Treatment of Gas-Solid Adsorption Data by the Error-in-Variables Method

A recently developed error-in-variables method of calculating regression parameters was applied to the modeling of gas-solid adsorption equilibria. The method accounts for error in all experimental variables in the regression calculations. Regression coefficients from pure component data calculated by the new method were used to predict multicomponent equilibria. The multicomponent predictions using pure component parameters calculated by the error-in-variables method were more accurate than predictions using parameters calculated by conventional least-squares regression.

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SCOPE

The error-in-variables method (EVM) was compared to the conventional least-squares method for calculating regression parameters. The physical system used in the study was a gas-adsorption model that correlates isothermal, pure-component gas-solid adsorption data and uses the resulting pure-component regression parameters to predict multicomponent adsorption equilibria. The multicomponent predictions using the EVM parameters were compared to the predictions obtained from parameters calculated by least-squares treatment.

The EVM described by Patino-Leal and Reilly (1982) allows measurement errors in all variables to be accounted for in the calculation of regression coefficients, whereas in least-squares regression only one variable is assumed to be error-corrupted and others are assumed to be independent and error-free. Patino-Leal and Reilly use vapor-liquid equilibrium as an example for the use of the EVM. The objective of this paper is to describe the application of the EVM to the gas-solid adsorption isotherm developed by Cochran et al. (1985) and to compare the predictive power of EVM-calculated regression coefficients to those regressed from standard nonlinear least-squares methods.

CONCLUSIONS AND SIGNIFICANCE

The error-in-variables method produced regression coefficients for pure-component gas-solid adsorption equilibria that were then used to predict binary and ternary mixture equilibria. The results of these predictions were compared to the predictions using the regression parameters from conventional least-squares methods. A decrease of 36.7% in errors in vapor phase predictions and 16.6% in total moles of adsorbed gas for the binary mixture was realized. For the ternary system studied the errors in the vapor phase predictions were reduced on the average of 31% from the errors produced by the least-squares approach. A negligible reduction in error in the predicted total moles adsorbed was realized for the ternary system.

The adsorption model used, the vacancy solution model, is derived from fundamental principles of solution thermodynamics. Therefore, the regression coefficients calculated from the experimental data have some physical significance. The error-in-variable method calculates regression parameters with more physical meaning than those calculated by conventional least-squares methods. Parameters with more physical significance lead to improved prediction of multicomponent equilibria.

More computer resources are needed for the error-in-variables method than the conventional least-squares approach. EVM regression of pure-component adsorption data requires approximately 10 s on an IBM 4341 computer, while conventional least-squares calculations require 4 s. More accurate regression parameters, however, are well worth the small increase in cost.

Introduction

The general error-in-variable method (EVM) was presented by Reilly and Patino-Leal (1981) and applied to the calculation of UNIQUAC parameters for vapor-liquid-equilibrium (VLE) systems (Patino-Leal and Reilly, 1982). In this treatment, the EVM was used to account for the measurement error in the VLE variables (temperature, pressure, vapor, and liquid composition) some of which are usually neglected in least-squares calculations. This work treats a new application of EVM in gas-solid adsorption equilibria. These are just two of the many possible applications of the EVM for the treatment of thermodynamic data.

The least-squares method of regression assumes that at least one experimental measurement is free from error relative to the other measured variables. For example, temperature vs. thermal conductivity data would be well suited to the treatment by least-squares if temperature is assumed to be the error-free, independent variable. For phenomena such as VLE and gas adsorption, however, the level of measurement error should not be neglected in any variable. In these cases the EVM could be used to provide more accurate regression parameters.

The most crucial consideration for any estimation problem is the quality of the input data and model to be regressed. Sophisticated regression methods such as EVM are not intended to eliminate inadequacies of data and models. The best application for the EVM is in the case of a theoretical model where accurate calculation of the parameters is desired based on all information concerning the available data.

Gas-Solid Adsorption Model

Cochran et al. (1985) developed an improved adsorption isotherm equation for pure components based on the vacancy solution theory of the form

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

The parameters n_i, b_i, and α_{iv} are then used to predict multicomponent equilibria by the following set of equations:

$$\phi_i y_i P = \frac{\gamma_i^s x_i n_m n_i^\infty \exp(\alpha_{iv}) \exp\left(\frac{\pi \bar{a}_i}{RT}\right)}{n_m^\infty b_i (1 + \alpha_{iv})} \tag{2}$$

where

$$\ln \gamma_i^s = 1 - \ln \sum_{j=1}^{n+1} \frac{x_j^s}{\alpha_{ij} + 1} - \left[\sum_{j=1}^{n+1} \frac{x_j^s}{\alpha_{ij} + 1}\right]^{-1} \tag{3}$$

$$x_i^s = \frac{x_i n_m}{n_m^\infty} \tag{4}$$

$$x_{n+1}^s = 1 - \sum_{i=1}^{n} x_i^s \tag{5}$$

$$\alpha_{ij} = \frac{1}{\alpha_{ji} + 1} - 1 \tag{6}$$

$$\alpha_{ij} = \frac{\alpha_{iv} + 1}{\alpha_{jv} + 1} - 1 \tag{7}$$

$$\frac{\pi \bar{a}_i}{RT} = -\left(1 + \frac{n_m^\infty - n_i^\infty}{n_m}\right) \ln(\gamma_v^s x_v^s) \tag{8}$$

$$n_m^\infty = \sum_{i=1}^{n} x_i n_i^\infty \tag{9}$$

Equations 2 through 9 are subject to the constraints

$$\sum_{i=1}^{n} y_i = 1 \tag{10}$$

$$\sum_{i=1}^{n} x_i = 1 \tag{11}$$

The vacancy solution model refers to the vacancy entity as the $n + 1$ component in a mixture of n gases. The fugacity coefficient in Eq. 2 is usually neglected because at the pressures considered the nonidealities in the vapor phase are not significant compared to those in the adsorbed phase. Equations 2 through 11 represent the equilibrium conditions for a multicomponent system and must be solved simultaneously to calculate the equilibrium conditions. The usual case for a binary system is that n_1, n_2, b_1, b_2, α_{1v}, α_{2v}, are calculated from pure-component data, and T and P are defined as the independent variables. Given x_1, Eqs. 2 through 9 reduce to a set of three equations and three unknowns y_1, y_2, and n_m. Varying x_1 will produce the phase diagram for the binary system at the defined T and P. This calculational procedure is readily extended to systems with more components. This development has been extended to include temperature dependence of the pure-component regression parameters n_i, b_i, and α_{iv} (Cochran et al., 1985).

The Error-in-Variables Model

The development of the EVM for calculating regression parameters can be found in Patino-Leal (1979), Reilly and Patino-Leal (1981), and Patino-Leal and Reilly (1982). These studies involve the problem of parameter estimation in terms of the error-in-variables model.

$$x_i = \xi_i + \epsilon_i \quad (i = 1, 2, \ldots, n) \tag{12}$$

where

$$f_k(\xi_i, \theta) = 0 \quad (k = 1, 2, \ldots, m) \tag{13}$$

is the mathematical relationship among the true values of the variable and parameters. This approach, as pointed out by Reilly and Patino-Leal, can be considered a maximum likelihood or Bayesian approach. The final equation used as an objective function to optimize and locate the parameter values is derived from a Bayesian approach. This approach leads to a final objective function that is more tractable than previous maximum likelihood models. The reader should refer to these excellent studies for more information concerning the statistical and computational background for the method.

In short, the EVM for regression equations that are nonlinear in the coefficients to be estimated, can be summarized as minimizing Q where:

$$Q = \sum_{i=1}^{n} (x_i - \xi_i')^T V_i^{-1} (x_i - \xi_i') \tag{14}$$

The vectors ξ_i' are the converged values of $\xi_i'^{(k)}$ found by an iterative method:

$$\xi_i'^{(k+1)} = x_i - VB_i^T(B_iVB_i^T)^{-1}[f(\xi_i'^{(k)}, \theta) + B_i(x_i - \xi_i'^{(k)})] \qquad k = 1, 2, 3, \ldots . \tag{15}$$

Equation 15 is used to iteratively calculate the estimated true values ξ_i' of the experimental points x_i. Equation 15 is used until ξ_i' converges satisfactorily for each experiment i. The $(m \times v)$ B_i matrix of partial derivatives is determined at each iteration for the iterative calculation of the vector ξ_i':

$$B_i = \begin{bmatrix} \dfrac{\partial f_1}{\partial \xi_1'} & \cdots & \dfrac{\partial f_1}{\partial \xi_v'} \\ \vdots & & \vdots \\ \dfrac{\partial f_m}{\partial \xi_1'} & \cdots & \dfrac{\partial f_m}{\partial \xi_v'} \end{bmatrix} \tag{16}$$

Then Eq. 14 is used to calculate Q as an input to a minimization routine to calculate new values of the regression parameters θ. When Q is minimized the resulting vectors ξ_i' are estimates of the "true" values of the measured variables x_i and the elements of the vector θ are the estimates of the regression parameters.

Application of EVM Method to Gas-Solid Adsorption

In order to test the effectiveness of the EVM when applied to gas-solid adsorption equilibria, regressions of several systems of pure component data were performed. The EVM requires an estimate of the variance-covariance matrix V. V can best be computed from repetitive experiments. Bilgic (1970) estimated experimental errors of 79.0 Pa for pressure, 2.68×10^{-5} kmol/kg for moles adsorbed, and 0.11 K for temperature. The values for pressure and moles adsorbed were used in the diagonal elements of V and were assumed to be constant from experiment to experiment. Temperature is not involved as a variable in Eq. 1, therefore the use of the variance for temperature in the calculations is superfluous. In other words, temperature measurements were taken as perfectly known.

The EVM and least-squares method were used to calculate values of the regression coefficients n_1^∞, b_1, and α_{1v} for 12 isothermal pure-component systems. Table 1 lists the regression coefficients for both the EVM and least-squares methods. While in some cases the coefficients obtained from the two methods are quite close, in a number of cases significant differences were obtained.

Even these large differences in the regression parameters produced only small changes in the visual appearance of the isotherms, as shown in Figure 1. For the most part, the EVM coefficients do not visually alter the slope or the fit of the pure component isotherm. Figure 2 is a comparison of the residuals of pressure ($P_{calc} - P_{exp}$) vs. volume adsorbed for two systems. For methane the vacancy solution model adequately fits the data. The residuals for ethane, however, show some error. We do not

Table 1. Least-Squares Method and Error-in-Variables Method Regression Coefficients

			Least Squares			Error-in-Variables			
Adsorbate	Adsorbent*	Temp. K	$n_i^s \times 10^3$ kmol/kg	b_i kmol/Pa · kg	α_{iv}	$n_i^s \times 10^3$ kmol/kg	b_i kmol/Pa · kg	α_{iv}	Reference
CH_4	A	293	4.78	1.30×10^{-5}	1.49	4.86	1.31×10^{-5}	1.53	Szepesy (1963)
C_2H_4	A	293	6.17	3.29×10^{-4}	3.06	6.19	3.43×10^{-4}	3.21	Szepesy (1963)
C_2H_6	A	293	6.14	3.12×10^{-3}	5.25	5.83	5.48×10^{-4}	3.18	Szepesy (1963)
N_2	B	172	4.82	5.78×10^{-3}	5.28	4.79	5.04×10^{-3}	5.11	Nolan et al. (1981)
CO	B	172	5.07	4.08×10^{-1}	8.35	5.05	$5.48 \times 10^{+1}$	13.3	Nolan et al. (1981)
C_2H_4	C	298	2.95	2.53×10^{-3}	2.46	2.94	2.81×10^{-3}	2.56	Hyun (1980)
C_2H_4	C	323	2.83	6.24×10^{-4}	2.00	2.88	6.96×10^{-4}	2.20	Hyun (1980)
CO_2	C	298	4.45	6.12×10^{-3}	3.85	4.41	4.12×10^{-3}	3.36	Hyun (1980)
CO_2	C	323	4.11	7.53×10^{-4}	2.41	4.16	8.53×10^{-4}	2.61	Hyun (1980)
CO_2	D	298	16.80	4.67×10^{-5}	3.01	12.90	4.24×10^{-5}	2.43	Wilson & Danner (1983)
CO	D	298	6.66	5.32×10^{-6}	1.70	6.47	5.32×10^{-6}	1.66	Wilson & Danner (1983)
CH_4	D	298	10.90	1.61×10^{-5}	2.71	7.34	1.48×10^{-5}	1.98	Wilson & Danner (1983)

*Adsorbents:
A, Nuxit-AL activated carbon
B, 10X molecular sieve
C, 13X molecular sieve
D, BPL activated carbon

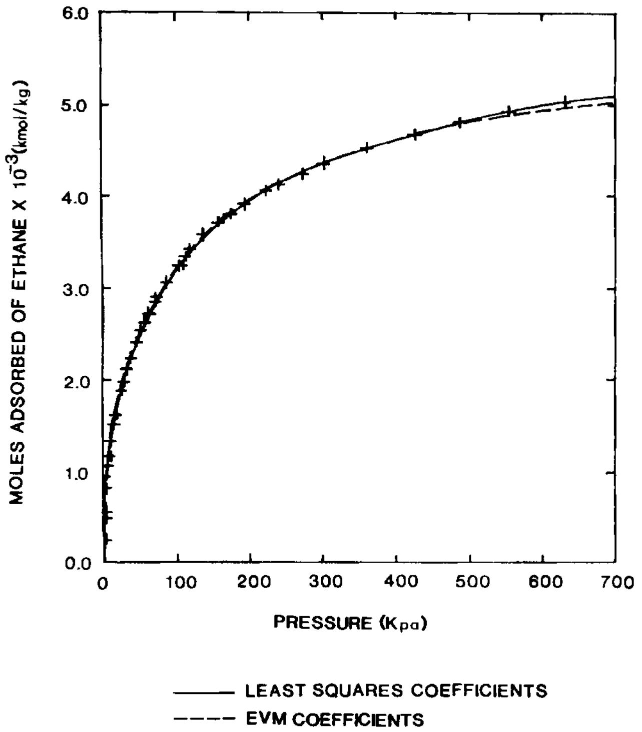

Figure 1. Pure isothermal least-squares and error-in-variables method regression of ethane on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

consider this behavior poor enough to warrant excluding any of the experimental points from the calculations.

The pure-component regression parameters from Table 1 were used to calculate phase diagrams for various binary and ternary systems. Given regressed values of n_1^∞, n_2^∞, b_1, b_2, α_{1v}, and α_{2v} from pure-component regressions, one chooses a value for the adsorbed phase mole fraction and calculates y_1 and n_m from Eqs. 2 through 11.

The prediction of the mixture equilibria using EVM-calculated component regression parameters was superior to predictions using least-squares-based parameters. For example, Figure 3 shows the prediction compared to experimental data of Szepesy (1963) of the binary equilibria system of CH_4 and C_2H_6 at 293 K on activated carbon adsorbent. The prediction using EVM coefficients shows far superior agreement with the data. In addition, total moles adsorbed for the same system was predicted with greater accuracy using EVM-calculated parameters, as seen in Figure 4. Additional cases indicated that the EVM-calculated coefficients predicted binary equilibrium much better than least-squares regressed coefficients, as seen in Figures 5 and 6. Table 2 summarizes the prediction accuracy for both EVM and the classical approach.

When the data and model are adequate, it seems clear that the EVM can estimate values that have more physical significance than those regressed by the standard least-squares technique. No regression method, however, can account for inadequate data or models. The adsorption system ethylene-carbon dioxide-molecular sieve type 13x is shown in Figure 7. This system has an adsorption azeotrope at approximately 8% ethylene. In this case neither regression method extracted pure-component parameters from the vacancy solution adsorption model,

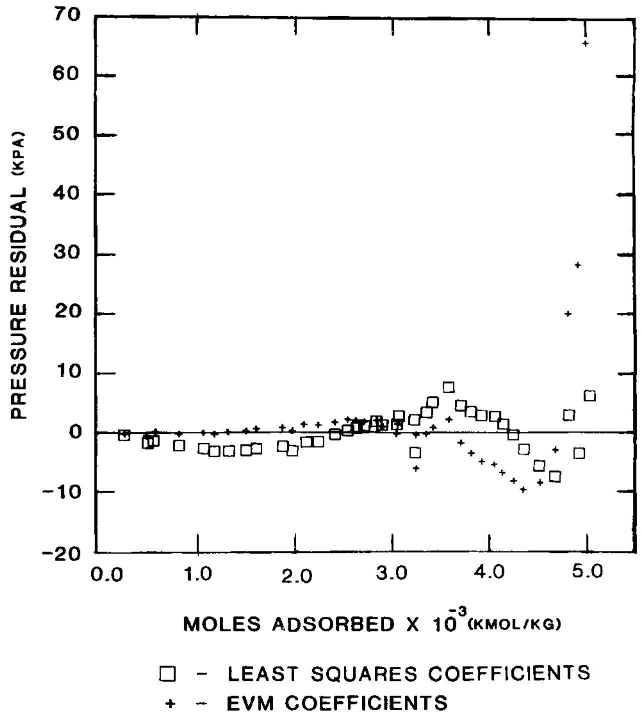

Figure 2a. Residual plot of pressure vs. volume adsorbed for ethane on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

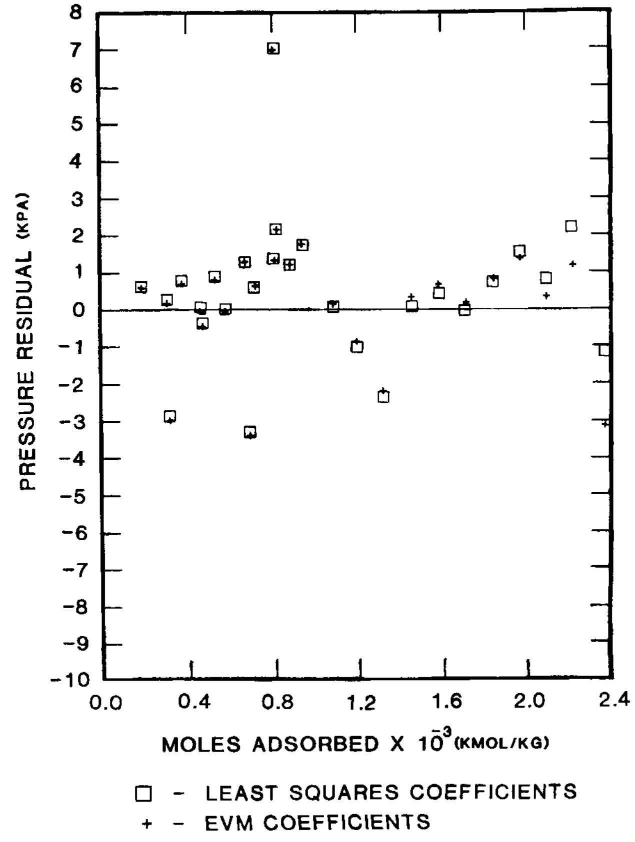

Figure 2b. Residual plot of pressure vs. volume adsorbed for methane on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

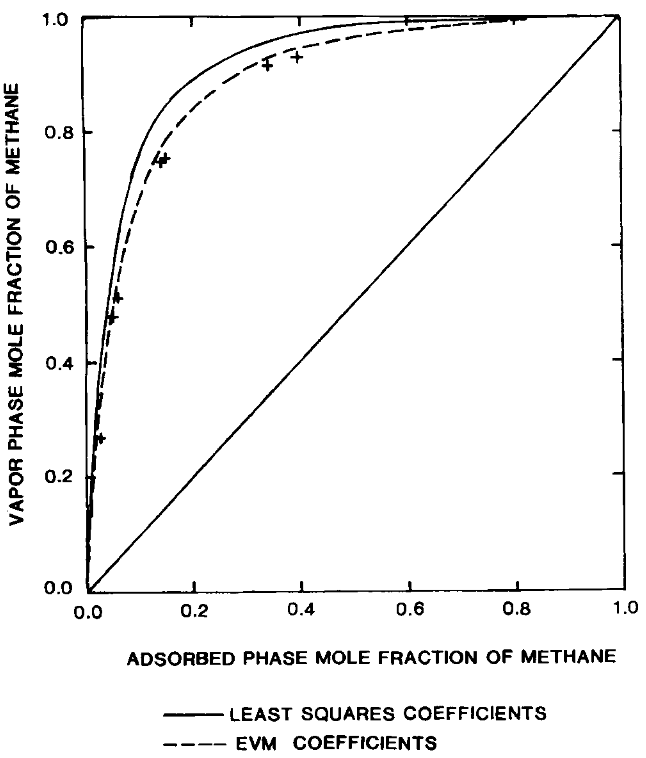

Figure 3. Binary mixture equilibria prediction and experimental data for methane-ethane mixture on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

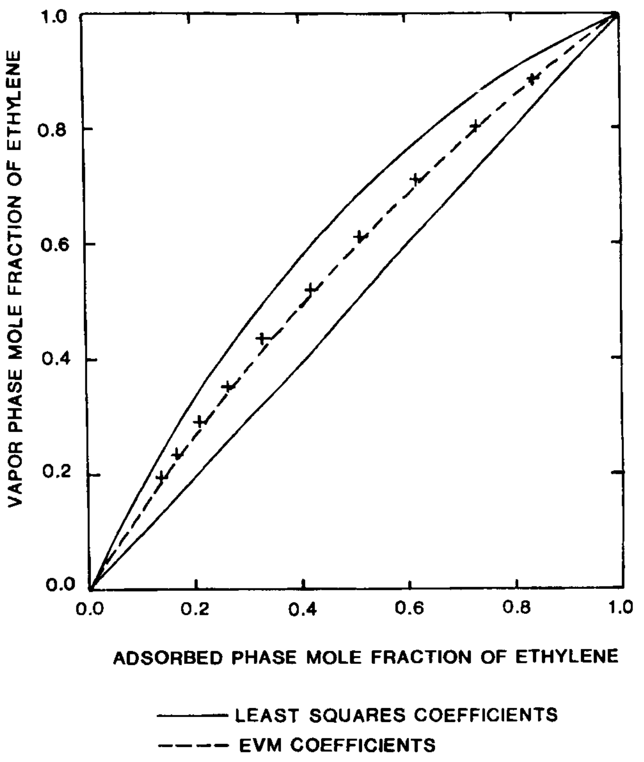

Figure 5a. Binary mixture equilibria prediction and experimental data for ethylene-ethane mixture on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

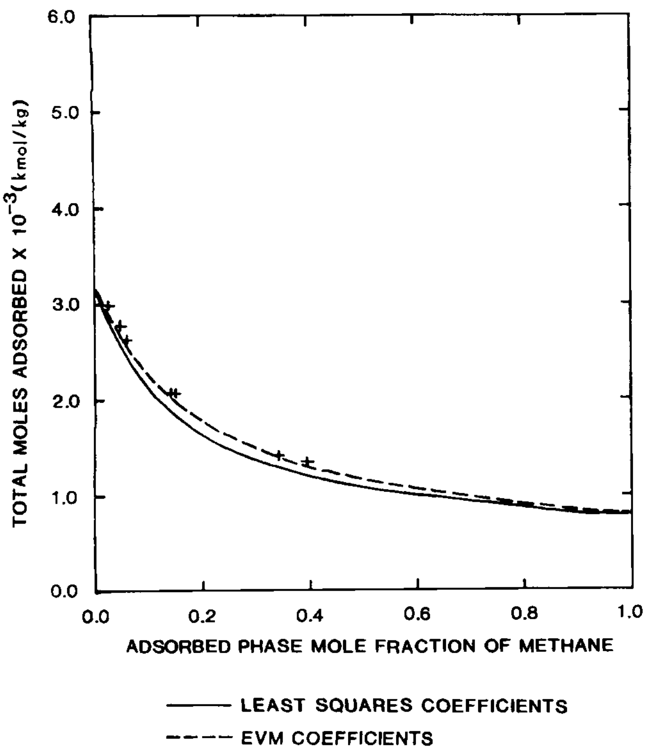

Figure 4. Total moles adsorbed prediction and experimental data for methane-ethane mixture on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

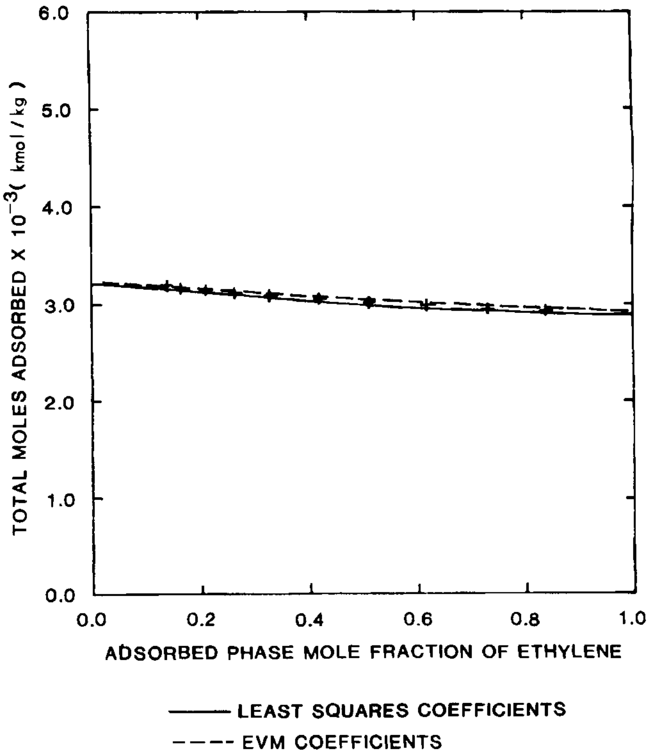

Figure 5b. Total moles adsorbed prediction and experimental data for ethylene-ethane mixture on Nuxit-AL activated carbon at 293 K (Szepesy, 1963).

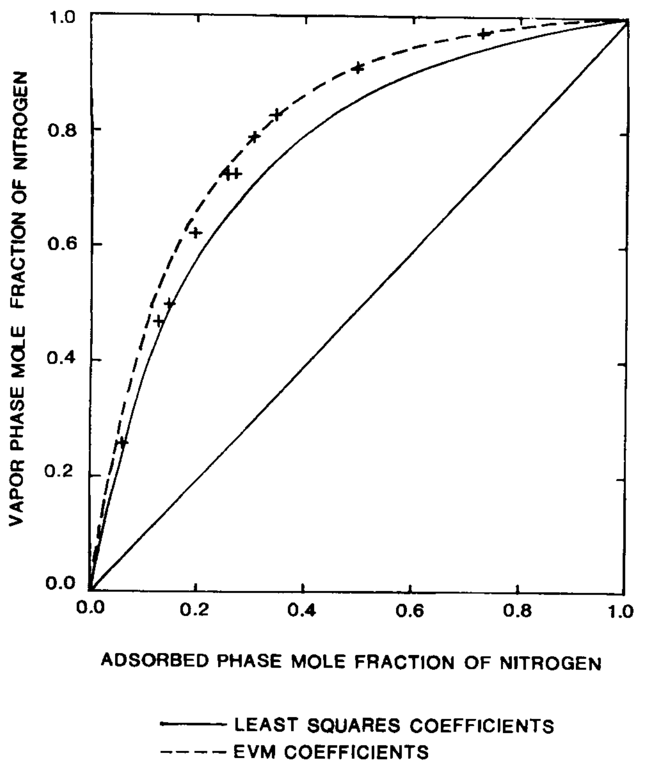

Figure 6a. Binary mixture equilibria prediction and experimental data for nitrogen-carbon monoxide mixture on molecular sieves types 10X at 172 K (Nolan et al., 1981).

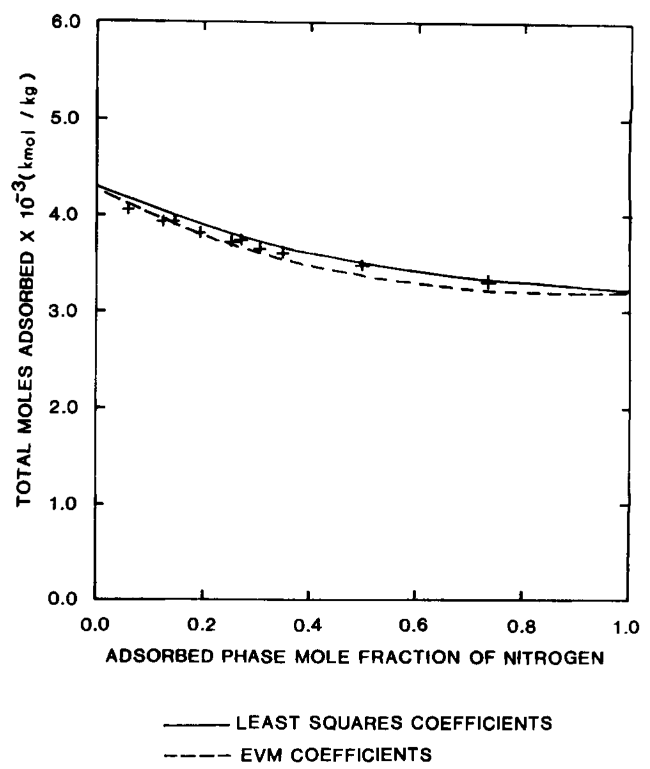

Figure 6b. Total moles adsorbed prediction and experimental data for nitrogen-carbon monoxide mixture on molecular sieves type 10X at 172 K (Nolan et al., 1981).

which predicted the azeotropic behavior. This may be caused by the inadequacy of the adsorption model or the data. For this highly nonideal system, numerous accurate low-pressure data are needed to correctly define the Henry's law parameter, which is very important in predicting the behavior in the low ethylene concentration region. It is suspected that the data are not adequate in this regard.

As shown by Table 2, however, for the binary systems where a substantial difference was observed between the predictions based on parameters extracted from the pure-component data by the two regression methods, the EVM was superior. For example, for the carbon monoxide-carbon dioxide system in Table 2 the EVM method reduced the average error in the prediction of the vapor phase mole fraction from 7.338 × 10^{-2} to

Table 2. Comparison of Predictions of Binary Mixture Equilibria

				Results				
				Least Squares Method		EVM Method		
System	Adsorbent*	Temp. K	No. of Points	Avg. Error in Vapor Phase mol frac.	Avg. Error of Moles Adsorbed kmol/kg	Avg. Error in Vapor Phase mol frac.	Avg. Error of Moles Adsorbed kmol/kg	Reference
CH_4-C_2H_4	A	293	7	1.168×10^{-2}	2.705×10^{-5}	1.352×10^{-2}	3.355×10^{-5}	Szepesy (1963)
CH_4-C_2H_6	A	293	7	8.084×10^{-2}	2.138×10^{-4}	2.151×10^{-2}	1.015×10^{-4}	Szepesy (1963)
C_2H_4-C_2H_6	A	293	10	6.216×10^{-2}	1.877×10^{-5}	1.120×10^{-2}	2.198×10^{-5}	Szepesy (1963)
N_2-CO	B	172	10	4.242×10^{-2}	6.346×10^{-5}	2.346×10^{-2}	5.654×10^{-5}	Nolan et al. (1981)
C_2H_4-CO_2	C	298	6	3.077×10^{-2}	4.751×10^{-5}	3.309×10^{-2}	4.391×10^{-5}	Hyun (1980)
C_2H_4-CO_2	C	323	5	3.027×10^{-2}	4.189×10^{-5}	3.014×10^{-2}	4.780×10^{-5}	Hyun (1980)
CO-CO_2	D	298	14	7.338×10^{-2}	3.176×10^{-4}	5.982×10^{-2}	2.482×10^{-4}	Wilson (1983)
CO-CO_2**	D	298	3	9.549×10^{-2}	6.261×10^{-4}	6.656×10^{-2}	4.761×10^{-4}	Wilson (1983)
CO-CH_4	D	298	9	9.253×10^{-3}	2.936×10^{-5}	1.659×10^{-2}	2.908×10^{-5}	Wilson (1983)
CH_4-CO_2	D	298	10	1.129×10^{-2}	5.835×10^{-5}	1.139×10^{-2}	1.092×10^{-4}	Wilson (1983)
Overall			81	4.370×10^{-2}	1.256×10^{-4}	2.767×10^{-2}	1.048×10^{-4}	

*See Table 1 for Adsorbents.
**System at 689.5 kPa. All other systems at 344.7 kPa.

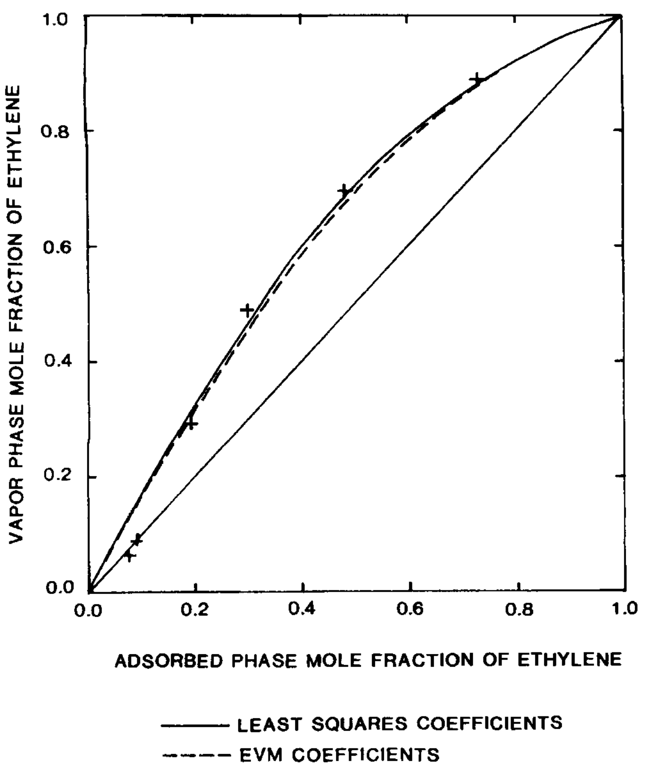

Figure 7a. **Binary mixture equilibria prediction and experimental data for ethylene-carbon dioxide mixture on molecular sieves type 13X at 298 K (Hyun, 1980).**

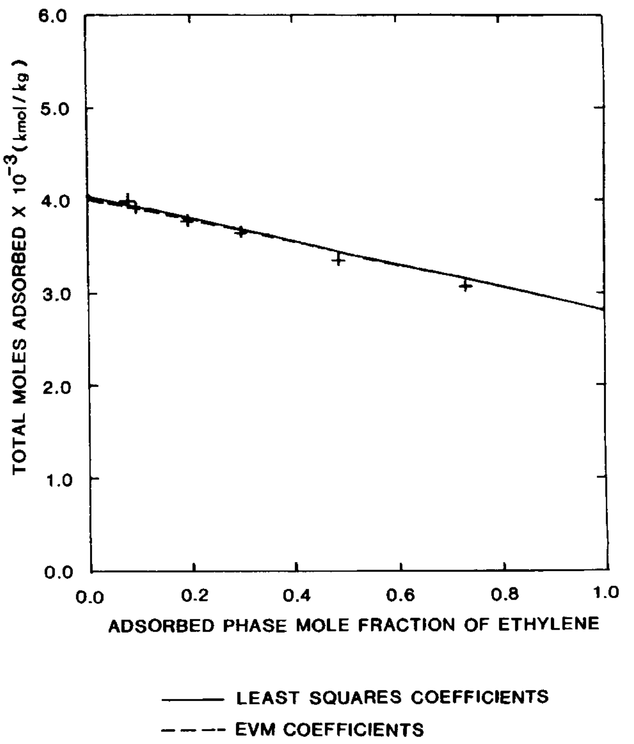

Figure 7b. **Total moles adsorbed prediction and experimental data for ethylene-carbon dioxide mixture on molecular sieves type 13X at 298 K (Hyun, 1980).**

5.982×10^{-2}, a reduction of 18.5%. For this same system, the error in the prediction of total moles adsorbed was reduced from 3.176×10^{-4} to 2.482×10^{-4} kmol/kg, a reduction of 21.8%. Table 3 gives the results of a prediction for the ternary system carbon monoxide-methane-carbon dioxide adsorbed on activated carbon. The ternary prediction in Table 3 shows a significant reduction in the error of the prediction of the vapor phase mole fractions of carbon monoxide and methane. The reduction in error of the prediction of the vapor phase mole fraction of carbon dioxide was not as large. For this ternary system there was a negligible reduction in the error in the prediction of total moles adsorbed.

Skjold-Jørgensen (1983) analyzed the maximum-likelihood method for determining parameters in activity coefficient models used to correlate vapor-liquid equilibria data. Skjold-Jørgensen emphasizes that no parameter estimation criterion can improve an inadequate model or poor experimental data. But, he says that for the limiting case of a good model and consistent data the choice of criterion is the maximum-likelihood one. Our treatment of the vacancy solution model with the EVM is an example of the benefits of using a method equivalent to the maximum-likelihood criterion to estimate parameters from a good model with good data. Even though the assumptions used in arriving at the criterion can be met only in ideal cases, application of the method has provided us with parameters with more physical significance. That is, even though we are not sure that our data are not corrupted with systematic error or that the vacancy solution is adequate to describe the adsorption phenomena, we have been able to predict multicomponent equilibria more accurately. We believe that the EVM approach can be used for any model because the results can be no worse than other empirical criteria such as least-squares. In such cases, however, caution must be used in drawing conclusions about the significance of the parameters.

The conventional maximum likelihood approach described by Skjold-Jørgensen requires the optimization of the true values of the variables as well as the parameters. Skjold-Jørgensen points out that a conditional likelihood function may be used along

Table 3. Comparison of Predictions of Ternary CO-CH_4-CO_2 System on Activated Carbon

Method	Error in Vapor Phase, mol/frac. CO	CH_4	CO_2	Avg. Error Moles Adsorbed kmol/kg
Least-squares	7.531×10^{-2}	1.817×10^{-2}	5.714×10^{-2}	2.121×10^{-4}
Error-in-variables	5.103×10^{-2}	8.734×10^{-3}	5.207×10^{-2}	2.116×10^{-4}

Type BPL activated carbon at 298 K (Wilson, 1983).

with error propagate expressions. In the first case, the unconditional criterion requires optimization of a large number of true values of the variables and the model parameters. This calculation would require a very large amount of computer resources. He states that the conditional likelihood requires the same computational complexity as the unconditional criteria. The error-in-variables method eliminates the nuisance parameters, the true values of the variables, from the optimization. The calculations involved in the EVM are greatly simplified.

Ricker (1984) concludes that "the gain in accuracy is, however, often small relative to the increased computational and experimental requirements imposed by the refined methods." We believe that arguments against maximum-likelihood criteria, and more specifically the error-in-variables method, because of increased computer costs are not valid. A regression performed on pure-component adsorption data requires less than 10 s on an IBM 4381 computer. The increased accuracy of the multicomponent equilibria prediction easily justifies the cost of the small amount of computer resources required. In general, we have found that the computer resources for an EVM calculation are not much different than those required for conventional nonlinear least-squares.

Notation

$\overline{a}_i$ = molar area of component i, m^2/kmol
b_i = Henry's law constant for the vacancy solution isotherm equation for component i, kmol/kg · kPa
B_i = $(m \times \upsilon)$ matrix of partial derivatives of each constraint equation with respect to each variable for experiment i
f_k = vector of k constraints
m = number of constraint equations
n = number of components in mixture; number of experiments in EVM
n_i = moles of component i absorbed, kmol/kg
n_i^∞ = limiting (maximum) adsorption uptake of pure component i, kmol/kg
n_m = total moles adsorbed of mixture, kmol/kg
n_m^∞ = limiting amount adsorbed of mixture, kmol/kg
P = total pressure of the system, kPa
Q = error-in-variable model objective function to be minimized
R = ideal gas constant, J/mol · K
T = temperature of adsorption system, K
υ = number of measurements in an observation
V = variance-covariance matrix $(\upsilon \times \upsilon)$
x_i = adsorbed phase mole fraction for vacancy solution isotherm equation; vector of experimental values for EVM; vector of υ experimental values for the ith experiment and jth replicate
x_i^s = mole fraction of component i in vacancy solution representing adsorbed phase
y_i = mole fraction of component i in gas phase

Greek Letters

α_{ij} = Flory-Huggins parameter for the vacancy solution equation for components i and j
γ_i^s = activity coefficient of component i in surface phase
ϵ_i = vector of υ errors for experiment i
ξ_i = vector of υ "true" values for experiment i
ξ_i' = estimated value of the vector of υ "true" values for experiment i
π = spreading pressure, N/m
θ = vector of unknown coefficients to be estimated; fraction of limiting adsorption
ϕ_i = fugacity coefficient of component i in gas phase

Superscripts

-1 = inverse operator
s = surface or absorbed phase
T = matrix transpose operator
∞ = value at limiting adsorption

Subscripts

i = experiment or observation i in the EVM algorithm; component i in the vacancy solution theory
j = component j
k = component k
m = mixture
υ = vacancy component

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