Reduction of Ion-Exchange Equilibria Data Using an Error in Variables Approach

Richard J. Vamos and Charles N. Haas
Pritzker Dept. of Environmental Engineering, Illinois Institute of Technology, Chicago, IL 60616

An error in variables method (EVM) was used to reduce binary ion-exchange equilibria data. Ion-exchange equilibria data were collected via batch equilibrium experiments. Three binary ion-exchange systems were studied: the Na^{+1}-Cd^{+2}, Na^{+1}-Cu^{+2}, and Cu^{+2}-Cd^{+2} systems with a strong acid synthetic ion-exchange resin. The Wilson model and a three-suffix, two-parameter Margules equation were used to model the dependency of the resin phase activity coefficients with resin-phase composition. The EVM was used to determine the best-fit estimates of the Wilson and Margules equation binary resin-phase activity coefficient parameters. Statistical analysis of the data fits indicates that although both equations were able to adequately model the resin phase nonidealities, the Wilson model provided the superior data fits based on the minimized objective functions.

Introduction

Ion-exchange processes are used extensively in water and wastewater treatment. Prediction of ion-exchange equilibria is needed to design and optimize such processes. Numerous binary equilibria studies have demonstrated that ion exchangers behave nonideally, in that the exchanger phase activity coefficients are nonunity and variable as a function of the exchanger phase composition (Davidson and Argersinger, 1953; El-Prince and Babcock, 1975; Smith and Woodburn, 1978; Vázquez et al., 1986). For binary systems, Gaines and Thomas (1953) presented a thermodynamically consistent method to measure these activity coefficients, and binary system equilibrium constants, from equilibrium data. The method is based upon interpreting the resin phase as a solid solution of the exchanger phase species in equilibrium with a thermodynamically distinct solution phase. Methods to make *a priori* predictions of exchanger phase activity coefficients are unavailable. However, empirical models which relate the exchanger phase activity coefficients to the exchanger phase composition have been used. These empirical models typically relate the exchanger phase activity coefficients to its composition using binary parameters. These binary parameters can be determined through reduction of the binary equilibria data. The empirical models used to describe the exchanger phase nonidealities, and the data reduction methods used to determine the binary parameters have often been the models and methods used to reduce binary vapor-liquid equilibrium data (Anderson and Prausnitz, 1978; Prausnitz et al., 1967). To date, methods typically used to reduce ion-exchange equilibria data, and determine the equilibrium constant and the binary exchanger phase activity coefficients, have been lacking in statistical rigor.

In this study, an error in variables method (EVM) to reduce the binary ion-exchange equilibria data is presented. The EVM approach differs from conventional least-squares regression in that measurement error in both the dependent and independent system variables is taken into account in the parameter estimation. In fact, there is no designation of variables as dependent or independent in the EVM approach, in contrast to least-squares regression where the dependent variables are assumed to be measured exactly, and only the independent variable is assumed to be measured with error. This problem of parameter estimation has been discussed, and similar approaches to determining best fit parameters have been developed and utilized, in the field of vapor-liquid equilibria data reduction (Prausnitz, 1969; Anderson et al., 1978; Anderson and Prausnitz, 1978a,b). Justification for using the EVM method instead of a straightforward least-squares regression approach has been previously

---

Correspondence concerning this article should be addressed to Richard J. Vamos who is currently at DePaul & Associates, Inc., One Northbrook Place, 5 Revere Drive, Northbrook, IL 60062.

Present address of Charles N. Haas: Environmental Studies Institute, Dept. of Civil and Architectural Engineering, Drexel University, Philadelphia, PA 19104.

provided by Patino-Leal and Reilly (1982) who compared various methods of reducing simulated binary vapor-liquid equilibria data. Using the EVM approach, ion-exchange equilibria data for three different binary systems were reduced to determine the binary equilibrium constants and the resin phase activity coefficient parameters. The binary systems studied were the Na^{+1}-Cd^{+2}, Na^{+1}-Cu^{+2} and Cu^{+2}-Cd^{+2} binary systems with Dowex 50W-X8 ion-exchange resins. The Wilson equation, and a three suffix, two parameter Margules model were used to model the dependence of the resin phase activity coefficients with resin phase composition.

Objectives of Study

One objective of the study was to compare two different binary activity coefficient expressions in terms of their abilities to model the exchanger phase nonidealities. The Wilson equation was chosen because a number of previous studies have used the Wilson equation with some success to model exchanger phase nonidealities (Smith and Woodburn, 1988; El-Prince and Babcock, 1975; Shallcross et al., 1988; Vázquez et al., 1986). Also, because the derivation of the Wilson equation resulted in the binary Wilson parameters defined in terms of component molar volumes and interaction energies (Wilson, 1964), there was some hope that future studies could compare observed Wilson parameters to predictions of the binary Wilson parameters based on estimates of component molar volumes and interaction energies. The Margules model was chosen as the alternative activity coefficient model because of its relative simplicity, and because it was desired to determine if the more sophisticated model (Wilson) provided better correlation to the data than a less sophisticated model. Also, a number of researchers have used models of similar mathematical form to the Margules equation (Hogfeldt and Soldatov, 1979) to describe exchanger phase nonidealities. In fact, for monovalent-monovalent ion-exchange systems, it can be demonstrated that the Margules equation and the exchanger phase activity coefficient expression used by Hogfeldt and Soldatov are identical (Vamos, 1990).

The second objective of the study was to demonstrate the EVM approach for reduction of ion-exchange equilibria data. Although EVM approaches to reducing binary vapor liquid equilibrium data have been demonstrated in the literature (Anderson et al., 1978), a review of the ion-exchange literature indicates that the EVM approach has not previously been applied for ion-exchange equilibria data reduction.

Binary Ion-Exchange Equilibria

Consider the following general binary ion-exchange reaction between soluble phase species A, and B, and an ion-exchange resin (Res):

$$z_B A\mathrm{Res} + z_A B^{z_B} \rightleftarrows z_A B\mathrm{Res} + z_B A^{z_A} \tag{1}$$

An equilibrium constant can be defined for Eq. 1 as:

$$K_{eq} = e^{\frac{-\Delta G}{RT}} = \frac{f_B^{z_A} N_B^{z_A} \gamma_A^{z_B} [A^{z_A}]^{z_B}}{f_A^{z_B} N_A^{z_B} \gamma_B^{z_A} [B^{z_B}]^{z_A}} \tag{2}$$

where the selectivity coefficient, K_a is defined as:

$$K_a = \frac{N_B^{z_A} \gamma_A^{z_B} [A^{z_A}]^{z_B}}{N_A^{z_B} \gamma_B^{z_A} [B^{z_B}]^{z_A}} \tag{3}$$

and the selectivity coefficient, and the equilibrium constant are related by:

$$K_{eq} = K_a \frac{f_B^{z_A}}{f_A^{z_B}} \tag{4}$$

The solution phase activity coefficients are defined using the conventional standard and reference states whereby the component solution phase activity coefficient approaches unity as the component molar concentration approaches zero. The exchanger phase standard and reference states are defined as the mono-ion exchanger in equilibrium with an infinitely dilute solution of that ion, such that for exchangeable component i:

$$\begin{gathered} \text{fugacity}_i \rightarrow 1 \text{ as } N_i \rightarrow 1 \\ a_i \rightarrow 1 \text{ as } N_i \rightarrow 1 \end{gathered} \tag{5}$$

With these definitions, the binary equilibrium constant and exchanger phase activity coefficients can be determined by applying the Gibbs-Duhem equation to the exchanger phase. Formally, the Gibbs-Duhem equation for the exchanger phase will include a term for the activities of the solvent and the nonexchangeable coions in the exchanger phase (Gaines and Thomas, 1953). However, for ion-exchange reactions in dilute solutions, it can generally be assumed that the free energy change due to solvent transfer between the solution and the exchanger, and the free energy change due to exchanger imbibement of coions, can be neglected (Barrer and Klinowski, 1974; Meares and Thain, 1968).

The resin phase activity coefficients (fs) can be modeled as functions of the resin phase mole fraction and two binary parameters. Note that K_a is not directly measured, but is derived from four system variables; the solution phase composition of the two components, and the mole fraction of the two components in the resin phase. Generally, the exchanger component mole fractions are calculated by measurements of the number of moles of each ion in the exchanger phase at equilibrium, and therefore are not directly measured. For the purposes of data reduction, Eq. 4 is typically rewritten as:

$$\ln K_a = \ln K_{eq} + z_B \ln f_A - z_A \ln f_B \tag{6}$$

where the model parameters are $\ln K_{eq}$, and the two binary resin phase activity coefficient parameters. Often, the model parameters have been determined by designating some function of the observed variables as the "dependent" variable, and transforming Eq. 6 into one that predicts a value of the dependent variable, given a set of values of the independent variables and model parameters (Smith and Woodburn, 1978; Shallcross et al., 1988; Vázquez et al., 1986). However, there is no obvious justification for defining one of the ion-exchange equilibria system variables as the "dependent" variable, and the other system variables as the "independent" variables. Such applications of least-squares regression analysis are inappropriate when the independent variables are measured with some error (Halfon, 1985).

A data reduction approach that accounts for error in all the measured variables, and does not arbitrarily define one system variable as the "dependent" variable, is the EVM, Britt and Luecke (1973) and Bard (1974) developed a theoretical basis for EVM to estimate parameters in systems where at least some of the system variables are measured with error. EVM approaches have been used to reduce binary vapor liquid equilibrium data (Anderson, Abrams, and Grens II, 1978) and biological oxidation kinetic data (Haas, 1989). The EVM approach has been used in this study to determine the best fit binary equilibrium parameters for the three binary ion-exchange systems observed. A description of the EVM method follows.

Error in Variables Method

The EVM approach to parameter estimation can be described as follows. For any general model, one may write a vector of constraint functions interrelating the variables and parameters for each observation, j, as:

$$F(A:x_j)=0 \tag{7}$$

where A is an unknown parameter vector whose best fit values are to be determined, x is the vector of system variables, and F is a vector function of constraints. In systems where variables are measured with error, one can define the vector of observed variables (measured with error) as x_j', and the vector of "true" variables (which one would obtain if the variables were measured without error, and the model fit the data perfectly) as x_j. Based upon this definition, a vector of measurement errors, e_j can be defined as:

$$e_j=x_j'-x_j \tag{8}$$

The variance/covariance matrix of the error vector e_j (which is assumed to be a realization from a multivariate normal with zero mean) is designated as V. This matrix V can be measured via analysis of replicate data, or can be estimated based on estimates of the precision in measuring the individual variables. If it is assumed that the measurement errors of the different variables are uncorrelated, then the matrix V is a diagonal matrix.

Britt and Luecke (1973) and Bard (1974) determined that the best fit estimates of the parameter matrix A can be calculated by minimizing an objective function Q, subject to the generalized constraint Eq. 7, where Q is defined as:

$$Q=\sum_{j}^{N_{\text{Obs}}}\sum_{i}^{r}(x_i'-x_i)_j^T V_j^{-1}(x_i'-x_i)_j \tag{9}$$

In Eq. 9, N_{Obs} is the number of observations and r is the number of variables. Minimization of the objective function Q can be viewed as a generalization of the least-squares approach, in that Q is minimized by simultaneously minimizing the weighted sum of the squared differences between the observed and predicted ("true") values of all the system variables. This is in contrast to conventional least-squares regression in which best fit parameters are determined by minimizing the sum of the squared differences between the observed and predicted values of a single dependent variable. Accounting for error in all of the variables has been demonstrated to produce parameter estimates that are more accurate and precise than those obtained by least-squares regression (Patino-Leal, 1979). In cases where both the dependent and independent variables are measured with error, applying the conventional least-squares approach to parameter estimation fails to account for the measurement error in the independent variables, producing biased estimates of the parameters even in linear systems (Halfon, 1985).

In EVM, the weighting of the squared differences between the observed and predicted values (matrix V in Eq. 9) is proportional to the relative precision of measurement of each of the variables. This weighting procedure allows for greater residual differences between observed and predicted values for variables that are measured less precisely than others, while requiring more precise estimates of the true values of variables that are measured with greater precision. Formally, the true values of the variables, x_j, are unknowns which are estimated along with the best fit parameters by the data reduction algorithm which solves the constrained optimization problem defined by Eq. 7 and Eq. 9.

It has been demonstrated (Britt and Luecke, 1973; Bard, 1974) that if the experimental data are from a series of independent experiments, and if the error vector e_j has a multivariate normal distribution, then minimizing Q maximizes the likelihood function, and the best fit parameters determined by minimizing Q are therefore maximum likelihood estimates of the parameters. (The objective function Q is equivalent to the log-likelihood function multiplied by -2.) It should be noted that the matrix V in Eq. 9 is subscripted to the observation j, and therefore can vary with the observations. This allows for heteroscedasticity (nonuniform error variance) in the system, and is significant because some data sets exhibit measurement error that changes significantly from observation to observation.

The above general description of EVM can be placed into the context of this study as follows. Each binary system observed in this study was described in terms of only a single constraint equation:

$$0=\ln K_{\text{eq}}-\ln K_a+z_B\ln f_A-z_A\ln f_B \tag{10}$$

which can be derived by rearrangement of Eq. 6. Each binary system statistical observation consisted of the four measured values, the molar concentrations of each of the two cations in the equilibrium solution phase (ESP), and the number of moles of each of the two cations recovered in the eluate. The parameters to be estimated were the two binary resin phase activity coefficient parameters, and the natural log of the binary equilibrium constant.

The parameter estimation problem generally defined by Eqs. 7 and 9 is fundamentally a constrained optimization problem, to which the method of Lagrangian multipliers may be applied. For nonlinear systems, this constrained optimization problem cannot be solved directly. Valko and Vajda (1987) developed an iterative procedure to implement the EVM method and solve the resultant constrained optimization problem. The algorithm developed by Valko and Vajda begins by first determining parameter estimates assuming the true values of the variables and the observations are equivalent. These parameter estimates are then used to calculate updated values of the true variables, which are then in turn used to determine updated parameter estimates. This iterative process is continued until the parameter estimates converge to within a given convergence criterion. The algorithm requires as an input the Jacobian matrix of the constraint Eq. 7 with respect to the measured variables, which can be determined by either numerical or analytical differentiation of the constraint equation.

A computer algorithm using the Valko-Vajda method to solve the EVM constrained optimization problem for binary ion-exchange equilibrium was modified from a computer algorithm developed by Haas (1989). This program, coded in Turbo Basic (Borland International, Version 1.0), used the simplex optimization method of Nelder and Mead (1965) to determine the solution to the unconstrained optimization problem (derived through linearization of the constraint equation) at each step in the iterative procedure. Each binary system was characterized by one constraint equation. The four measured variables supplied to the algorithm were the two solution phase molarities and the two resinate phase number of moles extracted from the resin. It is important to note here that, although the resin phase activity coefficients were calculated based on the resin phase mole fractions, the measured variables used to calculate the resin phase composition were the number of moles of each component measured in the eluate. In other words, the resinate mole fractions were calculated values, and could not be directly measured. This is significant in terms of defining the error covariance matrix.

The Jacobian matrix of the constraint equations was derived analytically by algebraic partial differentiation of the constraint equation (Eq. 10) with respect to each of the measured variables. The variance covariance matrix was assumed to be diagonal, with the diagonal elements derived from replicate experimental data. The replicate data provided measurements of the variance for each variable at different equilibrium compositions. This data was then further analyzed to determine estimates of the variance/covariance matrix of the observed variables for each of the three binary systems.

The EVM computer algorithm was used to provide the best estimates of the Wilson or Margules parameters, and the equilibrium constant; as well as the values for the predicted (true) variables for each observation. Implementing the program required inputting the data (including the variance covariance matrix), providing convergence criteria and a maximum number of iterations, and giving initial guesses for the parameters to be determined. The algorithm then updated the guesses for the best fit parameters, and calculated updated estimates for the "true" variables, until the number of iterations exceeded the desired maximum, or until the parameters and "true" variables exhibited a relative change less than the convergence criteria. Generally, the program had to be run several times, using improved values for the initial guess of the parameter vector, until the program reached the desired convergence criteria. To insure that the best fit estimates of the parameters were global optima, and not local optima, numerous initial guesses were used to demonstrate the achievement of the same set of best fit parameters, starting from different initial guesses.

Constraint Equations

Three different binary cationic exchange systems were observed in this study: the Na^{+1}-Cd^{+2}, Na^{+1}-Cu^{+2} and Cu^{+2}-Cd^{+2} systems, on the strong acid, synthetic ion-exchange resin Dowex 50W-X8. The ion-exchange reactions for these three systems can be expressed by:

$$2\mathrm{NaRes} + \mathrm{Cd}^{+2} \rightleftarrows \mathrm{CdRes} + 2\mathrm{Na}^{+1} \tag{11}$$

$$2\mathrm{NaRes} + \mathrm{Cu}^{+2} \rightleftarrows \mathrm{CuRes} + 2\mathrm{Na}^{+1} \tag{12}$$

$$\mathrm{CuRes} + \mathrm{Cd}^{+2} \rightleftarrows \mathrm{CdRes} + \mathrm{Cu}^{+2} \tag{13}$$

The equilibrium constants for these reactions can be expressed as:

$$K_{eq}^{\mathrm{NaCd}} = \frac{f_{\mathrm{Cd}} N_{\mathrm{Cd}} \gamma_{\mathrm{Na}}^2 [\mathrm{Na}^{+1}]^2}{f_{\mathrm{Na}}^2 N_{\mathrm{Na}}^2 \gamma_{\mathrm{Cd}} [\mathrm{Cd}^{+2}]} \tag{14}$$

$$K_{eq}^{\mathrm{NaCu}} = \frac{f_{\mathrm{Cu}} N_{\mathrm{Cu}} \gamma_{\mathrm{Na}}^2 [\mathrm{Na}^{+1}]^2}{f_{\mathrm{Na}}^2 N_{\mathrm{Na}}^2 \gamma_{\mathrm{Cu}} [\mathrm{Cu}^{+2}]} \tag{15}$$

$$K_{eq}^{\mathrm{CuCd}} = \frac{f_{\mathrm{Cd}} N_{\mathrm{Cd}} \gamma_{\mathrm{Cu}} [\mathrm{Cu}^{+2}]}{f_{\mathrm{Cu}} N_{\mathrm{Cu}} \gamma_{\mathrm{Cd}} [\mathrm{Cd}^{+2}]} \tag{16}$$

By taking the natural logarithm of both sides of the equilibrium constant expressions, and rearranging the resultant expression, the following constraint equations for each of the binary equilibrium systems can be derived as:

$$\ln K_{eq}^{\mathrm{NaCd}} - \ln K_{a}^{\mathrm{NaCd}} - \ln f_{\mathrm{Cd}} + 2\ln f_{\mathrm{Na}} = 0 \tag{17}$$

$$\ln K_{eq}^{\mathrm{NaCu}} - \ln K_{a}^{\mathrm{NaCu}} - \ln f_{\mathrm{Cu}} + 2\ln f_{\mathrm{Na}} = 0 \tag{18}$$

$$\ln K_{eq}^{\mathrm{CuCd}} - \ln K_{a}^{\mathrm{CdCu}} - \ln f_{\mathrm{Cd}} + \ln f_{\mathrm{Cu}} = 0 \tag{19}$$

where K_a is defined in Eq. 3. These constraint equations were used with the EVM method to reduce the data and determine the best fit sets of binary equilibrium constants and resin phase activity coefficient parameters.

Resin Phase Activity Coefficients

Modeling the quantitative dependence of the resinate activity coefficients on the resinate composition has been attempted by several authors. There are a number of possible expressions of the excess Gibbs free energy of mixing available in the literature. In this study, two alternative excess equations were considered, the Wilson equation (Wilson, 1964), and the Margules equation (Reid et al., 1977).

The Wilson equation (1964), originally developed and often applied to describe nonidealities in liquid organic mixtures (Van Ness and Abbott, 1982; Reid et al., 1977; Prausnitz, 1969), has been used with some success in modeling the compositional dependence of the resinate phase activity coefficients (Smith and Woodburn, 1988; El-Prince and Babcock, 1975; Shallcross et al., 1988; Vázquez et al., 1986). This approach implicitly treats the resinate phase as a nonrandomly mixed solid solution. The Wilson equation uses binary interaction parameters that are obtainable from binary equilibrium data. The general form of the Wilson equation is:

$$\frac{g_e}{RT} = -\sum_{i=1}^{r} \left[N_i \ln \left(\sum_{j=1}^{r} \Lambda_{ij} N_j \right) \right] \tag{20}$$

where g_e is the molar excess Gibbs free energy of mixing, r is the number of components in the system, N_i is the mole fraction of component i, and the Λs are the Wilson parameters. For ideal systems, the excess Gibbs free energy of mixing would be zero. The definition of the activity coefficient (Denbigh, 1981) is:

$$RT\ln f_i = \frac{\partial (n_T g_e)}{\partial n_i} \tag{21}$$

where the n_i are the number of moles of component i in the resin phase, and n_T is the total number of moles in the resin phase. Equations 22 and 23 give the following expressions for the activity coefficients in a binary system as a function of the mole fractions in the resinate phase and the Wilson parameters:

$$\ln f_1 = 1 - \ln(N_1 + N_2\Lambda_{12}) - \frac{N_1}{(N_1 + N_2\Lambda_{12})} - \frac{N_2\Lambda_{21}}{(N_1\Lambda_{21} + N_2)} \tag{22}$$

$$\ln f_2 = 1 - \ln(N_1\Lambda_{21} + N_2) - \frac{N_1\Lambda_{12}}{(N_1 + N_2\Lambda_{12})} - \frac{N_2}{(N_1\Lambda_{21} + N_2)} \tag{23}$$

Note that the Λs are strictly nonnegative, and that for ideal systems, $\Lambda_{12} = \Lambda_{21} = 1$ and $f_1 = f_2 = 1$.

Wilson parameters have been determined for binary systems in clays (El-Prince and Babcock, 1975), soils (Wiedenfeld and Hossner, 1978), and anion-exchange resins (Smith and Woodburn, 1978). Furthermore, it can be demonstrated that the binary data on cation exchange by Wilson, Davidson and Argersinger (1954) and Davidson and Argersinger (1953) are consistent with the Wilson (1964) equation.

The three-suffix, two parameter Margules model (Reid et al., 1977) is an empirical power series expansion of the excess Gibbs energy function in terms of two binary parameters and the component mole fractions. Like the Wilson model, Margules equations are often used to model activity coefficients in nonideal binary organic mixtures (Abbott and Van Ness, 1975; Abbott et al., 1975). For a binary system, the Margules expression for the excess Gibbs free energy function is:

$$g_E - N_1N_2[C + D(N_1 - N_2)] \tag{24}$$

which can be substituted into the definition of the activity coefficient (Eq. 21) to give the following:

$$\ln f_1 = (C + 3D)N_2^2 - 4DN_2^3 \tag{25}$$

$$\ln f_2 = (C + 3D)N_1^2 - 4DN_1^3 \tag{26}$$

In this study, the Wilson and the Margules equations were used as alternative descriptors of the nonidealities in the resinate phase.

Solution Phase Activity Coefficients

There are available numerous methods to estimate solution phase activity coefficients in aqueous systems (Harned and Owen, 1950; Robinson and Stokes, 1959; Pitzer, 1973). Some of the more well-known models are the Debye-Hückel, Davies, and Guggenheim-Scatchard models. In this study, the Pitzer (1973) model was used to estimate the solution phase activity coefficients (Shallcross et al., 1988).

Experimental Procedure

The ion-exchange resin used in all the experiments was a strong acid, synthetic resin, manufactured by Dow Chemical under the trade name Dowex 50W-X8, and marketed by J. T. Baker. This resin is a sulfonic acid resin formed by the sulfonation of polystyrene, and the cross-linking of the resultant polymer with divinyl-benzene at a nominal mole fraction of 8%. This resin has a nominal capacity of 4.9 mequiv./g. The resin used was in the form of spherical beads of diameters equivalent to a size range of 20 to 50 mesh. A typical resin particle diameter was on the order of 1 mm. The resin was preconditioned before use by three cycles of sequential column saturation to the two cations in the binary system, and the hydrogen ion. At the conclusion of the preconditioning process, the resins were left saturated to one of the two cationic forms which comprised the binary system of interest. The resins were then subjected to a final rinse with double distilled deionized water, and centrifuged.

The equilibrium experiments were performed using the method of batch equilibrium (Helfferich, 1962). Approximately 0.5 g (dry weight basis) of the moist, pretreated, centrifuged resins were placed in a 250 mL beaker and equilibrated to 100 mL (volume measured, and delivered via graduated cylinder) of solution. The initial solution contained one or more of the ions of interest, depending upon the desired equilibrium composition range. The total ionic strength of the initial solution was controlled to 0.1. Initial solutions were prepared by dissolving appropriate masses of the reagent grade nitrate salts of the cations of interest in double distilled deionized water. One drop of 0.1 Normal nitric acid was added to the initial solution to bring the pH to between 3.5 and 4.0; below the pH levels at which copper or cadmium exhibit hydrolysis. The control was 100 ml of the initial solution placed in a 250 mL beaker, with no addition of resin. The sample and control beakers were covered with two layers of parafilm, and placed on an agitator tray in a constant temperature room (22°C). Equilibrium was attained by agitating at constant temperature for 24 to 48 h (Helfferich, 1962). Kinetic experiments with the Na^{+1}-Cd^{+2} system demonstrated that this equilibrium time was sufficient (Vamos, 1990).

Upon reaching equilibrium, the resins were separated from the solution using a 10 mL minicolumn fitted with a glass frit at its effluent end. The minicolumn containing the moist, unrinsed, resins was then centrifuged for 10 min at 2,000 rpm, to remove any occluded solution. Then, the resins were rinsed by passing 20 mL of double distilled deionized water through the minicolumn. To determine the composition of the resin phase, 1 L of approximately four normal nitric acid was used to elute the resins through the minicolumn. The eluate and the equilibrium solution phase were then analyzed for the ions of interest using flame atomic absorption spectrophotometry. The number of moles of each binary component i (n_i) were calculated by multiplying the component concentrations in the eluate by the volume of total eluate (1 L).

Replicate experiments were performed for each of the binary systems studied following essentially the same procedure as described above. The major difference between the replicate

Table 1. Summary of Observed Data

System	No. of Data Points	Notes
Na-Cd	42	17 points from 4 sets of replicates
Na-Cu	47	15 points from 3 sets of replicates; one potential outlier
Cu-Cd	34	15 points from 3 sets of replicates; two potential outliers

experiments and the rest of the binary equilibria experiments was that the mass of dry resins used in the study were carefully weighed before the start of the experiment to insure that each of the replicates was done using the same quantity of resin. To insure that the initial solution phase composition for each of the replicate runs was also identical, a batch of initial solution was prepared of sufficient volume so that each experimental run of each replicate set used a portion of the same solution as the initial solution. Also, the volume of initial solution equilibrated with resins was carefully measured to insure minimal variability in the solution volume. By minimizing any systematic differences in the initial conditions of the replicate equilibrium experiments, the results of the replicate experimental runs could provide an accurate estimate of the pure error variance.

Results

The batch equilibrium experiments provided measurements of the composition of the equilibrium solution phase and resinate phase. The solution phase measurements gave the equilibrium concentrations (moles/liter) of the two system cations, while the resinate phase measurements provided the equilibrium total number of moles of the two cations present in the entire mass of resin used. To obtain estimates of the variance covariance matrix for each system, replicate experiments were performed. It was assumed that the covariance terms for each system were negligible compared to the diagonal elements of the variance covariance matrix. Therefore, the replicate data was used to provide estimates of the diagonal elements of the variance covariance matrices. Table 1 provides a summary of the full binary system data sets (including the replicate data). To provide an example data set, the sodium-copper binary system data set is provided in Appendix A. The replicate data are summarized for each of the binary systems in Tables 2-4. Included in Tables 2-4 are the range of variable observations so that the replicate data can be placed in context with the overall data sets.

Inspection of the variances provided in Tables 2-4 show that the variances were not constant, and generally increased with the magnitude of the measurement (Vamos, 1990). Therefore, using a constant variable variance term in the EVM data analysis would not be justified and could possibly result in nonnormal residuals. Preliminary data fits using a constant variance term based upon the mean variance on each variable from the replicate data confirmed this suspicion, with the resultant weighted residuals exhibiting nonnormality. A better estimate of the variance structure was found to be as (Vamos, 1990):

$$\text{Variance} = ((\text{Relative Error}) \times (\text{Concentration}))^2 \quad (27)$$

Relative errors for each variable and replicate set were calculated from the replicate data variances provided in Tables 2-4. The mean of the relative errors on each variable deter-

Table 2. Summary of Na-Cd Binary System Data

Measured Variable (Units)	Range of Variable Observed in Full Data Set	Replicate Set Mean (Variance)			
		Set 1	Set 2	Set 3	Set 4
$[Na^{+1}]$ (mol/L)	5.337e-3–9.097e-2	0.08379 (3.184e-6)	0.08007 (5.745e-6)	0.0785 (1.711e-6)	0.03903 (3.810e-7)
$[Cd^{+2}]$ (mol/L)	4.197e-5–2.608e-2	1.439e-3 (1.337e-9)	4.413e-3 (3.644e-8)	4.287e-3 (2.436e-8)	1.933e-2 (4.180e-8)
n_{Na} (mol)	1.475e-5–2.270e-3	1.366e-3 (2.172e-9)	8.073e-4 (4.622e-10)	7.281e-4 (2.254e-10)	1.625e-4 (6.475e-11)
n_{Cd} (mol)	3.055e-5–1.185e-3	5.062-4 (8.327e-11)	7.404e-4 (2.380e-11)	6.907e-4 (2.346e-11)	9.122e-4 (3.648e-11)

Table 3. Summary of Na-Cu Binary System Data

Measured Variable (Units)	Range of Variable Observed in Full Data Set	Replicate Set Mean (Variance)		
		Set 1	Set 2	Set 3
Na^{+1} (mol/L)	1.013e-3–9.489e-2	0.08342 (6.462e-6)	0.07240 (1.355e-6)	0.02762 (5.144e-8)
$[Cu^{+2}]$ (mol/L)	8.972e-5–3.372e-2	1.766e-3 (3.214e-9)	4.578e-3 (5.451e-9)	1.219e-2 (4.553e-7)
n_{Na} (mol)	4.461e-6–3.887e-3	1.349e-2 (2.191e-9)	8.848e-4 (5.721e-10)	1.986e-4 (1.954e-11)
n_{Cu} (mol)	9.208e-5–1.881e-3	5.766e-4 (7.906e-10)	8.476e-4 (6.410e-10)	1.170e-3 (3.304e-9)

Table 4. Summary of Cu-Cd Binary System Data

Measured Variable (Units)	Range of Variable Observed in Full Data Set	Replicate Set Mean (Variance)		
		Set 1	Set 2	Set 3
$[Cu^{+2}]$ (mol/L)	6.971e-4–3.180e-2	0.02900 (1.069e-6)	0.01593 (3.113e-7)	0.004288 (8.784e-9)
$[Cd^{+2}]$ (mol/L)	7.285e-4–3.000e-2	3.664e-3 (4.117e-8)	1.664e-2 (3.862e-7)	2.617e-2 (4.008e-7)
n_{Ca} (mol)	2.874e-5–1.728e-3	1.017e-3 (4.164e-10)	4.912e-4 (3.935e-9)	1.148e-4 (8.530e-12)
n_{Cu} (mol)	3.714e-5–1.904e-3	1.456e-4 (5.628e-11)	6.047e-4 (2.313e-9)	9.342e-4 (1.136e-9)

mined from the replicate data sets were used in the full data set data fits to calculate the variances (V in Eq. 9) of the four measured quantities for each data point using Eq. 27.

Initial fits of the data identified one potential outlier in the sodium-copper data set, and two potential outliers in the copper cadmium data set. The potential outliers were identified graphically by inspection of weighted residual plots. A sample of these residual plots will be provided later in this work. However, as there was no experimental justification in deleting these data points from the data set, the data was analyzed both with and without the potential outliers included.

Tables 5 and 6 summarize the binary system data fits using the Wilson model and the Margules model, respectively. Included are the best fit parameter estimates, the estimated variance for each parameter estimate, and the best fit minimized objective function. The parameter variance/covariance matrices were estimated as the inverse Hessian matrix of the log-likelihood function (Bard, 1974), where the log-likelihood function is the objective function (Eq. 9) multiplied by −0.5. This method of estimating the parameter variance/covariance matrix assumes that the posterior probability density function of the parameters can be approximated by a multivariate normal distribution (Patino-Leal, 1979). Bard (1974) has concluded that this method of approximating parameter variance/covariance matrices in multivariate, nonlinear systems is only accurate to an order of magnitude. Although other methods for estimating the parameter variance/covariance matrices are available (Patino-Leal, 1979), all of the methods rely upon statistical assumptions that are difficult to confirm, and provide estimated parameter variances with accuracies that are difficult to ascertain. This problem of estimating parameter variance/covariance matrices in multivariate nonlinear systems is a forefront topic of multivariate predictive statistics and is in no way inherent to the EVM method.

The convention that has been chosen in describing the binary systems is to give the component that is preferred in the resin phase as the second component. In other words, the binary system having the cations Na^{+1} and Cd^{+2} is described as the sodium-cadmium system (Na-Cd) because cadmium is preferred in the resin phase. Thus, the equilibrium constant associated with the Na-Cd system describes the reaction of cadmium replacing sodium in the resin phase. Furthermore, to designate the cations associated with the Wilson parameters, a number that corresponds to one of the cations is assigned in some of the following tables. In Table 5 for instance, Na is designated as 1, for the Na-Cd system. Thus, for that system, Λ_{12} corresponds to Λ_{NaCd}, and Λ_{21} corresponds to Λ_{CdNa}.

The effect of the outliers in the Na-Cu and Cu-Cd system data can be seen by comparison of the objective functions obtained when including or excluding the outliers. It can be demonstrated through calculation of the appropriate F-statistic that removing the outliers provides a statistically significant reduction of the best fit objective function, at a critical probability of 0.05. However, comparison of the resultant best fit parameters indicate that although the objective functions were significantly affected by the outliers, the best fit estimates of

Table 5. Summary of Best Fit Wilson Model of Binary Data

Binary System	No. of Data Points	Λ_{12} (Variance)	Λ_{21} (Variance)	$\ln K_{eq}$ (Variance)	Objective Function
Na-Cd (Na = 1)	42	0.1799 (2.521e-4)	2.2759 (3.492e-3)	1.3470 (1.524e-4)	95.7151
Na-Cu (Na = 1)	47	0.2383 (4.322e-4)	2.2210 (5.232e-3)	1.2786 (1.979e-4)	306.203
Na-Cu (Na = 1)	46*	0.1592 (1.405e-4)	2.4303 (3.238e-3)	1.2907 (1.992e-4)	58.5358
Cu-Cd (Cu = 1)	34	0.5434 (2.877e-2)	1.4277 (7.598e-2)	0.1783 (2.612e-4)	177.905
Cu-Cd (Cu = 1)	32**	0.4047 (1.261e-2)	1.6763 (5.341e-2)	0.1723 (2.671e-4)	26.0728

* One outlier deleted

** Two outliers deleted

Table 6. Summary of Best Fit Margules Model of Binary Data

Binary System	No. of Data Points	C	D	$\ln K_{eq}$	Objective Function
Na-Cd	42	0.09516 (2.151e-4)	−0.1413 (2.818e-4)	1.3484 (1.624e-4)	143.837
Na-Cu	47	0.01991 (1.694e-5)	−0.1340 (1.637e-4)	1.2793 (1.819e-4)	308.081
Na-Cu	46*	0.05150 (1.538e-4)	−0.1941 (2.731e-4)	1.2876 (1.932e-4)	114.045
Cu-Cd	34	0.13380 (7.004e-4)	−0.0454 (1.105e-3)	0.1771 (2.665e-4)	177.737
Cu-Cd	32**	0.13345 (1.261e-2)	−0.0636 (5.341e-2)	0.1717 (2.671e-4)	26.7132

* One outlier deleted

** Two outliers deleted

the activity coefficient parameters, and especially the equilibrium constant, were not greatly affected by the outliers. This robustness of the EVM method was previously pointed out by Patino-Leal (1979).

The best fit equilibrium constants for the three binary systems studied reflect that the selectivity order for the three cations of interest is cadmium-copper-sodium, in terms of decreasing preference of the resin for the cation of interest. This is in agreement with most published selectivity orders for cations on strong acid synthetic resins (Marcus and Howery, 1975).

Thermodynamic consistency

The thermodynamic consistency of the binary equilibrium data can be assessed by applying the triangle rule (Davidson and Argersinger, 1953) to the three binary equilibrium constants. The binary equilibrium constants were in general found to be in good agreement with the triangle rule, which predicts that the ratio of the K_{eq}(Na-Cd) to the K_{eq}(Na-Cu) should be equal to K_{eq}(Cu-Cd). For instance, applying the Wilson model data fits of the full data sets to the triangle rule gives:

$$\frac{K_{eq}^{NaCd}}{K_{eq}^{NaCu}} = 1.071; \quad K_{eq}^{CuCd} = 1.195 \qquad (28)$$

The agreement between the best fit Cu^{+2}-Cd^{+2} system equilibrium constant, and that predicted by the triangle rule from the Na^{+1}-Cd^{+2} and Na^{+1}-Cu^{+2} system best fit equilibrium constants was reasonable, and within the ranges of agreement taken as acceptable in the ion-exchange literature (Davidson and Argersinger, 1953; Bajpai, Gupta, and Rao, 1973; Chakravarti and Sengupta, 1983; Shallcross, Herrmann, and McCoy, 1988). A more formal test of the triangle rule (Vamos, 1990) indicated failure of the triangle rule test at a critical probability of 0.05. However, the test was based upon parameter variance estimates that, as has been previously discussed, are likely only accurate to within an order of magnitude.

Conventional selectivity plots

It is difficult to represent multivariate data graphically, since plots beyond three dimensions are practically impossible. Ion-exchange equilibria data is frequently depicted graphically by plotting the measured selectivity coefficient vs. the resin phase mole fraction of the preferred species. The measured selectivity is characterized by $\ln K_a$, which is a combination of four measured variables, and the calculated solution phase activity coefficients. A pseudo-predicted value of the natural logarithm of the selectivity coefficient ($\ln K_a$) was calculated using the measured values of the system variables, the best fit parameter set, and the constraint equation for the system of interest.

It is important to note that the best fit parameter sets listed in Tables 5 and 6 were *not* determined by minimizing the sum of squares of differences between $\ln K_a$ (measured) and $\ln K_a$ (predicted). Therefore, the plots involving $\ln K_a$ are for presentational purposes only, and should not be viewed from a statistical point of view. Figures 1 through 3 present the plots of $\ln K_a$ (measured and predicted) vs. resin phase mole fraction, where the predicted values of $\ln K_a$ are calculated using the EVM determined best fit $\ln K_{eq}$ and Wilson or Margules parameters. The predicted values of $\ln K_a$ in Figures 2 and 3 were calculated using the equilibrium constants and Wilson or Margules parameters determined upon data reduction of the complete data sets, that is, without outliers removed.

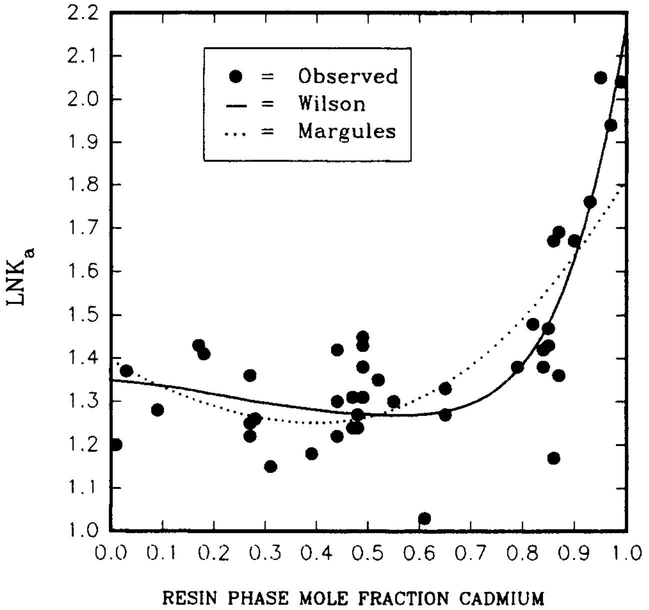

Figure 1. Measured and predicted natural log of selectivities vs. resin phase mole fraction of cadmium: sodium-cadmium binary system.

By definition, ideal ion-exchange systems are those in which the resin phase activity coefficients are unity, and thus $\ln K_a$ is invariant with respect to the resin phase mole fraction. Observing Figures 1 through 3, it seems clear that the systems studied were nonideal. Note also that the degree of nonideality varied among the systems studied. The copper cadmium system was relatively ideal, showing little variation in $\ln K_a$ with resin

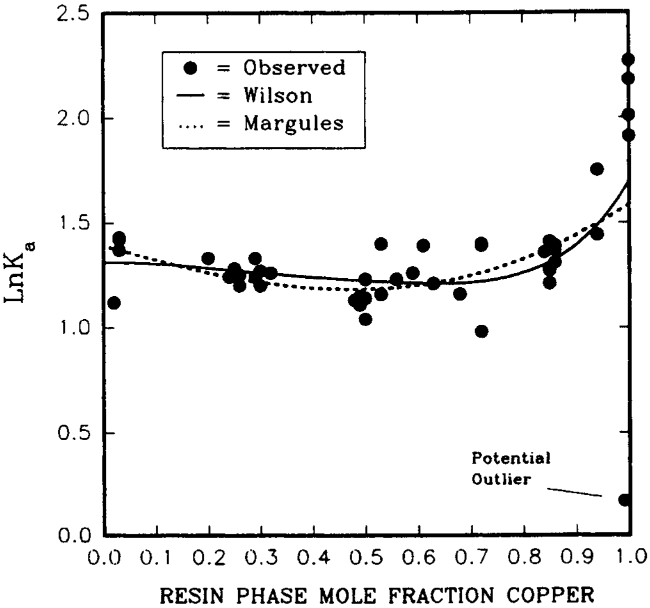

Figure 2. Measured and predicted natural log of selectivities vs. resin phase mole fraction of copper: sodium-copper binary system.

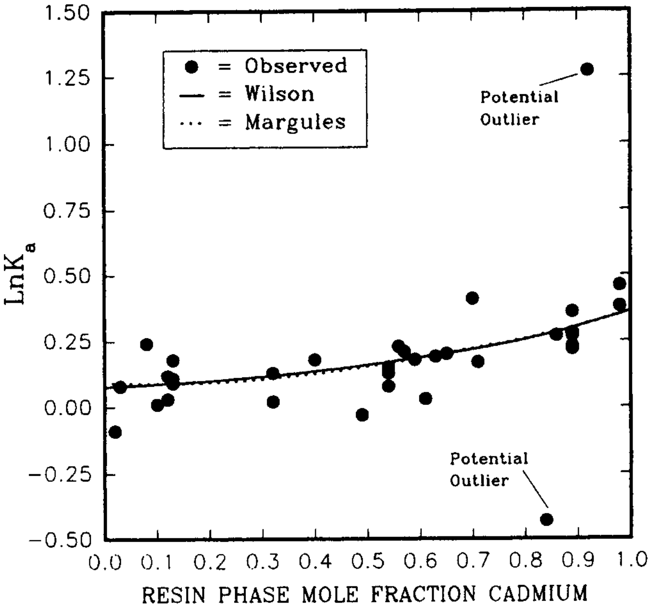

Figure 3. Measured and predicted natural log of selectivities vs. resin phase mole fraction of cadmium: copper-cadmium binary system.

phase composition. In contrast, the sodium-cadmium and sodium-copper binary systems were much less ideal, exhibiting significant variation in $\ln K_a$ with resin phase composition.

Again emphasizing that $\ln K_a$ was not the variable on which the data fits were determined, it is still interesting to note that in Figures 1 through 3, the curves resulting from using the Wilson model were in general better able to mirror the variation of the observed $\ln K_a$ with resin phase composition than the curves resulting from using the Margules model. The only exception was for the copper-cadmium binary system, where there was minor variation of the observed $\ln K_a$ with resin composition, and thus both "predicted" curves mirrored the observed values similarly. It is also worth noting that it is at the end points of the curves (near mole fractions of unity) where the differences between the Margules model and Wilson model calculated $\ln K_a s$ are the greatest. Finally, the potential outlying data points are clearly identifiable in the figures.

Discussion of Results

Test for nonideality

Figures 1 through 3 showed the variation of the observed $\ln K_a$ with resin phase composition. Early attempts at predicting ion-exchange equilibria assumed that the resin phase activity coefficients were unity, or in other words, the resin phase behaved ideally. An ideal ion-exchange system would then be characterized by a constant $\ln K_a$ with varying composition. Therefore, the binary systems observed in this study all appeared to exhibit some resin phase nonideality. Statistical tests (Vamos, 1990) indicated that in nearly all cases considered, three-parameter data fits ($\ln K_{eq}$, and the binary activity coefficient parameters) were significantly better than one-parameter ($\ln K_{eq}$ only) "ideal" data fits. The exception was the copper cadmium binary system with the outliers included, where no statistically significant difference between the three-parameter data fit, and the ideal model data fit was observed. However, this was mainly due to the two outliers, since the comparison with the outliers removed clearly indicated the superiority of the three parameter data fits.

Comparison of EVM to Simple Regression Model

It was of interest to see how the data fits using the EVM method compared to a data fit using a simple nonlinear regression technique. To make such a comparison, the sodium-copper binary system data was fit to a nonlinear regression model using SYSTAT (version 4.1). The regression model was based on the following constraint equation:

$$\ln K_a - \ln K_{eq} + 2\ln f_{Na} - \ln f_{Cu} \tag{29}$$

with K_a defined by:

$$K_a = \frac{\gamma_{Na}^2 [Na^{+1}]^2 N_{Cu}}{\gamma_{Cu} [Cu^{+2}] N_{Na}^2} \tag{30}$$

In this simple regression approach, $\ln K_a$ is viewed as the system dependent variable, and N_{Na} and N_{Cu} are taken as the system independent variables (expressed implicitly in Eq. 29 in the expressions for the resin phase activity coefficients). The system is optimized by finding the set of parameters ($\ln K_{eq}$ and the binary resinate phase activity coefficients) which minimize the sum of squares of the differences between the observed and predicted values for $\ln K_a$.

The regression model data fit of the sodium-copper binary system data was done using the Wilson model to account for the resinate phase nonidealities. The data fits were performed for the two cases of inclusion and removal of the system's potential outlying data points. It was found (Vamos, 1990) that the regression model and the EVM model were in close agreement in terms of the best fit parameter estimates for the two data sets tested. However, the regression model parameter confidence intervals were larger than the EVM model parameter confidence intervals, providing justification for the use of the EVM method instead of the more straightforward regression approach.

Residual plots

Although graphical comparisons between observed and predicted data are useful to assess the quality of data fits, residual plots and statistical analysis of the residuals are often more revealing in terms of the quality of the data fit. For instance, Haas (1989) performed an analysis of Smith and Woodburn's (1978) ternary ion-exchange system residuals, and demonstrated statistically significant trends in the residuals that were not evident in ternary plots of the observed and predicted resin phase equilibrium composition. Furthermore, since the data fits in this study were done by minimizing the differences between the observed and predicted variables in the system (the residuals), the proper method of analyzing the quality of the multivariable data fits is to look at the differences between the observed and predicted variables. The raw residuals in a multivariate system are defined as:

$$e_j = x_j - x_j' \tag{31}$$

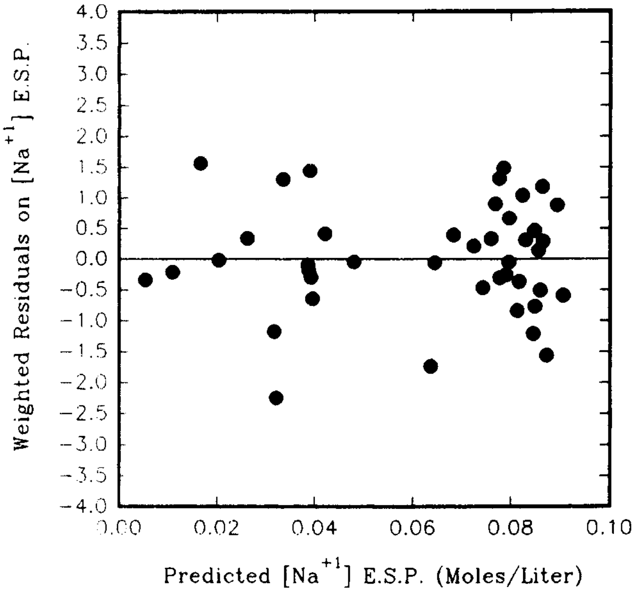

Figure 4. Weighted residuals on [Na^{+1}] ESP vs. Wilson model predicted [Na^{+1}] ESP: sodium-cadmium binary system.

where e_j is the vector of residuals for observation j, x_j is the vector of measured variables, and x_j' is the vector of predicted or "true" variables. For systems where the sample variance covariance matrix is a function of the observation, the analysis of the residuals must be done on the *weighted* residuals, which are related to the absolute residuals by:

$$e_{ji}^* = \frac{e_{ji}}{\sqrt{V_{j,ii}}} \qquad (32)$$

where the subscript j pertains to the observation number, the subscript i refers to the variable number, and the asterisk is used to distinguish between raw residuals and weighted residuals. The weighted residuals as defined by Eq. 32 are dimensionless quantities.

A plot of the appropriate weighted residuals for a given variable against the predicted values for that variable should give a scatter plot of values with a mean of zero, a standard deviation of unity and exhibit no trend with the predicted value of the variable. Weighted residuals with a variance significantly greater than unity may be evidence of significant lack of fit. Therefore, a test on lack of fit is to determine if the weighted residual variance is significantly greater than unity. Furthermore, one would hope that the residuals would be homoscedastic (constant variance), and normally distributed, because many common univariate and multivariate statistical tests require that the data be normally distributed. Heteroscedasticity generally indicates that the assumed sample variance covariance structure is invalid.

For example, for the sodium-cadmium binary system, a plot of the weighted residuals on the sodium equilibrium solution phase concentration (Na ESP) can be made by calculating the residuals on Na ESP as:

$$\begin{array}{c}\text{Weighted}\\ \text{Residual}\\ \text{on Na ESP}\end{array} = \frac{\begin{array}{c}[Na^{+1}]_{ESP}\\ \text{(Measured)}\end{array} - \begin{array}{c}[Na^{+1}]_{ESP}\\ \text{(Predicted)}\end{array}}{\sqrt{V_{ii}}} \qquad (33)$$

With each binary system having four system variables, four separate residual plots of the type defined by Eq. 33 can be made for each binary system. For the sodium-cadmium binary system, the residual plots based on the Wilson model data fit are given in Figures 4 through 7. The figures indicate that the residuals are well distributed, and do not display any obvious

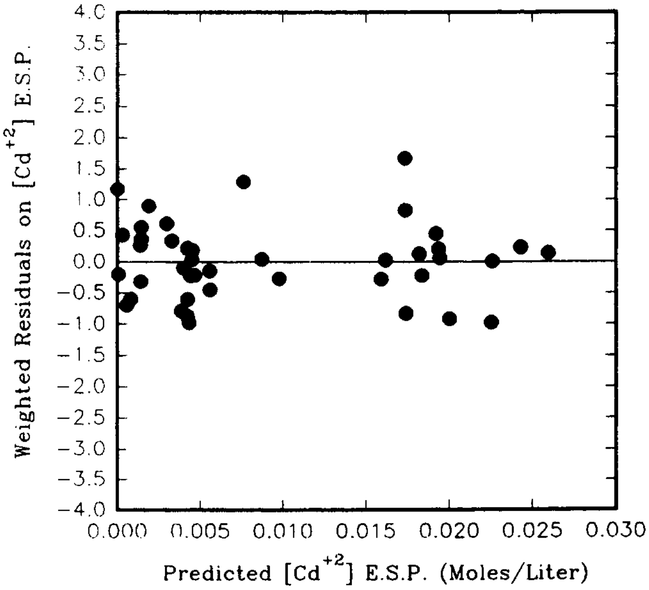

Figure 5. Weighted residuals on [Cd^{+2}] ESP vs. Wilson model predicted [Cd^{+2}] ESP: sodium-cadmium binary system.

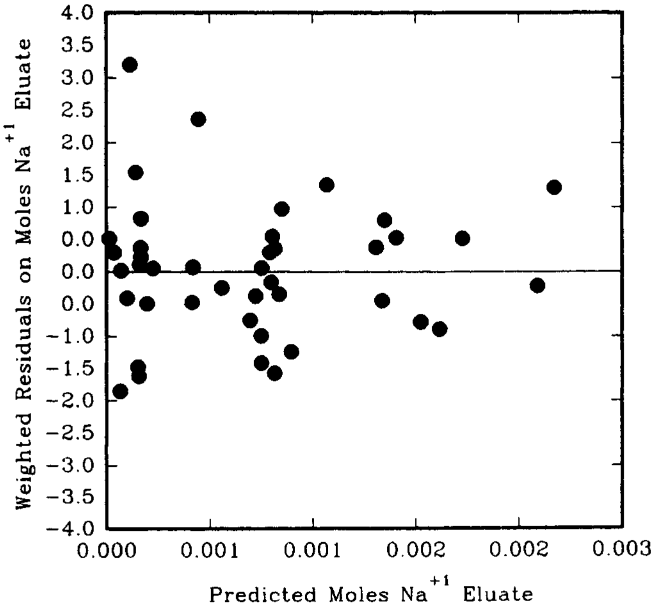

Figure 6. Weighted residuals on moles Na^{+1} eluate vs. Wilson model predicted mol Na^{+1} eluate: sodium-cadmium binary system.

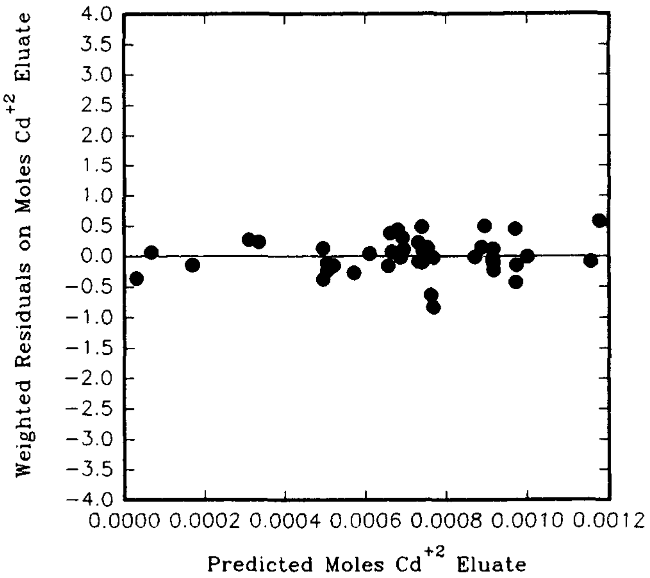

Figure 7. Weighted residuals on mol Cd^{+2} eluate vs. Wilson model predicted mol Cd^{+2} eluate: sodium-cadmium binary system.

trends or heteroscedasticity. This supports the assumptions made about the sample variance structure. A closer inspection of the weighted residual plots provided in Figures 4 through 7 reveal that the variance of the weighted residuals do appear to vary from variable to variable. However, it can be demonstrated through a chi-squared test that none of the weighted residual variances for the Na-Cd system variables are significantly greater than unity. Therefore, there is no significant evidence of lack of fit in terms of the weighted residual variances.

To provide an indication of the extent to which the potentially outlying data points varied from the rest of the data sets, two additional residual plots have been provided as Figure 8 and Figure 9. Figure 8 provides the residuals on the sodium equilibrium solution phase concentration for the Na-Cu system data fit with the potential outlier included, while Figure 9 provides the same residual plot for the data fit with the potential outlier excluded. The deviation of the outlier from the rest of the data set is clearly indicated in Figure 8. Also, it is clear that the weighted residuals resulting from the data fit with the outlier removed are distributed more appropriately than the weighted residuals resulting from the full data set reduction.

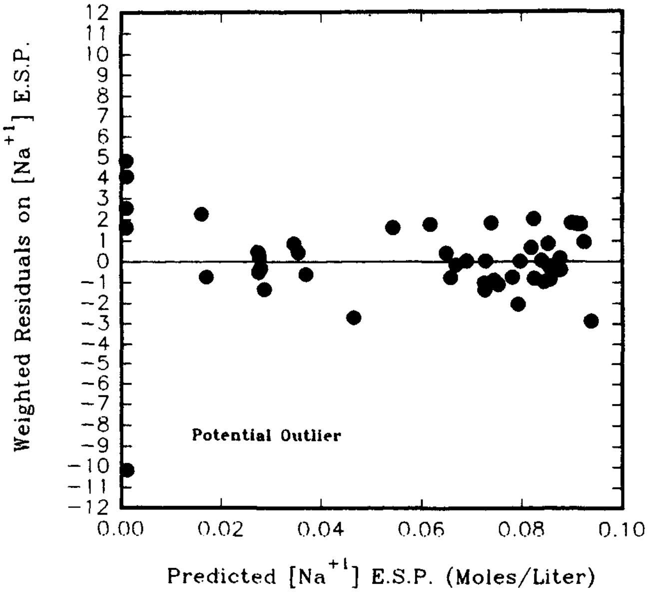

Figure 8. Weighted residuals on $[Na^{+1}]$ ESP vs. Wilson model predicted $[Na^{+1}]$ ESP: sodium-copper binary system; full data set.

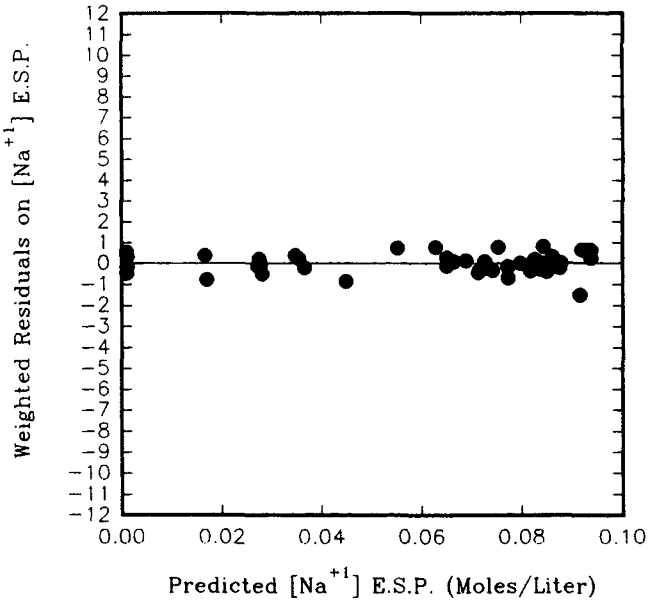

Figure 9. Weighted residuals on $[Na^{+1}]$ ESP vs. Wilson model predicted $[Na^{+1}]$ ESP: sodium-copper binary system; data fit with potential outlier removed.

Statistical Test of Residuals

A number of statistical tests were applied to the weighted residuals resulting from the data fits. The marginal weighted residuals were tested for univariate normality using the Lilliefors test (Lilliefors, 1967). To assess the quality of the data fits, the weighted residuals were tested against a hypothesis of their means being equal to zero. Both a univariate test on the marginal weighted residuals (Kleinbaum and Kupper, 1978) and a multivariate test on the weighted residual vector (Hotteling, 1931) were applied. Also, the marginal weighted residuals were tested for correlation with the measured value of the variable associated with the residual. Table 7 summarizes the results of these statistical tests of the weighted residuals for both the Wilson and the Margules model data fits.

The conclusions of the statistical tests on the residuals were the same for the Wilson and the Margules model data fits. The test for normality indicated that only some of the marginal weighted residuals were normally distributed. The test for normality failed for the full $Na^{+1}-Cu^{+2}$ and $Cu^{+2}-Cd^{+2}$ data sets. However, when the potential outliers were removed from these data sets, the marginal weighted residuals passed the test

Table 7. Summary of Statistical Tests of Residuals

System (Data Points)	Univariate Normality		Univariate Mean of Zero		Univariate Correlation with Measured Values		Hotteling T^2	
	Wilson	Margules	Wilson	Margules	Wilson	Margules	Wilson	Margules
Na-Cd (42)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Na-Cu (47)	Fail	Fail	Pass	Pass	Pass	Pass	Pass	Pass
Na-Cu (46*)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Cu-Cd (34)	Fail	Fail	Pass	Pass	Pass	Pass	Pass	Pass
Cu-Cd (32**)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass

*One outlier deleted
**Two outliers deleted

for normality. This provides additional justification for identification of the outliers. The tests on the magnitude of the weighted residuals indicated they were indistinguishable from both a univariate and multivariate mean of zero. Furthermore, the marginal residuals were not correlated with the measured value of the variable of interest.

Comparing Wilson and Margules Models

Based on the statistical analysis of the residuals, both the Wilson and Margules models were successful in modeling the resin phase nonidealities. To compare the two models directly, two statistical tests were made comparing the weighted residuals resulting from the two different model data fits. The first test was an F-test which compared the weighted residual variances of the four system variables. Table 8 summarizes the results of this statistical comparison.

In general, the results in Table 8 indicate that the weighted residuals variance terms using the Wilson model, although generally smaller, were not significantly smaller (significant if probability less than 0.05), than the corresponding terms obtained using the Margules model. The only binary system where the ratios of the variances of the weighted residuals were clearly significant was the Na^{+1}-Cu^{+2} system for the case where the data fits were determined with the one potential outlier removed. In this case, the Wilson model provides weighted residual variances that were significantly smaller than those provided by the Margules model.

Table 8. Summary of F-Test Comparison of the Weighted Residual Variance for Wilson and Margules Binary Data Fits

Binary System (Data Points)	F. Statistic (Probability)			
	Solution Phase		Resinate Phase	
	Comp. 1	Comp. 2	Comp. 1	Comp. 2
NaCd (42) Na = 1, Cd = 2	1.417 (0.140)	1.399 (0.149)	1.594 (0.075)	1.597 (0.074)
NaCu (47) Na = 1, Cu = 2	1.008 (0.489)	0.962 (0.550)	0.909 (0.623)	1.104 (0.372)
NaCu (46*) Na = 1, Cu = 2	1.661 (0.050)	1.664 (0.049)	1.902 (0.019)	2.001 (0.013)
CuCd (34) Cu = 1, Cd = 2	0.999 (0.501)	1.000 (0.500)	1.006 (0.494)	0.994 (0.506)
CuCd (32**) Cu = 1, Cd = 2	1.027 (0.471)	1.032 (0.466)	1.029 (0.470)	1.016 (0.483)

* One outlier deleted
** Two outliers deleted

The second test used to compare the Wilson and Margules model data fits was a multivariate comparison of the weighted residual vectors for the two model data fits, using the two sample Hotelling-T^2 test. Table 9 summarizes this comparison.

The results in Table 9 clearly indicate that the weighted mean residuals resulting from the binary system data fits using the Wilson and the Margules models were statistically indistinguishable. Based on the magnitude of the mean weighted residuals for the binary data fits, the Wilson and the Margules models fit the data equally well.

A final comparison between the Wilson and Margules model data fits involved a direct comparison of the best fit objective functions, which were given in Tables 5 and 6. A perusal of those tables indicate that except for the full Cu^{+2}-Cd^{+2} binary data set (where the minimized objective function for the Margules model is only smaller than that for the Wilson model by about 0.1 percent), the minimized objective functions using the Wilson model were smaller than the values obtained using the Margules model. In the case of the Na^{+1}-Cu^{+2} binary data set with 46 data points, the minimized objective function using the Margules model is approximately twice that obtained using the Wilson model. There is no readily implementable statistical test that can be made to test whether the differences in the

Table 9. Comparison of Wilson and Margules Model Weighted Residuals

Data Set (Data Points)	Calc. Test Statistic	Assoc. Probability
NaCd (42)	0.090	0.985
NaCu (47)	0.211	0.932
NaCu (46*)	0.075	0.990
CuCd (34)	0.00028	1.000
CuCd(32**)	0.003	1.000

* One outlier deleted
** Two outliers deleted

objective functions for the two models is significant. In other words, the only conclusion to be drawn in comparing the two models by their minimized objective functions is that the model which provides the smaller objective function was superior to the other for the given data set.

In summary, based on the values of the minimized objective functions for the binary system data fits, the Wilson model in general was somewhat superior to the Margules model. The one case in which the two models performed about equally in terms of the objective functions was for the copper cadmium binary system. This system was much more ideal than the other systems, and thus both models were equally capable of modeling the dependence of the resinate phase activity coefficients with resin phase mole fractions. The comparison of the weighted residuals and the variances of the weighted residuals, associated with the two models, did not in general distinguish between the two models.

Summary and Conclusions

An EVM data reduction technique was successfully used to model the three binary ion-exchange systems studied, and to determine the best fit system equilibrium constants and binary Wilson and Margules resin phase activity coefficient parameters. By using this method, the errors in data measurement of all the system variables were accounted for directly. This application of the EVM method was the first such application to ion-exchange equilibria data. It was found through the replicate experiments that the measurement errors were a function of the magnitude of the measurement. This was taken into account by using a relative variance structure for the measurement errors in the EVM method.

The Na^{+1}-Cd^{+2} and Na^{+1}-Cu^{+2} binary systems were demonstrated to be nonideal, in that the resin phase activity coefficients varied with resin phase composition. The nonidealities in the Cu^{+2}-Cd^{+2} binary system were found to be statistically insignificant when the full data set was analyzed. However, when the two potential outliers were removed from this data set, the nonidealities were found to be significant. The selectivity order on Dowex 50W-X8 for the three cations studied was found to be, in order of decreasing selectivity, Cd^{+2}-Cu^{+2}-Na^{+1}. Both the Wilson and Margules models were found to be successful in modeling the resin phase nonidealities for the three binary ion-exchange systems studied. Numerous univariate and multivariate statistical tests of the system residuals were used to verify the quality of the data fits and to compare the Wilson and Margules model data fits. Comparisons of the weighted residuals showed no statistically significant difference between the quality of the Wilson and Margules data fits. However, the Wilson model was found to provide the superior data fits, based upon the minimized objective functions.

Acknowledgment

The work described formed a portion of the PhD dissertation research of Richard J. Vamos, under the supervision of Dr. Charles N. Haas at the Pritzker Dept. of Environmental Engineering at the Illinois Inst. of Technology.

Notation

a_i = activity of component *i*
$[A]$ = molar concentration of component *A*
A, B = hypothetical ionic specie
C, D = binary Margules equation activity coefficient parameters
Cu-Cd = copper-cadmium binary system
g_e = excess molar Gibbs free energy
e_i = vector of measured errors for observation *i*
f_i = resin phase activity coefficient of component *i*
F = generalized constraint equation
J = Jacobian matrix
K_a = selectivity coefficient
K_{eq} = equilibrium constant
ln() = natural logarithm
n_i = number of moles of component *i*
n_T = total number of moles
N_i = resin phase mole fraction of component *i*
N_{Obs} = number of observations
N_{Par} = number of parameters
Na-Cd = sodium-cadmium binary system
Na-Cu = sodium-copper binary system
Q = EVM method objective function
r = number of variables
R = ideal gas constant
S = standard deviation
Res = ion-exchange resin
T = absolute temperature
V = error variance/covariance matrix
x = vector of system variables
z_i = valency of ionic component *i*

Greek letters

γ_i = solution phase activity coefficient of component *i*
ΔG = Gibb's free energy change
Λ_{ij} = binary Wilson activity coefficient parameter

Literature Cited

Abbott, M. M., J. K. Floess, G. E. Walsh, Jr., and H. C. Van Ness, "Vapor-Liquid Equilibrium: Part IV. Reduction of P-x Data for Ternary Systems," *AIChE J.*, **21**(1), 72 (1975).

Abbott, M. M., and H. C. Van Ness, "Vapor-Liquid Equilibrium: III. Data Reduction with Precise Expressions for G^E," *AIChE J.*, **21**(1), 62 (1975).

Anderson, T. F., D. S. Abrams, and E. A. Grens, II, "Evaluation of Parameters for Nonlinear Thermodynamic Models," *AIChE J.*, **24**(1), 20 (1978).

Anderson, T. F., and J. M. Prausnitz, "Application of UNIQUAC Equation to Calculation of Multicomponent Phase-Equilibria: 1. Vapor-Liquid-Equilibria," *Ind. Eng. Chem. Process Des. Dev.*, **17**(4), 552 (1978a).

Anderson, T. F., and J. M. Prausnitz, "Application of UNIQUAC Equation to Calculation of Multicomponent Phase-Equilibria: 2. Liquid-Liquid-Equilibria," *Ind. Eng. Chem. Process Des. Dev.*, **17**(4), 561 (1978b).

Bajpai, R. K., A. K. Gupta, and M. Gopala Rao, "Binary and Ternary Ion-Exchange Equilibria. Sodium-Cesium-Manganese-Dowex 50W-X8 and Cesium-Manganese-Strontium-Dowex 50W-X8 Systems," *J. Phys. Chem.*, **77**(10), 1288 (1973).

Bard, Y., *Nonlinear Parameter Estimation*, Academic Press, New York (1974).

Barrer, R. M., and J. Klinowski, "Ion-Exchange Selectivity and Electrolyte Concentration," *J. Chem. Soc. Farad. Trans. I*, No. 70, 2080 (1974).

Britt, H. I., and R. H. Luecke, "The Estimation of Parameters in Nonlinear, Implicit Models," *Technometrics*, **15**, 233 (1973).

Chakravarti, A. K., and M. Sengupta, "Multicomponent Ion Exchange Equilibria: II. Ca^{+2}-Mg^{+2}-H^+ on Amberlite IR 120," *J. Indian Chem. Soc.*, LX: 1124 (1983).

Davidson, A. W., and W. J. Argersinger, "Equilibrium Constants of Cation Exchange Processes," *Ann. NY Acad. Sci.*, **57**, 105 (1953).

Denbigh, K. B., *The Principles of Chemical Equilibrium*, 4th ed., Cambridge Univ. Press, Cambridge (1981).

Draper, N. R., and H. Smith, *Applied Regression Analysis*, Wiley, New York (1966).

El-Prince, A. M., and K. L. Babcock, "Prediction of Ion-Exchange Equilibria in Aqueous Systems with More than Two Counter-Ions," *Soil Sci.*, **120**, 332 (1975).

Gaines, G. L., and H. C. Thomas, "Adsorption Studies on Clay Minerals: II. A Formulation of the Thermodynamics of Exchange Adsorption," *J. Chem. Physics*, **21**, 714 (1953).

Haas, C. N., "On the Existence of Ternary Interactions in Ion Exchange," *AIChE J.*, **34**(4), 702 (1988).

Haas, C. N., "Error in Variables Parameter Estimation," *J. Env. Eng.*, **115**(1), 259 (1989).

Halfon, E., "Regression Methods in Ecotoxicology: A Better Formulation Using the Geometric Mean Functional Regression," *Environ. Sci. and Technol.*, **19**(8), 747 (1985).

Harned, H. B., and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, p. 454 (1950).

Helfferich, F., *Ion Exchange*, Chap. 5, McGraw-Hill, New York (1962).

Hogfeldt, E., and V. S. Soldatov, "On the Properties of Solid and Liquid Ion Exchangers: VII," *J. Inorg. Nucl. Chem.*, **41**, 575 (1979).

Hotteling, H., "The Generalization of Student's Ratio," *Ann. Math. Stat.*, **2**, 360 (1931).

Kleinbaum, D. G., and L. L. Kupper, *Applied Regression Analysis and Other Multivariate Methods*, Duxbury Press, Boston (1978).

Lilliefors, H. W., "On the Kolmogorov-Smirnov Test for Normality With Mean and Variance Unknown," *J. Amer. Statist. Assoc.*, **62**, 399 (1967).

Marcus, Y., and D. G. Howery, *Ion Exchange Equilibrium Constants*, IUPAC, Butterworths, London (1975).

Meares, P., and J. F. Thain, "The Thermodynamics of Cation Exchange. VI. Selectivity and Activity Coefficients in Moderately Concentrated Solutions," *J. Phys. Chem.*, **72**(8), 2789 (1968).

Nelder, J. A., and R. Mead, "A Simplex Method for Function Minimization," *Comp. J.*, **7**, 308 (1965).

Patino-Leal, H., "Advances in the Theory of the Error in Variables Model with Applications in Chemical Engineering," PhD Thesis, Univ. of Waterloo (1979).

Patino-Leal, H., and P. M. Reilly, "Statistical Estimation of Parameters in Vapor-Liquid Equilibrium," *AIChE J.*, **28**(4), 580 (1982).

Prausnitz, J. M., and P. L. Chueh, *Computer Calculations for High-Pressure Vapor-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1968).

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

Prausnitz, J. M., C. A. Eckert, R. V. Orye, and J. P. O'Connell, *Computer Calculations for Multicomponent Vapor-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1967).

Pitzer, K. S., "Thermodynamics of Electrolytes: I. Theoretical Basis and General Equations," *J. Phys. Chem.*, **77**, 268 (1973).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York (1977).

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London (1959).

Shallcross, D. C., C. C. Herrmann, and B. J. McCoy, "An Improved Model for the Prediction of Multicomponent Ion Exchange Equilibria," *Chem. Eng. Sci.*, **43**(2), 279 (1988).

Smith, R. P., and E. T. Woodburn, "Prediction of Multicomponent Ion Exchange Equilibria for the Ternary System Sulfate-Nitrate-Chloride from Data of Binary Systems," *AIChE J.*, **24**, 577 (1978).

Valko, P., and S. Vajda, "An Extended Marquadt Type Procedure for Fitting Error-in-Variables Models," *Comp. in Chem. Eng.*, **11**, 37 (1987).

Vamos, R. J., "Binary and Ternary Equilibria of Cationic Ion Exchange," PhD Diss., Illinois Institute of Technology, Chicago, IL (1990).

Van Ness, H. C., and M. M. Abbott, *Classical Thermodynamics of Non-Electrolyte Solutions*, McGraw-Hill, New York (1982).

Vázquez, G., A. Arce, and R. Méndez, "Ion-Exchange Equilibria: Study of the Na^+/Mn^{2+}, Na^+/Mn^{2+}, Na^+/Mn^{2+} Exchanges on Several Lewatit Cation Exchangers," *J. Chem. Eng. Data*, **31**(4), 466 (1986).

Wiedenfeld, R. P., and L. R. Hossner, "Cation Exchange Equilibria in a Mixed Soil System Containing Three Heterovalent Cations," *Soil Sci. Soc. Amer. Proc.*, **42**, 709 (1978).

Wilson, G. M., "Vapor-Liquid Equilibrium XI. A New Expression for the Excess Free Energy of Mixing," *J. Amer. Chem. Soc.*, **86**, 127 (1964).

Wilson, G. M., A. W. Davidson, and A. J. Argersinger, "The Effect of Ionic Strength on Equilibrium in Silver-Sodium Ion Exchange," *J. Amer. Chem. Soc.*, **76**, 3824 (1954).

Appendix A: Sodium-Copper Binary Equilibria Data Set

Run No.	$[Na^+]$ ESP (mol/L)	$[Cu^{+2}]$ ESP (mol/L)	mol Na^+ Eluate	mol Cu^{+2} Eluate
1	2.790e-02	1.323e-02	1.950e-04	1.118e-03
2	3.647e-02	2.189e-02	3.291e-04	1.881e-03
3	1.678e-02	2.919e-02	1.030e-04	1.680e-03
4	2.721e-02	1.118e-02	1.919e-04	1.084e-03
5	7.385e-02	4.560e-03	9.259e-04	8.495e-04
6	2.761e-02	1.186e-02	2.005e-04	1.215e-03
7	1.109e-03	3.148e-02	4.461e-06	1.777e-03
8	7.710e-02	6.623e-03	1.305e-03	1.464e-03
9	1.120e-03	3.207e-02	5.007e-06	1.777e-03
10	8.561e-02	6.566e-03	1.078e-03	1.225e-03
11	1.120e-03	3.207e-02	4.666e-06	1.777e-03
12	6.380e-02	1.393e-02	6.926e-04	1.781e-03
13	1.675e-02	2.266e-02	9.943e-05	1.690e-03
14	2.767e-02	1.225e-02	2.018e-04	1.225e-03
15	7.640e-02	6.288e-03	1.361e-03	1.385e-03
16*	1.013e-03	3.372e-02	1.064e-05	1.673e-03
17	1.078e-03	3.226e-02	4.815e-06	1.669e-03
18	6.489e-02	1.385e-02	6.593e-04	1.432e-03
19	7.652e-02	9.070e-03	9.712e-04	1.546e-03
20	2.771e-02	1.244e-02	2.037e-04	1.207e-03
21	8.303e-02	6.569e-03	1.151e-03	1.149e-03
22	9.419e-02	9.502e-05	3.316e-03	9.208e-05
23	8.131e-02	1.803e-03	1.362e-03	5.849e-04
24	8.520e-02	1.733e-03	1.310e-03	5.248e-04
25	8.920e-02	9.441e-05	3.887e-03	9.376e-05
26	7.977e-02	1.870e-03	1.280e-03	6.102e-04
27	9.419e-02	9.650e-05	3.151e-03	9.369e-05
28	7.327e-02	4.713e-03	8.608e-04	8.259e-04
29	8.582e-02	1.485e-03	1.925e-03	6.799e-04
30	7.122e-02	4.582e-03	8.865e-04	8.608e-04
31	6.907e-02	6.059e-03	1.130e-03	1.448e-03
32	7.279e-02	4.542e-03	8.899e-04	8.865e-04
33	3.505e-02	1.625e-02	3.244e-04	1.794e-03
34	7.086e-02	4.492e-03	8.610e-04	8.153e-04
35	8.672e-02	1.709e-03	1.405e-03	5.784e-04
36	9.315e-02	8.972e-05	3.768e-03	1.071e-04
37	9.489e-02	9.502e-05	3.193e-03	9.208e-05
38	6.670e-02	8.841e-03	5.369e-04	8.958e-04
39	8.442e-02	1.485e-03	1.945e-03	6.799e-04
40	8.296e-02	8.608e-04	2.909e-03	7.443e-04
41	8.411e-02	1.763e-03	1.386e-03	5.849e-04
42	6.541e-02	6.397e-03	1.015e-03	1.475e-03
43	8.791e-02	1.455e-03	1.987e-03	6.799e-04
44	8.721e-02	1.322e-03	2.323e-03	7.239e-04
45	5.599e-02	1.105e-02	6.332e-04	1.658e-03
46	4.426e-02	9.811e-03	7.298e-04	1.860e-03
47	3.568e-02	1.610e-02	3.538e-04	1.860e-03

* Outlier.

Manuscript received Mar. 1, 1993, and revision received June 29, 1993.