsorbate. At moderate pressures, the fugacity coefficients can be set equal to 1, and the equilibrium equations can be summed to eliminate y_i, permitting a simpler solution for n_m.
7. Select a different adsorbed phase composition and go to Step 4.

As an alternative to expressing the binary parameters in terms of parameters extracted from the pure-gas data as in Step 2, values for the binary parameters can be regressed from experimental, binary-mixture adsorption data. Regression of a value for α_{12} from binary data was a more time-consuming and difficult task than the regression of the pure-component parameters. Using values of b_1, n_1^∞ and α_{1v} for both components and an initial estimate of α_{12}, predicted values of the gas phase mole fractions and the amount of gas adsorbed were determined from experimental values of the pressure and the adsorbed phase mole fractions using the procedure outlined above. A sum-of-squared deviations between the experimental values and the predicted values of the gas phase mole fraction of one component was computed from which an adjusted value of α_{12} was calculated. The process was repeated until the sum-of-squared deviations became a minimum, thus determining the final value of α_{12}.

EVALUATION

Correlation of Pure-Component Adsorption Equilibria

The F-H VSM was tested on the following pure-gas adsorption data: H_2, CO, CO_2, C_2H_2 and various light paraffins and olefins on three types of activated carbon (Szepesy and Illés, 1963a, b; Wilson and Danner, 1983; Costa et al., 1981); light hydrocarbons on silica (Lewis et al., 1950); O_2, N_2, and CO on zeolite 10X (Danner and Wenzel, 1969; Dorfman and Danner, 1975; Nolan et al., 1981); and C_2H_4, C_2H_6, i-C_4H_{10}, and CO_2 on zeolite 13X (Danner and Choi, 1978; Hyun and Danner, 1982). These data constitute the major portion of all of the pure-component data for which reliable, corresponding gas-mixture data are available. All adsorbents are microporous solids.

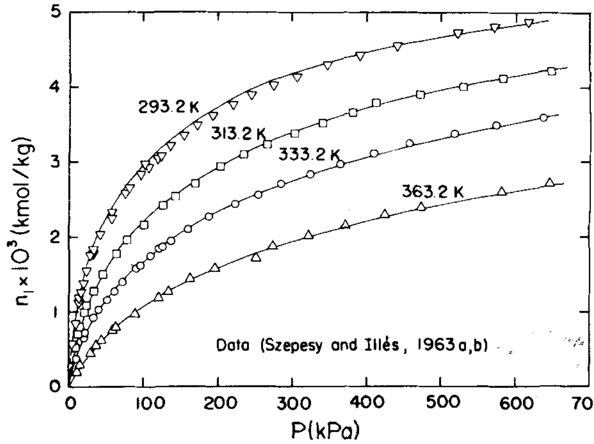

Figure 1. Adsorption isotherm of C_2H_4 on Nuxit-AL activated carbon. (Curves for the F-H VSM isothermal and temperature correlated methods coincide.)

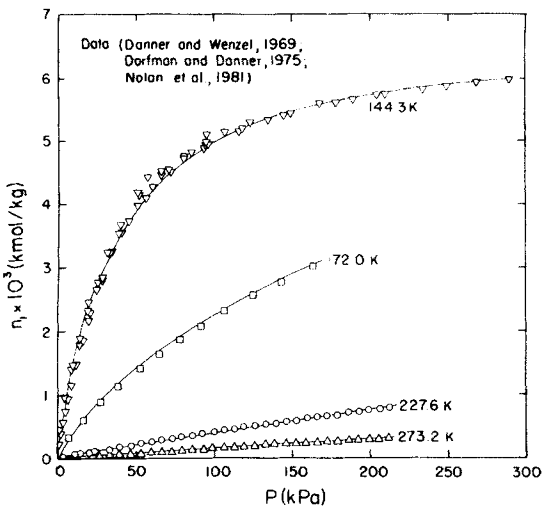

Figure 2. Adsorption isotherms of oxygen on zeolite 10X. (Curves for the F-H VSM isothermal and temperature correlated methods coincide.)

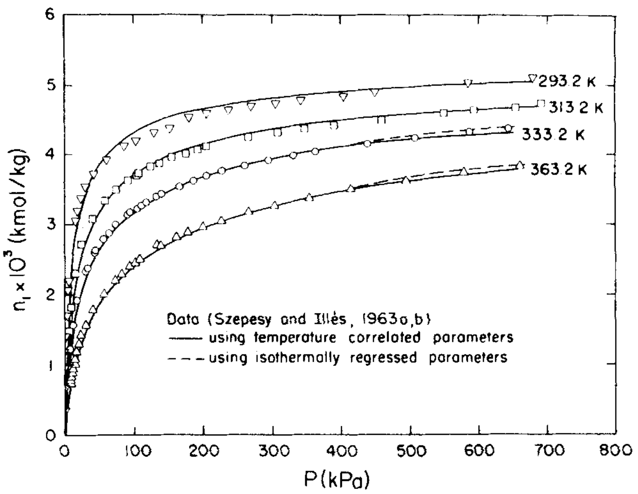

Figure 3. F-H VSM adsorption isotherms of C_3H_8 on Nuxit-AL activated carbon.

Whenever possible, pure-component parameters were regressed using both the isothermal and temperature correlation methods. Since some accuracy must be sacrificed when n_1^∞, b_1, and α_{1v} are forced to follow specified functions of temperature, the regressed isotherms obtained with the isothermal method are the optimal fits of the experimental data.

Typical examples of the fit of the pure-gas model to experimental data are given in Figures 1 through 3. The agreement between the predicted curves obtained with the isothermal and the temperature correlation methods indicates that Eqs. 22, 23, and 24 satisfactorily describe the dependence on temperature of n_1^∞, b_1, and α_{1v}. Furthermore, the close fit of the data illustrates the model's excellent accuracy. A similar degree of accuracy and correlation with temperature was achieved with the other data considered.

The values of n_1^∞, b_1, and α_{1v} regressed for the systems shown in Figures 2 and 3 are listed in Tables 1 and 2. The second set of n_1^∞, b_1, and α_{1v} values were calculated from the temperature independent regression parameters given in Table 3. Although the isothermal and temperature correlation methods produce two different sets of parameters, both sets predict essentially the same curves. Regression on multiple pure-component isotherms simultaneously forces the pure-component parameters obtained using the temperature correlation method to attain more reasonable values by insisting that the parameters not only provide a good fit of the data but also exhibit good temperature behavior. The temperature-independent parameters for all the systems for which three or more pure-component isotherms were available are given in Table 3.

The sensitivity of the regressed pure-component parameters to the pressure range of the experimental data sheds light on the parameter values found in Tables 1 and 2. Data in the pressure range encompassing low fraction of limiting adsorption, i.e., data below the characteristic knee-bend of the curve, contribute to the determination of the Henry's law constant, while data in the pressure range near saturation of the adsorbent, i.e., above the knee-bend, contribute to the determination of the limiting amount adsorbed. The nonideality parameter, α_{1v}, is not specifically related to any pressure region and acts as a secondary parameter.

Consider the results for the data of O_2 adsorbed on zeolite 10X that are given in Figure 2 and Table 1. The erratic temperature behavior of the n_1^∞ values obtained with the isothermal method and the finding of no temperature dependence of n_1^∞ with the temperature correlation method are a consequence of the insufficiency of data in the high pressure region. Except for the isotherm at 144.3 K, there were not enough data approaching saturation of the adsorbent to define values of n_1^∞. Conversely, the prevalence of low pressure data enabled precise values of b_1 to be determined. This is evident from the agreement between the b_1 values obtained with the two different regression methods.

The results for the data of C_3H_8 adsorbed on Nuxit-AL activated carbon (Figure 3, Table 2) illustrate the opposite effect. The large amount of data near saturtion of the adsorbent for all the isotherms enabled a reliable temperature dependence of n_1^∞ to be determined. This is evident by the agreement between the n_1^∞ values obtained with the two different regression methods. However, the lack of a linear portion in the low pressure region caused erratic behavior in the isothermally regressed values of b_1. In this case, the correlation of b_1 with temperature is imperative in assuring that the most accurate and coherent values of b_1 are obtained.

Systems which have very large initial slopes in their isotherms such as those shown in Figure 4 are difficult to analyze correctly. The extremely steep initial slopes cause the Henry's law constants to be very large. Even small deviations between the model and the data at low pressure or small experimental errors in the low pressure data can cause the Henry's law constant to deviate significantly

TABLE 1. PARAMETERS OF THE F-H VSM FOR OXYGEN AND NITROGEN ON ZEOLITE 10X

		Isothermally Regressed Parameters			Values Calculated from the Temperature Independent Regression Parameters		
Adsorbate	Temp. K	$n_1^\infty \times 10^3$ kmol/kg	b_1 kmol/kg·kPa	α_{1v}	$n_1^\infty \times 10^3$ kmol/kg	b_1 kmol/kg·kPa	α_{1v}
Oxygen	144.3	6.68	1.93×10^{-4}	0	7.01	2.24×10^{-4}	0.781
	172.0	19.3	4.16×10^{-5}	2.36	7.01	4.07×10^{-5}	0.781
	227.6	4.98	4.68×10^{-6}	0.581	7.01	4.70×10^{-6}	0.781
	273.2	4.38	1.60×10^{-6}	0	7.01	1.54×10^{-6}	0.781
Nitrogen	144.3	5.38	7.15×10^{-3}	3.72	5.32	5.67×10^{-3}	3.28
	172.0	4.82	5.78×10^{-3}	5.28	5.32	6.85×10^{-4}	3.28
	227.6	7.31	4.64×10^{-5}	3.55	5.32	4.65×10^{-5}	3.28
	273.2	5.53	8.13×10^{-6}	2.65	5.32	1.16×10^{-5}	3.28

TABLE 2. PARAMETERS OF THE F-H VSM FOR PROPANE ON NUXIT-AL ACTIVATED CARBON

Temp.	Isothermally Regressed Parameters			Values Calculated from the Temperature Independent Regression Parameters		
K	$n_1^\infty \times 10^3$ kmol/kg	b_1 kmol/kg·kPa	α_{1v}	$n_1^\infty \times 10^3$ kmol/kg	b_1 kmol/kg·kPa	α_{1v}
293.2	5.22	7.02×10^{-2}	6.65	5.20	1.86×10^{-2}	5.19
313.2	4.94	3.12×10^{-3}	4.03	4.97	7.28×10^{-3}	4.92
333.2	4.72	2.99×10^{-3}	4.49	4.78	3.19×10^{-3}	4.69
363.2	4.40	3.75×10^{-4}	3.06	4.54	1.10×10^{-3}	4.41

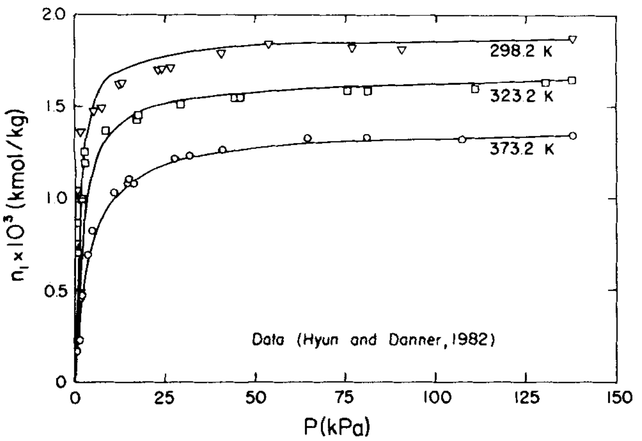

Figure 4. Adsorption isotherms of i-C_4H_{10} on zeolite 13X. (Curves for the F-H VSM isothermal and temperature correlated methods coincide.)

from its true value. Since the prediction of multicomponent equilibria strongly depends on the value of b_1, the equilibria of gas mixtures with components that have isotherms of this type are difficult to predict accurately.

Prediction of Binary Mixture Adsorption Equilibria

The F-H VSM was examined with experimental adsorption data on binary mixtures with the following components: CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, and n-C_4H_{10} on Nuxit-AL activated carbon at 293.2 and 333.2 K and approximately 101.3 kPa (Szepesy and Illés, 1963c); CO, CO_2, and CH_4 on BPL activated carbon at 298.2 K and 344.7 and 689.5 kPa (Wilson and Danner, 1983); CH_4, C_2H_4, C_2H_6, and C_3H_6 on AC-40 activated carbon at 293.7 K and 10 kPa (Costa et al., 1981); C_2H_2, C_2H_4, C_3H_6, and C_3H_8 on silica at 273.2, 298.2, and 313.2 K and 101.3 kPa (Lewis et al., 1950); O_2, N_2, and CO on zeolite 10X at 144.3, 172.0, 227.6 and 273.6 K and 101.3 kPa (Danner and Wenzel, 1969; Nolan et al., 1981); and CO_2, C_2H_4, C_2H_6, and i-C_4H_{10} on zeolite 13X at 298.2, 323.2, and 373.2 K and 138 kPa (Danner and Choi, 1978; Hyun and Danner, 1982). These systems represent essentially all of the types of systems for which reliable gas-mixture adsorption data are available. The F-H pure-component equations correlated the pure-gas data corresponding to these binary mixtures very well.

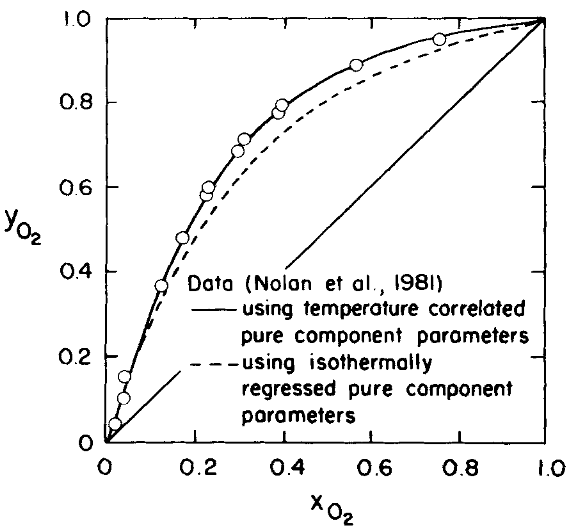

Figure 5. Adsorption phase diagram for O_2-N_2 mixtures on zeolite 10X at 273.2 K and 101.3 kPa as predicted by F-H VSM.

The predicted adsorption phase diagrams obtained using the pure-gas parameters that were extracted via the temperature correlation regression method were significantly more accurate than those obtained using the parameters that were determined with the isothermal method. An illustration of this point is given in Figure 5.

TABLE 3. TEMPERATURE-INDEPENDENT REGRESSION PARAMETERS FOR THE F-H VSM

Adsorbent	Adsorbate	$n_{o1}^\infty \times 10^3$ kmol/kg	r_1 K	$b_{o1} \times 10^9$ kmol/kg·kPa	$-q_1 \times 10^{-7}$ J/kmol	m_1 kg/kmol
Nuxit AL Activated Carbon	CH_4	10.5	0	5.94	1.886	352
	CO_2	12.4	0	2.49	2.426	276
	C_2H_2	11.0	0	2.35	2.762	375
	C_2H_4	5.91	0	4.78	2.646	604
	C_2H_6	5.71	0	5.60	2.707	630
	C_3H_6	2.14	270	2.85	3.759	1,079
	C_3H_8	2.56	208	7.87	3.577	1,191
	n-C_4H_{10}	1.93	217	33.30	3.993	1,886
Silica	C_2H_4	4.58	0	0.561	2.644	703
	C_3H_6	4.61	0	2.16	2.806	768
	C_3H_8	8.98	0	0.917	2.681	435
Zeolite 10X	O_2	7.01	0	5.89	1.265	254
	N_2	5.32	0	11.30	1.575	805
	CO	6.03	0	136.00	1.566	987
Zeolite 13X	C_2H_4	2.91	0	1.25	3.532	1,093
	C_2H_6	2.88	0	1.36	2.775	438
	i-C_4H_{10}	0.408	457	74.30	2.971	2,171
	CO_2	4.35	0	0.913	3.753	929

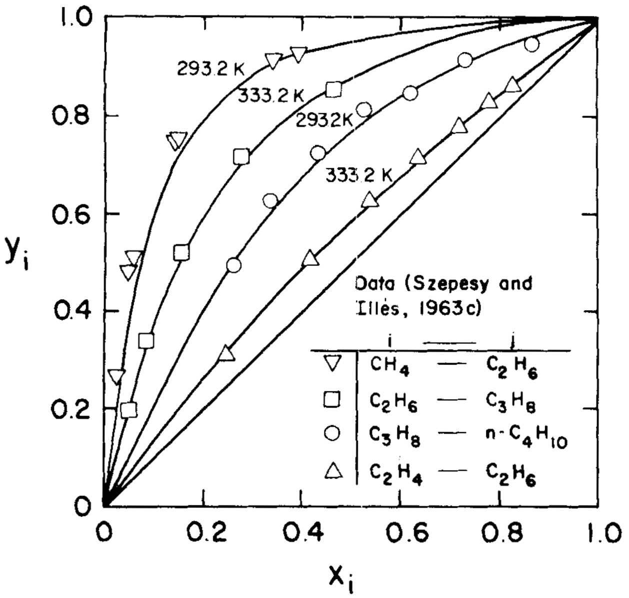

Figure 6. Adsorption phase diagrams for mixtures adsorbed on Nuxit-AL activated carbon at approximately 101.3 kPa as predicted by F-H VSM.

The total amounts adsorbed, however, were predicted equally well with either set of pure-gas parameters. Since the pure-component and gas-mixture adsorption models are consistent, predicted values of the total moles adsorbed vary smoothly between the pure component end points. Since both sets of parameter values produce nearly identical fits of pure-gas data, the total amount adsorbed curves determined with the two sets of parameter values are nearly identical.

All subsequent multicomponent equilibria results presented in this paper use pure-gas parameters determined using temperature correlation. Examples of the prediction of experimental phase diagrams and total amount adsorbed curves are given in Figures 6 and 7, which are typical of the accuracy observed.

Regression of a value for α_{12} from the binary mixture data did not significantly improve the correlation of binary data over the calculation of a value for α_{12} using Eq. 21. For the system shown in Figure 5, no difference in the predicted adsorption phase diagram, which is given by the solid line, was observed with the calculated value of α_{12} of -0.510 and the regressed value of -0.603. The agreement between the calculated and regressed α_{12} values for the other systems examined was similar to that given for this system. The largest deviation was observed with the data for the adsorption of binary mixtures of O_2 and CO on zeolite 10X at 144.3 K and 101.3 kPa. The calculated value of α_{12} for this system was -0.701 while the regressed value was 1.037. The adsorption phase diagram and total amount adsorbed curves are given in Figures 8 and 9, respectively. Even in this most prominent case, differences in the equilibria predictions that were made with the regressed and the calculated values of α_{12} are minor. This indicates that the use of binary data in correlating multicomponent adsorption equilibria with the F-H VSM offers no advantage over the use of only the single-gas data. Furthermore, this suggests that Eq. 21 determines a satisfactory value of the binary parameter.

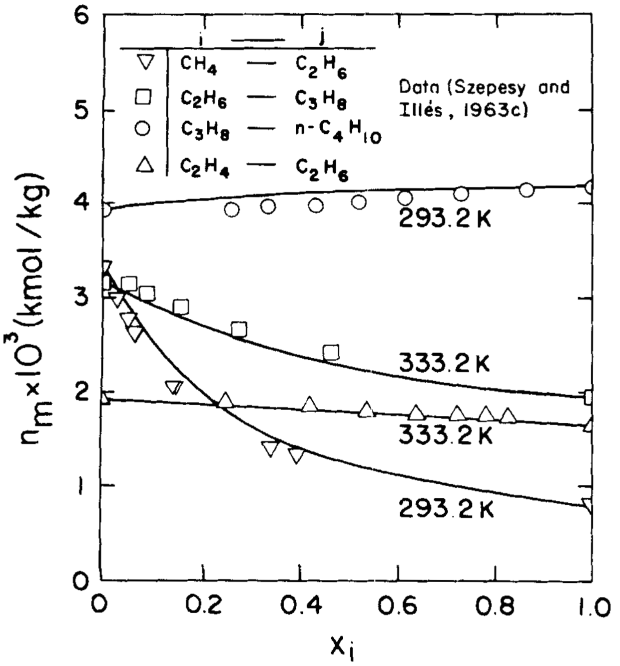

Figure 7. Total amount of mixtures adsorbed on Nuxit-AL activated carbon at approximately 101.3 kPa as predicted by F-H VSM.

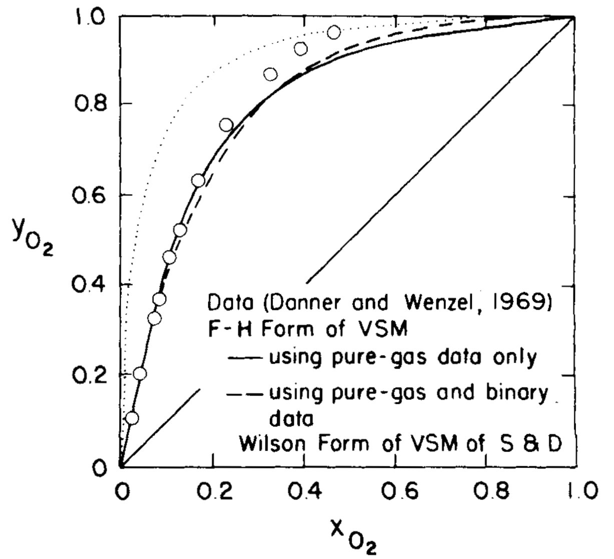

Figure 8. Adsorption phase diagrams for O_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa.

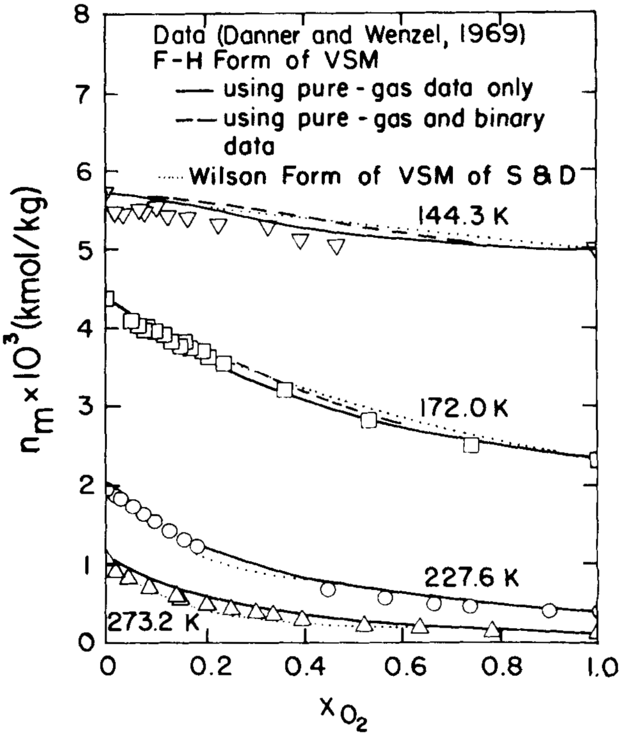

Figure 9. Total Amount of O_2-CO adsorbed on zeolite 10X at 101.3 kPa.

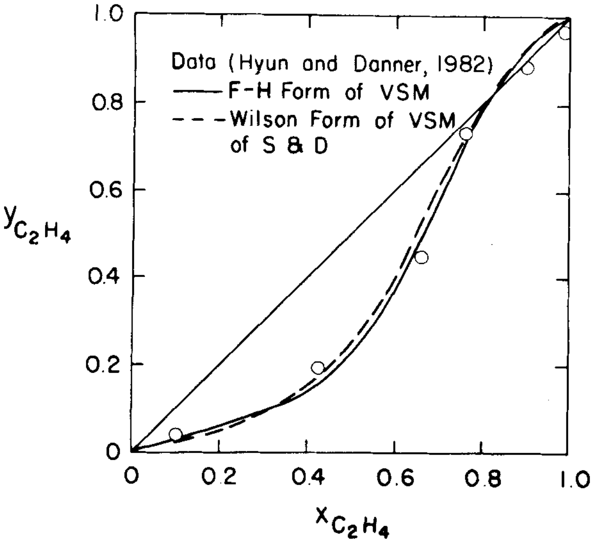

Figure 10. Adsorption phase diagram for i-C_4H_{10}-C_2H_4 Mixtures on zeolite 13X at 373.2 K and 137.8 kPa.

Comparisons between the Wilson form of the VSM of S&D and the F-H form presented in this paper are shown in Figures 8 to 10. Figures 8 and 9 are for the system O_2-CO-zeolite 10X, one of the systems which was most difficult to predict. While there is not much difference in the total volume adsorbed predictions, there is considerable improvement in the adsorption phase equilibrium diagram when the F-H VSM is used. Little difference is evident in the adsorption phase equilibrium diagram for the i-C_4H_{10}-C_2H_4-zeolite 13X system shown in Figure 10. These are only a few of the many systems that have been examined. The conclusion is that when only pure-component data are available, the Flory-Huggins form of the VSM gives significantly better predictions than the Wilson form.

Prediction of Ternary Mixture Adsorption Equilibria

The F-H gas mixture adsorption model was evaluated with the following ternary mixture adsorption data: CH_4-C_2H_4-C_2H_6 and C_2H_4-C_2H_6-C_3H_6 on AC-40 activated carbon at 293.2 K and 13.3 kPa (Costa et al., 1981), CO-CH_4-CO_2 on BPL activated carbon at 298.2 K and 344.7 kPa (Wilson and Danner, 1983), and O_2-N_2-CO on zeolite 10X at 144.3 and 172.0 K and 101.3 kPa (Dorfman and Danner, 1975; Nolan et al., 1981). The model was also tested with data on the adsorption of the quaternary mixture, H_2-CO-CH_4-CO_2, on BPL activated carbon at 298.2 K and 344.7 kPa (Wilson and Danner, 1983). Since hydrogen acts as an inert diluent, however, only three of the components were adsorbed.

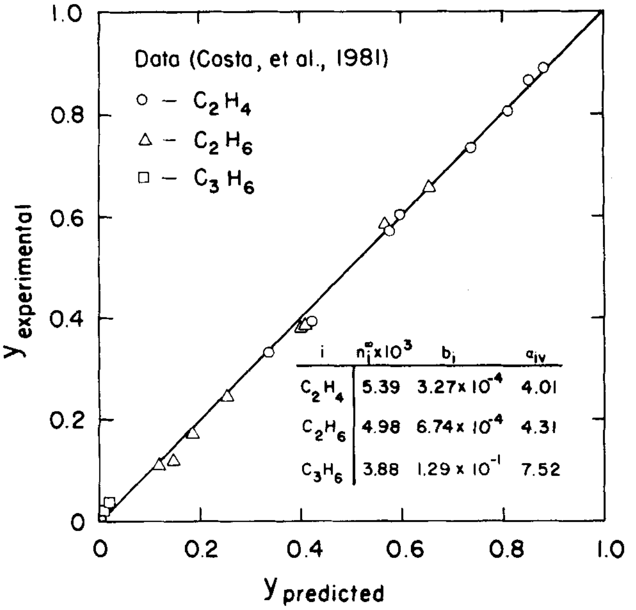

Figure 11. Prediction of gas phase mole fractions for C_2H_4-C_2H_6-C_3H_6 mixtures adsorbed on AC-40 activated carbon at 293.2 K and 13.33 kPa with the F-H VSM.

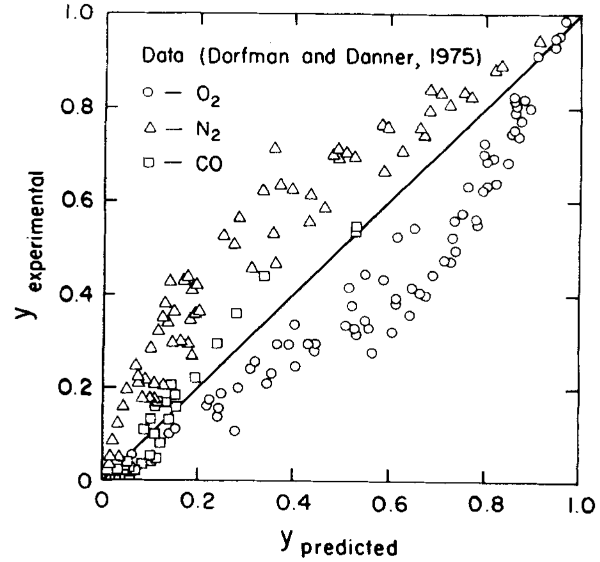

Figure 12. Prediction of gas phase mole fractions for O_2-N_2-CO mixtures adsorbed on Zeolite 10X at 144.3K and 101.3 kPa with the Wilson form of the VSM of S&D.

An example of the prediction of ternary phase equilibria with the F-H VSM from only pure-gas data is given in Figure 11. The accuracy here is excellent. The additional use of binary adsorption data in determining values for the binary parameters, as opposed to calculating those values from the pure-gas parameters with Eq. 21, did not significantly change the adsorption equilibria predictions. As observed with binary data, this suggests that Eq. 21 determines satisfactory values of the binary parameters.

The most poorly predicted set of ternary data was for the O_2-N_2-CO-zeolite 10X system at 144.3 K and 101.3 kPa. The predictions based on the Wilson form of the VSM of S&D are shown in Figure 12 while those obtained with the F-H VSM are shown in

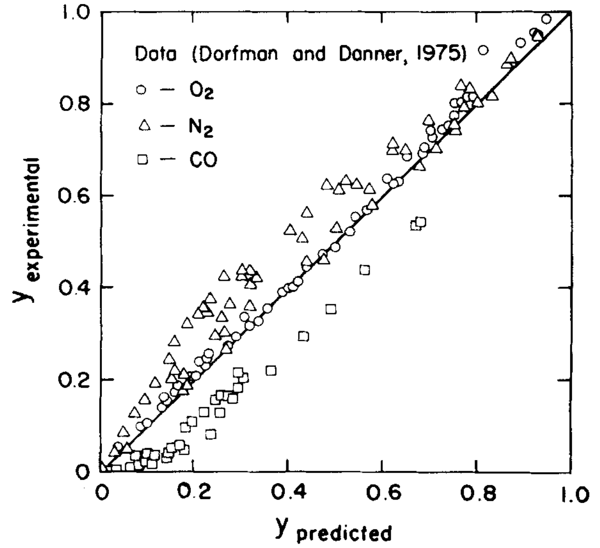

Figure 13. Prediction of gas phase mole fractions for O_2-N_2-CO mixtures adsorbed on zeolite 10X at 144.3 K and 101.3 kPa with the F-H VSM.

Figure 13. Considerable improvement has been obtained using the F-H form, although the accuracy is still not satisfactory in this particular case. The deviations in the total volumes adsorbed are not shown for this case but were relatively good with either VSM form (6.2% average error for the Wilson form, and 4.4% for the F-H form).

SUMMARY

The systems evaluated in this study are typical of the kinds of systems in which physical adsorption might be used for bulk separations—i.e., supercritical or low boiling gases and mixtures of nonpolar fluids. For mixtures of polar-nonpolar fluids or of components having significantly different molecular sizes, the selectivity of adsorption for the polar or larger component is typically very high, making very accurate thermodynamic data predictions unnecessary. Also, regeneration of the adsorbent may be difficult. For higher boiling components, distillation is usually the preferred separation technique. All of these factors explain why there are essentially no adsorption equilibria data for mixtures of these types. Such data would be very useful, however, for testing the limitations of the VSM and extending its range of application.

In summary, it is recommended that when only pure-component adsorption data are available, multicomponent gas adsorption equilibria should be predicted using the F-H form of the VSM. In most practical circumstances this will be the case. Even when binary data are available for all pairs in a system, there is no advantage to using regressed Flory-Huggins binary parameters, α_{ij}. There is the possibility of regressing binary interaction parameters for the Wilson VSM form and using these parameters to predict multicomponent equilibria. This approach has been examined and in some cases proven to be beneficial. Results of this study will be presented in a future paper.

ACKNOWLEDGMENTS

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NOTATION

a_i = molar area of component i, m^2/kmol
b_i = Henry's law constant of compound i, kmol/kg·kPa
b_{oi} = temperature independent constant characterizing each adsorbate-adsorbent system, kmol/kg·kPa
G^E = excess Gibbs free energy, J/kmol
m_i = temperature-independent constant of proportionality, kg/kmol
M = number of components in vacancy solution
n_i = moles of component i adsorbed per mass of adsorbent, kmol/kg
n_m = total moles adsorbed of mixture, kmol/kg
n_i^∞ = limiting amount adsorbed of pure component i, kmol/kg
n_m^∞ = limiting amount adsorbed of mixture, kmol/kg
n_{oi}^∞ = temperature-independent constant characterizing each adsorbate-adsorbent system, kmol/kg
N = number of components
P = equilibrium adsorption pressure, kPa
q_i = isosteric heat of adsorption of component i at infinite dilution, J/kmol
r_i = temperature independent constant characterizing each adsorbate-adsorbent system, K
R = gas constant, J/kmol·K
T = temperature of adsorption system, K
v_i^l = molar liquid volume, m^3/kmol
x_i = mole fraction of component i in adsorbed mixture
x_i^l = liquid phase mole fraction of component i
x_i^s = mole fraction of component i in vacancy solution representing adsorbed phase
y_i = gas phase mole fraction of component i

Greek Letters

α_{ij} = parameter describing nonideality in adsorbed phase induced by interaction between species i and j
γ_i^s = activity coefficient of component i in surface phase
θ = fraction of limiting adsorption
Λ_{ij} = Wilson's parameter for interaction between species i and j
ϕ_i = fugacity coefficient of component i in gas phase

Superscripts

E = excess thermodynamic quantity
l = liquid phase
s = surface or adsorbed phase
∞ = limiting or maximum value

Subscripts

i,j = component, i,j
m = mixture
v = vacancy

LITERATURE CITED

Bering, B. P., and V. V. Serpinskii, "Adsorption-Equilibrium and Thermodynamics of Vacancy Solutions," *Bull. Acad. Sci., USSR, Div. Chem. Sci.* (English Translation) **12**, 2,616 (1973).

——, "The Theory of Adsorption-Equilibrium, Based on Thermodynamics of Vacancy Solutions," *Bull. Acad. Sci., USSR, Div. Chem. Sci.* (English translation) **11**, 2,342 (1974).

Cochran, T. W., "Vacancy Solution Models for Gas Mixture Adsorption," MS Thesis, The Pennsylvania State Univ., University Park, PA (1982).

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**, 5 (1981).

Danner, R. P., and E. C. F. Choi, "Mixture Adsorption Equilibria of Ethane and Ethylene on 13X Molecular Sieves," *Ind. Eng. Chem. Fund.*, **17**, 248 (1978).

Danner, R. P. and L. A. Wenzel, "Adsorption of Carbon Monoxide-Nitrogen, Carbon Monoxide-Oxygen, and Oxygen-Nitrogen Mixtures on Synthetic Zeolites," *AIChE J.*, **15**, 515 (1969).

Dorfman, L. R., and R. P. Danner, "Equilibrium Adsorption of Nitrogen-Oxygen-Carbon Monoxide Mixtures on Molecular Sieve Type 10X," *AIChE Symp. Ser. 152*, **71**, 30 (1975).

Dubinin, M. M., "New Results in Investigations of Equilibria and Kinetics of Adsorption of Gases on Zeolites," 4th Int. Conf. on Molecular Sieves, Univ. Chicago (April, 1977).

Flory, P. J., "Thermodynamics of High Polymer Solutions," *J. Chem. Phys.*, **10**, 51 (1942).

Huggins, M. L., "Some Properties of Solutions of Long-Chain Compounds," *J. Phys. Chem.*, **10**, 151 (1942).

Hyun, S. H., and R. P. Danner, "Equilibrium Adsorption of Ethane, Ethylene, Isobutane, Carbon Dioxide and Their Binary Mixtures on 13X Molecular Sieves," *J. Chem. Eng. Data*, **27**, 196 (1982).

Kaul, B. K., "Correlation and Prediction of Adsorption Isotherm Data for Pure and Mixed Gases," AIChE Annual Meet. Los Angeles (1982).

Lewis, W. K., E. R. Gilliland, B. Chertow, and W. P. Cadogan, "Adsorption Equilibria: Hydrocarbon Gas Mixtures," *Ind. Eng. Chem.*, **42**, 1,319 (1950).

Lucassen-Reynders, E. H., "A Surface Equation of State for Mixed Surfactant Monolayers," *J. Colloid Interface Sci.*, **41**, 156 (1972).

——, "Interactions in Mixed Monolayer I. Assessment of Interaction between Surfactants," *J. Colloid Interface Sci.*, **42**, 554 (1973).

——, "Adsorption of Surfactant Monolayers at Gas/Liquid and Liquid/Liquid Interfaces," *Prog. Surf. Membrane Sci.*, **10**, 253 (1976).

Nolan, J. T., T. W. McKeehan, and R. P. Danner, "Equilibrium Adsorption of Oxygen, Nitrogen, Carbon Monoxide and Their Binary Mixtures on Molecular Sieve Type 10X," *J. Chem. Eng. Data*, **26**, 112 (1981).

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

Suwanayuen, S., and R. P. Danner, "Vacancy Solution Theory of Adsorption from Gas Mixtures," *AIChE J.*, **26**, 76 (1980b).

Szepesy, L. and V. Illés, "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 (1963a).

———, "Adsorption of Gases and Gas Mixtures. II: Measurement of the Adsorption Isotherms of Gases on Activated Carbon under Pressures of 1 to 7 atm.," *Acta. Chim. Hung.*, **35**, 53 (1963b).

———, "Adsorption of Gases and Gas Mixtures. III: Investigation of the Adsorption Equilibria of Binary Gas Mixtures," *Acta. Chim. Hung.*, **35**, 245 (1963c).

Wilson, R. J., and R. P. Danner, "Adsorption of Synthesis Gas-Mixture Components on Activated Carbon," *J. Chem. Eng. Data*, **28**, 14 (1983).

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Longitudinal and Lateral Dispersion in Packed Beds: Effect of Column Length and Particle Size Distribution

Longitudinal and lateral dispersion coefficients were measured at various axial positions in a packed bed in the Peclet number range from 10^2 to 10^4. Three different types of packings were used: uniform size particles, a narrow size distribution, and a wide size distribution. For the case of uniform particles the longitudinal dispersivities were found to be strong functions of position in the bed unless the dispersion length satisfies a constraint dependent on the value of the Peclet number. Generally, the larger the Peclet number, the larger the required length for constant axial dispersivities to be achieved. For the case of the wide size distribution, longitudinal dispersivities were larger than in the uniform particle case, and they required a longer dispersion length to achieve a constant value. This suggests a characteristic length for dispersion larger than the mean hydraulic radius. The lateral dispersivities were found to be insensitive to the distribution of particle sizes or location in the bed.

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SCOPE

The dispersion equation is used to calculate the average concentration of a solute in a porous medium under flow conditions (Bear, 1972; Dullien, 1979). The dispersive term accounts for the spread of the solute about the mean pulse position due to molecular diffusion and the coupling of interparticle velocity and concentration gradients (Whitaker, 1967; Gray, 1975). It consists of the double scalar product of a dispersion tensor, or total dispersivity tensor (Brenner, 1980) with the second derivative of the average solute concentration in the porous medium. For the case of an isotropic porous medium, the total dispersivity tensor has non-zero components only along the diagonal. The diagonal element corresponding to the mean direction of flow is called the longitudinal dispersion coefficient and it contributes to the spread of solute pulses along the flow direction. The other on-diagonal elements are called the lateral dispersion coefficients and they contribute to the spread of the solute in the directions orthogonal to the mean flow.

There have been many experimental measurements of the longitudinal dispersion coefficient in packed beds and its dependence on the Peclet number (Harleman and Rumer, 1963; Edwards and Richardson, 1968; Rifai et al., 1956; Carberry and Bretton, 1958; Ebach and White, 1958; Pfannkuch, 1963; Blackwell et al., 1959; Gunn and Pryce, 1969). The Peclet number dependence of the lateral dispersion coefficient has not been measured as extensively but there are some data at low Peclet numbers (Harleman and Rumer, 1963; Gunn and Pryce, 1969; Grane and Gardner, 1961; Hassinger and von Rosenberg, 1968; Blackwell, 1962). Implicit in these studies is the assumption that the dispersion coefficients are constants that depend on the value of the Reynolds and Schmidt numbers only, and are independent of position in the packed bed or porous medium. However, G. I. Taylor (1953, 1954) in his original work on dispersion in capillary tubes was very careful to point out that dispersion models become valid only after a sufficiently long time has passed since the insertion of the solute pulse. How long this time is in a particular experiment was shown to depend on the value of the molecular diffusivity, the tube radius, and the average fluid velocity. More recently, Brenner (1980) showed that dispersion models are valid asymptotically in time for the case of dispersion in spatially periodic porous media, while

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