The Vacancy Solution Model of Adsorption—Improvements and Recommendations

The vacancy solution model of adsorption which uses an activity coefficient equation of the Wilson form has been improved (1) by incorporating temperature dependency into the model, and (2) by development of a functional relationship between the adsorbate-adsorbate binary interaction parameters. This reduces the number of regression parameters and improves the predictive capabilities of the model. Comparisons of this improved model with the Flory-Huggins activity coefficient form of the vacancy solution model are presented for binary and ternary systems. For a priori predictions from pure-component data, the Flory-Huggins form is recommended. If experimental binary data are available for all pairs, the form that most accurately correlates the binary data should be used to predict higher-order systems.

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SCOPE

The vacancy solution model (VSM) of adsorption has been nurtured with one primary objective in mind: to facilitate the prediction of multicomponent adsorption equilibria from pure-component data. Because of the difficulty of obtaining gas-mixture adsorption data experimentally, a predictive scheme is needed. To be useful, the procedure must include a method of interpolating and extrapolating to different temperatures and pressures. If, on the other hand, binary adsorption data are available, it is important to use this information as effectively as possible when predicting multicomponent systems.

Suwanayuen and Danner (1980a,b) presented a form of the VSM based on the Wilson activity coefficient equation, incorporating no temperature dependency and having two independent adsorbate-adsorbate interaction parameters. Cochran et al. (1985) introduced the Flory-Huggins activity coefficient into the VSM, incorporated temperature dependency, and reduced the number of binary interaction parameters. They were able to predict gas-mixture adsorption equilibria quite well for many systems using only pure-gas data. However, a number of systems involving zeolites led to less than satisfactory results. Furthermore, no significant improvements were attained by regressing a binary interaction parameter from the binary adsorption data.

In an attempt to improve the predictions for zeolite systems, temperature dependence has been introduced into the Wilson form of the VSM and the number of binary regression parameters has been reduced. This modified Wilson form and the Flory-Huggins form of the VSM are examined in terms of their abilities to correlate or predict binary and ternary equilibria with and without parameters extracted from the binary data.

CONCLUSIONS AND SIGNIFICANCE

Temperature dependency has been introduced into the Wilson form of the vacancy solution model. This allows pure-component isotherms to be predicted at temperatures where no data are available, and gas-mixture adsorption equilibria to be predicted within this expanded temperature range. A relationship between the two adsorbate-adsorbate binary interaction parameters has been developed. Thus the number of regression parameters that must be determined is decreased with no reduction in the accuracy of the method.

When pure-component isotherms are available at a number of temperatures, the temperature-dependent model should be used in preference to the isothermal model. In this way the regressed parameters attain more reasonable values. If only pure-component data are available, the Flory-Huggins form of the vacancy solution model should be used to predict gas-mixture adsorption equilibria. If binary data are also available, predictions of the binary equilibria using only the pure-gas data with the Flory-Huggins form should be compared to the data. If these predictions are accurate, the Flory-Huggins form should be used to predict multicomponent equilibria using only the parameters extracted from the pure-component data. If the predictions are inaccurate, the Wilson form with

one binary interaction parameter regressed for each set of binary data should be evaluated against the experimental data. If it correlates the binary data better than the Flory-Huggins form, then the Wilson form should be used. By following this protocol one can expect reasonable prediction of multicomponent adsorption equilibria in the most efficient manner.

INTRODUCTION

Suwanayuen and Danner (1980a,b) presented a vacancy solution model (VSM) based on a formulation using the Wilson equation for the activity coefficients in the vacancy solutions. They showed that parameters regressed from the pure-component isotherms can be used to predict the adsorption equilibria of multicomponent systems at the same temperature as the isotherms. The lack of an explicit temperature dependency is a definite disadvantage of their method. In this paper, the desired temperature dependency is introduced.

In the work of Suwanayuen and Danner the interactions between unlike adsorbates were either neglected or were estimated using the isosteric heat of adsorption at infinite dilution and the coordination number of the molecule in the adsorbed phase. Hyun and Danner (1982) found that this method of estimation gave poorer quantitative agreement with the data than using the ideal values of unity. No satisfactory, a priori method of calculating these interaction parameters has been found. Kaul (1984) showed that excellent binary correlations and ternary predictions can be obtained for O_2-N_2-CO-zeolite 10X systems if two Wilson binary interaction parameters are regressed for each binary pair. As discussed below, we have determined a functional relationship between the two Wilson binary interaction parameters, which means that only one binary parameter needs to be regressed from the available binary data.

Cochran et al. (1985) presented a VSM using activity coefficient equations of the Flory-Huggins type. (See erratum on p. 2082 of this issue.) They found that their approach was superior to using the isothermal Wilson form as originally given by Suwanayuen and Danner. To complete the picture, the Flory-Huggins form must be compared with the improved Wilson formulation presented below.

TEMPERATURE DEPENDENCE IN WILSON VSM

The pure-component isotherm equation for the Wilson form of the VSM as presented by Suwanayuen and Danner (1980a) contains a Henry's law constant, b_1, the limiting amount adsorbed, n_1^∞, and two Wilson interaction parameters, Λ_{1v} and Λ_{v1}

$$P = \left[\frac{n_1^\infty}{b_1}\frac{\theta}{1-\theta}\right]\left[\Lambda_{1v}\cdot\frac{1-(1-\Lambda_{v1})\theta}{\Lambda_{1v}+(1-\Lambda_{1v})\theta}\right] \cdot \exp\left[-\frac{\Lambda_{v1}(1-\Lambda_{v1})\theta}{1-(1-\Lambda_{v1})\theta}-\frac{(1-\Lambda_{1v})\theta}{\Lambda_{1v}+(1-\Lambda_{1v})\theta}\right] \quad (1)$$

The fraction of limiting adsorption, θ, is the ratio of the amount adsorbed, n_1, and the limiting amount of adsorption, n_1^∞,

$$\theta = \frac{n_1}{n_1^\infty} \quad (2)$$

To enable correlation of a body of pure gas adsorption data at various temperatures, each of the parameters in Eq. 1 must be related to temperature by an appropriate function. The Henry's law constant (specifically dn_1/dP at the origin), which accounts for the adsorbate-adsorbent interactions at infinite dilution, is theoretically related to the isosteric heat of adsorption at infinite dilution, q_1.

$$b_1 = b_{o1}\exp\left(-\frac{q_1}{RT}\right) \quad (3)$$

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

No such theoretical relationship is available for the temperature dependence of the limiting amount of adsorption. Instead an empirical equation of the same form as Eq. 3 was found to be quite useful.

$$n_1^\infty = n_{o1}^\infty\exp\left(\frac{r_1}{T}\right) \quad (4)$$

TABLE 1. PURE-COMPONENT REGRESSION PARAMETERS FOR THE TEMPERATURE-CORRELATED, WILSON FORM OF THE VSM

Adsorbent	Adsorbate	Temp. K	$n_{o1}^\infty \times 10^3$ kmol/kg	r_1 K	b_{o1} kmol/kg · kPa	$-q_1/R$ K	a_v/a_1	$\frac{\lambda_{11}-\lambda_{v1}}{R}$ K	$\frac{\lambda_{vv}-\lambda_{v1}}{R}$ K
Zeolite 10X	O_2	144.3, 172.0,							
$A = 672\ m^2/g$		227.6, 273.2	6.94	0	6.36×10^{-9}	1,507	0.353	70.95	−73.08
	N_2	144.3, 172.0,							
		227.6, 273.2	5.52	0	3.32×10^{-9}	2,160	0.363	162.8	27.64
	CO	144.3, 172.0,							
		227.6, 273.2	7.78	0	4.70×10^{-7}	1,498	0.0598	865.3	−327.2
Zeolite 13X	C_2H_4	298.2, 323.2,							
$A = 420\ m^2/g$		373.2	3.11	0	1.26×10^{-9}	4,138	0.0796	1013	−741.4
$Vp = 0.29\ cm^3/g$	C_2H_6	273.2, 298.2,							
		323.2, 373.2	2.82	0	2.53×10^{-9}	3,036	0.224	52.60	−249.8
	i-C_4H_{10}	298.2, 323.2,							
		373.2	0.212	705.8	1.31×10^{-8}	3,982	9.09×10^{-5}	3960	$-\infty$
	CO_2	298.2, 323.2	4.47	0	2.02×10^{-13}	7,112	12.1	−933.3	1,130

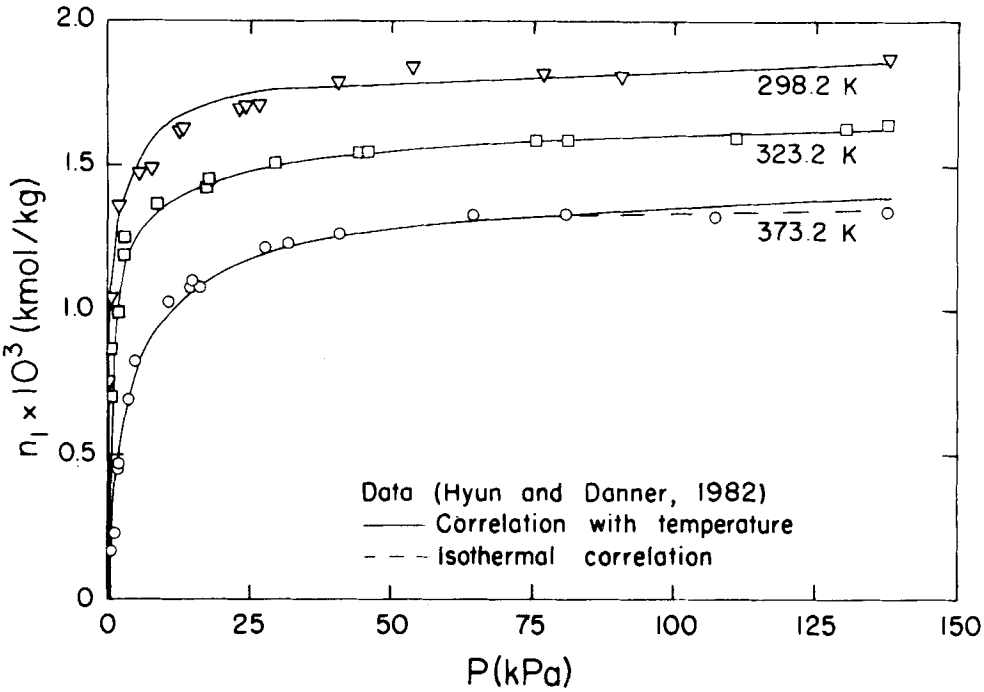

Figure 1. Isotherms for i-C_4H_{10} on zeolite 13X; predictions using Wilson form of VSM.

The original application of the Wilson equation for activity coefficients was in the area of vapor-liquid equilibria where the Wilson parameters were defined as (Prausnitz, 1969):

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp -\left(\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{5}$$

Here V_i is the molar liquid volume of species i, and λ_{ij} represents the potential energy of interaction between species i and j. Note that Λ_{ij} is not equal to Λ_{ji}, which can be obtained from Eq. 5 with all i and j interchanged. For gas adsorption the two-dimensional analog of Eq. 5 is:

$$\Lambda_{ij} = \frac{a_j}{a_i} \exp -\left(\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{6}$$

Here a_i refers to the molar area of an adsorbed gas or vacancy. For a pure-component isotherm the temperature dependence of Λ_{1v} should be able to be expressed in terms of two constant values, (a_v/a_1) and $(\lambda_{1v} - \lambda_{11})$, while Λ_{v1} is given in terms of $[1/(a_v/a_1)]$ and $(\lambda_{v1} - \lambda_{vv})$. Thus, to correlate pure-component adsorption data with temperature, values for seven temperature-independent constants—b_{o1}, q_1, n_{o1}^{∞}, r_1, (a_v/a_1), $(\lambda_{1v} - \lambda_{11})$, and $(\lambda_{v1} - \lambda_{vv})$—are regressed from pure-gas adsorption data using Eqs. 1-4 and 6.

The above correlation scheme was tested with data for O_2, N_2, and CO adsorbed on zeolite 10X at 144.3, 172.0, 227.6, and 273.2 K (Danner and Wenzel, 1969; Dorfman and Danner, 1975; Nolan et al., 1981) and with the data for C_2H_4, C_2H_6, i-C_4H_{10}, and CO_2 adsorbed on zeolite 13X at 273.2, 298.2, 323.2, and 373.2 K (Danner and Choi, 1978; Hyun and Danner, 1982). The regression parameters are given in Table 1. The behaviors of n_{o1}^{∞}, b_{o1}, $-q_1/R$ appear to be quite reasonable. Most systems are far removed from their saturation pressure; therefore, the temperature dependency of n_1^{∞}, cannot be ascertained (i.e., the regressed value of r_1 was zero). For the case of isobutane on zeolite 10X, however, the isotherms have essentially reached saturation as shown in Figure 1, and a nonzero value of r_1 was obtained. Estimates of n_1^{∞} may be obtained by assuming that the pores of the adsorbent are filled with adsorbate liquid. This concept breaks down, however, above the critical point. Even for subcritical temperatures it is insufficiently accurate to provide more than an estimate.

Because most practical gas-mixture adsorption applications occur at coverages considerably below saturation, the Henry's law constant is much more important in the mixture predictions than the limiting amount of adsorption. Thus, the lack of accurate definition of the temperature dependency of n_1^{∞} is often not of much concern. The interaction parameters a_v/a_1, $(\lambda_{1v} - \lambda_{11})/R$, and $(\lambda_{v1} - \lambda_{vv})/R$ are not as statistically significant as the other parameters; thus, they tend to fluctuate more erratically. They may in fact take on physically unrealistic values. This is a reminder that one should not try to infer too much physical significance from parameters of a model that involves numerous simplifying assumptions and regression parameters. The value of the model depends not on the theoretical significance of the parameters but on the ability of the resulting functional relationship to describe the phenomena of interest. A complete analysis of parametric sensitivity is available from Cochran (1982).

The isotherms for isobutane on zeolite 13X and for carbon monoxide on zeolite 10X shown in Figures 1 and 2 are typical examples of the correlations obtained. The temperature-correlated parameters usually represented the isotherms as well as did the specific isotherm parameters. Thus, it was concluded that the temperature functions selected for the pure-component parameters are quite satisfactory.

Using data at multiple temperatures simultaneously insures that the parameters behave more reasonably with temperature than those obtained from fitting several individual isotherms. These temperature-correlated parameters have been found to be more accurate for predicting multicomponent equilibria. A good example of this is shown in Figure 3 for the case of ethane-isobutane mixtures adsorbed on zeolite 13X. The solid line, which was obtained from parameters calculated from the temperature functions (i.e., Eqs. 3, 4, and 6, represents the binary data much better than the dashed line, which is based on parameters regressed using only the data for the two pure components at 298.2 K. No results are shown for the total moles adsorbed (n_T) as a

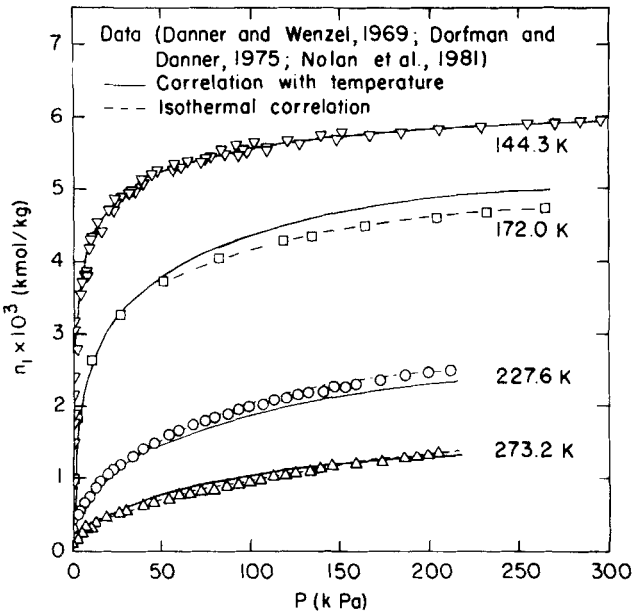

Figure 2. Isotherms for CO on zeolite 10X; predictions using Wilson form of VSM.

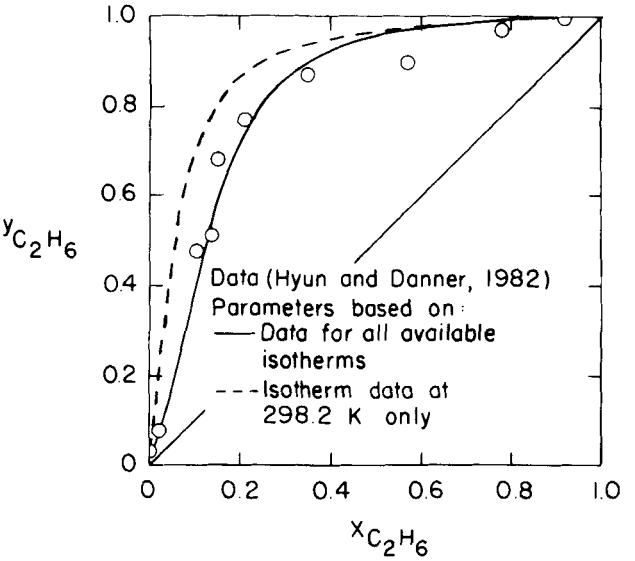

Figure 3. Adsorption phase diagram for C_2H_6–*i*-C_4H_{10} mixtures on zeolite 13X at 298.2 K and 137.8 kPa; predictions using Wilson form of VSM.

function of composition (x_i) because this criterion is not a good method of discriminating between the two cases. Since in each case the parameters correlate the pure-component isotherms well, n_T at the end points (x_i = 0,1) is predicted accurately. The variation of n_T with x_i is not a complex function and there is no significant difference between the predictions of n_T.

BINARY INTERACTION PARAMETERS IN WILSON VSM

For a multicomponent system, the Wilson activity coefficient equations contain two binary interaction parameters for each pair of species, Λ_{ij} and Λ_{ji}. In the vacancy solution model these parameters for the vacancy-adsorbate pairs are determined from the regression of the pure-component data as described in the previous section. For gas-mixtures, however, there is also a pair of these interaction parameters for every adsorbate-adsorbate pair. If the interactions between different adsorbed species are considered negligible when compared to interactions between the adsorbate and adsorbent, these interaction parameters can be set equal to unity. If binary adsorption equilibria data are available, one would prefer to make use of this information optimally when predicting equilibria for higher-order systems involving these same pairs. In the Wilson form of the VSM this suggests that two absorbate-adsorbate interaction parameters should be regressed from each binary set of data. Kaul (1984) showed this approach could be quite successful in some cases. When we used this approach, we found that in many cases there was a strong inverse correlation between the two parameters. This caused an instability in the regression procedure and in many cases the algorithm failed to converge. While this may have been caused in part by inefficient programming, the algorithm used was reasonably sophisticated and had been successful for the other applications in this work. Thus, we looked for a theoretical relationship between the interaction parameters.

Combining the equations that are formed by applying Eq. 6 to Λ_{1v} and Λ_{v1}, one obtains:

$$\frac{\Lambda_{1v}}{\Lambda_{v1}} = \left(\frac{a_v}{a_1}\right)^2 \exp\left(\frac{\lambda_{11} - \lambda_{vv}}{RT}\right) \tag{7}$$

Applying the same reasoning to the pairs Λ_{2v}:Λ_{v2} and Λ_{12}:Λ_{21}, and then combining the results, an equation is obtained that relates the ratio of the adsorbate-adsorbate binary interaction parameters to the Wilson parameters that are regressed from the pure-component data.

$$\frac{\Lambda_{12}}{\Lambda_{21}} = \frac{\Lambda_{1v}\Lambda_{v2}}{\Lambda_{v1}\Lambda_{2v}} \tag{8}$$

Since the righthand side of Eq. 8 is determined strictly from the pure-component parameters, a direct relationship exists between the binary parameters and only one of them needs to be regressed from the binary data. As shown in the next section, this not only alleviates the convergence problem, but also results in a model which is more self-consistent.

EVALUATION OF MODIFIED WILSON VSM

Binary parameters were regressed from the experimental data for the binary mixtures of O_2, N_2, and CO adsorbed on zeolite 10X at 144.3, 172.0, 227.3, and 273.2 K (Danner and Wenzel, 1969; Dorfman and Danner, 1975; Nolan et al., 1981), for C_2H_6–*i*-C_4H_{10}, C_2H_4-CO_2, and C_2H_6-C_2H_4 mixtures adsorbed on zeolite 13X at 298.2 and 323.2 K (Danner and Choi, 1978; Hyun and Danner, 1982), and for i-C_4H_{10}–C_2H_4 mixtures adsorbed on zeolite 13X at 298.2, 323.2, and 373.2 K (Hyun and Danner, 1982). Attempts were made to regress isothermal values for both Λ_{12} and Λ_{21} directly. Convergence problems were encountered in over 60% of the cases studied. The results obtained for the O_2-N_2-CO-zeolite 10X systems are shown in Table 2. On the other hand, when one of the independent interaction parameters was eliminated by the use of Eq. 8, and only one binary parameter was determined by regression, all calculations converged easily. In the cases where both procedures converged, the two sets of isothermal values of the binary interaction parameters were usually reasonably close to each other. This lends credence to the use of Eq. 8 to eliminate one of the parameters when carrying out the regression. More important, perhaps, the correlations of the binary mixture data obtained in the two cases were

TABLE 2. REGRESSED BINARY INTERACTION PARAMETERS FOR THE WILSON FORM OF THE VSM—BINARY MIXTURES ON ZEOLITE 10X AT 1,013 kPa

Adsorbates	Temp. (K)	Regression of Both Binary Parameters		Regression of Only One Binary Parameter			
				Isothermal		Temperature-Correlated	
		Λ_{12}	Λ_{21}	Λ_{12}	Λ_{21}*	Λ_{12}**	Λ_{21}*
O_2-N_2	144.3	1.042	1.375	1.194	1.199	1.149	1.154
	172.0	0.586	1.721	1.036	1.051	0.993	1.008
	227.6	†	†	0.616	0.632	0.826	0.848
	273.2	0.808	1.139	0.929	0.962	0.750	0.777
O_2-CO	144.3	0.635	18.350	0.494	20.367	0.460	18.960
	172.0	0.545	13.970	0.868	11.075	0.907	11.569
	227.6	0.129	12.360	1.762	5.071	2.146	6.176
	273.2	3.541	6.089	3.957	5.295	3.348	4.480
N_2-CO	144.3	†	†	0.000	0.000	0.021	0.854
	172.0	†	†	0.112	1.413	0.092	1.162
	227.6	†	†	0.345	0.968	0.613	1.718
	273.2	3.027	1.962	2.378	3.073	1.629	2.105

* Calculated from Λ_{12} and Eq. 8.
** By correlation of isothermal values with $\log \Lambda_{12} = A + (B/T)$.
† No convergence obtained.

identical. Thus, there is no reason to attempt to regress values for both binary parameters.

To make optimal use of the binary data we wish to have the binary parameters not on an isothermal basis, but as functions of temperature. One approach to this would have been to substitute Eq. 6 for Λ_{12} and regress for (a_1/a_2) and $(\lambda_{12} - \lambda_{11})$ and then use Eq. 8 to calculate Λ_{21}. In this approach, however, one is again trying to regress two parameters from the binary data and serious computational problems result. To avoid this problem the isothermally determined values of Λ_{12} were correlated with temperature through linear regression of the logarithm of Λ_{12} as a function of the inverse of temperature. Then the corresponding values of Λ_{21} were calculated from Eq. 8. These temperature correlated values are given in Tables 2 and 3. In the cases where only two temperatures are available, the temperature-correlated values are constrained to be equal to the isothermal values; therefore, they are not listed in the tables. The correlations of the binary mixture data (i.e., phase compositions and total moles adsorbed) obtained with the temperature-correlated parameters were identical to those made with the isothermal binary parameters. Note that according to Eq. 1 the ideal case is described by the Langmuir equation form, i.e., when $\Lambda_{1v} = \Lambda_{v1} = 1$. The values given in Tables 2 and 3 indicate significant deviations from this ideal situation. The zero values for Λ_{12} and Λ_{21} in Table 3 result from $\Lambda_{v1} = 0$ for i-C_4H_{10}.

TABLE 3. REGRESSED BINARY PARAMETERS FOR THE WILSON FORM OF THE VSM—BINARY MIXTURES ON ZEOLITE 13X AT 137.8 kPa

Adsorbates	Temp. K	Regression of Only One Binary Parameter†			
		Isothermal		Temperature-Correlated	
		Λ_{12}	Λ_{21}*	Λ_{12}**	Λ_{21}*
i-C_4H_{10}–C_2H_4	298.2	2.860	0.000	2.960	0.000
	323.2	2.043	0.000	1.932	0.000
	373.2	0.956	0.000	0.977	0.000
C_2H_6–*i*-C_4H_{10}	298.2	0.000	16.650	‡	‡
	323.2	0.000	4.946	‡	‡
C_2H_4–CO_2	298.2	3.400	0.217	‡	‡
	323.2	2.650	0.454	‡	‡
C_2H_6–C_2H_4	298.2	0.189	3.120	‡	‡
	323.2	0.259	2.930	‡	‡

* Calculated from Λ_{12} and Eq. 8.
** By correlation of isothermal values with $\log \Lambda_{12} = A + (B/T)$.
† Lack of convergence prevented simultaneous regression for both binary parameters in all cases.
‡ Temperature-correlated values are constrained to be the same as the isothermal values when only two temperatures are available.

An example of the effect of using binary interaction parameters in the Wilson form of the VSM is shown in Figure 4, the adsorption phase diagram for O_2-CO on zeolite 10X at 144.3 K and 101.3 kPa. Here the temperature-correlated values determined by regression for a single binary parameter were used (0.460 and 18.960 in Table 2). The improvement over the Wilson form using only the pure-component data is significant. No significant differences were observed in the analysis of the total moles adsorbed.

If binary data are available for the determination of the adsorbate-adsorbate interaction parameters, the hope is that the use of these data will improve multicomponent predictions. Unfortunately, there are few data sets available containing more than two adsorbing components. Dorfman and Danner (1975) have published data for the adsorption of ternary mixtures of O_2, N_2, and

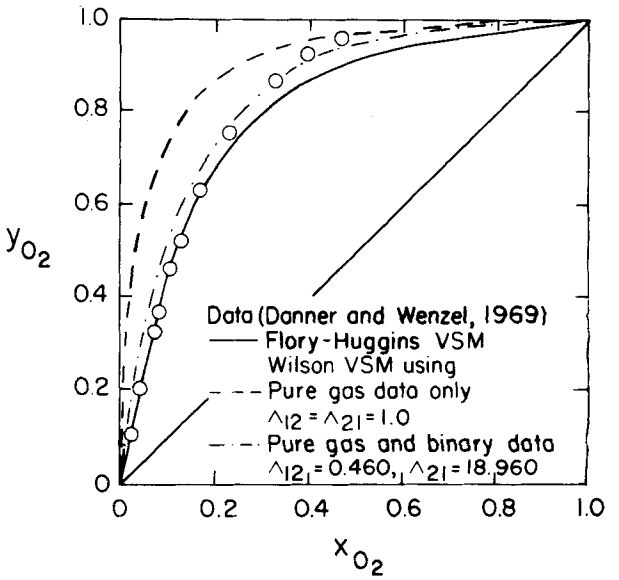

Figure 4. Adsorption phase diagram for O_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa.

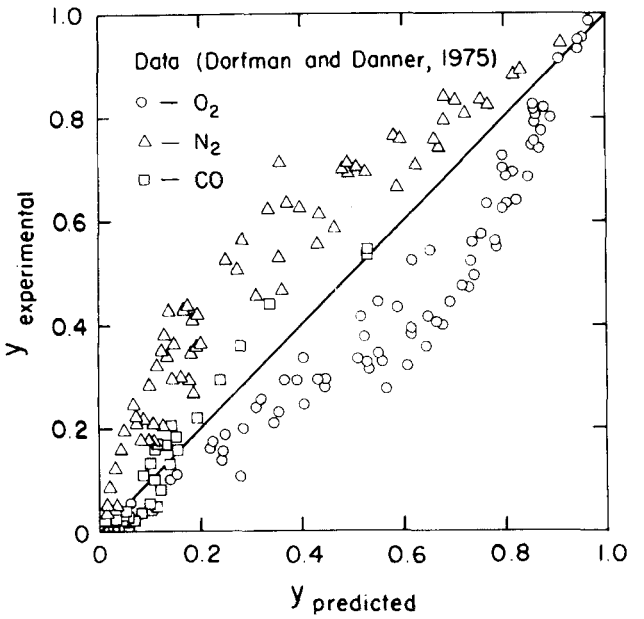

Figure 5. Prediction of gas phase mole fractions for O_2-N_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with Wilson form of VSM and all adsorbate-adsorbate binary interaction parameters set equal to 1.0.

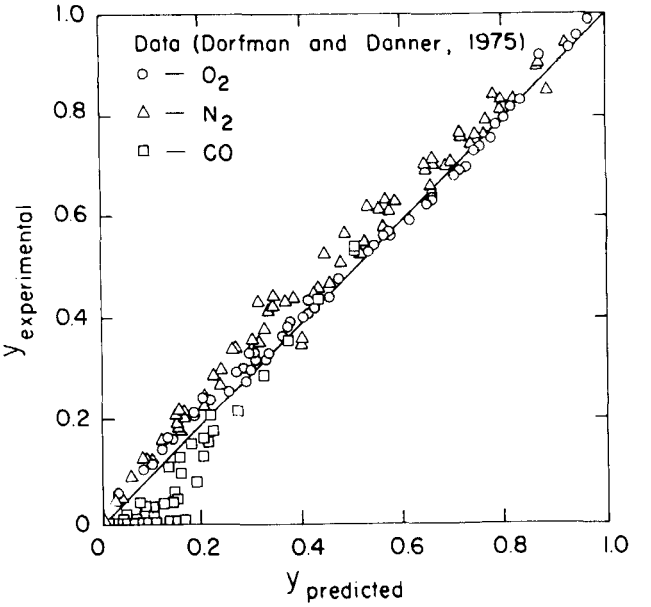

Figure 6. Prediction of gas phase mole fractions for O_2-N_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with Wilson form of VSM and regressed binary interaction parameters for all adsorbate-adsorbate pairs.

CO on zeolite 10X at 144.3 K and 101.3 kPa. In Figure 5 the experimental gas phase mole fractions are compared with the corresponding predicted values when the Wilson form of the VSM is used and all adsorbate-adsorbate binary interaction parameters are set equal to unity. There is considerable bias in the results; the nitrogen values are predicted low and the oxygen values are predicted high. Figure 6 shows the marked improvement that can be obtained for this system if a binary interaction parameter regressed from the experimental binary data is used for each adsorbate pair. These values are given in the last two columns of Table 2. Kaul (1984) also obtained good predictions for this ternary system using only pure and binary data. He used two regressed binary parameters for each adsorbate pair, however. No results are presented for the prediction of the total moles adsorbed because this criterion is not a good discriminator.

COMPARISON OF THE VSM FORMS

Four forms of the VSM have been presented to date. Suwanayuen and Danner (1980a,b) used the two-suffix Margules activity coefficient equation in the VSM and showed that it led to an isotherm equation equivalent to the Fowler equation, which is generally not satisfactory for adsorption equilibria. These authors then presented the original Wilson form as discussed above. The other two forms that must be considered are the modified Wilson form presented here with temperature-dependent parameters and a functional relationship between the two binary parameters for any species pair, and the Flory-Huggins form published by Cochran et al. (1985). Cochran et al. showed their formulation to be superior to the original Wilson form. A comparison between the Flory-Huggins form and the modified Wilson form is needed.

Figure 4 contains predictions of the adsorption phase diagram for the O_2-CO mixtures on zeolite 10X. The Flory-Huggins form is superior to the Wilson form when only pure-gas data are used to make the predictions. The Wilson form with binary interaction parameters, however, is the best. As reported by Cochran et al. (1985), no improvement is realized in the Flory-Huggins case by the use of a regressed binary interaction parameter in place of the value predicted from pure component information.

Figure 7 shows the prediction of ternary O_2-N_2-CO mixtures on zeolite 10X using the Flory-Huggins form where again the predictions are based only on pure-gas data. Comparing Figures 5, 6, and 7 shows that the Flory-Huggins form predicts the ternary data better than the Wilson form when only pure-gas data are used, but the modified Wilson model with a regressed binary interaction parameter is better than the Flory-Huggins form.

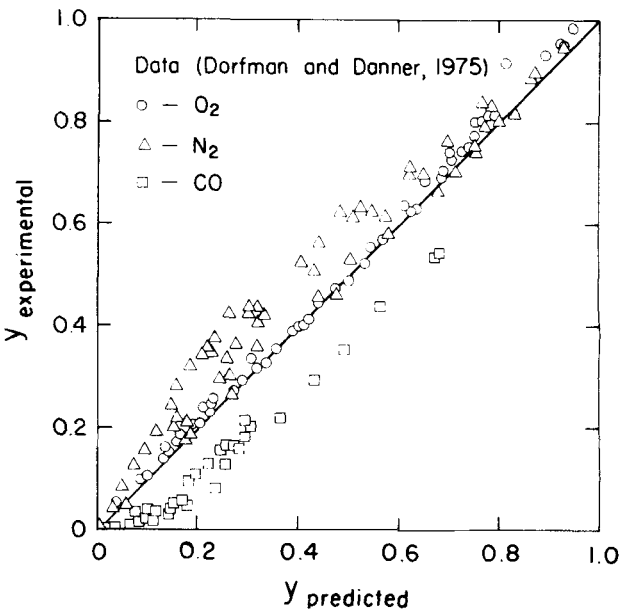

Figure 7. Prediction of gas phase mole fractions for O_2-N_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with Flory-Huggins form of VSM.

Results analogous to the above were found for a number of other systems involving zeolites. For systems involving carbon or silica adsorbents the Flory-Huggins form using only pure-gas data gave good results. If only pure-gas data are available, the Flory-Huggins form is preferred. But for some systems, particularly zeolite systems, if binary data are available for all pairs in the mixture, the use of the modified Wilson form is preferred in order to make optimal use of the experimental data. The modified Wilson form, however, is considerably more complex and more likely to produce regression difficulties.

Kaul (1984) suggests that if there is high surface coverage, binary parameters are needed with the Wilson form of the VSM. Our results do not support this assertion. We found excellent predictions from pure component data only for example, for C_2H_4–C_2H_6–i-C_4H_{10}–CO_2 systems on zeolite 13X and for the C_3H_6–n-C_4H_{10} system on carbon. These systems are high-coverage systems (θ = 0.8–0.95). It is difficult to generalize the reason for poor predictions, but it appears the less polar both the adsorbent and the adsorbates are, the better the results will be.

In using any form of the vacancy solution model the most critical and difficult aspect is the nonlinear regression on the pure-component data. The pure-component vacancy solution model is easily understood, but one must also be fluent in the techniques of (or computer library subroutines for) nonlinear regression. The algorithm for VSM predictions of multicomponent equilibria is somewhat involved, but computer programs can be written and run within a few hours by people without special expertise. CPU time is a matter of seconds.

RECOMMENDATIONS

When using the vacancy solution model to predict multicomponent adsorption equilibria, we make the following recommendations.

- If isothermal data are available for the pure components at a number of temperatures, parameters in the temperature-dependent equations should be used in preference to regressing isothermal parameters.
- When only pure-component data are available, the Flory-Huggins form as published by Cochran et al. (1985) should be used. (For erratum, see p. 2082 of this issue.)
- If both pure-component and binary data for every pair in the mixture are available, compare the experimental binary data with the predictions of the Flory-Huggins form based only on the pure-gas data. If the predictions are accurate, use the Flory-Huggins form to predict the multicomponent equilibria. If the binary predictions are not of satisfactory accuracy, the modified Wilson form described in this paper—i.e., with one regressed binary parameter for each binary pair and the second parameter calculated from Eq. 8—should be evaluated with the experimental binary data. If it correlates the binary data better than the Flory-Huggins form, the Wilson form should be used to predict the multicomponent equilibria.

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NOTATION

A = surface area of adsorbent, m^2/g
a_i = molar area of component i, $m^2/kmol$
b_i = Henry's law constant of component i, kmol/kg·kPa
b_{oi} = temperature-independent constant characterizing each adsorbate-adsorbent system, kmol/kg·kPa
n_i = moles of component i adsorbed per mass of adsorbent, kmol/kg
n_i^∞ = moles of component i adsorbed at saturation, kmol/kg
n_{oi}^∞ = temperature-independent constant characterizing each adsorbate-adsorbent system, kmol/kg
n_T = total moles of mixture adsorbed per mass of adsorbent, kmol/kg
P = equilibrium pressure, kPa
q_i = isosteric heat of adsorption of component i at infinite dilution, kJ/kmol
R = gas constant, kJ/kmol·K
r_i = temperature-independent constant characterizing each adsorbate-adsorbent system, K
T = temperature, K
V_i = liquid molar volume of component i, $m^3/kmol$
V_p = pore volume of adsorbent, cm^3/g

Greek Letters

θ = fraction of limiting adsorption
Λ_{ij} = Wilson parameter for interaction between species i and j
λ_{ij} = potential energy of interaction between species i and j, kJ/kmol

Subscripts

i,j = component i, j
v = vacancy

LITERATURE CITED

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

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

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. No. 152*, **71**, 30 (1975).

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," *Ind. Eng. Chem. Proc. Des. Dev.*, **23**, 711 (1984).

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).

Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, NJ, 230 (1969).

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

——, "Vacancy Solution Theory of Adsorption from Gas Mixtures," *AIChE J.*, **26**, 76 (1980b).

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