RIGOROUS TREATMENT OF ADSORPTION DATA FOR MULTICOMPONENT PREDICTIONS

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Abstract — Three considerations in the rigorous treatment of adsorption data for multicomponent adsorption equilibria are discussed below: (1) choice of pure-component model for the ideal adsorbed solution theory; (2) variable sensitivity analysis for the choice of independent variable sets; and (3) the error-in-variables method for binary interaction parameters. The O'Brien and Myers model gave better agreement with adsorption data than the Langmuir model for single components. However, in the prediction of binary and ternary component adsorption equilibria, IAS theory combined with the O'Brien and Myers model did not show any improvement over the IAS theory with Langmuir model. Sensitivity analysis showed that large sensitivities of dependent variables to independent variables can give large deviations in the prediction of binary component adsorption. This motivated the use of the error-in-variables method, which was shown to be superior to conventional least-squares in calculating the Wilson binary parameters for the prediction of ternary component equilibria with O_2-N_2-CO adsorption data on zeolite 10X. Smaller deviations in the predictions of total amount of adsorption were found from the parameters regressed by EVM, but the errors in the prediction of mole fraction were not reduced significantly compared to the traditional least squares approach.

INTRODUCTION

While equilibrium data for gas adsorption have some similarities to vapor-liquid equilibrium (VLE), the essential difference between VLE and gas adsorption is the presence of the solid adsorbent in the latter case, which introduces an additional degree of freedom [1]. The amount adsorbed, n_i (or solid phase mole fraction, x_i) is measured as a function of temperature T, pressure P, and gas phase mole fraction y_i.

The techniques used in fitting VLE data are generally applicable to parameter estimation in adsorption systems. Several methods have been proposed to estimate the constants in thermodynamic models describing vapor-liquid equilibrium. A number of authors have shown that the results are influenced by the choice of independent and dependent variable sets, use of different functions of measured variables, and the weighting factors in regression, as summarized by Kemeny [2, 3].

Similar problems arise in the prediction of multicomponent adsorption equilibria from pure-component adsorption data. Richter et al. [4] demonstrated that calculations of mixed-gas equilibria are very sensitive

to deviations of adsorption equations from the pure-component adsorption data; multicomponent predictions also depend on the regression technique (the choice of least squares criterion) used to extract parameters from the pure-component adsorption data. Ritter and Yang [5] showed that for the same model significantly different results can be obtained depending on the selection of the independent variable sets $\{P, T, x_i\}$ or $\{P, T, y_i\}$. High and Danner [6] showed that multicomponent predictions using pure component parameters calculated by the error-in-variables method (EVM of Reilly and Patino-Leal [7]) were more accurate than predictions using parameters calculated by conventional least-squares regression.

For the rigorous prediction of multicomponent equilibria the following additional topics have been studied in this paper: (1) choice of rigorous pure-component isotherm model; (2) variable sensitivity study for binary mixture equilibria; (3) EVM for the estimation of binary interaction parameters.

REVIEW OF ADSORPTION MODELS

Below we present the basic equations governing

four different adsorption models: Langmuir model, O'
Brien and Myers model, the ideal adsorbed solution
theory (IAS) and the vacancy solution model (VSM).

1. Langmuir Isotherm

The Langmuir isotherm is a widely-used pure-com-
ponent adsorption model and described by the follow-
ing equation:

$$n_i = m_i \frac{\eta_i}{1 + \eta_i} \tag{1}$$

where $\eta_i = K_i P_i$; K_i is the Langmuir constant, m_i is
the limiting adsorption amount, P_i is the pure compo-
nent partial pressure, and the amount adsorbed is n_i.

2. O'Brien and Myers Isotherm

Recently, O'Brien and Myers [8, 9] derived an equa-
tion for adsorption on heterogeneous surfaces based
on a logical series-expansion extension to the Lang-
muir isotherm:

$$n_i = m_i \left[\frac{\eta_i}{1 + \eta_i} + \frac{\sigma_i^2 \eta_i (1 - \eta_i)}{2(1 + \eta_i)^3} \right] \tag{2}$$

where $\eta_i = K_i P_i$. K_i, m_i, and σ_i are parameters represen-
ting the Langmuir constant, the limiting adsorption
amount, and the variance of the energy distribution
of the adsorption sites, respectively. P_i is the pure com-
ponent partial pressure, and the amount adsorbed is
n_i.

Talu and Myers [1] have suggested various rules
for evaluating the reliability of adsorption models and
data. Equation (2) has a finite slope at low pressure,
namely

$$\lim_{p \to 0} \frac{dn}{dp} = m_i K_i \left(1 + \frac{\sigma^2}{2} \right) \tag{3}$$

so that the O'Brien and Myers model can be consid-
ered a rigorous thermodynamic model based on Talu
and Myers' rule.

3. Ideal Adsorbed Solution (IAS) Theory

For the prediction of the multicomponent adsorption
equilibria from pure-component adsorption isotherms,
the theory of ideal adsorbed solutions was originally
proposed by Myers and Prausnitz [10]. The theory
is based on the assumption that the adsorbed phase
can be treated as an ideal solution of the adsorbed
components. IAS theory is attractive since (1) it requi-
res no mixture data and (2) it is an application of solu-
tion thermodynamics to the adsorption problem. There
is no restriction on the type of isotherm equation, he-
nce one that fits the experimental data can be chosen.
For the calculation of multicomponent equilibria, the
so-called FastIAS technique was developed by O'Brien
and Myers [9].

4. Vacancy Solution Model (VSM)

The pure-component isotherm equation for the Wil-
son form of the VSM as presented by Suwanayuen
and Danner [11] contains a Henry's law constant, b_i,
the limiting amount adsorbed, n_i^∞, and two Wilson in-
teraction parameters, Λ_{iv} and Λ_{vi}.

$$P = \left[\frac{n_i^\infty}{b_i} \frac{\theta}{1 - \theta} \right] \left[\Lambda_{iv} \frac{1 - (1 - \Lambda_{vi})\theta}{\Lambda_{iv} + (1 - \Lambda_{iv})\theta} \right]$$
$$\exp \left[-\frac{\Lambda_{vi}(1 - \Lambda_{vi})\theta}{1 - (1 - \Lambda_{iv})\theta} - \frac{(1 - \Lambda_{vi})\theta}{\Lambda_{vi} + (1 - \Lambda_{iv})\theta} \right] \tag{4}$$

The fraction of limiting adsorption, θ, is the ratio of
the amount adsorbed n_i to the limiting amount of ad-
sorption n_i^∞.

$$\theta = \frac{n_i}{n_i^\infty} \tag{5}$$

Cochran et al. [12] developed a vacancy solution
model (VSM) using the Flory-Huggins activity coeffi-
cient equations.

$$P = \frac{n_i^\infty}{b_i} \frac{\theta}{1 - \theta} \exp \left[\frac{\alpha_{iv}^2 \theta}{1 + \alpha_{iv} \theta} \right] \tag{6}$$

where α_{iv} is the Flory-Huggins (F-H) parameter.

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 phase, an equa-
tion for the distribution of the adsorbate between two
phases can be obtained using Wilson or F-H activity
coefficient equations.

The above equations contain an inconsistency [1,
13]; selectivity measured at different gas phase com-
positions does not extrapolate to the same limit (Hen-
ry's law). However, while VSM violates Henry's law,
VSM is still useful for the prediction of multicompo-
nent equilibria with non-ideal gases.

ERROR-IN-VARIABLES METHOD

In a classical regression approach, the measure-
ments of the independent variables are assumed to be
free of error, while the observations of the dependent
variables, the response of the system, are subject to
errors. However, in some engineering problems obser-
vations of the independent variables also contain er-
rors.

In the error-in-variables method (EVM), unlike the
least-squares approach, measurement errors in all var-
iables are treated in the calculation of regression co-
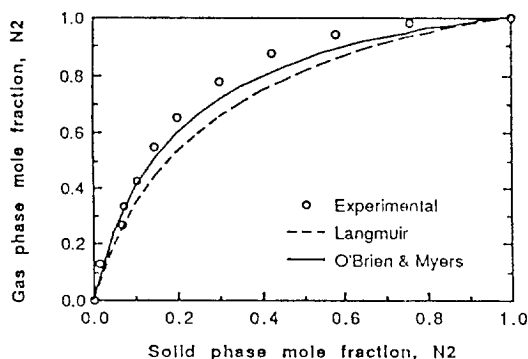efficients. EVM provides both parameter estimates and

Fig. 1. Binary mixture equilibria prediction for N_2-CO on molecular sieve 10X at 144.3 K and 101.3 kPa. Data from Danner and Wenzel [17].
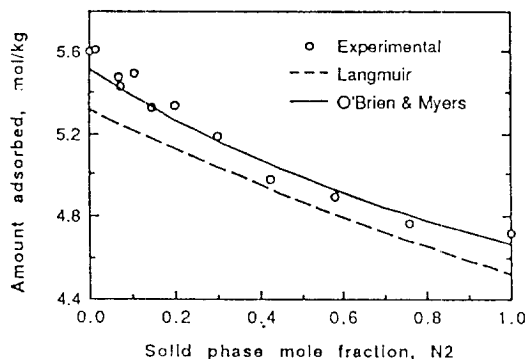

Fig. 2. Total amount adsorbed prediction for N_2-CO on molecular sieve 10X at 144.3 K and 101.3 kPa. Data from Danner and Wenzel [17].

reconciled data estimates.

EVM estimates the parameters by minimizing the error norm function with respect to $\hat{z}$ and $\hat{\theta}$

$$\Psi(\hat{z}_1,\cdots,\hat{z}_m,\ \hat{\theta})= \sum_{i-1}^{m} (z_i-\hat{z}_i)^T V_i^{-1}(z_i-\hat{z}_i) \qquad (7)$$

subject to $f(\hat{z}_i,\ \hat{\theta})=0$, $i=1,2,\cdots,m$.

The efficient solution of the above parameter estimation problem can be obtained by the algorithms of Reilly and Patino-Leal [7], Valko and Vajda [14] and Kim et al. [15].

RESULTS AND DISCUSSION

1. Choice of Pure-Component Isotherm Model

Richter et al. [4] pointed out that the failure of

IAS theory combined with the Langmuir model to agree with experimental data may be due to: (1) nonidealities in the adsorbed phase or (2) the poor fit of the adsorption equation with experimental data for adsorption of single gas. In order to find a pure component model to predict multicomponent adsorption equilibria well by IAS theory, the Langmuir and O' Brien and Myers model were compared.

Figures 1 and 2 show the improved predictions of gas phase mole fraction and amount adsorbed obtained with O'Brien and Myers model vs. the Langmuir model for a N_2-CO mixture on zeolite 10X. Table 1 gives some comparisons of the two models for other gas mixtures. In general, the errors in the amount adsorbed decreased by 15%, but the errors in the gas phase mole fraction were not reduced significantly. Even though the O'Brien and Myers model fits the

Table 1. Comparison of predictions of binary mixtures

		Langmuir		O'Brien and Myers	
		Avg. error in y_i's	Avg. error in $n_i \times 10^3$ [kmol/kg]	Avg. error in y_i's	Avg. error in $n_i \times 10^3$ [kmol/kg]
MS10X	O_2-N_2	0.0275	0.081	0.0304	0.059
	O_2-CO	0.0465	0.132	0.0886	0.108
	N_2-CO	0.0684	0.186	0.0344	0.057
	O_2-N_2-CO	0.0583	0.112	0.0627	0.156
MS13X	i-C_4H_{10}-C_2H_4**	0.0687	0.136	0.0784	0.089
	C_2H_4-CO_2*	0.0578	0.241	0.0573	0.099
	C_2H_4-CO_2**	0.0312	0.198	0.0329	0.095
AC40	CH_4-C_2H_6-C_2H_4	0.0311	0.940	0.0261	0.942
	C_2H_4-C_2H_6-C_3H_6	0.0253	0.894	0.0257	0.892

1. MS10X data from Danner and Wenzel (1969). 144.3 K
2. MS13X data from Hyun and Danner (1982). 298* and 323 K**
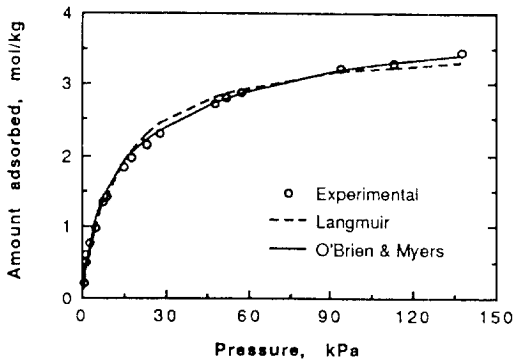3. AC40 data from Costa et al. (1981). 293 K

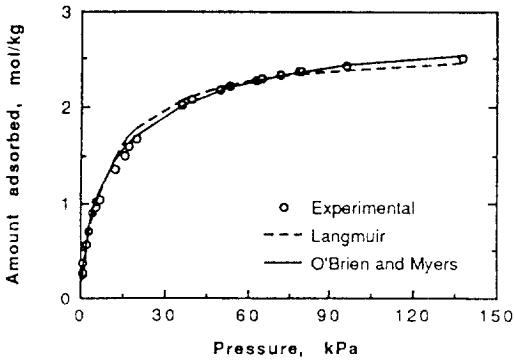Fig. 3. Predictions of CO_2 isotherm on zeolite 13X. Data from Hyun and Danner [20].

Fig. 4. Predictions of C_2H_4 isotherm on zeolite 13X. Data from Hyun and Danner [20].

pure-component experimental data well, as shown in Figures 3 and 4, the three-parameter O'Brien and Myers model could not make much improvement over the Langmuir model in predicting multicomponent equilibria.

O'Brien and Myers model has a third parameter, the variance of adsorption energy distribution, which treats the nonideality in the adsorbed phase in a pure-component isotherm. Because IAS theory is based on the assumption that the adsorbed phase can be treated as an ideal solution of the adsorbed components, the IAS using O'Brien and Myers model cannot handle nonidealities in the adsorbed phase in a multicomponent case. Another possible explanation is that the amount of experimental data was insufficient to extract three parameters for the O'Brien and Myers model as shown in O_2 case in Table 2; in other words, the O'Brien and Myers model was over-parameterized for O_2 data.

2. Variable Sensitivity Analysis

Parameter values usually contain errors or uncer-

Table 2. Pure component parameters on zeolite 10X at 144.3 K. Data from Danner and Wenzel [17]

		Langmuir model	O'Brien and Myers model
O_2	M_i, kmol/kg	7.048×10^{-3}	7.048×10^{-3}
	K_i, 1/kPa	2.484×10^{-2}	2.484×10^{-2}
	σ_i, —	—	0.0
N_2	M_i, kmol/kg	4.721×10^{-3}	5.226×10^{-3}
	K_i, 1/kPa	2.251×10^{-1}	1.745×10^{-1}
	σ_i, —	—	1.467
CO	M_i, kmol/kg	5.405×10^{-3}	5.710×10^{-3}
	K_i, 1/kPa	5.950×10^{-1}	6.913×10^{-1}
	σ_i, —	—	1.746

tainties. Information concerning the sensitivity of the predictions to changes or variations in a parameter is usually carried out by a sensitivity analysis. Similarly it is very important to check how much the predicted values of the dependent variables change due to uncertainties or errors in the independent variables. A sensitivity test may provide suitable information of the choice of the input variable sets.

Errors in the independent variables (X) influence the prediction errors in the dependent variables (Y) by the error propagation law [3]. The variances of the dependent variables, σ_y^2, can be calculated as

$$\sigma_{Yi}^2 = \sum_{j=1}^{nv} \left(\frac{\partial Y_i}{\partial X_j} \right)^2 \sigma_{Xj}^2, \quad i=1,\cdots,n \qquad (8)$$

where σ_X^2 is the variance of the independent variables, nv is the number of independent variables and n is the number of dependent variables. $\partial Y_i/\partial X_j$ is the sensitivity of Y_i variables with respect to the X_j variables and can be calculated either analytically or numerically. In the prediction of gas phase mole fraction, for example, the errors in pressure, P, and solid phase mole fraction, x, can be propagated to gas phase model fraction, y, as

$$\sigma_y^2 = \left(\frac{\partial y}{\partial P} \right)^2 \sigma_P^2 + \left(\frac{\partial y}{\partial x} \right)^2 \sigma_x^2 \qquad (9)$$

If the sensitivities of the dependent variables to independent variables are large, small errors in the independent variables can cause a large deviation in the prediction of a given dependent variable. Alternatively, the relative sensitivity,

$$\frac{dY_i/Y_i}{dX_j/X_j} \qquad (10)$$

can be computed to give a more meaningful measure [16].

Table 3. Relative sensitivities of the IAS theory with the Langmuir isotherm model using simulated data

$\theta_1 = (7, 1)$ and $\theta_2 = (4, 0.7)$ with $\theta = (M_i, \text{mol/kg}, K_i, 1/\text{atm})$.

Case		% Relative sensitivity		Avg. % R.S.*
		Output		
1		n_t	y	82.77
Input	P	52.78	−7.51	
	x	68.89	201.9	
2		P	x	75.17
Input	n_t	182.4	7.99	
	y	−58.04	52.28	
3		n_t	x	36.31
Input	P	54.93	4.49	
	y	31.44	54.38	
4		P	y	136.9
Input	n_t	189.8	−14.07	
	x	−133.6	210.0	

*Avg. % R.S. = Avg. (|% R.S.|)

Table 4. Relative sensitivities of the IAS theory with the O'Brien and Myers isotherm model using simulated data

$\theta_1 = (7, 1, 1)$ and $\theta_2 = (4, 0.7, 0.5)$ with $\theta = (M_i, \text{mol/kg}, K_i, 1/\text{atm}, \sigma_i, -)$.

Case		% Relative sensitivity		Avg. % R.S.*
		Output		
1		n_t	y	93.66
Input	P	42.60	−5.80	
	x	74.40	251.8	
2		P	x	85.99
Input	n_t	229.0	6.35	
	y	−64.77	43.81	
3		n_t	x	30.04
Input	P	44.10	2.96	
	y	27.73	45.36	
4		P	y	173.8
Input	n_t	237.1	−13.29	
	x	−184.4	260.4	

*Avg. % R.S. = Avg. (|% R.S.|)

Tables 3 and 4 show the relative sensitivities on the prediction of binary adsorption equilibria using the IAS theory with Langmuir and O'Brien and Myers isotherm models for four different cases; (1) prediction of n_t and y from P and x; (2) prediction of P and x from n_t and y; (3) prediction of n_t and x from P and y; (4) prediction of P and y from n_t and x. In these calculations, 10 simulated data points were used. In both models, the average absolute relative sensitivity for case 3, predictions of n_t and x from P and Y, is the smallest. In case 1, the prediction of n_t and y from P and x, the prediction y is quite sensitive to variable x. It means that if there are small errors in x, this will lead large deviations between the predictions of y and the experimental values.

The results of a sensitivity analysis can explain the unusual results of Ritter and Yang [5]. In the prediction of equilibrium adsorption of multicomponent gas mixtures, they found that from the same model significantly different results can be obtained depending on the selection of the independent variable set, {T, P, x$_i$} or {T, P, y$_i$}. When they used IAS with the Langmuir isotherm model, the errors in the prediction of n_t and x$_i$ from {P, T, y$_i$} were greater than the errors in the prediction of n_t and y$_i$ from {P, T, x$_i$}. These results are consistent with this sensitivity analysis.

3. EVM for Binary Interaction Parameters

High and Danner [6] compared the least-squares approach (LS) and EVM in parameter estimation for the F-H vacancy solution model. The dependent variable used in LS was pressure, P, instead of amount adsorbed, n_t, because P is explicitly related to the amount adsorbed in the VSM equation (Equation (6)). Large differences in the regression parameters were found by High and Danner. The experimental errors in pressure were relatively smaller than the errors in amount adsorbed, but larger errors in amount adsorbed was neglected in the calculation of parameters in LS by choosing P as a dependent variable. However, when n_t was chosen as a dependent variable, there was not much difference in the estimates by LS and EVM, because the error in P is relatively small. Therefore EVM had little advantage in the calculation of parameters for pure-component adsorption equations and data when n_t was chosen as a dependent variable.

The calculation of binary interaction parameters for the Wilson form of the VSM is similar to the calculation of parameters for activity equations in VLE. In the VLE calculation, EVM has been more effective than LS. Cochran et al. [12] predicted ternary component adsorption equilibria of O_2-N_2-CO on zeolite 10X at 144.3K, when binary interaction parameters were involved. They did not describe the parameter estimation criteria in their paper.

For the comparison of EVM with the other approaches, two adsorbate-adsorbate interaction parameters for the Wilson form of VSM were regressed by EVM from each binary set of data for the binary mixtures of O_2, N_2 and CO adsorbed on zeolite 10X at 144.3K (data from Danner and Wenzel [17]). Experimental errors were chosen as $\sigma_p = 79$ Pa, $\sigma_x = \sigma_y = 0.005$ and $\sigma_n = 2.68 \times 10^{-4}$ kmol/kg [6]. Both binary interaction

Table 5. Wilson binary interaction parameters regressed by EVM for binary mixtures on zeolite 10X at 144.3 K. Data from Danner and Wenzel [17]

Adsorbate	Regression of both binary parameters		Regression of only one binary parameter	
	Λ_{12}	Λ_{21}	Λ_{12}	Λ_{21}*
O_2-N_2	0.633	2.005	1.199	1.192
O_2-CO	0.419	21.542	0.494	20.281
N_2-CO	0.506	0.0	0.079	3.258

*Λ_{21} was calculated by Equation (11).

Table 6. Comparison of predictions of O_2-N_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with the Wilson form of VSM. Data from Dorfman and Danner [19]

|	Average error in vapor phase mole fraction	Average error in moles adsorbed $\times 10^6$ [kmol/kg]
Using only Λ_{12} from Cochran and Danner (1985b)	0.0318	0.147
Using both Λ_{12} and Λ_{21} regressed by EVM	0.0363	0.119
Using only Λ_{12} regressed by EVM	0.0336	0.114

parameter Λ_{12} and Λ_{21} were regressed and listed in the second and third columns of Table 5.

Another regression was done for only Λ_{12} and the corresponding values of Λ_{21} were calculated from the functional relationship between the adsorbate-adsorbate interaction parameter.

$$\Lambda_{21} = \frac{\Lambda_{r1}\,\Lambda_{2i}}{\Lambda_{1i}\,\Lambda_{i2}}\Lambda_{12} \tag{11}$$

where Λ_{ir} and Λ_{ii} were calculated from the temperature-correlated parameters for pure-component Wilson form of VSM of Cochran and Danner [18]. These parameters are given in the 4th and 5th columns in Table 5.

The predictions using both binary interaction parameters, Λ_{12} and Λ_{21}, regressed by EVM show the reduction of deviations in amount adsorbed and gave small errors in gas phase mole fractions as shown in Table 6. Figure 5 shows the predictions for gas phase mole fraction by EVM which were quite good. The quality of fit is similar to that obtained by Cochran et al. [18]. Figures 6 and 7 show the improvement of the prediction of amount adsorbed from the parameters regressed by EVM over the calculation from
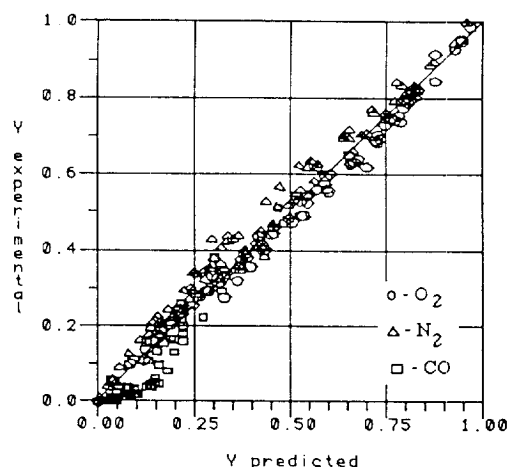
Fig. 5. Comparison of predicted and experimental vapor phase mole fractions for O_2-N_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with Wilson form of VSM and parameters estimated by EVM. Data from Dorfman and Danner [19].
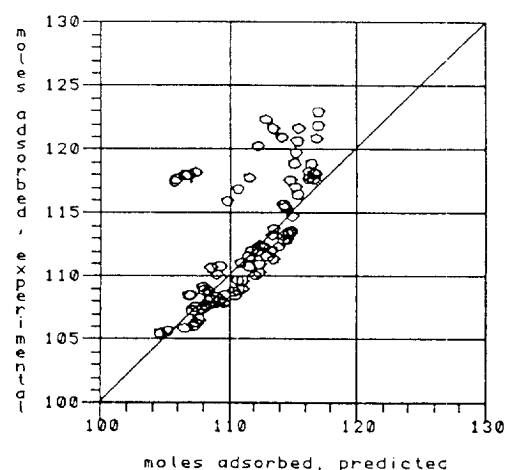
Fig. 6. Comparison of predicted and experimental amount adsorbed for O_2-N_2-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with Wilson form of VSM and parameters estimated by EVM. Data from Dorfman and Danner [19].

the parameters of Cochran et al. [18].

IAS theory was also compared with VSM. When only the pure-component parameters were used (i.e., Λ_{12} and Λ_{21} are set equal to unity when the interactions between different adsorbed species are assumed to be negligible), IAS theory gave more accurate results than the Wilson form of VSM as shown in Table
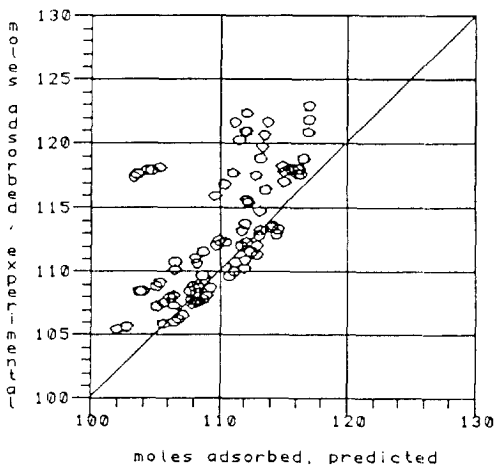
Fig. 9. Comparison of predicted and experimental amount adsorbed for O₂-N₂-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa with Wilson form of VSM and parameters of Cochran et al. [18]. Data from Dorfman and Danner [19].

Table 7. Comparison of predictions of O₂-N₂-CO mixtures on zeolite 10X at 144.3 K and 101.3 kPa. Data from Dorfman and Danner [19]

	Average error in vapor phase mole fraction	Average error in moles adsorbed $\times 10^3$ [kmol/kg]
IAS with Langmuir model	0.0583	0.112
IAS with O'Brien and Myers model	0.0627	0.156
Wilson form of VSM $\Lambda_{12}=\Lambda_{21}=1$	0.0978	0.398

7. However, these results are worse than those by VSM using the interaction parameters.

CONCLUSIONS

In this work, three aspects of the rigorous treatment of adsorption data for multicomponent adsorption equilibria were considered: (1) choice of pure-component model for the ideal adsorbed solution theory; (2) variable sensitivity analysis for the choice of independent variable sets; and (3) the error-invariables method for binary interaction parameters in VSM.

The O'Brien and Myers model fitted experimental data better than the Langmuir model for single components. However, in the prediction of binary and ternary component adsorption equilibria, the IAS theory

with the O'Brien and Myers' model did not show much improvement over the IAS theory with the Langmuir model. This might be due to nonidealities in the adsorbed phase or possibly the O'Brien and Myers model was over-parameterized in some data sets.

The deviations in the prediction of dependent variables depend on sensitivities of dependent variables to independent variables and errors in the independent variables. The variable sensitivity analysis showed that in the calculations of binary component adsorption equilibria, the prediction of y and n_t from P and x was worse than the prediction of n_t and x from P and y.

EVM was applied to the calculation of the Wilson binary parameters for the predictions of ternary component equilibria with O₂-N₂-CO adsorption data on zeolite 10X. Smaller deviations in the predictions of total amount of adsorption were found from the parameters regressed by EVM, but the errors in the prediction of mole fraction were not reduced compared to the least-squares approach.

NOMENCLATURE

b_i : Henry's law constant [kmol/kg/kPa]
f : a vector of functions that comprise model
K_i : Langmuir constant [1/kPa]
m : number of experiments
m_i : Langmuir constant
n_i : amount adsorbed [kmol/kg]
n_i^* : limiting amount adsorbed [kmol/kg]
n_t : total amount of adsorption
nv : number of independent variables
P : equilibrium adsorption pressure [kPa]
T : temperature [K]
V : variance and covariance matrix
x_i : solid phase mole fraction
y_i : gas phase mole fraction
$\hat{z}$: a vector of estimates
z : a vector of measured variables

Greek Letters
α_{ij} : nonideality parameter in VSM
$\Lambda_{ij}, \Lambda_{ji}$: Wilson interaction parameter
Λ_{ij} : Wilson binary interaction parameter

$\hat{\theta}$: a vector of parameter estimates
θ : fraction of limiting adsorption
σ_i : O'Brien and Myers constant

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