J. Chem. Eng. Data **2005,** *50,* 1995−2002

Modeling Solution Phase Behavior in Multicomponent Ion Exchange Equilibria Involving H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} Ions

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Eight different ion exchange equilibrium models are tested to determine which gives the most accurate predictions of equilibrium behavior for multicomponent ion exchange. The eight models differ only in the way in which they account for solution phase phenomena. Nonidealities in the exchanger phase are accounted for by applying the Wilson model. The solution phase models considered include a model that assumes ideal solution behavior and others that apply the extended Debye−Hückel equation, the Meissner and Kusik electrolyte solution theory, and the Pitzer electrolyte solution theory. Each of these methods for accounting for solution phase nonidealities are applied twice, once assuming incomplete ion dissociation and once assuming that ion dissociation was complete. The models are tested using an extensive set of equilibrium data for the 10 binary, 10 ternary, 5 quaternary, and 1 quinternary systems involving exchange of the five H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} cations on a commercial resin. The results show that for nearly all of the systems studied the greatest single improvement in the accuracy of the model predictions is achieved when incomplete dissociation of the ions is considered even if neither the extended Debye−Hückel equation nor the models of Meissner and Kusik or Pitzer are applied to the solution phase. The application of Pitzer's theory yields significantly superior results to those of Meissner and Kusik and the other models.

Introduction

A range of semi-theoretical models have been proposed to predict multicomponent ion exchange equilibrium behavior. Many of these models rely on analysis of the experimental data from the constitutive binary systems to predict the behavior in multicomponent systems.

It has long been recognized that the exchange of two ionic species between a solution phase and an exchanger phase may be represented by the reversible stoichiometric equation of the type:

$$z_b A^{\pm z_a} + z_a \underline{B^{\pm z_b}} \Leftrightarrow z_b \underline{A^{\pm z_a}} + z_a B^{\pm z_b} \qquad (1)$$

where z_a and z_b are the valencies of the ionic species A and B, respectively, and the underscore denotes that the ion is in the exchanger rather than the solution phase.

Many equilibrium models are based on the assumption that the distribution of the exchanging ions between the two phases may be represented through the definition of the binary equilibrium constant:

$$K_{AB} = \left(\frac{a'_A}{a_A}\right)^{z_b} \times \left(\frac{a_B}{a'_B}\right)^{z_a} \qquad (2)$$

where a_i and a'_i are the activities of ionic species i in the solution and exchanger phases, respectively. By defining the equilibrium constant in terms of activities, the models are able to account for the nonideal behavior usually exhibited in both phases.

Early workers often assumed that both phases behaved ideally.[1,2] Though computationally simple, the predictions made by these models were inevitably inaccurate.

The model proposed by Elprince and Babcock[3] was one of the first to account for nonideal behavior in both phases. They applied the Wilson[4] model to estimate the exchanger phase activity coefficients. The Wilson equation applied to the exchanger phase to calculate the activity coefficients is

$$\ln \bar{\gamma}_i = 1 - \ln\left\{\sum_{j=1}^{M} y_{mj}\Lambda_{ij}\right\} - \sum_{k=1}^{M}\left\{\frac{y_{mk}\Lambda_{ki}}{\sum_{j=1}^{M} y_{mj}\Lambda_{kj}}\right\} \qquad (3)$$

Here $\bar{\gamma}_i$ is the exchanger phase activity coefficient of component i, y_{mi} is the mole fraction of component i in the exchanger phase, M is the number of counterion species in the exchanger phase, and Λ_{ij} is the Wilson binary interaction parameter defined such that $\Lambda_{ij} = 1$ when $i = j$ and $\Lambda_{ij} > 0$ when $i \neq j$. Since for an ideal exchanger phase, $\Lambda_{ij} = 1 = \Lambda_{ji}$ for all i and j, deviation of the parameters from unity is an indication of the nonideality of the exchanger phase. For a binary system, only two parameters (Λ_{AB} and Λ_{BA}) are required to calculate the activity coefficient. Once determined for a binary system of two counterions, these values may be used to calculate the exchanger phase activity coefficients in a multicomponent system, assuming that the values are independent of the presence of any other exchanging ion species.

This model was improved upon by Smith and Woodburn,[5] who applied the extended Debye−Hückel equation to calculate the activity coefficients in the aqueous solution phase. They also applied the Wilson model to estimate the exchanger phase activity coefficients. Using data for the three constitutive binary systems, they were able to successfully predict the equilibrium behavior of the SO_4^{2-}−NO_3^-−Cl^- ternary system.

Later Shallcross et al.[6] proposed the use of the Pitzer electrolyte solution theory[7] to predict the aqueous phase

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10.1021/je050232j CCC: $30.25

activity coefficients. In all other respects the model was identical to the Smith and Woodburn model.[5] The analytical techniques used to fit this model to the binary equilibrium data were improved upon by Mehablia et al.[8,9]

As an alternative to the Pitzer model, Martinez et al.[10] proposed the use of the Meissner and Kusik[11] electrolyte solution theory to calculate the solution phase activity coefficients. While their model was developed for binary ion exchange systems only, de Lucas et al.[12] successfully developed and tested a model for a four-component system that used the Meissner and Kusik model.[11]

Most of the preceding models use the Wilson model to predict the activity coefficients in the exchanger phase. Vamos and Haas[13] conducted a study to compare the effectiveness of the Wilson and Margules equations to estimate the exchanger activity coefficients. They concluded that the performance of the Wilson model was slightly superior to that of the Margules equation.

Shallcross et al.[6] also recognized that not all the ions in the solution would be available for exchange with the exchanger phase because they would not be present as free ions but rather as ion pairs. They employed the method described by Kester and Pytkowicz[14] to determine the concentrations of the free ions in the solution phase available for ion exchange.

In this study we compare the performance of different models to account for the nonideal behavior of the solution phase. The solution phase models considered include the ideal behavior model, the application of the extended Debye−Hückel equation, the Meissner and Kusik electrolyte solution theory, and the Pitzer electrolyte solution theory. All four solution phase models are tested either assuming or not assuming incomplete ion dissociation. We assume that the nonidealities in the exchanger phase may be accounted for by the Wilson model.

To thoroughly test the different models, they are applied to extensive ion exchange equilibrium data for all binary, ternary, and quaternary systems as well as the five-component system involving the ions H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} on the gel-type Amberjet 1200H resin manufactured by Rohm and Hass.[15] Data are available for all systems at four different solution concentrations: 0.10 mol·L^{-1}, 0.20 mol·L^{-1}, 0.50 mol·L^{-1}, and 1.00 mol·L^{-1}.[16]

Solution Phase Behavior

Ideal Behavior. The simplest model of all, the activity coefficients for all ions, are assumed to be equal to one.

Extended Debye−Hückel Equation. Debye and Hückel[17] presented their limiting law:

$$\ln \gamma = -A|z_c z_a|I^{1/2} \tag{4}$$

where γ is the solution activity coefficient, A is the Debye−Hückel coefficient, I is the ionic strength, and z_i is the charge of ion i.

The Debye−Hückel limiting law had the serious limitation that it could only be applied with confidence to very low ionic strength solutions. An improved Debye−Hückel equation was proposed in which the term α represents the ionic atmosphere concept:[18]

$$\ln \gamma = -\frac{A|z_c z_a|I^{1/2}}{1 + \beta\alpha I^{1/2}} \tag{5}$$

Here α is the interaction coefficient between cation (c) and anion (a). This extension equation performs satisfactory up to 0.1 M.

Table 1. Extended Debye−Hückel Equation Parameters for Use in Equation 6

compound	$\alpha \cdot 10^{10}$	δ	reference
Na^+	3.97	0.075	Truesdell and Jones[21]
H^+	4.47	0.08	Robinson and Stokes[19]
K^+	3.63	0.19	Robinson and Stokes[19]
Ca^{2+}	4.73	0.12	Robinson and Stokes[19]
Mg^{2+}	5.02	0.14	Robinson and Stokes[19]
Cl^-	3.5	0.15	Truesdell and Jones[21]

The extended Debye−Hückel equation includes a term that accounts for the reduction of the dielectric constant with increasing concentration:

$$\ln \gamma_i = -\frac{Az_i^2 I^{1/2}}{1 + \beta\alpha_i I^{1/2}} + \delta_i I \tag{6}$$

where $A = 0.5115$ and $\beta = 3.281 \times 10^7$. Values for α_i and δ_i are species-dependent and are tabulated values presented by Robinson and Stokes.[19] Values for α_i and δ_i are also available for a range of ionic species.[20,21] According to Robinson and Stokes,[19] the extended Debye−Hückel equation (eq 6) fits the activity coefficients in electrolyte solutions to within the accuracy of the experimental data up to concentrations of at least 1 N. Table 1 presents the values for the parameters required in eq 6 for the present study.

Meissner and Kusik Electrolyte Solution Theory. Meissner and Kusik[11] defined the reduced activity coefficient as

$$\Gamma = \gamma_{ca}^{1/(z_c - z_a)} \tag{7}$$

where Γ is the reduced activity coefficient, γ_{ca} is the mean ionic activity coefficient, and z_c and z_a are the absolute number of charges on the cation and anion, respectively. They presented an equation for the prediction of activity coefficients in aqueous electrolyte solutions, based on parameter q, the Kusik−Meissner parameter:

$$\Gamma^0 = [1 + B(1 + 0.1\mathrm{I})^q - B]\Gamma^* \tag{8}$$

with

$$\left.\begin{aligned} &B = 0.75 - 0.065q_M \\ &\ln \Gamma^* = -\frac{A\sqrt{I}}{1 + C\sqrt{I}} \\ &C = 1 + 0.055q_M \exp(-0.023I^3) \\ &A = 0.5107 \end{aligned}\right\} \tag{9}$$

Here Γ^0 is the reduced activity coefficient of pure solution at 25 °C, and q_M is the Kusik−Meissner parameter at 25 °C. Note that the equation for Γ^* is of a similar form to the Debye−Hückel equation. A is 0.5107 for the monovalent ions and 0.4895 for divalent ions.

Meissner and Kusik[11] developed their method to calculate the activity coefficients of electrolytes in multicomponent solutions. For the electrolyte of cation i and anion j, the reduced activity coefficient is

$$\ln \Gamma_{ij} = \frac{z_i}{z_i + z_j}\frac{(W_{i2}I_2 \ln \Gamma_{i2}^0 + W_{i4}I_4 \ln \Gamma_{i4}^0 + ...)}{I} + \frac{z_i}{z_i + z_j}\frac{(W_{j1}I_1 \ln \Gamma_{j1}^0 + W_{j3}I_3 \ln \Gamma_{j3}^0 + ...)}{I} \tag{10}$$

Table 2. Meissner and Kusik[11] Model Parameters for Use in Equation 9

compound	A	$B\cdot 10^{-8}$	q_M
Na	0.5107	0.3258	3.12
H	0.5107	0.3258	5.96
K	0.5107	0.3258	11.21
Ca	0.4895	0.1511	18.22
Mg	0.4895	0.1015	15.19

Here the odd numbers indicate cations and the even numbers indicate anions, z_i is the valency of ion i, I_i is the ionic strength of the ion i, I is the total ionic strength of the solution, Γ_{ij}^0 is the reduced activity coefficient of electrolyte ij in a pure solution, and W_{ij} is the weighting factor.

The weighting factor is defined as

$$W_{ij} = \frac{0.5(z_i + z_j)^2}{z_i z_j} \tag{11}$$

Meissner[22] proposed a method for calculating q at 25 °C used in eq 9:

$$q_{ij,\mathrm{mix}} = \frac{I_1 q_{1j}^0 + I_3 q_{3j}^0 + ...}{I} + \frac{I_2 q_{i2}^0 + I_4 q_{i4}^0 + ...}{I} \tag{12}$$

The Meissner and Kusik model is considered very accurate and has been used in recent studies.[23] However, because of the lack of availability of the q parameter for a wide range of electrolytes, its application is relatively limited. Table 2 presents the values for the parameters for eq 9 for the present study.

Pitzer's Electrolyte Solution Theory. The application of Pitzer's electrolyte solution theory first proposed in 1973 and subsequently updated in 1991 has been described many times. What follows is a brief description of the application of the theory to the calculation of solution activity coefficients. More detailed discussions are presented elsewhere.[7,15,24−27]

The estimation model developed by Pitzer for single ions in aqueous solutions incorporates terms that relate to both binary and ternary interaction between the ions, as well as incorporating a Debye−Hückel electrostatic term. The expression for the activity coefficient of the single cation (M) in an aqueous solution of cations (c) and anions (a) is given by Pitzer[24] as

$$\begin{aligned}\ln \gamma_\mathrm{M} = {} & \mathrm{z}_\mathrm{M}^2 f^\gamma + \sum_\mathrm{a} m_\mathrm{a}\left[B_\mathrm{Ma} + \left(\sum_\mathrm{c} m_\mathrm{c} z_\mathrm{c}\right) C_\mathrm{Ma}\right] + \\ & 2\sum_\mathrm{c} m_\mathrm{c}\theta_\mathrm{Mc} + \sum_\mathrm{c}\sum_\mathrm{a}\left[z_\mathrm{M}^2 B'_\mathrm{ca} + z_\mathrm{M} C_\mathrm{ca} + \psi_\mathrm{Mca}\right] + \\ & {}^1/_2\sum_\mathrm{a}\sum_\mathrm{a'} m_\mathrm{a} m_\mathrm{a}'\left[z_\mathrm{M}^2\theta_\mathrm{a'a'} + \psi_\mathrm{Maa'}\right] + \frac{z_\mathrm{M}^2}{2}\sum_\mathrm{c}\sum_\mathrm{c'} m_\mathrm{c} m_\mathrm{c'}\theta'_\mathrm{cc'}\end{aligned} \tag{13}$$

where

$$f^\gamma = -A_\phi\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{\ln(1 + 1.2\sqrt{I})}{0.6}\right] \tag{14}$$

$$B_\mathrm{MX} = \beta_\mathrm{MX}^{(0)} + \frac{2\beta_\mathrm{MX}^{(1)}}{\alpha^2 I}\left[1 - \left(1 + \alpha\sqrt{I}\right)\exp(-\alpha\sqrt{I})\right] \tag{15}$$

$$B'_\mathrm{MX} = \frac{2\beta_\mathrm{MX}^{(1)}}{\alpha^2 I^2}\left[-1 + \left(1 + \alpha\sqrt{I} + \frac{\alpha^2 I}{2}\right)\exp(-\alpha\sqrt{I})\right] \tag{16}$$

$$C_\mathrm{MX} = \frac{C_\mathrm{MX}^{(0)}}{2|z_\mathrm{M} z_\mathrm{X}|^{0.5}} \tag{17}$$

The above equations are valid for 1−1, 1−2, and 2−1 electrolytes. In these equations z_i is the charge of ionic species i, and I is the ionic strength. A_φ is temperature-dependent, being defined as

$$A_\phi = \frac{1}{3}\,\frac{2\pi N_\mathrm{o}\rho_\mathrm{w}^{0.5}}{1000}\left(\frac{e^2}{\epsilon kT}\right)^{1.5} \tag{18}$$

where N_o is Avogardo's number, ρ_w and ϵ are the density and the static dielectric constant of the pure solvent, k is Boltzmann's constant, T is the absolute temperature, and e is the electron charge. At 25 °C, A_φ equals 0.392 for water. A value of 2.0 for α is recommended by Pitzer.[7]

The β and θ terms in the above equations represent measurable combinations of the second virial coefficients and may be derived from single electrolyte data. The C and ψ terms are measurable combinations of the virial coefficients and may be derived from data of two-salt systems. Values for $\beta_\mathrm{MX}^{(0)}$, $\beta_\mathrm{MX}^{(1)}$, and $C_\mathrm{MX}^{(0)}$ are species-dependent and are tabulated in the literature.[24]

The values used for the Pitzer parameters are presented in Tables 3 and 4. Values for θ_MN and ψ_MNX for systems other than those listed in Table 3 are assumed to be zero.

Incomplete Ion Dissociation. When a salt $\mathrm{M}_x\mathrm{X}_m$ is introduced into an aqueous solution, not all the molecules will immediately dissociate into the separate ions. An equilibrium will be established corresponding to the equation:

$$\mathrm{M}_x\mathrm{X}_m \leftrightarrow x\mathrm{M}^{m+} + m\mathrm{X}^{x-} \tag{19}$$

having a stability constant defined as

$$K_\mathrm{S}^\mathrm{MX} = \frac{[\mathrm{M}_x\mathrm{X}_m]}{[\mathrm{M}^{m+}]_\mathrm{f}^x[\mathrm{X}^{x-}]_\mathrm{f}^m} \tag{20}$$

where $[\mathrm{M}]_\mathrm{f}$ is the free ion concentration of species M, and m and x are the valences of cation M and anion X, respectively.

Some of the ions present in the solution will not be available for ion exchange because they are not present as free ions but rather as ion pairs. Thus for the binary system of Ca^{2+} and Na^+ ions with Cl^- ions as the nonexchanging anions, some of the ions will be present as CaCl^+ and NaCl ion pairs. We assume that all CaCl_2 dissociates to at least CaCl^+ and Cl^-.

To calculate the free ion concentrations of each of the species the method of Kester and Pytkowicz[14] is used. As an example consider the system involving the exchange of Na^+ and Ca^{2+} in the presence of Cl^-. Since sodium is present as either Na^+ or NaCl then

$$[\mathrm{Na}]_\mathrm{t} = [\mathrm{Na}^+]_\mathrm{f} + [\mathrm{NaCl}] \tag{21}$$

where $[\mathrm{Na}]_\mathrm{t}$ is the total concentration of sodium present in whatever form. According to the definition of the stability constant we may write

$$[\mathrm{NaCl}] = K_\mathrm{S}^\mathrm{NaCl}[\mathrm{Na}^+]_\mathrm{f}[\mathrm{Cl}^-]_\mathrm{f} \tag{22}$$

Table 3. Single Salt Pitzer Parameters[24]

MX	$\beta_{MX}^{(0)}$	$\beta_{MX}^{(1)}$	$C_{MX}^{(0)}$
HCl	0.20332	−0.01668	−0.00372
NaCl	0.07722	0.25183	0.00106
KCl	0.04661	0.22341	−0.00044
$CaCl_2$	0.32579	1.38412	−0.00174
$MgCl_2$	0.35573	1.61738	−0.00174

Table 4. Binary Salt Pitzer Parameters[24]

MX−NX	θ_{MN}	ψ_{MNX}
NaCl−HCl	0.0368	−0.0033
KCl−HCl	0.0067	−0.0081
$CaCl_2$−HCl	0.0682	0.0043
$MgCl_2$−HCl	0.0891	0.0006

Table 5. Salt Dissociation Constants for Use in Equation 26[14]

MX	A'_{MX}	B'_{MX}
HCl	−1.179	−0.982
NaCl	−0.537	−1.002
KCl	−0.491	−0.464
$CaCl^+$	1.073	−0.442
$MgCl^+$	0.651	−0.011

Substitution into eq 21 yields upon rearrangement

$$[Na^+]_f = \frac{[Na]_t}{1 + [Cl^-]_f K_S^{NaCl}} \tag{23}$$

Similar equations may be written for the free ion concentrations of the other ionic species, namely

$$[Ca^{2+}]_f = \frac{[Ca]_t}{1 + [Cl^-]_f K_S^{CaCl^+}} \tag{24}$$

$$[Cl^-]_f = \frac{[Cl]_t}{1 + [Ca^{2+}]_f K_S^{CaCl^+} + [Na^+]_f K_S^{NaCl}} \tag{25}$$

Since the total concentrations of the ionic species present are known and values for the stability constants are tabulated for many ion pairs, the three above equations may be solved to determine the concentrations of free ions available for ion exchange for the Na^+−Ca^{2+} binary system with Cl^-.

Kester and Pytkowicz[14] proposed that the stability constant (K_S^{MX}) may be related to the solution ionic strength (I) through an equation of the form:

$$\ln(K_S^{MX}) = A' + B'I \tag{26}$$

where A' and B' are constants, whose values are tabulated for a range of salts. Table 5 presents the parameters required in eq 26 to calculate the stability constants (K_S^{MX}).

Exchanger Phase Behavior

The Wilson[4] model is used to estimate the exchanger phase activity coefficients. For a single binary system, eq 3 reduces to

$$\ln \bar{\gamma}_1 = 1 - \ln(y_{m1} + y_{m2}\Lambda_{12}) - \left[\frac{y_{m1}}{y_{m1} + y_{m2}\Lambda_{12}} + \frac{y_{m2}\Lambda_{21}}{y_{m1}\Lambda_{21} + y_{m2}}\right] \tag{27}$$

since, as has already been noted, $\Lambda_{11} = 1 = \Lambda_{22}$. A similar expression may be written for the activity coefficient for the ion $\bar{\gamma}_2$.

Thus, following Wilson's model, values for the two binary interaction parameters, namely, Λ_{12} and Λ_{21}, must be known before the resin phase activity coefficients can be calculated. Once these values are determined, they may be used together with their counterparts from the other binary systems (e.g., Λ_{13} and Λ_{31}; Λ_{23} and Λ_{32}) to predict the activity coefficients in a multicomponent system.

Smith and Woodburn[5] proposed that values for the Wilson binary interaction parameters may be calculated along with the equilibrium constant using equilibrium data from a single binary system. They achieved this by first defining an equilibrium quotient (λ) for each ion exchange reaction as

$$\lambda_{AB} = \left(\frac{\gamma_B C_B}{y_B}\right)^{z_a}\left(\frac{y_A}{\gamma_A C_A}\right)^{z_b} \tag{28}$$

This equilibrium quotient is related to the equilibrium constant by

$$\lambda_{AB} = K_{AB}\frac{\bar{\gamma}_B^{z_a}}{\bar{\gamma}_A^{z_b}} \tag{29}$$

Thus, the equilibrium quotient would be equal to the equilibrium constant if the resin phase were ideal. Smith and Woodburn choose to use the equilibrium quotient as it is a quantity that can be determined from experimental binary equilibrium data if the solution phase activity coefficients are known.

Substitution of eq 3 into eq 29 yields upon rearrangement the equation:

$$\ln \lambda_{AB} = \ln K_{AB} - \sum_{k=1}^{M}\omega_k\left[1 - \ln\left(\sum_{l=1}^{M} y_{ml}\Lambda_{kl}\right) - \sum_{n=1}^{M}\left(\frac{y_{mn}\Lambda_{nk}}{\sum_{l=1}^{M} y_{ml}\Lambda_{nl}}\right)\right] \tag{30}$$

where ω_k is the stoichiometric coefficient of species k in the exchanger phase.

Mehablia et al.[8] proposed the use of the Gaines and Thomas[28] approach to first calculate the equilibrium constant. Then a two-parameter regression is performed to determine the Wilson binary interaction parameters. This has the advantage of decoupling the effect of variations of the equilibrium constant from variations in the Wilson binary interaction parameters:

$$\ln K_{AB} = (z_B - z_A) + \int_0^1 \ln(\lambda_{AB})\, dy_A \tag{31}$$

Since the equilibrium quotient is readily determined from simple binary batch equilibrium tests, a value for the equilibrium constant may be estimated by integrating the area under a plot of $\ln(\lambda_{AB})$ against resin equivalent ionic fraction. The method of Mehablia et al.[8] will be used to evaluate the equilibrium constants and Wilson binary interaction parameters for each of the constitutive binary systems.

Experimental Procedures

For the present study, ion exchange equilibrium data were collected using a simple batch technique for selected binary, ternary, and quaternary systems involving H^+,

Na^+, K^+, Ca^{2+}, and Mg^{2+} ions with Cl^- as the nonexchanging anion. The ion exchanger used in the experiments was the commercially available gel-type Amberjet 1200H manufactured by Rohm and Haas. The spherical resin beads had a mean diameter of (650 ± 50) μm. All solutions used in the studied were prepared from analytical grade chemicals and high-quality distilled and deionized water.

Experimental equilibrium data were obtained for the 10 binary, 10 ternary, 5 quaternary, and 1 quinternary systems involving H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} ions. In all systems, Cl^- was the only nonexchanging anion present. The full experimental data are presented elsewhere by Vo and Shallcross.[16]

To remove any water-soluble residues or undesired cations remaining on the resin after the manufacturing process, the resin samples were subjected to a preconditioning process that left them in the desired form. To determine the cation exchange capacity of the resin, a sample of the dry resin in the H^+ form was placed in a flask. A known amount of deionized water was then added to the flask. Analytical grade NaCl was then introduced. The salt immediately went into solution forming a concentrated solution of Na^+ ions, which displaced all the H^+ ions from the resin, converting the resin completely to the Na^+ form. The concentration of the H^+ ions in the solution was then determined by titrating with a standard NaOH solution under stirring action directly into the flask still containing the resin. When repeated five times the cation exchange capacity was found to be (5.05 ± 0.03) mmol/g of dry resin in the H^+ form.

A sample of the resin in a known form was put in contact with a 100 mL solution of a known composition and concentration in an Erlenmeyer flask. The resin and solution phases were then allowed to equilibrate over 3 days under intermittent shaking at 21 °C. Preliminary tests confirmed that a period of 3 days was sufficient to ensure that equilibrium had been attained. The amount of resin used and the composition of the solution phase were varied to achieve a wide range of equilibrated compositions. All binary and multicomponent systems were studied at four different solution phase concentrations, namely, 0.10 $mol \cdot L^{-1}$, 0.20 $mol \cdot L^{-1}$, 0.50 $mol \cdot L^{-1}$, and 1.00 $mol \cdot L^{-1}$.

The concentration of ions in the solution at equilibrium was measured using appropriate techniques such as titration, inductively coupled plasma, and atomic adsorption spectrophotometry. Once the equilibrium composition of the solution phase was measured, the equilibrium composition of the exchanger phase was calculated by a simple material balance. Samples of the resin used for the equilibrium experiments were also analyzed to determine their moisture content. The experimental program is described more fully elsewhere.[15]

Model Comparisons

In this work we compare the performance of eight different models to account for the nonideal behavior of the solution phase. The solution phase models considered include the ideal behavior model, the application of the extended Debye−Hückel equation, the Meissner and Kusik electrolyte solution theory, and the Pitzer electrolyte solution theory. All four solution phase models are tested either assuming or not assuming incomplete ion dissociation. For the cases when we assume that ion dissociation is complete, we refer to the ideal model as model ID, the application of the extended Debye−Hückel equation as model DH, the Meissner and Kusik electrolyte solution theory as model MK, and the Pitzer electrolyte solution theory as model PI. The corresponding models that incorporate the assumption that ion dissociation is incomplete will be referred to as the ID/IA, DH/IA, MK/IA, and the PI/IA models, respectively.

Model ID/IA assumes that the activity coefficients in the solution phase are equal one, but that not all the ions are available for ion exchange with the exchanger phase. Model DH is very similar to the model of Smith and Woodburn except for the way in which the equilibrium constants and Wilson binary interaction parameters are calculated from the constitutive binary system data. Model PI/IA is essentially the model proposed by Mehablia et al.[8]

To quantify the accuracies of the predictions of the ion exchange equilibrium model, this work uses the relative residue. It is defined as

$$R = \frac{\sum_{i=1}^{N}\left[\sum_{j=1}^{M}\left(\frac{\chi_{\text{model}} - \chi_{\text{experiment}}}{\chi_{\text{experiment}}}\right)_j^2\right]_i}{NM - 1} \qquad (32)$$

Here M is the number of set of equilibrium data, N is the number of cationic species, and χ is the quantity of interest, either the equivalent ionic fraction in the solution phase or that in the exchanger phase. For the same systems, the model that yields the lowest value for the relative residue (R) will be the one that agrees most closely with the observed experimental equilibrium data.

Analysis of Binary System Data. The eight ion exchange equilibrium models were fitted to the experimental data for each of the 10 binary systems allowing values for the equilibrium constant (K_{AB}) and the two Wilson binary interaction parameters (Λ_{AB} and Λ_{BA}) to be calculated. The values for these three fitted parameters are presented in Table 6 for each binary system and each equilibrium model.

The values for the relative residue presented in Table 7 for the eight models allow the accuracy of the model predictions to be compared. We see that for all 10 binary systems the predictions of the PI/IA model, which applies the Pitzer electrolyte solution theory and considers incomplete dissociation, yields the most accurate predictions.

The results also show that, at least for the 10 binary systems considered, the four methods of considering for nonideal behavior of the solution phase generally may be arranged in order of increasing accuracy in the model predictions as

ideal < Debye−Hückel < Meissner and Kusik < Pitzer

Furthermore, for most of the binary predictions the greatest single improvement to the accuracy of the model predictions is achieved when incomplete dissociation of the ions is considered even if neither the extended Debye−Hückel equation nor the models of Meissner and Kusik or Pitzer are applied to the solution phase. Once incomplete ion dissociation is considered, then the application of Pitzer's theory yields significantly superior results to those of Meissner and Kusik.

Analysis of Multicomulticomponent System Data. The eight equilibrium models were also used to predict the behavior of the 10 ternary, 5 quaternary, and 1 quinternary system using the values for the three fitted parameters calculated previously using the constitutive binary system data and presented in Table 6.

The relative residue values for these systems are also presented in Table 7 for each of the eight models. As before the predictions of the PI/IA are the most accurate. We also

Table 6. Model Parameters Fitted to the Ten Binary Systems for Each of the Eight Different Models

		without ion association			with ion association		
solution phase model	system AB	K_{AB}	Λ_{AB}	Λ_{BA}	K_{AB}	Λ_{AB}	Λ_{BA}
ideal ID and ID/IA	NaH	1.76	1.75	2.14	1.70	1.91	1.03
	KH	4.40	0.96	3.06	4.38	1.61	1.10
	MgH	85.7	2.01	2.20	8.30	2.04	1.67
	CaH	107.9	1.59	0.36	112.8	2.24	0.97
	KNa	1.36	1.41	2.14	1.21	1.22	2.12
	MgK	10.04	2.12	4.42	10.7	2.16	2.40
	CaK	8.01	2.85	1.32	13.3	2.45	1.06
	MgNa	29.2	2.57	4.02	25.9	1.24	4.34
	CaMg	2.29	3.19	4.35	2.37	4.10	2.66
	CaNa	37.2	2.90	4.07	40.0	2.97	3.41
Debye−Hückel DH and DH/IA	NaH	1.80	2.08	1.85	1.92	2.05	1.87
	KH	4.01	1.93	1.33	3.95	1.23	1.40
	MgH	82.4	1.75	0.92	85.1	1.93	0.75
	CaH	102.9	2.02	0.81	103.0	1.94	0.81
	KNa	1.57	1.94	1.13	1.36	1.58	0.99
	MgK	9.77	1.45	2.52	10.55	1.41	1.39
	CaK	15.1	3.05	1.00	13.4	2.02	1.22
	MgNa	34.9	2.90	2.02	33.2	2.52	2.45
	CaMg	2.37	2.73	0.75	2.79	2.09	1.02
Meissner and Kusik MK and MK/IA	NaH	1.88	2.13	0.42	2.11	2.31	0.80
	KH	4.36	1.27	1.96	4.24	1.05	2.05
	MgH	87.2	2.17	0.20	86.0	2.34	0.31
	CaH	104.3	1.64	1.13	104.0	1.82	0.97
	KNa	1.42	1.47	0.94	1.49	1.34	0.83
	MgK	94.6	2.63	0.95	7.47	2.16	0.69
	CaK	16.5	1.49	1.27	14.8	1.46	1.33
	MgNa	24.6	3.49	1.78	28.6	4.53	2.08
	CaMg	1.99	2.89	3.11	1.94	2.34	3.62
	CaNa	35.2	4.34	1.24	39.8	5.16	0.80
Pitzer PI and PI/IA	NaH	2.30	2.04	0.93	2.01	1.91	1.64
	KH	3.91	1.25	1.60	3.84	1.04	1.66
	MgH	84.3	1.44	0.88	82.0	1.80	0.74
	CaH	112.3	1.23	1.05	98.0	1.42	1.07
	KNa	1.32	1.11	0.80	1.22	1.18	0.65
	MgK	7.62	2.71	0.33	7.01	2.23	0.67
	CaK	14.8	1.83	0.95	12.4	1.14	1.07
	MgNa	23.5	3.72	1.25	20.8	4.21	2.30
	CaMg	1.86	5.25	2.29	1.92	4.27	3.63

Table 7. Values for the Relative Residue for Each System for Each of the Eight Different Models[a]

system	ID	DH	MK	PI	ID/IA	DH/IA	MK/IA	PI/IA
NaH	0.000245	0.000227	0.000195	0.000186	0.000184	0.000141	0.000108	0.000079
NaK	0.000245	0.000215	0.000203	0.000205	0.000205	0.000167	0.000165	0.000061
NaCa	0.000283	0.000254	0.000243	0.000221	0.000195	0.000171	0.000122	0.000075
NaMg	0.000296	0.000230	0.000212	0.000225	0.000195	0.000156	0.000086	0.000050
KH	0.000280	0.000263	0.000216	0.000219	0.000186	0.000175	0.000120	0.000057
KMg	0.000248	0.000219	0.000183	0.000160	0.000164	0.000136	0.000084	0.000076
KCa	0.000290	0.000271	0.000216	0.000184	0.000203	0.000142	0.000098	0.000088
MgH	0.000246	0.000200	0.000164	0.000150	0.000129	0.000105	0.000100	0.000065
MgCa	0.000275	0.000226	0.000219	0.000230	0.000225	0.000175	0.000171	0.000167
CaH	0.000232	0.000162	0.000150	0.000149	0.000141	0.000072	0.000060	0.000059
KNaH	0.00356	0.00328	0.00315	0.00318	0.00302	0.00275	0.00269	0.00250
NaHCa	0.00407	0.00374	0.00359	0.00352	0.00341	0.00307	0.00295	0.00271
NaHMg	0.00443	0.00408	0.00352	0.00344	0.00320	0.00283	0.00242	0.00215
KNaCa	0.00484	0.00453	0.00414	0.00361	0.00322	0.00280	0.00231	0.00226
KNaMg	0.00460	0.00436	0.00420	0.00410	0.00386	0.00349	0.00270	0.00239
KHCa	0.00447	0.00465	0.00410	0.00398	0.00383	0.00360	0.00340	0.00318
KHMg	0.00428	0.00423	0.00416	0.00425	0.00375	0.00316	0.00370	0.00308
NaMgCa	0.00472	0.00435	0.00417	0.00385	0.00385	0.00368	0.00337	0.00315
HMgCa	0.00373	0.00335	0.00325	0.00319	0.00303	0.00276	0.00273	0.00268
KMgCa	0.00531	0.00447	0.00419	0.00423	0.00422	0.00401	0.00377	0.00338
CaMgNaK	0.00620	0.00509	0.00477	0.00451	0.00481	0.00442	0.00364	0.00382
KNaHMg	0.00523	0.00452	0.00420	0.00401	0.00387	0.00363	0.00353	0.00324
KNaCaMg	0.00486	0.00462	0.00439	0.00442	0.00395	0.00360	0.00378	0.00306
KHCaMg	0.00476	0.00427	0.00412	0.00399	0.00380	0.00358	0.00348	0.00287
NaHCaMg	0.00564	0.00513	0.00477	0.00463	0.00435	0.00396	0.00384	0.00298
KNaHCaMg	0.01236	0.01088	0.01012	0.01012	0.00971	0.00903	0.00858	0.00841

[a] ID, ideal solution phase; DH, extended Debye−Hückel equation applied to solution phase; MK, Meissner and Kusik electrolyte solution theory applied to solution phase; PI, Pitzer electrolyte solution theory applied to solution phase; /IA, with incomplete ion dissociation incorporated into model.

see that the value of the relative residue increases with increasing number of exchanging ions in the system.

The model predictions for five of the models are compared graphically with the actual experimentally deter-

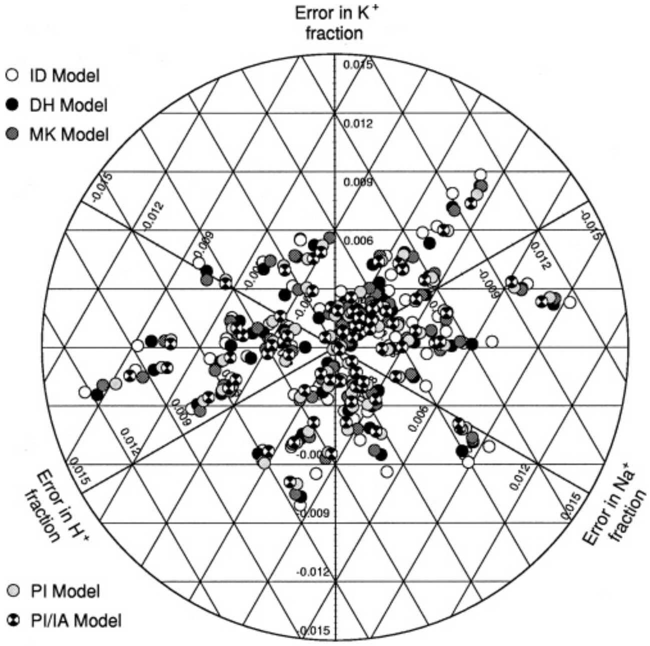

Figure 1. Ternary error diagram for the prediction of the exchanger-phase composition for the $K^+-Na^+-H^+$ system using five different ion exchange equilibrium models.

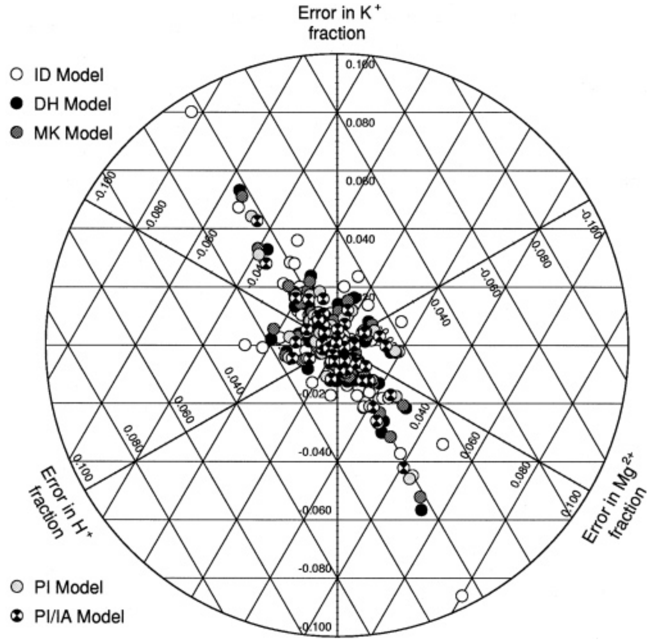

Figure 2. Ternary error diagram for the prediction of the exchanger-phase composition for the $K^+-H^+-Mg^{2+}$ system using five different ion exchange equilibrium models.

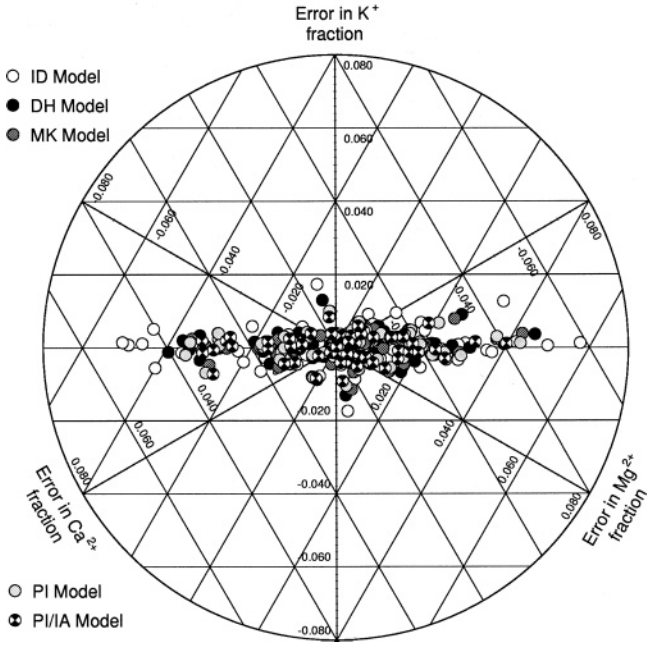

Figure 3. Ternary error diagram for the prediction of the exchanger-phase composition for the $K^+-Mg^{2+}-Ca^{2+}$ system using five different ion exchange equilibrium models.

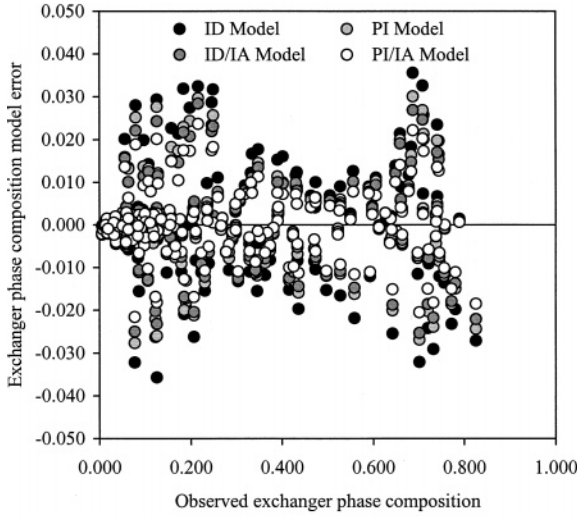

Figure 4. Errors in the predictions for the equilibrium exchanger-phase compositions for the four models for the $K^+-Na^+-Mg^{2+}-Ca^{2+}$ quaternary system.

mined equilibrium exchanger phase compositions for the $K^+-Na^+-H^+$ system in Figure 1. This is an example of a ternary error diagram as originally proposed by Shallcross and Vo.[29] Each point on this diagram represents the error in the exchange phase equilibrium composition predicted by a model as compared with the actual experimentally determined composition. The better the agreement between the model predictions and the experimental data, the closer the data point will be to the diagram's origin. The data in this diagram represents 76 sets of equilibrium compositions for four different solution concentrations ranging from 0.10 $mol \cdot L^{-1}$ to 1.00 $mol \cdot L^{-1}$. Clearly from Figure 1 the predictions made using model PI/IA are the most accurate. Moreover the four methods considered for modeling the nonideal behavior of the solution phase generally may be arranged in order of increasing accuracy in the model predictions as

$$\text{ideal} < \text{Debye−Hückel} < \text{Meissner and Kusik} < \text{Pitzer}$$

This observation is confirmed in Figures 2 and 3, which are the comparable diagrams for the $K^+-H^+-Mg^{2+}$ and the $K^+-Mg^{2+}-Ca^{2+}$ ternary systems. These are representative of the 1−1−2 and 1−2−2 valence systems studied.

As the triangular error diagram is only applicable to ternary systems the data for four- and five-component systems must be presented in a different form. Figure 4 presents the error in the exchanger phase model predictions for $K^+-Na^+-Mg^{2+}-Ca^{2+}$ four-component system. Each predicted exchanger phase composition is represented by four points on the diagram, one for each of the four

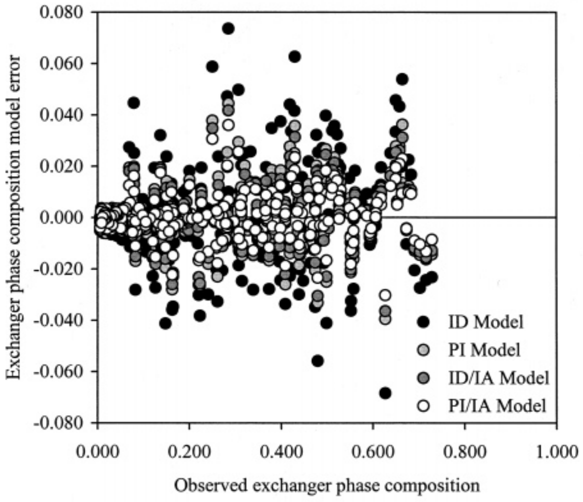

Figure 5. Errors in the predictions for the equilibrium exchanger-phase compositions for the four models for the $K^+-Na^+-H^+-Mg^{2+}-Ca^{2+}$ quinternary system.

exchanging ions. The data in this diagram represents 60 sets of equilibrium compositions for four different solution concentrations ranging from 0.10 $mol \cdot L^{-1}$ to 1.00 $mol \cdot L^{-1}$. We note that the ID model predictions are the poorest of the four models studied with PI/IA model giving the best set of predictions. This is confirmed by the relative residue data presented in Table 7. This system is representative of the five four-component systems studied. Figure 5 presents the comparable diagram for the $H^+-Na^+-K^+-Mg^{2+}-Ca^{2+}$ system. In this diagram, the data represent 77 sets of equilibrium compositions for four different solution concentrations ranging from 0.10 $mol \cdot L^{-1}$ to 1.00 $mol \cdot L^{-1}$.

Concluding Remarks

Eight ion exchange equilibrium models differing in the way in which they account for solution phase phenomena were applied to extensive equilibrium data involving exchange of up to five cations. This work clearly shows that, at least for the five cation species studied, the four methods of considering for nonideal behavior of the solution phase generally may be arranged in order of increasing accuracy in the model predictions as:

$$\text{ideal} < \text{Debye–Hückel} < \text{Meissner and Kusik} < \text{Pitzer}$$

Furthermore for most of the systems considered, the greatest single improvement to the accuracy of the model predictions is achieved when incomplete dissociation of the ions is considered even if neither the extended Debye–Hückel equation nor the models of Meissner and Kusik or Pitzer are applied to the solution phase. Once incomplete ion dissociation is considered, then the application of Pitzer's theory yields significantly superior results to those of Meissner and Kusik.

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Received for review June 16, 2005. Accepted September 14, 2005.

JE050232J