DEVELOPMENT OF A GENERALIZED MULTICOMPONENT

ION EXCHANGE REACTION

EQUILIBRIUM MODEL

By

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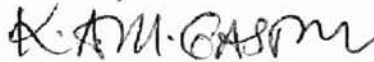
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PREFACE

A generalized multicomponent ion exchange reaction equilibrium model is developed in this work. The equilibrium model calculates the interfacial concentrations of ions on an ion exchange resin and operates independently of the form of the resin. The model is shown to be numerically stable. A survey of non-ideal generalized multicomponent equilibrium models available in the literature is also included. Recommendations about implementing non-ideal reaction equilibria in an ion exchange column model are presented.

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NOMENCLATURE

A_i parameter of ion i

a_s interfacial area (L^2/L^3)

B_i parameter of ion i

C_i concentration of species i in the bulk solution (meq/L^3)

C_i^* concentration of species i at the surface of the resin (meq/L^3)

C_T total equivalent concentration in the bulk solution (meq/L^3)

C_T^* total equivalent concentration at the surface of the resin (meq/L^3)

D_i self-diffusivity of species i (L^2/T)

D_e effective diffusivity (L^2/T)

F Faraday's constant (coulombs/mole)

ΔG^{rxn} the Gibbs free energy of reaction.

J_i flux of species i in the film $(meq/T.L^2)$

k_A^B the equilibrium constant of the exchange reaction $A^+ + BX \Leftrightarrow .AX + B^+$

K_A^B selectivity coefficient for ion B in solution compared to A in the

        resin

N_i relative valence of ion i

n number of counterions

P exponent in Franzreb's flux expressions

q_i concentration of species i in the resin (meq/L^3)

Q capacity of the resin (meq/L^3)

r radius of the film (L^{-1})

R ideal gas constant (energy/mol K)

T	temperature $(°C, K)$
X_i^*	equivalent ionic fraction of ion i in the solution phase
Y_i	equivalent ionic fraction of ion i in the resin phase
z_i	charge of ionic species i
z_j	charge of ionic species j
z_{ref}	mean counterion valence in pseudo-equilibrium model.
z_Y	mean coion valence in Franzreb's flux expressions

Greek Letters

γ_I	activity coefficient of species i in the solution phase.
$\ddot{\gamma}_i$	activity coefficient of species i in the resin phase.
Λ_{ij}	parameter for the Wilson activity coefficient model.
λ_t	coefficient in mole fraction constraint polynomial.
λ_A^B	equilibrium quotient of the exchange reaction $A^+ + BX \Leftrightarrow .AX + B^+$
	electric potential (ergs/coulomb)
	+1 for cations; -1 for anions

Superscripts

bar	refers to resin phase
*	interfacial equilibrium condition

Subscripts

ref	reference ion
i	counterion species
j	coion species
T	total concentration

CHAPTER I

INTRODUCTION

Ultrapure water is defined in this work as water with impurity concentrations less than 1 part per billion (ppb). The manufacture of mass quantities of ultrapure water typically requires several units to remove impurities from surface or well waters. Different units are used to remove different contaminants. For example, particulate matter is normally removed via filtration, dissolved gases are removed with vacuum degasification, organic contaminants may be removed with granular activated carbon, or a combination of ozonation, ultraviolet light and vacuum degasification. The removal of ionic species from solution is typically performed with reverse osmosis membranes and ion exchange columns. Reverse osmosis membranes are typically effective in removing up to 99% of the ionic contaminants but do not produce effluent ionic concentrations less than 1 ppb. The final polishing of water to ultrapure standards is normally accomplished with ion exchange columns.

Ion exchange is the branch of science which deals with the partitioning of ionic species between different phases of an overall system. The phases under consideration for this study are the aqueous solution phase and a solid resin phase. The ion exchange reaction is defined as the stoichiometric reaction of exchangeable species between the resin and liquid phases while maintaining electroneutrality and exchange capacity. The electroneutrality assumption is required because otherwise an electric current would be

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generated within the solution phase, and the exchange capacity definition recognizes a finite number of exchange sites within the exchanging phase.

Ion exchange resins are a vital part of the water purification industry. Applications of ion exchange resins include microelectronics manufacturing, pharmaceutical production, paper pulp processing, and condensate polishing for steam turbine cycles.

Ion exchange resins are typically composed of a polystyrene matrix crosslinked with divinyl benzene. Functional groups are attached to the divinyl benzene to provide exchange sites. The typical functional group for strong acid cationic resins is sulfate, while strong base anionic resins have tert-methyl amine functional groups.

Mixed Bed Ion Exchange

Mixed bed ion exchange (MBIE) is a mixture of cationic and anionic resin within the same column used to deionize an influent stream. The idea was first conceived by Kunin (1951). MBIE is often used in ultra pure water manufacture because it combines the ion exchange reaction in the resin with the neutralization reaction that occurs between free hydrogen and hydroxyl ions in the bulk solution. This reduces the bulk solution phase concentrations of hydrogen and hydroxyl ions and promotes the mass transfer and reaction equilibria of these ions from the resin into the solution phase. MBIE is the industrial standard of eliminating the final traces of ionic species from ultrapure water. With sufficient pretreatment from reverse osmosis membranes or electrodeionization units, MBIE columns can produce effluent water with an effluent ionic concentration ranging from as low as 50 parts per trillion (ppt) to 30 ppm.

Cationic resin is in the hydrogen form when all of the exchange sites have hydrogen ions attached. Similarly anionic resin is in the hydroxyl form when all of the exchange sites have hydroxyl groups attached. Ion exchange resins are typically in the hydrogen or hydroxyl forms for ultrapure water applications, where the exchanged hydrogen and hydroxyl ions combine according to the dissociation of water; however, different forms of the resin can be used depending upon the application. For example, cation resin is often used in the sodium form for softening applications, where the hardness ions, such as calcium or magnesium, are exchanged preferentially for sodium. This allows the softening resin to be regenerated cheaply with a concentrated brine solution. The power industry often uses cationic resin in the ammonia or morpholine form to increase the pH of water for corrosion control.

Ion Exchange Mechanism

The mechanism of ion exchange is divided into five steps (Lou, 1993). These are:

1. Diffusion of the counterions from the bulk solution through a film outside the resin.

2. Diffusion of the counterions within the resin phase.

3. Chemical reaction between the counterions and the exchange site.

4. Diffusion of the displaced ion out of the resin.

5. Diffusion of the exchanged ion from the resin surface through the film into the bulk solution.

Steps 1 and 5 have been shown by several authors (Boyd et al., 1947; Helfferich, 1962) to be the rate limiting steps in the ion exchange reaction. Film diffusion models

have been discussed by several authors (Helfferich, 1962; Zecchini, 1991; Bulusu, 1994). The film diffusion models assume a linear driving force requiring two solution concentrations per ion as boundary conditions, a bulk solution concentration, and the interfacial concentration on the surface of the resin (Haub, 1984). Several film diffusion models have been developed in the literature. The Ultra Pure Water Research group at Oklahoma State University applies a model adapted from the work of Franzreb (1993). The flux is expressed mathematically as,

$$J_i = \frac{D_i}{\delta}\left((1 - \frac{N_i}{P})(C_i^* - C_i) + N_i A_i(1 + \frac{1}{P})(C_T^* - C_T)\right) \qquad (I\text{-}1)$$

where J_i is the ionic flux of species i in meq/cm^2 s. The variables D_i, δ, P, N_i, and A_i are ion specific variables described in detail in Appendix C and by other authors (Bulusu, 1994; Sunkavalli 1996). The individual and total solution ionic concentrations, C_i and C_T, can be found by from applying bulk neutralization solution chemistry. The individual and total interfacial concentrations, C_i^* and C_T^*, are calculated from multicomponent reaction equilibrium.

Assuming film diffusion is the rate limiting step allows the assumption of instantaneous reaction equilibrium. This work develops expressions for multicomponent chemical reaction equilibrium between arbitrary counterions and the exchange sites. By modeling the ion exchange equilibrium, we may estimate the interfacial ionic concentrations on the surface of the resin, and supply the necessary boundary conditions required to estimate the ionic fluxes into and out of the resin. Figure I-1 illustrates graphically the ion exchange reaction for sodium and hydrogen on a cationic resin. Notice the sodium and hydrogen concentration differences between the bulk solution and

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the interface provides driving forces for diffusion of the sodium ions into the resin phase and the diffusion of hydrogen ions from the resin into the solution phase.

An analogous figure applies to anionic resin with typical anions such as Cl^-, F^-, SO_4^{2-}, or NO_3^- exchanging with hydroxyl groups (OH^-).
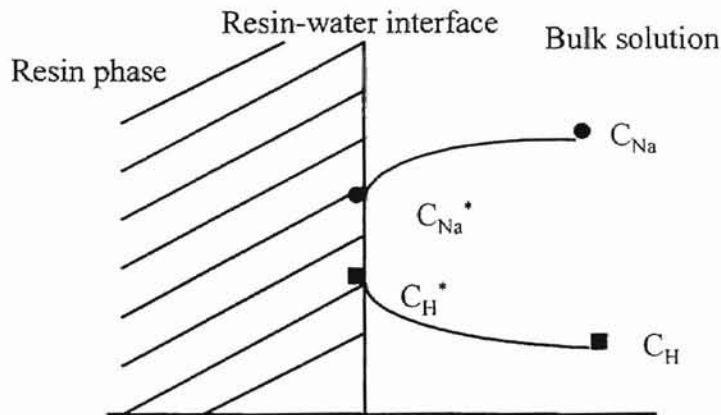
Figure I-1. Graphical representation of ion exchange resin surface in an aqueous solution.

Objective

The objectives of this work are defined below:

1. Develop a model to predict interfacial concentrations for up to 10 ions with arbitrary valences given the number of ions, resin loading, selectivities, and resin capacity.

2. The model must be suitable for cation and anion exchange equilibrium.

3. A computer subroutine is to be used to implement the model, and the subroutine must be completely stable.

4. The subroutine must allow for the number of exchanging ions to be varied.

Earlier works by Bulusu (1994) and Sunkavalli (1996) have developed a multicomponent equilibrium model for use in the mixed bed ion exchange model;

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however, it is unstable when the reference ion loading in the selectivity expression is equal to zero, and the model is unable to predict the column performance after the reference ion is completely exchanged.

CHAPTER II

LITERATURE REVIEW

Multicomponent ion exchange equilibrium has been studied by several authors, each providing different insights in compensating for the non-ideal effects present within the ion exchange resin and solution phase. The objective of this chapter is to provide an introduction to multicomponent ion exchange equilibrium methods presented in the literature.

Multicomponent Ion Exchange Theory

The ion exchange reaction occurring between a resin exchanger and a solution phase ion is represented by the following binary reaction,

$$z_B A^{\pm z_A} + z_A \overline{B^{\pm z_B}} \Leftrightarrow z_B \overline{A^{\pm z_A}} + z_A B^{\pm z_B} \tag{II-1}$$
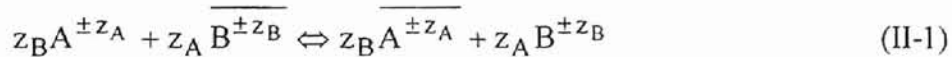
with the overbar denoting the resin phase. De Lucas et al. (1992) classified the methods for multicomponent ion exchange equilibria into four main groups:

1. Models assuming ideal exchange equilibria with a constant separation factor and activity coefficients equal to unity in the resin phase

2. Models assuming regular systems with a linear transformation between the separation factor and the composition in the solid phase

3. Models which emulate the ion exchange reaction as a phase equilibrium

4. Theoretical models which consider non-ideal or real systems

Equilibrium Constant and Selectivity

Three different forms of the equilibrium constant are commonly encountered in the literature. These are the equilibrium constant, k_A^B, the selectivity coefficient, K_A^B, and the equilibrium quotient, κ_A^B. Each of these variables are discussed below.

The equilibrium constant, k_A^B, for this reaction is usually defined as (Argersinger et al., 1950)

$$k_A^B = \left(\frac{\overline{a_A}}{a_A}\right)^{z_B} \left(\frac{a_B}{\overline{a_B}}\right)^{z_A} \tag{II-2}$$

where a_i is the activity of species i and again the overbar denoting the species is in the resin phase. The activity is defined in many chemistry and thermodynamics texts as

$$a_i = \gamma_i X_i^* C_T \tag{II-3}$$

or for the resin phase

$$\overline{a_i} = \overline{\gamma_i} Y_i Q \tag{II-4}$$

where

γ_i = the activity coefficient of species i in either the resin or solution phase.

X_i^* = the equivalent ionic fraction of ion i in the solution phase.

Y_i = the equivalent ionic fraction of species i in the resin phase.

Inserting the definitions of activity for both the resin and solution phase yields

$$k_A^B = \left(\frac{\overline{\gamma_A} Y_A}{\gamma_A X_A^*}\right)^{z_B} \left(\frac{\gamma_B X_B^*}{\overline{\gamma_B} Y_B}\right)^{z_A} Q^{(z_A - z_B)} C_T^{*(z_B - z_A)} \tag{II-5}$$

Assuming isothermal conditions, we see by inspection that in order to calculate the equilibrium solution concentrations for a binary system we must know the equilibrium constant, initial loading of the resin, the capacity of the resin, the total interfacial concentration of ions in the solution phase, and four individually calculated activity coefficients.

Estimation of the equilibrium constant has been discussed by many authors (Argersinger et al., 1950; Högfeldt, 1990), and the method of calculation is the topic of considerable debate. In many applications the solution phase concentration is assumed to be ideal, and the resin phase activity coefficients are lumped with the equilibrium constant to yield the selectivity coefficient. Work by Allen et al. (1989) states the selectivity coefficient is a function of the solution concentration, with the selectivity coefficient increasing almost 20 fold when the solution concentration was varied from 0.1 eq/l to 1.0 eq/l. Mehablia (1994) applied the method of Gaines and Thomas (1953) which successfully separated the equilibrium constant from the resin and solution ionic concentrations, yielding a thermodynamically consistent mass action equilibrium constant coupled with an activity coefficient model.

Kunin (1960) made several observations about ion exchange equilibria that are useful in qualitatively predicting the selectivity of an exchanging species:

1. At low concentrations and normal temperatures (between 50-100 °F) , the selectivity increases with increasing valence of the exchanging species:

$$Na^+ < Ca^{2+} < Al^{3+} < Th^{4+}$$
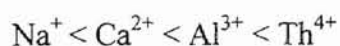
2. Assuming constant valence with normal temperatures and low concentrations, the selectivity of an exchanging species increases with increasing atomic number:

monovalent: Li < Na < K < Rb < Cs; divalent Mg < Ca < Sr < Ba

3. High molecular weight organic ions and metallic anionic complexes exhibit high exchange potentials.

4. Ions with high activity have greater exchange potential.

5. Increasing the degree of resin crosslinking increases the selectivity, and decreasing crosslinking reduces the selectivity to a limit of unity.

Several different methods are employed to calculate the equilibrium constant from isotherm data (Högfeldt, 1990). Generally these methods calculate the equilibrium constant by integrating the equilibrium quotient with respect to the resin phase equivalent ionic fraction of the exchanging ion. The selectivity is estimated by integrating the equilibrium quotient with respect to the reference ion concentration

$$\ln K_A^B = \int_0^1 \ln \kappa_A^B dY_A \qquad \text{(II-6)}$$

The equilibrium quotient, κ, is defined by Smith and Woodburn (1978) as the product of the equilibrium constant and the ratio of the resin phase activity coefficients at an arbitrary resin loading. The equilibrium quotient is written mathematically as,

$$\kappa_A^B = k_A^B \frac{\gamma_B}{\gamma_A} \qquad \text{(II-7)}$$

Values of the equilibrium quotient are obtained from experimental data and the integration is performed using graphical or numerical methods. The methods differ primarily in their approach in estimating the ratio of activity coefficients as a function of the resin phase concentration.

Solution Phase Concentration

The bulk solution phase concentration can be measured directly with a variety of instruments, such as an ion chromatograph, or indirectly by using a conductivity meter. Mehablia et al. (1994) suggested the possibility of the formation of ion pairs in the solution phase inhibiting the availability of exchangeable ions in solution. Mehablia (1994) applied the method of Kester and Pykowicz (1969) to determine the concentration of exchangeable ions within the solution phase, and have generated equilibrium curves of the Na^+-H^+ system with various sodium electrolytes (NaF, $NaSO_4$, $NaNO_3$, and NaCl) illustrating the effect of ion pair formation.

Resin Capacity

The resin capacity can be measured by several techniques. A simple method for capacity measurement is performed by mixing a known volume of ion exchange resin in the hydrogen form with a salt solution of known volume and concentration. For cationic resin, the hydrogen exchanges preferentially for the sodium. The equivalents of sodium exchanged can be measured by titrating the solution with a standard sodium hydroxide solution (Mehablia et al., 1994, 1996).

Solution Phase Activity Coefficients

Several solution phase activity coefficient models have been used to model ion exchange equilibrium. Smith and Woodburn (1978) applied the extended form of the Debye-Hückel model to predict the activity coefficients. However, Shallcross (1988) noted the activities of the Debye-Hückel equation are influenced only by the ionic strength of other ions present. Horvath (1985) recommends the activity coefficient model

proposed by Pitzer (1973, 1979, 1991). Pitzer's correlations are more accurate for multicomponent solutions; however, they are substantially more complex than the Debye-Hückel model. There are three species dependent parameters, two parameters which are derived from binary electrolyte data, and two parameters which are derived from single electrolyte data leading to a total of seven required parameters.

Resin Phase Activity Coefficients

Resin phase activity coefficients have been modeled with excess Gibbs free energy models such as the regular solution model, sub-regular solution model, or the Wilson activity model. Grant et al. (1989) compared these activity coefficient models with equilibrium data obtained from ion exchange resins and montmorillonite clay. The study showed all three of the models can accurately predict the resin phase activity coefficients of binary reactions. The Wilson model provided the most accurate results for both binary and ternary systems given binary and ternary equilibrium data respectively; however, accurate ternary predictions were not achieved from binary data. Mehablia et al. (1994, 1996) obtained accurate ternary and quaternary equilibrium concentration predictions for sodium, calcium, potassium and hydrogen from binary data. Appendix B discusses both non-ideal solution and resin activity coefficients in greater detail.

Many ion exchange processes are used for multicomponent systems; however, very little experimental work has been performed for systems with three or more exchangeable species. Multicomponent equilibrium for many species has been approximated by Bulusu (1994) and Sunkavalli (1996) by assuming constant selectivity and ideal solutions and applying mole fraction constraints to solve for the interfacial

concentrations in terms of one variable. The derivation of this model is detailed in

Chapter III.

CHAPTER III

MODEL DEVELOPMENT

The primary objective of the equilibrium model is to develop a subroutine that provides reasonably accurate interfacial concentrations for up to 10 cations or 10 anions given the following variables; 1) selectivities referenced to a common ion, 2) ion valences, 3) total interfacial concentration, 4) resin capacity and 5) arbitrary resin loading.

The selectivities and ion valences are obtained from a selectivity database collected by the Ultrapure Water Research Group. They are normally referenced to hydrogen ions (H^+) for cations, and hydroxyl ions (OH⁻) for anions. Selectivities may also be referenced to a different ion. The reference ion may be switched to the appropriate ion by applying the following relation,

$$K_B^C = \frac{\left(K_A^C\right)^{z_B}}{\left(K_A^B\right)^{z_C}} \tag{III-1}$$

where the subscripts and superscripts A, B, and C refer to arbitrary ions, and z_i is the charge of ion i.

The resin capacity is obtained from a resin database developed by the Ultra Pure Water Research Group. The capacity units used within the code are meq/ml. The total interfacial concentration is calculated iteratively within the ionic flux expressions of the column model (Bulusu 1994).

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The algorithm for calculating the interfacial concentrations is presented below, and is coded in another work (Sunkavalli, 1996).

Ideal multicomponent ion exchange equilibrium

The focus of this section is to develop the expressions that are used to calculate the interfacial ionic concentrations. Ideal multicomponent equilibrium expressions are developed in terms of binary equilibrium expressions, and then mole fraction constraints are applied to calculate the interfacial concentrations for each ion.

The ion exchange reaction for a binary reaction is defined in general form as

$$z_M A^{Z_A} + z_A \overline{M}^{Z_M} \Leftrightarrow z_M \overline{A}^{Z_A} + z_A M^{Z_M} \tag{III-2}$$

where ion A is the reference ion of the exchanger, typically H^+ or an amine for a cationic exchanger, or OH^- for an anionic exchanger, and i is an arbitrary counter ion with valence z_i. The overbar denotes the ion in the resin phase.

Smith and van Ness (1992) define the ideal equilibrium constant with the law of mass action, written below as

$$K = \prod -\overline{x_i} Y^{v_i} \tag{III-3}$$

where x_i is the mole fraction of species i and v_i is the stoichiometric number of species i.

Writing this expression for the ion exchange reaction yields

$$K_A^B = \left(\frac{q_B}{C_B^*} \right)^{Z_A} \left(\frac{C_A^*}{q_A} \right)^{Z_B} \tag{III-4}$$

where

q_i = the resin phase concentration of species i in meq/ml

$$\lambda_i = Y_i \left(K_A^i \right)^{-1/z_A} \left(Y_A \right)^{-z_i/z_A} \left(\frac{Q}{C_T^*} \right)^{z_i/z_A} \qquad \text{(III-12)}$$

the interfacial equivalent ionic fraction for ionic species i is written as

$$X_i^* = \lambda_i \left(X_A^* \right)^{z_i/z_A} \qquad \text{(III-13)}$$

Currently for n ions there are (n-1) equations and (n+1) unknowns, namely the interfacial equivalent ionic fractions and the total interfacial concentration. By applying equivalent ionic fraction constraints, another equation is supplied and a polynomial expression for the solution of the interfacial concentrations is written in terms of X_A^*.

$$\sum_{i=1}^{n} X_i^* = \sum_{i=1}^{n} \lambda_i \left(X_A^* \right)^{z_i/z_A} = 1 \qquad \text{(III-14)}$$

This polynomial can be solved using various types of numerical search algorithms. Bulusu (1994) applied a Newton-Raphson iteration, and the present author has solved the equations with Ridder's method.

After solution of the polynomial expression for the equivalent ionic fraction X_A^*, the remaining interfacial concentrations are found by substituting the value for X_A^* into Eq. (III-14) and solving for each equivalent ionic fraction.

Throughout the development of these equations the total interfacial concentration C_T^* is still unknown. This quantity is found by an iterative procedure. The equations are developed by Franzreb (1993) and summarized below. The derivation of Franzreb's flux expressions is in Appendix B.

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$$C_T^* = \left(\dfrac{\sum\limits_{i=1}^{n}(1+N_i)D_iX_i}{\sum\limits_{i=1}^{n}(1+N_i)D_iX_i^*} \right)^{\!\!1/P+1} \qquad \text{(III-15)}$$

where

N_i = the negative of the ratio of the counterion valence to the mean coion valence, expressed mathematically as

$$N_i = -\dfrac{z_i}{z_Y}. \qquad \text{(III-16)}$$

where

$$z_Y = \dfrac{\sum\limits_{i=1}^{n} z_i^2 C_i}{\sum\limits_{i=1}^{n} z_i C_i} \qquad \text{(III-17)}$$

D_i = the ionic diffusion coefficient of species i.

P = an exponent applied in the ionic flux expressions expressed mathematically as

$$P = \dfrac{\sum\limits_{i=1}^{n} N_i D_i\left(X_i^* - X_i^o\right)}{\sum\limits_{i=1}^{n} D_i\left(X_i^* - X_i^o\right)} \qquad \text{(III-18)}$$

Notice the interfacial concentrations appear in the selectivity expressions and the total interfacial concentration expression. This requires an iterative solution applying the following algorithm (Bulusu, 1994).

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Table I-I. Algorithm for calculating the total interfacial concentration.

1.	Assume $C_T^* = C_T^o$
2.	Calculate X_i^*'s by applying Eq. (III-13)
3.	Substitute the values for X_i^* into Eqs. (III-15) and (III-16) and calculate C_T^*.
4.	Substitute C_T^* into Eq. (III-13) and repeat steps 2 and 3 until the relative difference is equal to or below a predetermined tolerance.

Arbitrary resin loading is the primary disadvantage of the current equilibrium model. As stated previously, the reference ion equivalent ionic fraction is in a denominator of the selectivity expression solved for the solution equivalent ionic fraction. When the resin becomes completely loaded with ions other than the reference ion, the equivalent ionic fraction of the reference ion approaches zero. This possible zero may cause failure of the computer code and is unacceptable in commercial software applications.

A common situation where the reference ion loading approaches zero is during column breakthrough with a multicomponent feed. Consider a feed with sodium and calcium ions exchanging on a cationic resin. As the column operates for an extended period of time, almost all of the hydrogen is exchanged for sodium. Eventually, the resin will be in the sodium form and begin exchanging calcium ions for sodium ions. At this moment, the hydrogen loading is approximately zero, and the column model neglects the hydrogen from the equilibrium calculations (Sunkavalli, 1996).

Run time is also an important consideration during the model development. A typical run of the column model may execute the interfacial concentration subroutine up to 12 million times, requiring several hours of computer time. This limits significantly the complexity of the equilibrium model.

Possible solutions and the pseudo-ion concept

The author has considered two possibilities to avoid having a zero loading of the reference ion. The first alternative is to switch the reference ion when the loading of the current reference ion approaches zero. There are several problems with this solution. The first problem is determining at which loading we must switch the reference ion. The second problem is deciding which ion to use at the new reference. Consider the hypothetical situation when the resin is equally loaded with five different ions. What criteria do we apply in choosing the reference ion? Should we choose the ion with the largest or smallest selectivity? Or should we consider the valence of the ion? Implementing a decision tree that selects the proper reference would be quite difficult, and the stability of the code would be in question.

The second alternative is to create a reference ion from the ions that are currently loaded on the resin. This concept of a pseudo-ion has been applied by Franzreb (1993) in the calculation of the ionic fluxes, and offers several advantages.

The pseudo-ion has a resin phase equivalent ionic fraction of 1.0 because the pseudo-ion is defined by the properties of all of the ions loaded on the resin. This eliminates the potential for a zero within the denominator.

The pseudo-ion is independent of the reference ion. This is beneficial when calculating the behavior of resins in another form. Selectivity data are typically represented in the hydrogen or hydroxyl forms. By using the pseudo-ion algorithm, the form of the resin does not matter, as long as the selectivity data have a common reference ion.

Mean selectivity derivation

Consider the thermodynamic definition of an ideal equilibrium constant for a reaction,

$$\frac{\Delta G^{rxn}}{RT} = \ln\left(k_A^B\right) \tag{III-19}$$

(de Bokx et al, 1992) where $\Delta G^{rxn}/RT$ is the dimensionless form of the Gibb's free energy of reaction for ions A and B with respect to the exchanger ion on the resin. The Gibb's free energy is a molar property. This allows us to take the arithmatic average of the Gibb's free energy for several reactions by applying the relationship

$$\overline{M} = \sum_{i=1}^{n} x_i M_i \tag{III-20}$$

(Smith et al., 1992). Thus the average Gibb's free energy of several reactions is represented by the following relationship.

$$\sum_{i=1}^{n} y_i \frac{\Delta G_i^{rxn}}{RT} = \sum_{i=1}^{n} y_i \ln\left(k_A^i\right) \tag{III-21}$$

Moving the coefficient of the logarithm to the exponent of the selectivity coefficient and defining the mean Gibb's free energy with Eq. (III-21) yields the following expression.

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$$\overline{\frac{\Delta G^{rxn}}{RT}} = \sum_{i=1}^{n} \ln\left(k_A^i\right)^{y_i} \tag{III-22}$$

Applying the property of logarithms

$$\sum_{i=1}^{n} \ln(X_i) = \ln\left(\prod_{i=1}^{n} X_i\right) \tag{III-23}$$

allows us to reduce the expression to the final form.

$$\overline{\frac{\Delta G^{rxn}}{RT}} = \ln\left(\prod_{i=1}^{n} k_A^{i \ y_i}\right) \tag{III-24}$$

By noting the similarity of Eqs. (III-19) and (III-24), we can substitute the selectivity coefficient for the equilibrium constant and define the mean selectivity coefficient (or the selectivity of the pseudo-ion with respect ion A) with the following relationship.

$$K_A^{ref} = \prod_{i=1}^{n} K_A^{i \ y_i} \tag{III-25}$$

where the superscript 'ref' refers to the reference ion.

Mean Valence and Reference Switching

We have now developed an expression that gives the mean selectivity coefficient for several ion exchange reactions given the selectivities and loadings for individual binary reactions. However, in order to use the pseudo-ion as our reference ion by applying Eq. (III-1), we need to define a mean ionic valence. Franzreb (1993) applies the following definition for the mean ionic valence

$$z_{ref} = \frac{\sum_{i=1}^{n} z_i^2 C_i}{\sum_{i=1}^{n} z_i C_i} \qquad \text{(III-26)}$$

where

z_{ref} = the mean ionic valence

z_i = the charge of ion i

C_i = the concentration of ion i in mol/l

Notice the relationship allows the possibility of fractional charges. Fractional charges have been applied by Franzreb (1993) in calculating the ionic mass transfer.

Also note the units of concentration in the mean ionic valence are mol/l. Selectivity data are normally represented in terms of equivalents, thus the units must be converted to mol/l by applying the following relation.

$$(Y_i Q)_{mole} = \frac{(Y_i Q)_{eqiv.}}{|z_i|} \qquad \text{(III-27)}$$

These units are only applied within a subroutine that calculates the mean ionic valence, thereafter they are no longer used.

The system is specified for transforming the selectivity data to a common pseudo-ion. Rewriting Eq. (III-1) in terms of the pseudo-ion variables referenced to ion A yields

$$K_{ref}^i = \frac{\left(K_A^i\right)^{z_{ref}}}{\left(K_A^{ref}\right)^{z_i}} \qquad \text{(III-28)}$$

We now have all of the variables required to complete the multicomponent ion exchange equilibrium expression.

Calculation of the Interfacial Concentrations

A polynomial is generated by relating the individual solution phase equivalent ionic fractions to the pseudo-ion solution phase equivalent ionic fraction and applying the equivalent ionic fraction constraint.

$$\sum_{i=1}^{n} X_i = \sum_{i=1}^{n} \lambda_i \left(X_{ref}\right)^{z_i/z_{ref}} = 1 \qquad \text{(III-29)}$$

where λ_i is defined by

$$\lambda_i = Y_i \left(K_{ref}^i\right)^{-1/z_{ref}} \left(Y_{ref}\right)^{-z_i/z_{ref}} \left(\frac{Q}{C_T^*}\right)^{1-z_i/z_{ref}} \qquad \text{(III-30)}$$

Recall the value of Y_i is known, Y_{ref} is equal to 1.0, the total capacity is defined by the resin, and the total interfacial concentration C_T^* is calculated iteratively with Franzreb's flux expressions.

Eq. (III-31) is written in the following form to facilitate the search for a root with an appropriate numerical method.

$$f\left(X_{ref}^*\right) = 1 - \sum_{i=1}^{n} \lambda_i \left(X_{ref}^*\right)^{z_i/z_{ref}} \qquad \text{(III-31)}$$

The resulting polynomial has been shown to have a root between 0.0 and 1.0. The function is then solved for zero using Ridder's search algorithm described in Appendix B. This algorithm was chosen because it has guaranteed convergence when the root is properly bracketed, and the convergence is slightly faster than the bisection method.

The value of X_{ref}^* has no actual physical significance, it is merely used as a reference to calculate the interfacial equivalent ionic fractions for each ion. This is

accomplished by first calculating the interfacial equivalent ionic fraction of the ion with respect to the pseudo-ion using the following relation.

$$X^*_{i,ref} = \lambda_i \left(X^*_{ref} \right)^{z_i/z_{ref}} \tag{III-32}$$

These interfacial equivalent ionic fractions are in the correct proportion to each other, but they do not sum to exactly 1.0. Normalizing the fractions to 1.0 by applying

$$X^*_i = \frac{X^*_{i,ref}}{\sum\limits_{i=1}^{n} X^*_{i,ref}} \tag{III-33}$$

yields interfacial equivalent ionic fractions for each ion. The resulting fractions are then multiplied by the total interfacial concentration with the following relation,

$$C^*_i = X^*_i C^*_T \tag{III-34}$$

to yield the interfacial concentration for each ion which can be used in the algorithm developed by Franzreb (1993).

Model Constraints

The author has found two limitations to the model in its present form:

1. The resin phase equivalent ionic fractions must sum to exactly 1.0

2. All valences and selectivities must be positive real numbers.

The first limitation is a result of the definition of equivalent ionic fractions. If the numbers do not sum to exactly one, the root will not be within 0.0 and 1.0. This should not be a problem because the resin loading fractions sum to 1.0 by definition, however, a flag has been entered into code to ensure the loading fractions sum to 1.0 to prevent possible failure of the subroutine.

The second limitation is also a minor problem because only the absolute values of the charges are considered in both the cationic and anionic interfacial concentration calculations, and the selectivities are always defined as positive real numbers. A flag has been inserted into code to insure these constraints have been satisfied.

CHAPTER IV

RESULTS AND DISCUSSION

The pseudo-ion model was written into code and the following tests were

performed:

1. Equilibrium Y-X isotherms were generated for several binary ion exchange reactions.

    The ion pairs were Na^+-H^+, K^+-H^+ and Ca^{2+}-H^+.

2. The new equilibrium model was compared to the version presented in Chapter III and

    to experimental data.

3. Interfacial concentrations were plotted as a function of pH for several ions and the

    equilibrium leakages were compared to data given by Arizona Public Service.

4. Run-times were determined for two different numerical methods.

Equilibrium isotherms

A separate driver program included in Appendix D was written to receive input

and execute the subroutine. Equilibrium curves were generated by assuming constant

total solution concentrations, selectivities, capacities and valences. The initial loadings of

the binary system were then varied. Table IV-I illustrates the input data used to generate

the equilibrium curves.

Figure IV-1 shows an isotherm generated for the Na^+-H^+ binary exchange reaction

and a 1:1 line. The abscissa of the plot is the resin phase equivalent ionic fraction of

hydrogen, and the ordinate is the solution phase equivalent ionic fraction of hydrogen.

Mathematically, the equilibrium isotherm of monovalent ions is similar to the separation

factor used in vapor liquid equilibrium calculations. Notice the curve is a monotonic,

concave downward function that yields X_H values greater than the Y_H values. This

indicates the interfacial solution phase equivalent ionic fraction of hydrogen is greater

than the interfacial solution phase equivalent ionic fraction of sodium at equilibrium.

Table IV-I. Input data for interfacial concentration subroutine

Parameter	Na^+-H^+	K^+-H^+	Ca^{2+}-H^+
Selectivity	1.5	2.5	4.4
Valence	1	1	2
Capacity (meq/ml)	1.9	1.9	1.9
Solution concentration (meq/ml)	0.001	0.001	0.001

Figure IV-2 is an isotherm for the K^+-H^+ system. A comparison of the K^+-H^+

isotherm to the Na^+-H^+ isotherm shows the effect of atomic coefficient on the reaction

equilibria of ions of the same valency. The curve is steeper and yields higher interfacial

equivalent ionic fractions of hydrogen for equivalent hydrogen loadings. Figure IV-3 is

an isotherm for the Ca^{2+}-H^+ reaction. The curve is much steeper than the previous two

cases because the calcium ion is divalent, leading to a squared concentration term in the

equilibrium expression. Notice the solution fraction of hydrogen is almost 1.0 at

hydrogen loading is higher than 0.15. This implies calcium ions on the surface of the

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resin exchange completely with hydrogen until the resin is almost completely loaded with

calcium.
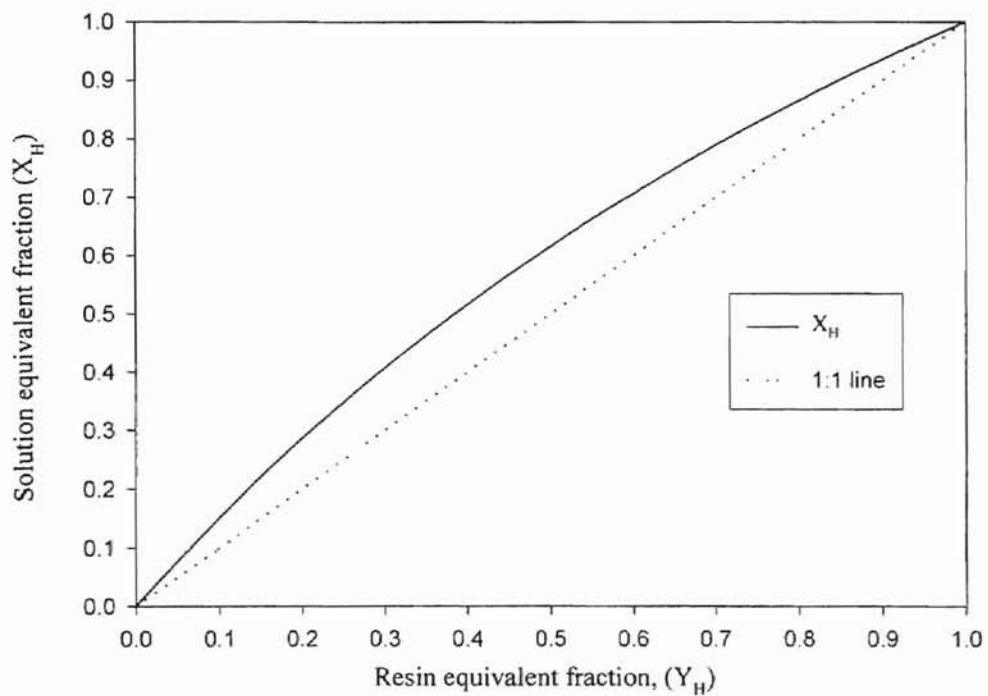
Figure IV-1. Equilibrium isotherm for the Na^+-H^+ binary ion exchange reaction.
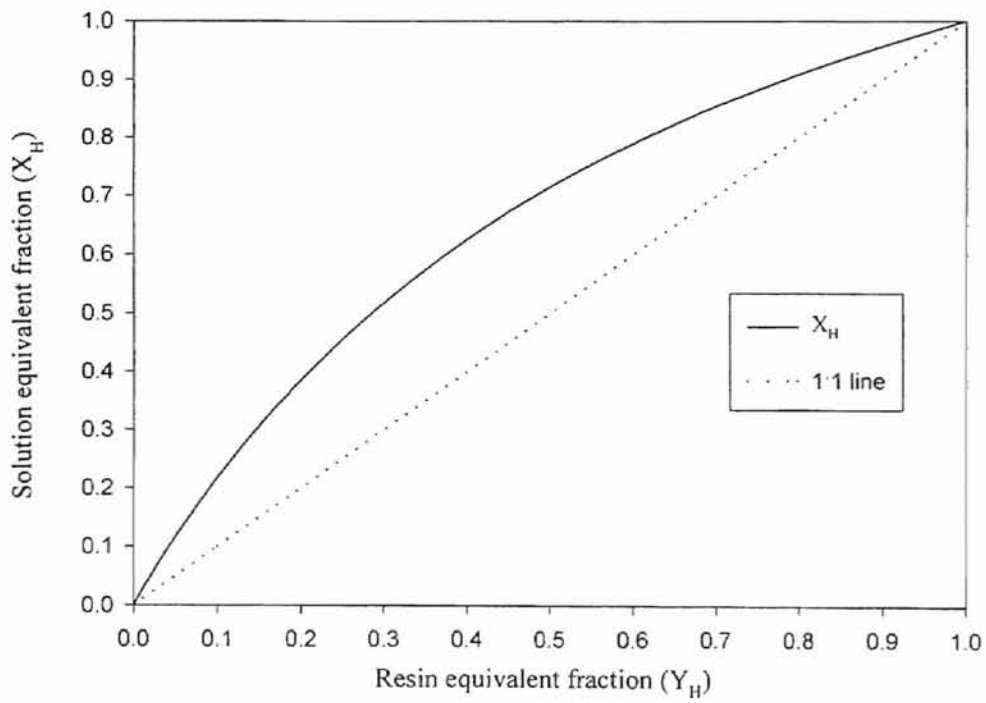
Figure IV-2. Equilibrium isotherm for the K^+-H^+ binary ion exchange reaction.
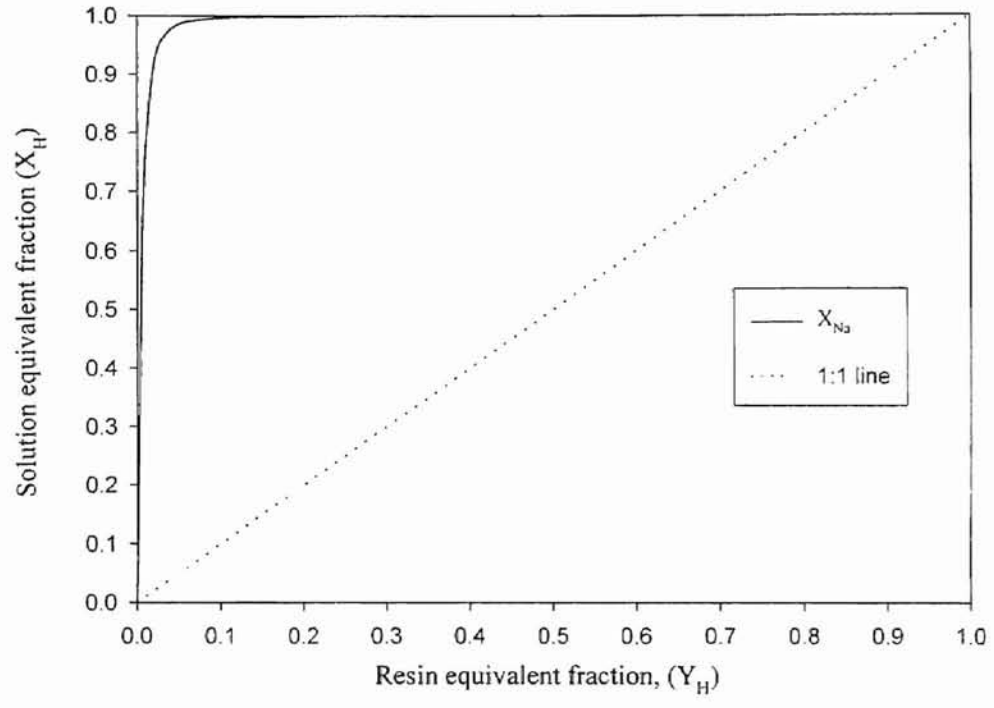
Figure IV-3. Equilibrium isotherm of the Ca^{2+}-H^+ binary ion exchange reaction.

Model comparison

The input data in Table IV-I were used to generate isotherms with the original version of the multicomponent code included in Appendix D. The results were compared to the results obtained from the pseudo-ion model. Both models generated identical results for the Na^+-H^+, K^+-H^+, and Ca^{2+}-H^+ systems.

Equilibrium isotherms of different resin forms

An additional benefit of the pseudo-ion equilibrium model is the ability to model the equilibrium of a resin loaded with another ion besides the reference ion in the selectivity expression. The only requirements for this calculation are the selectivities of the counterions with respect to a common reference. As stated in Chapter I, water softeners normally have resin in the sodium form to remove hardness ions such as magnesium or calcium. Figure IV-4 and Figure IV-5 show the isotherms of the Ca^{2+}-Na^+ and Ca^{2+}-Mg^{2+} binary systems. Notice the Ca^{2+}-Na^+ isotherm strongly resembles the Ca^{2+}-H^+ system. This is attributed to the charge difference of the calcium and sodium ions. The Ca^{2+}-Mg^{2+} isotherm; however, appears as a monovalent system, indicating the influence of charge upon the exchange reaction.

Comparison of model with experimental data

Experimental data from the literature (Mehablia et al., 1994; Smith 1965) were compared to the equilibrium model for the Na^+-H^+ and Ba^{2+}-Na^+ binary systems. A statistical analysis was performed with the regression macro in the Data Analysis package of Microsoft Excel™.

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Figure IV-6 is a comparison of the experimental data for the Na^+-H^+ presented by

Mehablia et al. (1994). The total solution concentration of the experimental isotherm was

0.7 N, and the selectivity of sodium with respect to hydrogen was 1.5. Good agreement

was obtained between the model and the data. The standard error for the comparison was

0.017, and the R^2 was 0.996. Figure IV-7 is a plot of the residuals for the comparison.

The residual plot shows a sufficiently random scatter throughout the range of data.

Figure IV-8 is a comparison of the model to experimental data presented by Smith

(1965). The total solution concentration of the experimental isotherm was 0.01 N, and

the selectivities of barium and sodium with respect to hydrogen were 10.5 and 1.5,

respectively. The equilibrium model deviated significantly from the experimental

interfacial concentrations for most data points. The standard error for this comparison

was 0.046, and the R^2 value was 0.76. Figure IV-9 is a plot of the residuals for this

comparison. The residual plot shows a wide range of scatter. The error can be attributed

to an ideal model being applied to a highly non-ideal system and experimental error.

The effect of total interfacial ionic concentration

Isotherms were generated for the K^+-H^+ and Ca^{2+}-H^+ systems with varying total

interfacial concentrations. The equilibrium isotherm for the Na^+-H^+ system is not

affected by varying the total interfacial concentration. This is expected mathematically

because the ratio of the capacity to the interfacial concentration in Eq. (III-29) is raised to

the difference of the valence of the exchanging ions. Sodium and hydrogen are both

monovalent ions, and the difference of valences is zero.

Figure IV-10 shows two isotherms of the Ca^{2+}-H^+ system with varying total

interfacial ionic concentrations. Calcium is a divalent ion and the difference of the

charges of the exchanging ions is 1.0. The ratio of the capacity to the interfacial

concentration term is no longer unity, and the term changes the coefficients of the

polynomial used to calculate the interfacial concentration. Notice the equilibrium curve

becomes steeper as the total interfacial concentration decreases. This effect has been

observed for all binary systems with ions of different valence.
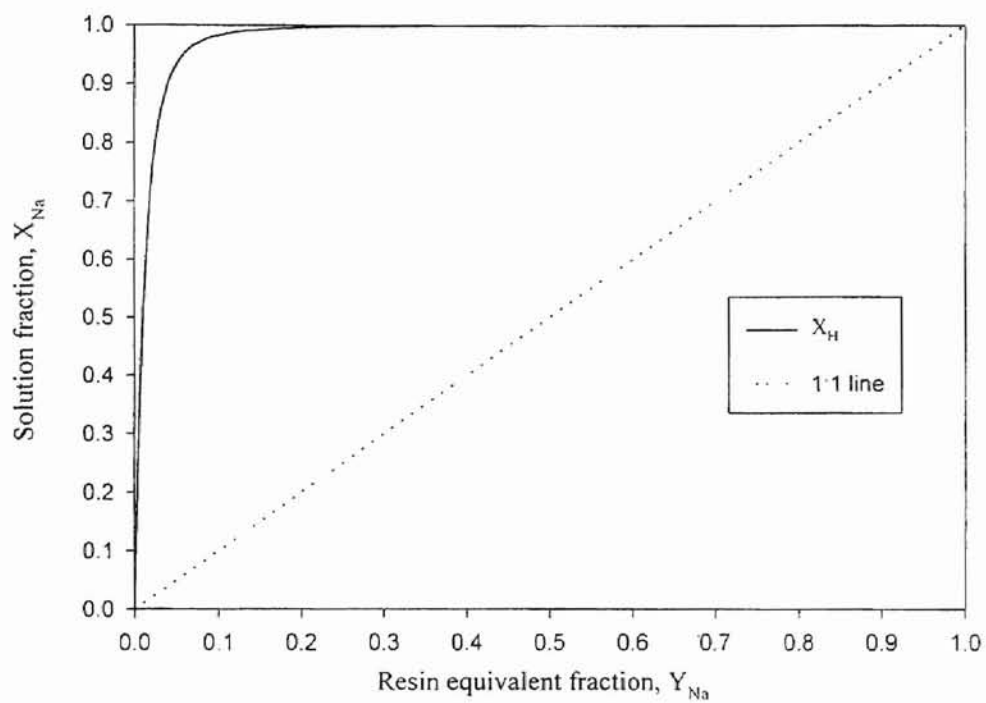
Figure IV-4 Equilibrium isotherm of the Ca^{2+}-Na^+ binary reaction
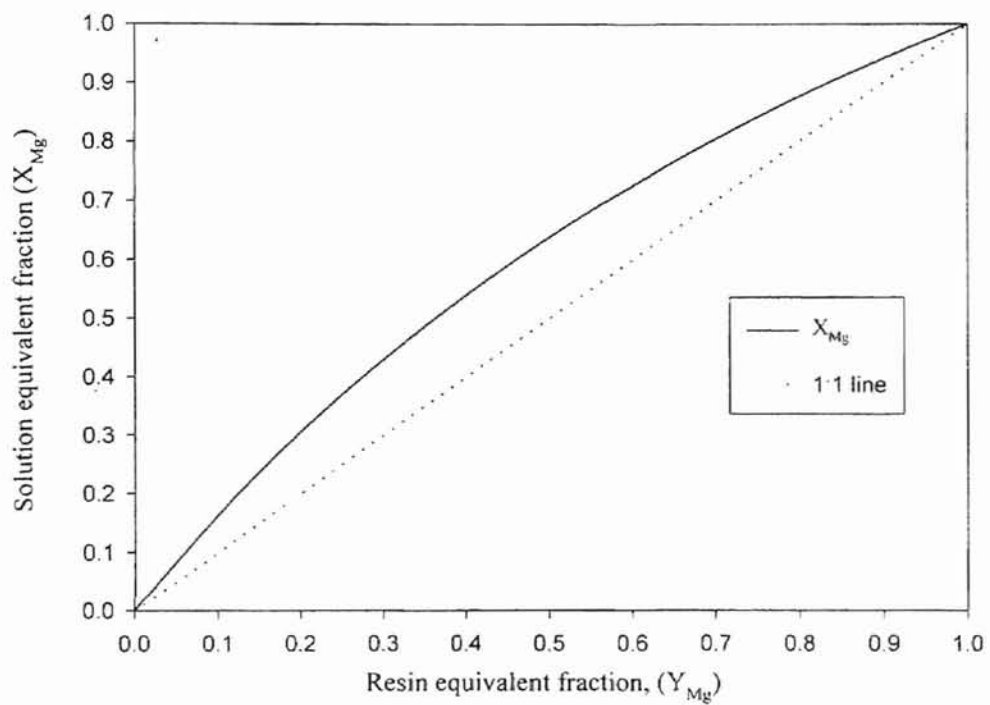
Figure IV-5 Equilibrium isotherm of the Ca^{2+}-Mg^{2+} binary reaction.
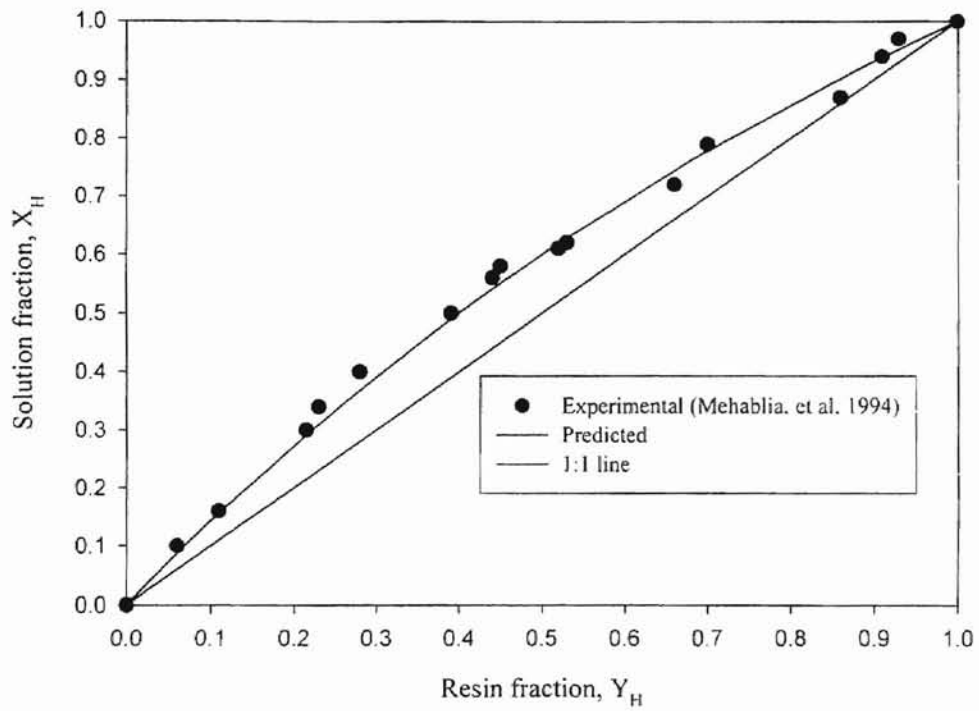
Figure IV-6 Comparison of model prediction to experimental data for the Na^+-H^+ binary system
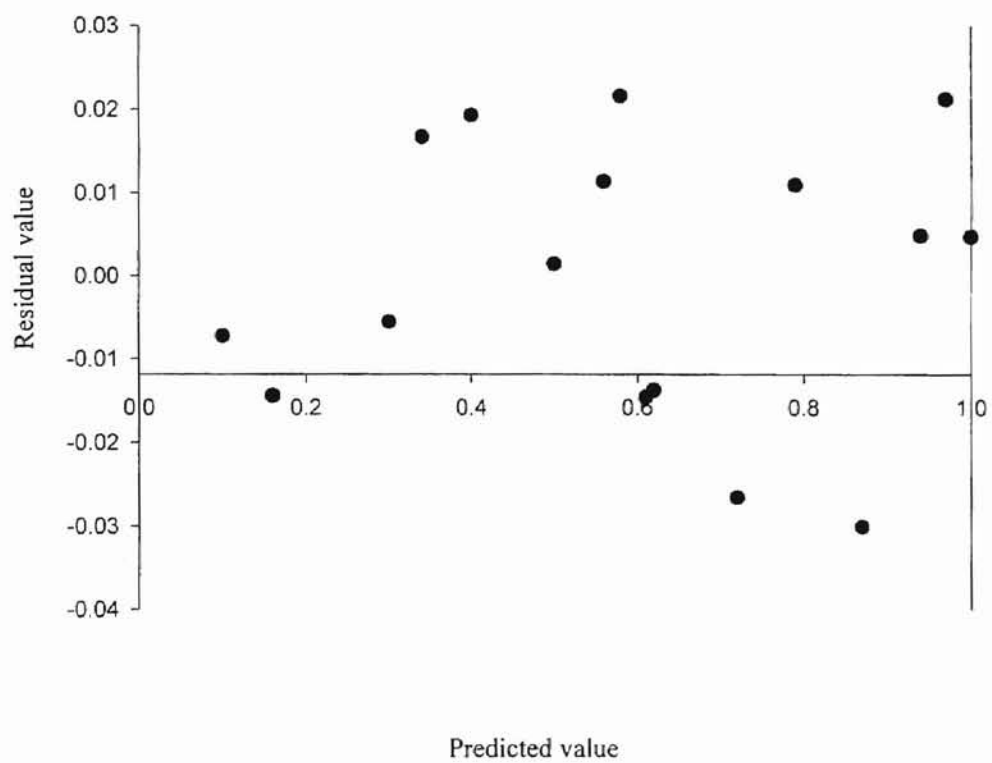
Figure IV-7 Residual plot for the Na^+-H^+ binary system
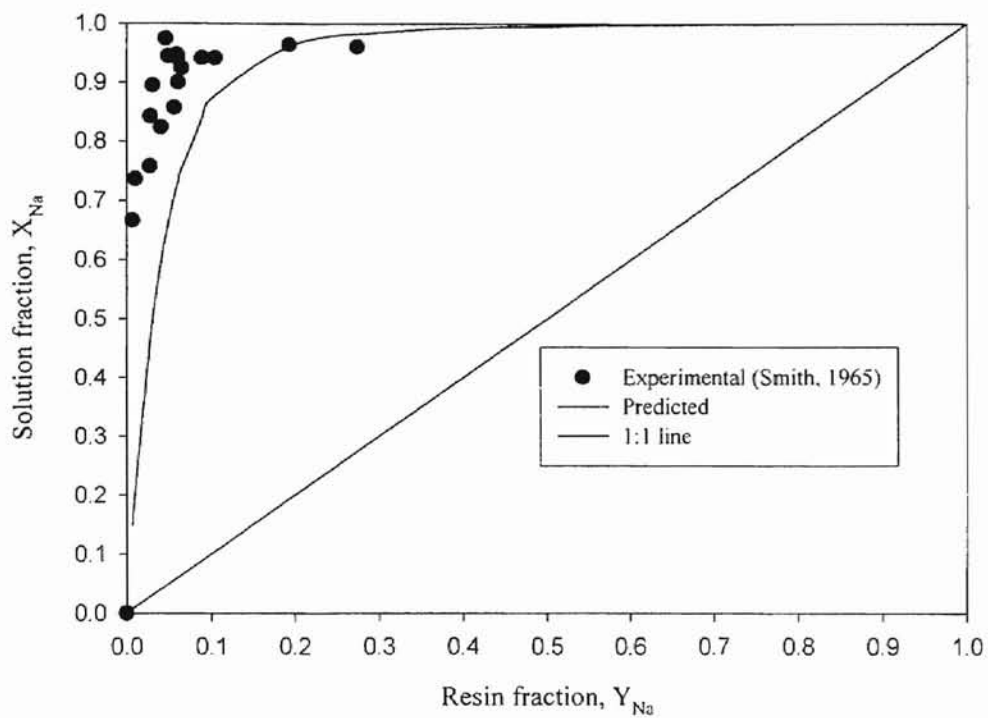
Figure IV-8 Comparison of model prediction to experimental data for the Ba^{2+}-Na^+ binary system
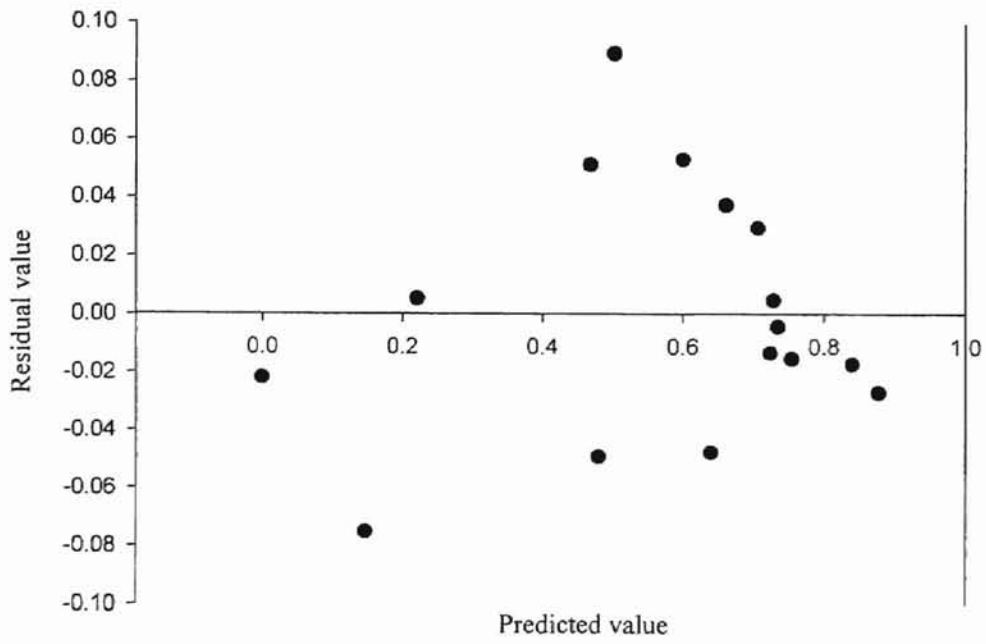
Figure IV-9 Residual plot for the Ba^{2+}-Na^+ binary system
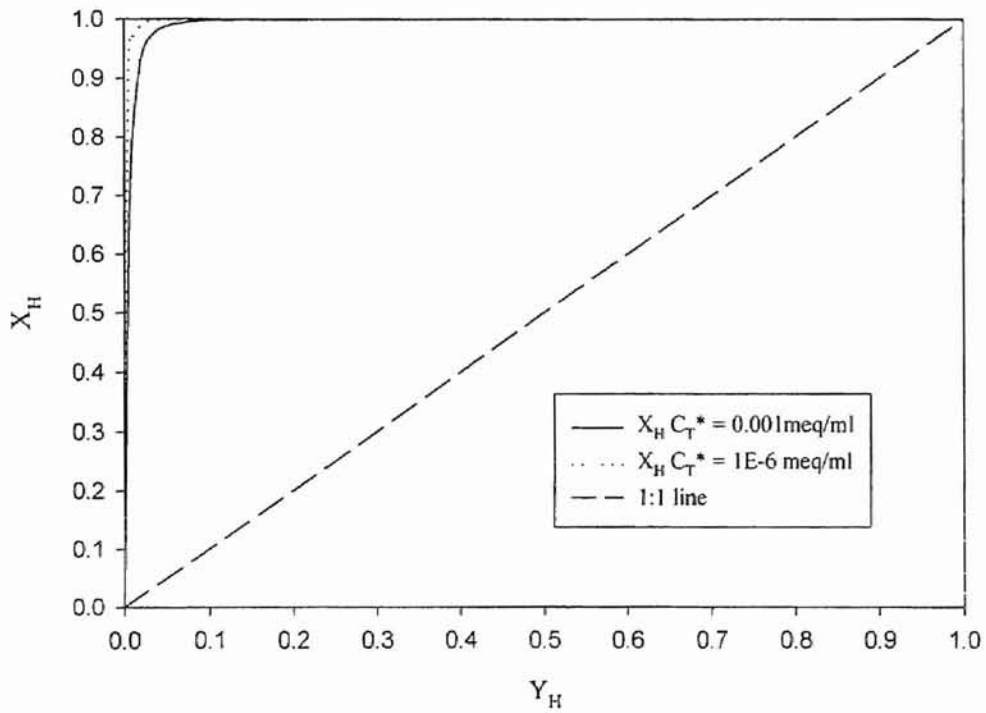
Figure IV-10. Comparison of Ca^{2+}-H^+ equilibrium isotherms for different total interfacial concentrations.

The effect of pH on equilibrium leakages.

Arizona Public Service (APS) presented effluent data from a mixed bed ion exchange column with high peaks of chloride and sulfate. The equilibrium leakage of chloride is expected to be between 10-90 ppt from an effluent stream if the resin is loaded with approximately 0.1% chloride. Data provided show sulfate and chloride effluent concentrations ranging from 100-200 ppb. Given freshly regenerated resin (loadings of approximately 0.1% of SiO_4^-, BO^-, and SO_4^{2-}), predict,

1. The effluent concentrations of chloride and sulfate assuming resin that is 99% hydroxyl form.

2. The chloride loading required to have an equilibrium leakage of 200 ppb.

Model input parameters

Tables I and II summarize the input parameters used for the two simulations.

Table IV-II. Input parameters for calculating interfacial ionic concentrations of hydroxyl form anionic resin.

Ion	Selectivity	Loading	pH range
OH^-	1	0.995	7-9 for all
Si^-	2.5	0.001	
Cl^-	16	0.002	
BO^-	0.15	0.001	
SO_4^{2-}	64	0.001	

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Table IV-III. Input data for calculating the interfacial ionic concentrations of anionic resin in the chloride form.

Ion	Selectivity	Loading	pH range
OH⁻	1	0.047	7-9 for all
Si⁻	2.5	0.001	
Cl⁻	16	0.95	
BO⁻	0.15	0.001	
SO_4^{2-}	64	0.001	

Figure IV-11 illustrates the predicted equilibrium leakages for chloride, sulfate, silicates, and borate given the loadings stated in the data. Notice the equilibrium leakage for chloride ranges between 1-40 ppt for a pH range between 7-9, and the sulfate leakage is negligible. Figure IV-12 shows the given conditions would have a borate leakage ranging from 0.1-3.0 ppb. Borate was not present in the data at these concentrations.

Figure IV-13 demonstrates the chloride loading would have to be approximately 95% to achieve the equilibrium leakages described in the given data. It was not possible to attain both chloride and sulfate leakages in the 200 ppb range.

From these simulations the author concludes the chloride and sulfate peaks cannot be attributed to equilibrium leakages. APS engineers have determined there was an external source of chloride and sulfate from a solvent within a polymer liner of a service vessel.
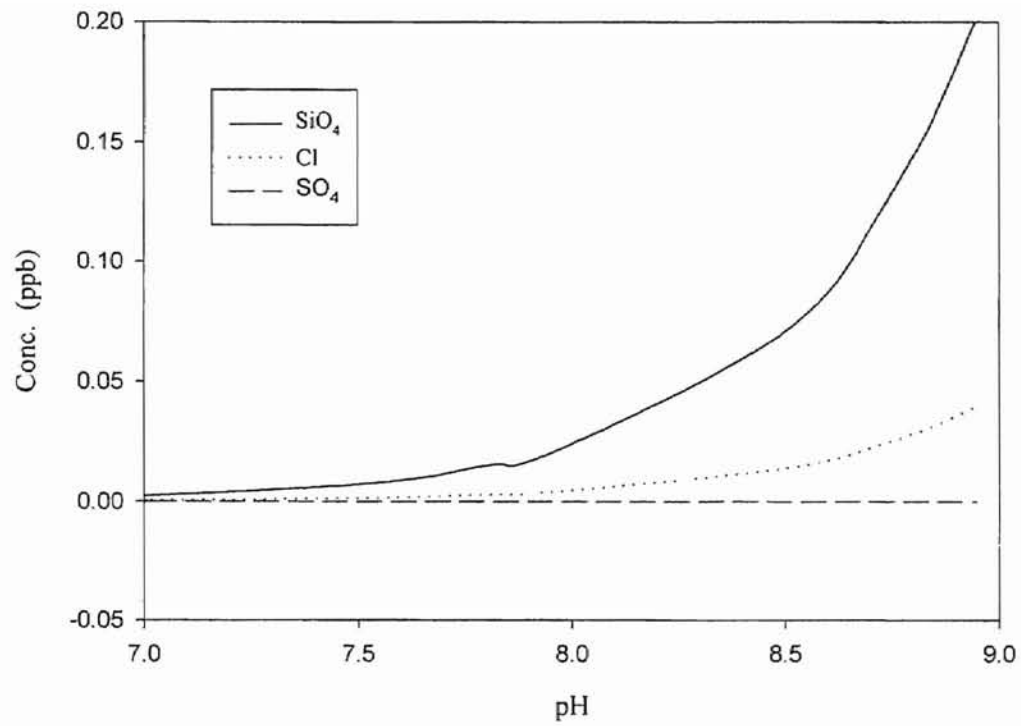
Figure IV-11. Equilibrium leakages of silicate, chloride and sulfate from a hydroxyl form resin as a function of the pH of the bulk solution.
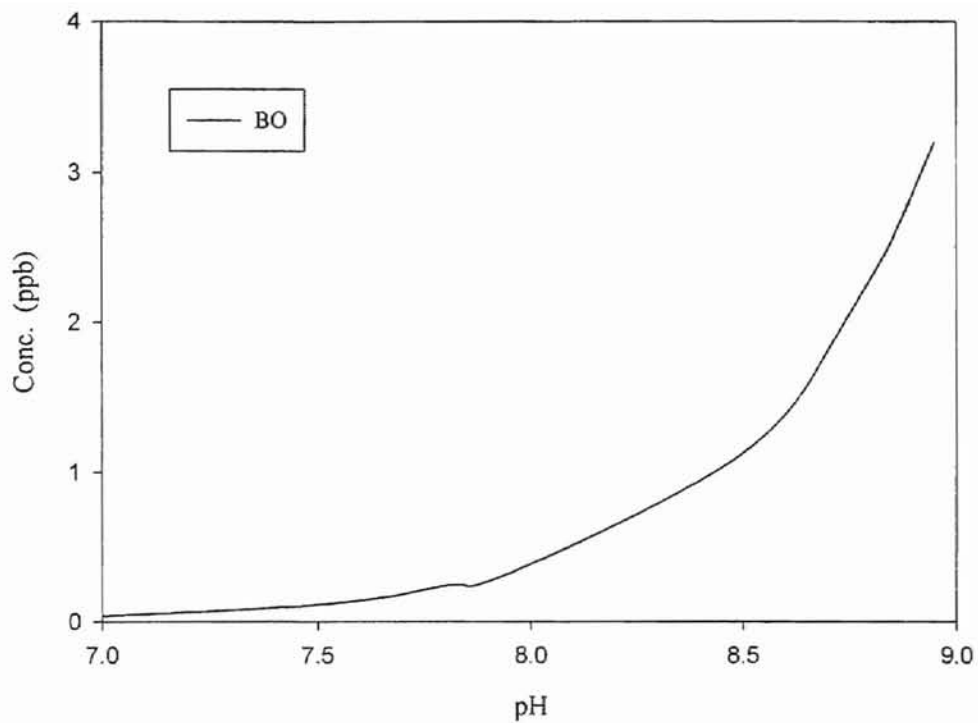
Figure IV-12. Equilibrium leakage of borate from a hydroxyl form resin as a function of pH of the bulk solution.
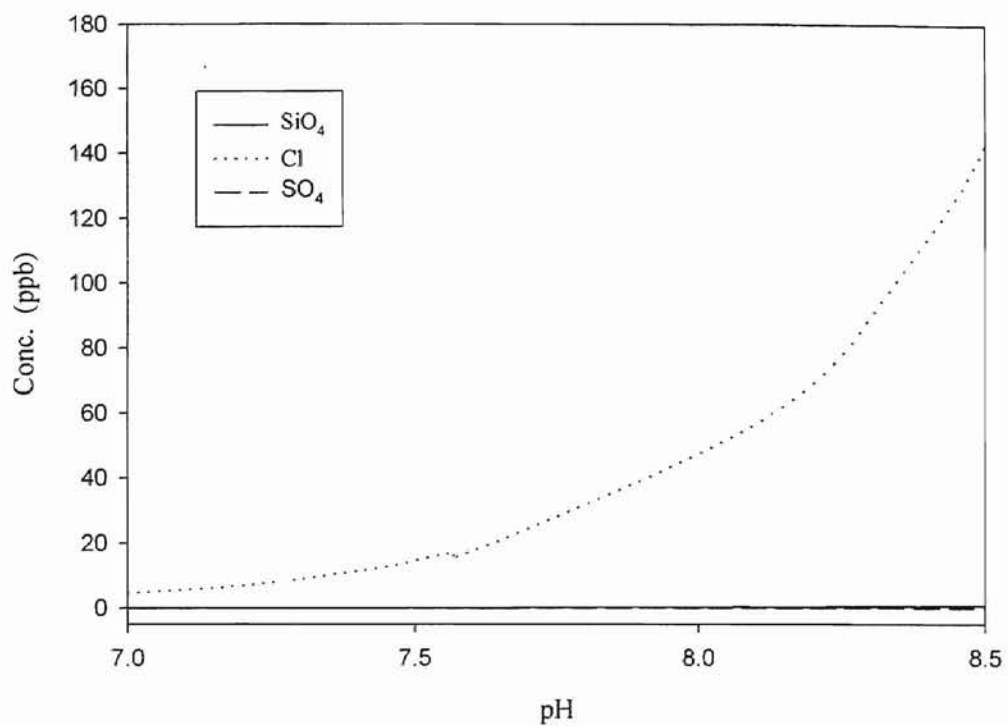
Figure IV-13. Equilibrium leakage of chloride, sulfate and silicate from a chloride form resin as a function of pH of the bulk solution.

Numerical method run time comparison

Two numerical methods were considered for solving the polynomial in Eq. (III-29), the *regula falsi* (false position) search method, and Ridder's method. The criteria for numerical method selection are 1) robustness of the algorithm, 2) convergence behavior, and 3) run time of the algorithm.

Both numerical methods converged readily within 5 iterations when the relative tolerance was set at 1E-8, and program failure occurred only when the root was not bracketed between 0.0 and 1.0.

1. The interfacial concentration model was compiled with default input values for the loading, selectivity, and valence.

2. Record the system time with the ITIME subroutine in FORTRAN Power Station.

3. Execute the subroutine one million times without reading or writing data to the hard drive.

4. Record the system time after execution.

5. Subtract the initial time from the final time and write the difference to an output file.

Programs were written for both numerical methods, and compiled with FORTRAN Power Station optimized for a Pentium processor. The programs were executed with a 133 MHz Intel Pentium processor with an Intel motherboard, 48MB EDO RAM, and 256 KB Pipeline burst cache. The operating system was Windows 95. The results are described below in Table IV-IV.

Table IV-IV. Run time comparison of Ridder's method and regula falsi algorithms.

Numerical Method	Run-time
Regula-falsi	4 minutes, 14 seconds
Ridder's Method	4 minutes, 9 seconds

Referencing the example in Chapter III, where the subroutine is called 8 million times in a single execution of the column model, Ridder's Method reduces the run time by 40 seconds. The run time reduction from Ridder's method within the column model is determined by the time and distance step sizes within the column model.

Compiler caveat

Coding of the equilibrium model revealed a compilation error which occurs with Microsoft™ FORTRAN Power Station. The error occurred when the loading of the reference ion of the selectivity data had a value of 0.1. The pseudo-ion equilibrium model, as well as the previous equilibrium model coded by Sunkavalli, would predict a high value of the solution phase equivalent ionic fraction. The error was not present if the loading were 0.099 or 0.101, instead appearing as a discontinuity in the equilibrium isotherm. The code was successfully compiled with another compiler, and Microsoft has been notified of the error. No response was received from Microsoft when this document was printed

CHAPTER V

FUTURE MODEL MODIFICATIONS

This section describes future model modifications that may be developed to incorporate non-ideal multicomponent reaction equilibrium into the model. The following topics discussed in this chapter:

1) Solution phase activity coefficient models.

2) Resin phase activity coefficient models.

3) Application of non-ideal multicomponent models to solve for interfacial solution concentrations.

The author has not been able to adapt the pseudo-ion model developed in Chapter III for non ideal systems. The following approach should be applied to the method developed by Sunkavalli (1996).

Solution phase activity coefficients

The model developed in Chapter III assumes ideal solution phase activity coefficients. This is a reasonable assumption for ultrapure water manufacture while the columns are in service because the impurity concentrations are normally less than 1 ppm. The ideal solution phase assumption does not apply when the ionic concentrations are greater than 0.05 N. A situation where high ionic solution concentrations are encountered in industry is during regeneration of the resin, where typically the solution concentration

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ranges from 4-6 wt% HCl for cationic resin, or 6-10 wt% NaOH for anionic resin. For these situations an electrolyte activity coefficient model must be applied. Early ion exchange equilibrium models (Smith et al. 1978) applied the extended Debye-Hückel equation for calculating the solution activity coefficients. Written mathematically, the extended Debye-Hückel approximation represents the solution phase activity coefficient by,

$$\ln \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I \qquad (V-1)$$

According to Horvath (1985), the constant A is a temperature dependent constant with a value of 0.51 for water at 25 °C. The constants a_i and b_i are species dependent parameters found in several papers published by Truesdell et al., (1973).

Horvath (1985) recommends the activity coefficient model developed by Pitzer (1973, 1979, 1991), which is applicable to monovalent and divalent systems. The model incorporates three species dependent terms, two terms that relate to binary interactions, two terms relating to ternary interactions as well as a Debye-Hückel electrostatic term. Pitzer's model is very complex, and requires a large database of parameters that are not practical for a MBIE column model. However, Pitzer's correlations should be applied if calculating the equilibrium constant or resin phase activity coefficients from binary data.

Resin phase activity coefficients

The resin phase activities have been approximated with an excess Gibbs free energy model. Smith et al. (1978) recommended using the Wilson activity coefficient model to correlate the excess Gibbs free energy because the model is especially suited to

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athermal systems, which is typical in MBIE columns. The Wilson model has been

applied successfully to ion exchange reactions by Smith et al. (1978) and Mehablia et al.

(1994, 1996), and its application to multicomponent systems is presented below;

however, the model is normally applied to miscible polar-non polar vapor/liquid

equilibrium systems (Reid et al., 1987), and it is not normally applied to electrolyte

systems.

The defining relation of the Wilson model is

$$\frac{\Delta G^E}{RT} = -\sum_{i=1}^{M} Y_i \ln \left\{ \sum_{j=1}^{M} \Lambda_{ij} Y_j \right\} \tag{V-2}$$

where,

$\dfrac{\Delta G}{RT} =$ the excess Gibb's free energy of the reaction

Differentiating with respect to n_i yields the following

$$\ln \gamma_i = 1 - \ln \left\{ \sum_{j=1}^{M} Y_j \Lambda_{ij} \right\} - \sum_{k=1}^{M} \left\{ \frac{Y_k \Lambda_{ki}}{\sum\limits_{j=1}^{M} Y_j \Lambda_{kj}} \right\} \tag{V-3}$$

Notice that there are two parameters for each binary reaction e.g. Λ_{12} and Λ_{21}.

These values must be determined experimentally from equilibrium data. The following

section outlines the procedure necessary to calculate the binary interaction parameters

from equilibrium data.

Estimation of the equilibrium constant and binary interaction parameters

In order to calculate the binary equilibrium constant, we begin by defining the equilibrium quotient λ_{AB},

$$\lambda_A^B = \left(\frac{\gamma_B C_B}{y_B}\right)^{z_A} \left(\frac{y_A}{\gamma_A C_A}\right)^{z_B} \tag{V-4}$$

Combining equations (III-9) and (V-4), we can see that the equilibrium quotient is related to the equilibrium constant by the following relation

$$\lambda_A^B = K_A^B \frac{\overline{\gamma_B^{z_A}}}{\gamma_A^{z_B}} \tag{V-5}$$

Notice that the equilibrium quotient equals the equilibrium constant when the resin phase is ideal.

If binary equilibrium data are available, the equilibrium quotient can be related to the selectivity coefficient and the resin phase activity coefficients for a binary system. Gaines and Thomas have introduced a relation to calculate the selectivity coefficient directly from binary equilibrium data. Expressed mathematically,

$$\ln K_A^B = (z_A - z_B) + \int_0^1 \ln(\lambda_A^B) dY_A \tag{V-6}$$

The equilibrium concentrations are determined experimentally from binary batch equilibrium data. The Wilson coefficients are then found by applying a nonlinear least squares regression algorithm such as the Marquardt method.

Substitution of Eq. (V-3) into Eq. (V-5) and rearranging yields the following equation.

$$\ln \lambda_A^B = \ln K_A^B - \sum_{k=1}^{M} \omega_k \left\{ 1 - \ln\left(\sum_{l=1}^{M} Y_{ml}\Lambda_{kl} \right) - \sum_{n=1}^{M} \left(\frac{Y_{mn}\Lambda_{nk}}{\sum_{i=1}^{M} Y_{ml}\Lambda_{nl}} \right) \right\} \qquad \text{(V-7)}$$

where

ω_k = the stoichiometric coefficient of species k in the exchanger phase.

This equation is then combined with the objective function defined as

$$F = \sum_{i=1}^{N} \left(\frac{\lambda_i^{exp} - \lambda_i^{fit}}{\lambda_i^{exp}} \right)^2 \qquad \text{(V-8)}$$

Mehablia et al. suggest using the following form of the objective function in order to account for the increase of experimental error at lower concentrations.

$$F' = \frac{\displaystyle\sum_{i=1}^{N} \left(X_i^*\left(1-X_i^*\right)Y_i\left(1-Y_i\right) \right)^2 \left(\frac{\lambda_i^{exp} - \lambda_i^{fit}}{\lambda_i^{exp}} \right)^2}{\displaystyle\sum_{i=1}^{N} \left(X_i^*\left(1-X_i^*\right)Y_i\left(1-Y_i\right) \right)^2} \qquad \text{(V-9)}$$

Inspection of Eqs. (V-8) and (V-9) show as the difference between the experimental and fitted values of the equilibrium quotient decrease, the value of the objective function decreases. As shown in Eq. (V-7), the equilibrium quotient is dependent upon the equivalent fractions, selectivity coefficient, and Wilson parameters. The equivalent fractions are constant and the selectivity coefficient is determined by the binary equilibrium experiments. Figure I-1 was referenced to Smith et al., (1978).

```
┌─────────────────────────────┐
│   Choose Wilson Parameter   │◄──────┐
└─────────────────────────────┘       │
              │                        │
              ▼                        │
┌─────────────────────────────┐       │
│   Find Equilbrium Constant  │       │
└─────────────────────────────┘       │
              │                        │
              ▼                        │
┌─────────────────────────────┐       │
│  Compute Objective Function │       │
└─────────────────────────────┘       │
              │                        │
              ▼                        │
          ╱─────────╲                  │
        ╱             ╲                 │
      ╱    Minimum?     ╲───────────────┘
        ╲             ╱            No
   Yes    ╲─────────╱
              │
              ▼
┌─────────────────────────────┐
│ Best Set for Wilson Coefficient │
└─────────────────────────────┘
```
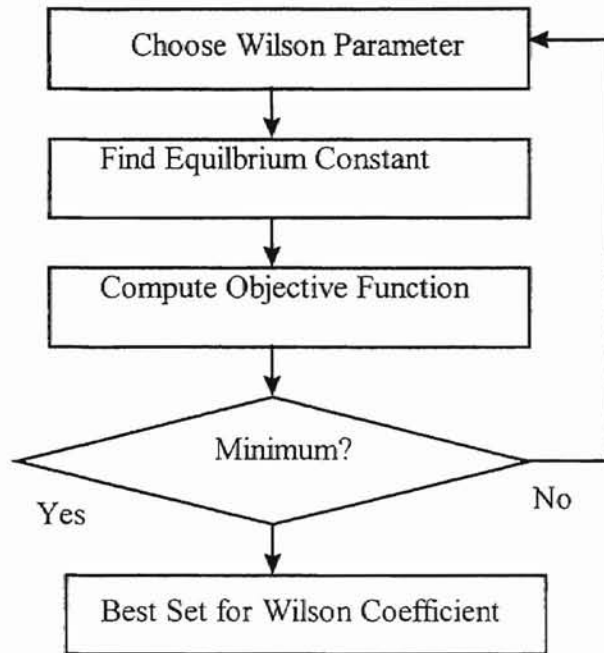
Figure V-1. Algorithm for regressing the equilibrium constant and Wilson binary interaction parameters from experimental data.

The values for the Wilson parameters can then be stored into a database with binary interaction parameters of other ion systems measured at a common temperature. These parameters may then be applied in Eq. (V-3) for calculation of the individual ion resin phase activity coefficients.

Interfacial concentrations of non-ideal multicomponent systems

Consider the equilibrium expressions of a ternary system of ions A, B, and C. Three selectivity expressions and one mole fraction constraint may be written for this system yielding,

$$k_A^B = \left(\frac{\overline{\gamma_A} Y_A}{\gamma_A X_A^*} \right)^{z_B} \left(\frac{\gamma_B X_B^*}{\overline{\gamma_B} Y_B} \right)^{z_A} Q^{(z_A - z_B)} C_T^{*(z_B - z_A)} \qquad (V\text{-}10)$$

$$k_B^C = \left(\frac{\overline{\gamma_B Y_B}}{\gamma_B X_B^*}\right)^{z_C} \left(\frac{\gamma_C X_C^*}{\overline{\gamma_C Y_C}}\right)^{z_B} Q^{(z_B - z_C)} C_T^{*(z_C - z_B)} \tag{V-11}$$

$$k_A^C = \left(\frac{\overline{\gamma_A Y_A}}{\gamma_A X_A^*}\right)^{z_C} \left(\frac{\gamma_C X_C^*}{\overline{\gamma_C Y_C}}\right)^{z_A} Q^{(z_A - z_C)} C_T^{*(z_C - z_A)} \tag{V-12}$$

$$\sum_{i=1}^{n} X_i^* = 1 \tag{V-13}$$

Assuming known activities, capacity, and total ionic interfacial concentration, the system is overspecified with four equations and three unknowns. The values of X_A^*, X_B^*, and X_C^* can be solved with two of the three equilibrium expressions and the mole fraction constraint (Mehablia et al., 1996).

Extending the system to include four ions, A, B, C, and D, introduces three more equilibrium expressions which include ion D, as shown below.

$$k_A^D = \left(\frac{\overline{\gamma_A Y_A}}{\gamma_A X_A^*}\right)^{z_D} \left(\frac{\gamma_D X_D^*}{\overline{\gamma_D Y_D}}\right)^{z_A} Q^{(z_A - z_D)} C_T^{*(z_D - z_A)} \tag{V-14}$$

$$k_B^D = \left(\frac{\overline{\gamma_B Y_B}}{\gamma_B X_B^*}\right)^{z_D} \left(\frac{\gamma_D X_D^*}{\overline{\gamma_D Y_D}}\right)^{z_B} Q^{(z_B - z_D)} C_T^{*(z_D - z_B)} \tag{V-15}$$

$$k_C^D = \left(\frac{\overline{\gamma_C Y_C}}{\gamma_C X_C^*}\right)^{z_D} \left(\frac{\gamma_D X_D^*}{\overline{\gamma_D Y_D}}\right)^{z_C} Q^{(z_C - z_D)} C_T^{*(z_D - z_C)} \tag{V-16}$$

Maintaining the previous assumptions, the system is now overspecified with seven equations and four unknowns. The mole fraction constraint must be satisfied and is by default included in the equation set, leaving six given equations and three equations required for problem solution. Applying the elementary statistical combination, C_3^6,

leads to a total of 20 possible solution sets. The interfacial solution fractions may be calculated via non-linear optimization; however, Mehablia et al. (1996) identified the most sensitive set of equations by recognizing each set of equations from the possible twenty combinations has a common ion in the expression. A comparison of the model results to the data obtained showed the best estimations were obtained when the most highly selective ion was chosen as the common ion.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

An ideal multicomponent ion exchange reaction equilibrium model has been successfully developed to calculate the interfacial ionic concentrations on the surface of both cationic and anionic ion exchange resins. The model operates independently of the form of the resin, and the results are in very close agreement with the model previously developed by Sunkavalli (1996). The model showed good agreement when compared to a monovalent binary system; however, the model agreement was only adequate when compared to a divalent binary system.

The implementation of a non-ideal multicomponent reaction equilibrium model has been investigated. Incorporating non-ideal multicomponent equilibrium into a MBIE model will require binary equilibrium data from which resin phase activity coefficient parameters can be regressed. After the thermodynamic parameters are regressed, the simultaneous set of equations generated by the mole fraction constraints may be solved in terms of the ion with the highest selectivity.

The author recommends investigating the possibility of extending the pseudo-ion model to non-ideal reaction equilibrium, and the development of a binary reaction equilibria database for estimating thermodynamic parameters.

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APPENDIXES

APPENDIX A

NUMERICAL METHOD SELECTION

The X_{ref}^* term in Eq. (III-29) may have fractional exponents which prevents an analytical solution, however, we have the advantage of a bracketed root between 0.0 and 1.0. A numerical search algorithm must be employed to solve for the reference interfacial equivalent ionic fraction. Three numerical methods were researched; the Newton-Raphson iteration, *regula falsi* (false position) and Ridder's method. Ridder's method was selected for it's robustness and convergence properties.

The convergence properties of a numerical search algorithm is quantitatively defined by the following relationship,

$$\varepsilon_{n+1} = \text{constant} \times \left(\varepsilon_{n+1}\right)^m \qquad \text{(A-1)}$$

where,

ε_{n+1} = the new interval resulting from an iteration

ε_n = the interval used in the current iteration

m = an exponent denoting the order (superlinearity) of a search algorithm.

Simple numerical methods, such as the bisection method, are considered linear models because the method calculates additional significant figures linearly with each iteration. More complex numerical algorithms such as the Newton-Raphson iteration have

superlinear convergence, however, erratic local behavior in the function may diverge the solution to infinity.

Newton-Raphson Iteration

The Newton-Raphson iteration was considered for this work because it converges quadratically (m = 2), however, it was discarded because occasional convergence problems occurred when testing multicomponent systems. The convergence problems were attributed to the analytical derivatives calculated within a separate function. Numerical derivatives of the function were considered, but this would add a function call and iteration to the algorithm and extend the run time of the procedure.

Regula Falsi (False Position) Method

The false position method was found to be adequate for solving Eq. (III-29), and may be used instead of Ridders' method. Ridders' method is actually an extension of the false position method, thus the false position method shall be discussed in detail before discussing Ridders' method. The convergence properties of the false position method are variable for reasons discussed below.

The false position method converges quickly for any function that is smooth and continuous near a root (Press et al., 1992). Consider any arbitrary smooth function such as below.

The false position method assumes the function is linear in the local area of interest, and finds the next estimate of the root at the point where the approximating line crosses the x-axis. One of the boundary points is discarded in favor of the latest estimate of the root after each iteration. Notice for this example that boundary point 1 may be active for many steps. It is this property of the algorithm which causes the difficulty in

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predicting the convergence behavior. The false position method is often superlinear ($m >$ 1); however, the exact order is function specific (Press et al., 1992).
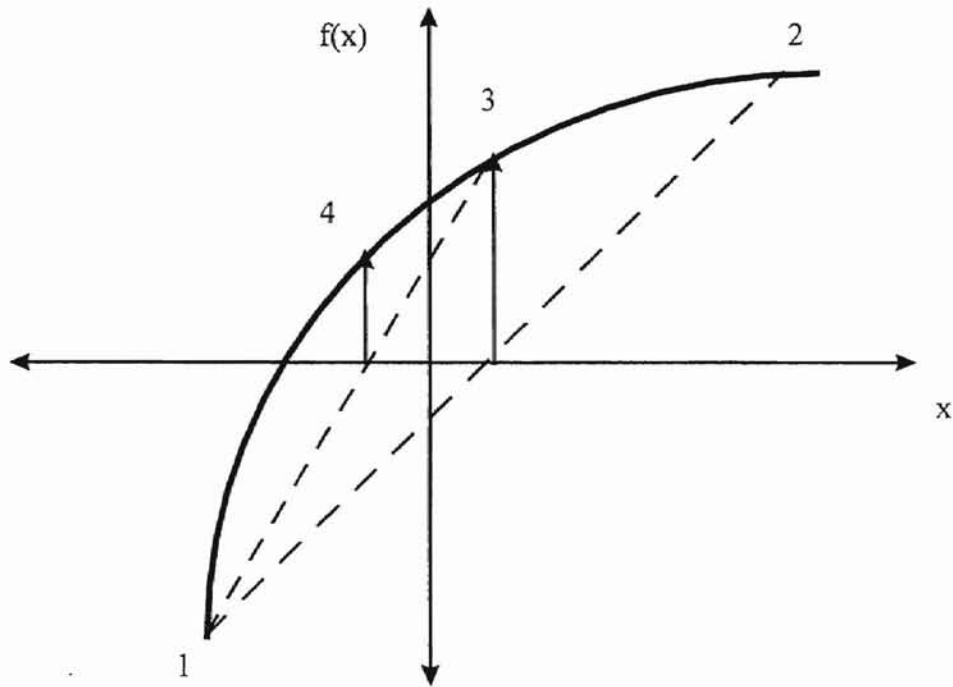
Figure A-1 Graphical representation of the false position method. Interpolation lines are drawn through the most recent point that brackets the root.

Ridders' Method

Ridders' method is a powerful extension of the false position method with guaranteed solution and superlinear convergence. The algorithm begins the iteration by evaluating the function at the midpoint of the interval.

$$x_3 = \frac{(x_2 + x_1)}{2} \tag{A-2}$$

The method then factors out a unique exponential function which turns the residual function into a straight line. This is accomplished by solving the following equation for e^Q.

$$f(x_1) - 2f(x_3)e^Q + f(x_2)e^{2Q} = 0 \tag{A-3}$$

Eq. (A-3) is a quadratic equation in e^Q, which can be solved to give

$$e^Q = \frac{f(x_3) + \text{sign}[f(x_2)]\sqrt{f(x_3)^2 - f(x_1)f(x_2)}}{f(x_2)} \tag{A-4}$$

where the 'sign' function refers to the sign of the function evaluated at x_2.

The method now employs the false position method, but not to the functional values at x_1, x_2, and x_3. Instead the values $f(x_1)$, $f(x_3)e^Q$, and $f(x_2)e^{2Q}$ are used. The following updating formula yields a new guess for the root at x_4.

$$x_4 = x_3 + (x_3 - x_1)\frac{\text{sign}[f(x_1) - f(x_2)]f(x_3)}{\sqrt{f(x_3)^2 - f(x_1)f(x_2)}} \tag{A-5}$$

The updating formula has several beneficial properties.

- The updated root, x_4, is guaranteed to lie in the interval (x_1, x_2), thus the method can never jump out of the brackets (Press et al., 1992).

- The convergence of successive applications of the updating formula is quadratic, i.e. $m = 2$. However, the method requires two function evaluations, reducing the convergence of the algorithm to $\sqrt{2}$ (1.414). This results in doubling the number of significant digits with each two function evaluations (Press et al., 1992).

- Linearizing the function with an exponential factor as opposed to curve fitting with a parabola yields an algorithm of exceptional robustness.

The author must note the 'sign' function present in Eqs. (A-4) and (A-5) may not have the same syntax or may not be present in some versions of FORTRAN 77. If the Ridders' method subroutine is incompatible with a specific compiler, the author recommends applying the false position search algorithm in Appendix C.

APPENDIX B

TOTAL INTERFACIAL CONCENTRATION DERIVATION

The total interfacial concentrations of cations and anions are found as a result of

the derivations of flux expressions for the MBIE model. Flux expressions describing

multicomponent ion exchange process are derived using Nernst-Planck model and basic

principles of ion exchange. Haub and Foutch (1984) and Zecchini and Foutch (1990)

successfully applied Nernst-Planck model to describe film diffusion controlled mixed bed

ion exchange process. The expression for the total interfacial concentration is coded for

arbitrary multicomponent species by Sunkavalli (1996).

The Nernst-Planck equation is used to describe the flux of a given species within

the static film that is assumed around the resin bead. Neglecting the curvature of the film,

this expression is:

$$J_i = -D_i \left(\frac{\partial C_i}{\partial r} + \frac{C_i z_i F}{RT} \frac{\partial \phi}{\partial r} \right)$$ (B-1)

where is the electric potential and z_i is the ion valence. Assuming pseudo steady state

allows the replacement of partial derivatives by ordinary derivatives. The flux

expressions derived in this model are based on bulk-phase neutralization.

The conditions that must be satisfied within the film surrounding the resin are; 1)

electroneutrality, 2) no coion flux, and 3) no net current flow. Mathematically,

$$\sum z_i C_i = \sum z_j C_j \qquad \text{(Electroneutrality)} \qquad \text{(B-2)}$$

where 'i' stands for counterions and 'j' stands for coions

$$z_j J_j = 0 \qquad \text{(No coion flux)} \qquad \text{(B-3)}$$

$$\sum z_i J_i = \sum z_j J_j \qquad \text{(No net current flow)} \qquad \text{(B-4)}$$

From Equations (B-3) and (B-4) we have

$$\sum z_i J_i = 0 \qquad \text{(B-5)}$$

The total equivalent ion concentration can be defined as:

$$C_T = \omega \sum_{i=1}^{n} z_i C_i = \omega_j \sum_{j=1}^{m} z_j C_j \qquad \text{(B-6)}$$

where 'n' is the number of counterions, 'm' is the number of coions and $\quad =+1$ for cations

and -1 for anions.

Using the no coion flux condition (Eq. B-3), we have

$$\frac{d\phi}{dr} = -\frac{RT}{F} \frac{z_j \dfrac{dC_j}{dr}}{z_j^2 C_j} \qquad \text{(B-7)}$$

From the no coion flux condition we have that the sum of the coion fluxes in the film is

also zero. Now the electric potential term in the Nernst-Planck equation can be

eliminated in terms of the total equivalent concentration as:

$$\frac{d\phi}{dr} = -\frac{RT}{F} \frac{\displaystyle\sum_{j=1}^{m} z_j \dfrac{dC_j}{dr}}{\displaystyle\sum_{j=1}^{m} z_j^2 C_j} \qquad \text{(B-8)}$$

Introducing a mean coion valence defined as

$$z_Y = \frac{\sum\limits_{j=1}^{m} z_j^2 C_j}{\sum\limits_{j=1}^{m} z_j C_j} \qquad (B\text{-}9)$$

and combining with the definition for total concentration (Eq. B-6), Eq. (B-8) reduces to

$$\frac{d\phi}{dr} = \frac{-RT}{z_Y F} \frac{1}{C_T} \frac{dC_T}{dr} \qquad (B\text{-}10)$$

Now the Nernst-Planck expression for counterions can be written as:

$$J_i = -D_i \left(\frac{dC_i}{dr} - \frac{C_i z_i}{C_T z_Y} \frac{dC_T}{dr} \right) \qquad (B\text{-}11)$$

Using the no net current flow condition (Eq. B-5) and (Eq. C-11), we get

$$\sum_{i=1}^{n} z_i D_i \frac{dC_i}{dr} + \sum_{i=1}^{n} z_i D_i N_i \frac{C_i}{C_T} \frac{dC_T}{dr} = 0 \qquad (B\text{-}12)$$

where

$$N_i = -\frac{z_i}{z_Y} \qquad (B\text{-}13)$$

For monovalent system of ions or equal valence system of ions, the above

equation could be easily integrated to obtain a relation between C_i and C_T. This is not

possible in the case of arbitrary valences. At this point the method proposed by Franzreb

(1993) is used to proceed further. In this method, Eq. (B-11) is differentiated to eliminate

the unknown J_i. This leads to a homogeneous second order differential equation:

$$\frac{d^2 C_i}{dr^2} + \frac{N_i}{C_T} \frac{dC_i}{dr} \frac{dC_T}{dr} + N_i \frac{C_i}{C_T} \left(\frac{d^2 C_T}{dr^2} - \frac{1}{C_T} \left(\frac{dC_T}{dr} \right)^2 \right) = 0 \qquad (B\text{-}14)$$

This method leads to an exact solution for the case of equal valences and only an approximation for the case of arbitrary valences. For counterions of equal valences, summation of Eq. (B-14) for all the ions leads to

$$\sum_{i=1}^{n}\frac{d^2C_i}{dr^2}+\frac{1}{C_T}\frac{dC_T}{dr}\sum_{i=1}^{n}N_i\frac{dC_i}{dr}+\frac{1}{C_T}\frac{d^2C_T}{dr^2}\sum_{i=1}^{n}N_iC_i-\frac{1}{C_T^2}\left(\frac{dC_T}{dr}\right)^2\sum_{i=1}^{n}N_iC_i=0 \quad (B\text{-}15)$$

Substituting Eq. (C-6) and its derivatives in the above leads to

$$\frac{d^2C_T}{dr^2}=0 \qquad\qquad (B\text{-}16)$$

From the above equation it can be understood that for the case of counterions of equal valences, the profile of the total concentration in the film is linear. Zecchini and Foutch (1990) arrived at the same conclusion in their model for univalent ternary ions. The above equation combined with Eq. (B-6) can be used to obtain relationships between the derivatives of C_i and C_T. Substitution of all these derivatives in Eq. (B-16) leads to

$$\frac{d^2C_i}{dC_T^2}+\frac{N_i}{C_T}\frac{dC_i}{dC_T}-\frac{N_iC_i}{C_T^2}=0 \qquad\qquad (B\text{-}17)$$

This is the Euler's differential equation the solution of which is

$$z_iC_i=A_iC_T+B_iC_T^{-P} \qquad\qquad (B\text{-}18)$$

For the case of equal valences, we have $P=N_i$. Using the boundary conditions

$$r=0, C_T=C_T^\bullet$$
$$r=\delta, C_T=C_T^o$$

the values of the parameters A_i and B_i can be determined as follows:

$$A_i=\frac{1}{C_T^o}\left(z_iC_i^o-B_i\left(C_T^o\right)^{-P}\right) \qquad\qquad (B\text{-}19)$$

and

$$B_i = \omega \frac{X_i^\bullet - X_i^o}{\left(C_T^\bullet\right)^{-P-1} - \left(C_T^o\right)^{-P-1}} \tag{B-20}$$

Equation (B-18) gives us a relation between the individual ion concentrations, C_i and the total equivalent concentration, C_T. Substituting for C_i and its derivative in the modified Nernst-Planck Equation (B-11), we get the following flux expression:

$$J_i = -\frac{D_i}{z_i}\frac{dC_T}{dr}\left[\left(A_i - PB_iC_T^{-P-1}\right) + N_i\left(A_i + B_iC_T^{-P-1}\right)\right] \tag{B-21}$$

For the case of arbitrary valences, Eq. (B-18) is only an approximation. In this case however, N_i is not the same for all the counterions and hence, P cannot be equal to N_i. Combining the above equation with the condition of no net current flow (Eq. B-5) results in

$$\left(\sum_{i=1}^{n}D_iA_i + \sum_{i=1}^{n}N_iD_iA_i\right) + \left(\sum_{i=1}^{n}N_iD_iB_i - P\sum_{i=1}^{n}D_iB_i\right)C_T^{-P-1} = 0 \tag{B-22}$$

The only way the above equation can hold true is when both the terms are equal to zero. That leads to

$$\sum_{i=1}^{n}\left(1+N_i\right)D_iA_i = 0 \tag{B-23}$$

Substitution of A_i (Eq. B-19) in to above and some mathematical manipulations gives the desired expression for total interfacial concentration, $C_T^\bullet$:

$$C_T^\bullet = \left(\frac{\sum_{i=1}^{n}(1+N_i)D_iX_i^o}{\sum_{i=1}^{n}(1+N_i)D_iX_i^\bullet}\right)^{1/P+1} C_T^o \tag{B-24}$$

Equating the second parentheses term to zero and substitution of B_i would give us the expression for the exponent P as:

$$P = \frac{\sum_{i=1}^{n} N_i D_i \left(X_i^* - X_i^o \right)}{\sum_{i=1}^{n} D_i \left(X_i^* - X_i^o \right)} \qquad \text{(B-25)}$$

In an equal valance case, P is equal to Ni and in an arbitrary case, it would be in the neighborhood of Ni. The concentrations involved in this work are very low and lead to lot of numerical errors and instability. Because of numerical discrepancies, sometimes the value of P computed in the code is unusually high and leads to problems in further computations. Hence the expression for P (Eq. B-26) is modified as follows:

$$P = \frac{\sum_{i=1}^{n} N_i D_i \left(X_i^* - X_i^o \right)}{\sum_{i=1}^{n} D_i \left(X_i^* - X_i^o \right)} \qquad \text{(B-26)}$$

Once again substitution of the above equations into (B-11) and integrating between the boundary conditions given earlier, We would get the final desired form of the ionic flux expression:

$$J_i = \frac{D_i}{\delta} \left((1 - \frac{N_i}{P})(C_i^* - C_i^o) + N_i A_i (1 + \frac{1}{P})(C_T^* - C_T^o) \right) \qquad \text{(B-27)}$$

APPENDIX C

COMPUTER CODE

Note: This code is the intellectual property of Oklahoma State University. Any use in whole or in part without the expressed written consent of the Oklahoma State University School of Chemical Engineering is prohibited.

```
*----------------------------------------------------------------*
*   Driver for SUBROUTINE intercon                               *
*----------------------------------------------------------------*
      PROGRAM Intdrive
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 K(15),z(15),Y(15),X(15),Q,Cto
      INTEGER flag,n
      READ(*,*) m
      DO 50 j=1,m
        READ(*,*) n, Q, Cto
        READ(*,*) (K(i),i=1,n)
        READ(*,*) (z(i),i=1,n)
        READ(*,*) (y(i),i=1,n)
        CALL Intercon(Y,X,K,z,Cto,Q,n,flag)
        IF (flag.eq.1)THEN
        WRITE(*,*)'Program failure:  Check output for cause'
        ENDIF
          DO 15, i = 1,n
        WRITE(*,105) Y(1),X(1)
15    CONTINUE
50    CONTINUE
100   FORMAT(1x,a3,5x,a12,5x,a7,5x,a8)
105   FORMAT(1X,e13.6,5x,e13.6)
      STOP
      END
```

```
*----------------------------------------------------------------------*
*        This subroutine calculates the interfacial liquid phase       *
*    equivalent ionic fractions for a multicomponent ion exchange      *
*    system for either a cationic or anionic resin.  The given variables *
*    are Y(i), K(i), z(i), Q, Cto, n, and flag, where the dimensioned  *
*    variables are input in the main program.                          *
*        The required input variables are:                             *
*        K(i) = the selectivity of ion i with respect to a common      *
*               reference, i.e. hydrogen, hydroxyl, amines etc.        *
*        z(i) = the absolute value of the charge of ion i, i.e. 1      *
*               for either hydrogen or hydroxyl ions.                  *
*        Y(i) = the mole fraction of ion i loaded within the resin     *
*               at the time of calculation.                      *     *
*        Q    = the capacity of the resin (mol/liter)                  *
*        Cto  = the total interfacial concentration of the ions.       *
*        n = the number of counterions                                 *
*        flag = a sentinel variable, default = 0, 1 if code in error   *
*----------------------------------------------------------------------*


      SUBROUTINE Intercon(Y,X,K,z,Cto,Q,n,flag)
      IMPLICIT REAL*8(A-H,O-Z)
      EXTERNAL pol
      REAL*8 Y(15),X(15),K(15),Kt(15),z(15),Cto,Q,Kref,lam(15),ord(15),
     1     xsum
      INTEGER flag,n


*----------------------------------------------------------------------*
*        Ensure the input data are suitable for execution.             *
*----------------------------------------------------------------------*


      Ytest = 0.0
      flag = 0
      DO 5 i=1,n
        Ytest = Ytest + Y(i)
5     CONTINUE
      IF (ABS(Ytest-1.0).gt.1.0e-5) THEN
        WRITE(*,*) 'Initial loadings must sum to 1.0'
        flag = 1
        RETURN
      ELSEIF (Cto.le.0.0) THEN
        WRITE(*,*) 'Total interfacial concentration equals zero'
        RETURN
```

```
      ENDIF

*-----------------------------------------------------------------------*
* Calculate the mean selectivity, mean valence, and switch the reference *
* reference ion to the pseudo-ion                                        *
*-----------------------------------------------------------------------*

      CALL Selmean(K,Kref,Y,Yref,n,flag)
      CALL Chargemean(z,zref,Y,Q,n,flag)
      CALL Selref(K,Kt,z,n,Kref,zref,flag)
      IF (zref.eq.0.0) THEN
        WRITE(*,*)'zref equals zero'
        flag = 1
      ENDIF


*-----------------------------------------------------------------------*
* Calculate coefficients and exponents of the mole fraction constraint   *
*  polynomial.                                                           *
*-----------------------------------------------------------------------*

      DO 10 i = 1,n
        lam(i) = Y(i)*(Kt(i)**(-1/zref))*(Yref**(-z(i)/zref))*(Q/Cto)
     1        **(1-(z(i)/zref))
        ord(i) = z(i)/zref
10    CONTINUE
      x1=0.0
      xacc=1e-9
      x2=1.0
      xroot = zriddr(pol,x1,x2,xacc,lam,ord,n,flag)
      DO 22 i = 1,n
        X(i)=lam(i)*xroot**(ord(i))
22    CONTINUE
      xsum = 0.0
      DO 23 i = 1,n
        xsum = xsum + X(i)
23    CONTINUE
      DO 24 i=1,n
        X(i) = X(i)/xsum
24    CONTINUE
      RETURN
      END
*-----------------------------------------------------------------------*
*  Function pol                                                          *
*  Uses the coefficients and exponents generated in the main program to  *
*  calculate the functional value of the mole fraction constraint equation *
```

```
*----------------------------------------------------------------*

      FUNCTION pol(X,lam,ord,n)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 X,lam(15),ord(15)
      INTEGER n
      pol = -1.
      DO 25 i = 1,n
        pol = pol + lam(i)*X**(ord(i))
 25   CONTINUE·
      RETURN
      END


*----------------------------------------------------------------*
*   Subroutine Selref                                            *
*   This subroutine changes the reference ion in the selectivity *
*   coefficient array for either cations or anions of arbitrary valence *
*   The variables used are:                                      *
*      K = Selectivity array with common reference ion           *
*      Kref = Selectivity of new reference with respect to the old reference *
*      n = number of cations or anions in system                 *
*      z = ion charge array                                      *
*      zref = reference ion charge                               *
*----------------------------------------------------------------*

      SUBROUTINE Selref(K,Kt,z,n,Kref,zref,flag)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 K(15),Kt(15),Kref,z(15),zref
      INTEGER n,flag
      DO 10 i = 1,n
          if (Kref.eq.0.0) then
            write (*,*) 'Reference Selectivity equals zero'
            flag = 1
            return
          endif
          Kt(i)=(K(i)**zref)/(Kref**z(i))
 10   CONTINUE
      RETURN
      END


*----------------------------------------------------------------*
*   Subroutine Selmean                                           *
*   This subroutine calculates the mean selectivity coefficient  *
*   given the current resin loading.  See the documentation      *
*   enclosed with this code for the derivation of the mean selectivity *
```

```
*   coefficient                                                        *
*       Variables used:                                               *
*          K(i)= Selectivity array with respect to reference ion      *
*          Y(i)= Current resin loading (meq/ml)                       *
*          Yref = Equivalent ionic fraction of new reference ion,     *
*                 by definition it has a value of 1.0                 *
*          n = number of cations or anions (includes dissociative species *
*          Kref = the selectivity of the new reference ion with       *
*                 respect to the old one.                             *
*---------------------------------------------------------------------*


      SUBROUTINE Selmean(K,Kref,Y,Yref,n,flag)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 K(15),Kref,Y(15),Yref
      INTEGER n,flag
      Kref = 1.
      Yref = 1.
      DO 10 i = 1,n
          if (K(i).le.0.0) then
            write(*,*) 'Negative selectivity'
            flag = 1
            return
          endif
          Kref = Kref*(K(i)**Y(i))
10    CONTINUE
      RETURN
      END


*---------------------------------------------------------------------*
*   Subroutine Chargemean                                    *        *
*   This subroutine calculates the mean ionic valence as described by *
*   Franzreb's flux expressions                                       *
*   The variables used are:          .                                *
*      Q = the total capacity of the resin (meq/ml)                   *
*      z(i) = the charge array of either cations or anions            *
*      zn = the summation term in the numerator of Franzreb's         *
*         expression                                                  *
*      zd = the summation term in the denominator of Franzreb's       *
*         expression                                                  *
*      zref = the mean ionic valence                                  *
*      Y(i) = the equivalent fraction array of cations or             *
*         anions (meq/ml)                                             *
*      Yt(i) = mole fraction resin loading array (mol/l)              *
*      n = the number of either cations or anions                     *
```

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```
*-----------------------------------------------------------------------*

      SUBROUTINE Chargemean(z,zref,Y,Q,n,flag)
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 z(15),Y(15),Qt(15),Q,zn,zd,zref
      INTEGER n,flag
      zn = 0.
      zd = 0.
      zref = 0.

c         Convert equivalent ionic capacities to molar capacities

      DO 5 i = 1,n
        Qt(i) = Q*Y(i)/ABS(z(i))
5   CONTINUE

C         Apply mean valence relationship

      DO 10 i = 1,n
        zn = zn + (z(i)**2)*Qt(i)
        zd = zd + z(i)*Qt(i)
10  CONTINUE
      IF (zd.eq.0.0) THEN
        flag = 1
        WRITE(*,*) 'mean valence denominator equals zero'
        RETURN
      ELSE
      ENDIF
        zref = zn/zd
      RETURN
      END

c   Apply Ridder's method to search for polynomial root.

      FUNCTION zriddr(pol,x1,x2,xacc,lam,ord,n,flag)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER MAXIT
      REAL*8 zriddr,x1,x2,xacc,pol,lam(15),ord(15)
      PARAMETER (MAXIT=60,UNUSED=-1.11E30)
          INTEGER n,flag
      EXTERNAL pol
      INTEGER j
      REAL*8 fh,fl,fm,fnew,s,xh,xl,xm,xnew
      fl=pol(x1,lam,ord,n)
      fh=pol(x2,lam,ord,n)
```

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```fortran
      IF((fl.gt.0..and.fh.lt.0.).or.(fl.lt.0..and.fh.gt.0.))THEN
        xl=x1
        xh=x2
        zriddr=UNUSED
        DO 11 j=1,MAXIT
          xm=0.5*(xl+xh)
          fm=pol(xm,lam,ord,n)
          s=sqrt(fm**2-fl*fh)
          if(s.eq.0.)return
          xnew=xm+(xm-xl)*(sign(1.,fl-fh)*fm/s)
        IF (abs(xnew-zriddr).le.xacc) RETURN
          zriddr=xnew
          fnew=pol(zriddr,lam,ord,n)
        IF (fnew.eq.0.) RETURN
        IF (sign(fm,fnew).ne.fm) THEN
          xl=xm
          fl=fm
          xh=zriddr
          fh=fnew
        ELSEIF(sign(fl,fnew).ne.fl) THEN
          xh=zriddr
          fh=fnew
        ELSEIF(sign(fh,fnew).ne.fh) THEN
          xl=zriddr
          fl=fnew
        ELSE
          pause 'Ridders' method ineffective'
        ENDIF
        IF (abs(xh-xl).le.xacc) RETURN
11    CONTINUE
        WRITE (*,*)'Ridders' method exceeded maximum iterations'
          flag = 1
      ELSEIF (fl.eq.0.) THEN
        zriddr=x1
      ELSEIF (fh.eq.0.) THEN
        zriddr=x2
      ELSE
        WRITE(*,*)'root must be bracketed in zriddr'
        flag = 1
      RETURN
      ENDIF
      RETURN
      END
```

Notes:

Subroutine requires same driver as 'SUBROUTINE Intercon'

```
      SUBROUTINE multc(Y,X,K,z,Cto,Q,n,flag)
      EXTERNAL pol
      REAL*8 Y(15),X(15),K(15),z(15),lam(15),Q,Cto,ord(15),Ytest,X1,X2
1     ,Xacc,pol,zriddr
      INTEGER n,flag
```

```
*--------------------------------------------------------------------------*
*     Calculate the values of lam for each component, and calculate        *
*     the order of the concentration as determined by the ratio of         *
*     the ion valence to the reference ion valence.                        *
*--------------------------------------------------------------------------*
      DO 1 ii=1,n
        IF (K(ii).le.0.0)THEN
          WRITE(*,*) 'Negative or zero selectivity value'
          flag = 1
          RETURN
        ENDIF
1     CONTINUE
      Ytest = 0.0
      DO 2 ii=1,n
        Ytest=Y(ii)+Ytest
2     CONTINUE
      IF(ABS(1.0-Ytest).gt.1.0e-8)THEN
        WRITE(*,*)'Initial loadings do not sum to 1.0'
        flag = 1
        RETURN
      ENDIF
      IF (z(1).eq.0.0) then
          write(*,*)'Reference ion valence in multc equals zero'
          flag = 1
          RETURN
      ELSEIF(Cto.eq.0.0) THEN
          WRITE(*,*)'Interfacial concentration equals zero'
          flag = 1
          RETURN
      ENDIF
      DO 10 i = 1,n
        lam(i) = Y(i)*(K(i)**(-1/z(1)))*(Y(1)**(-z(i)/z(1)))*(Q/Cto)
```

```
   1       **(1-(z(i)/z(1)))
          ord(i) = int(z(i)/z(1))
   10  CONTINUE


*----------------------------------------------------------------------*
*     Construct the polynomial and solve for the correct root using     *
*     the Ridder false position method.  The polynomial is found in     *
*     FUNCTION pol                                                       *
*----------------------------------------------------------------------*

          X1 = 0.0
          X2 = 1.0
          xacc = 1e-8
          flag=0
          Xr = zriddr(pol,x1,x2,xacc,lam,ord,n,flag)
          X(1)=Xr
          DO 22 i = 2,n
            X(i)=lam(i)*X(1)**(ord(i))
   22  CONTINUE
          xsum = 0.0
          DO 23 i = 1,n
            xsum = xsum + x(i)
   23  CONTINUE
          IF (ABS(1.0-xsum).GE.1e-4)THEN
          WRITE(*,*)'Interfacial concentrations do not sum to 1.0'
           flag = 1
           RETURN
          ENDIF
          RETURN
          END


*----------------------------------------------------------------------*
*  FUNCTION pol                                                          *
*  Calculates functional value of the polynomial derived from the mole  *
*  fraction constraint.                                                 *
*----------------------------------------------------------------------*

          FUNCTION pol(X,lam,ord,n)
          IMPLICIT REAL*8(A-H,O-Z)
          REAL*8 X,lam(15),ord(15)
          INTEGER n
          pol = -1.
          DO 25 i = 1,n
              pol = pol + lam(i)*X**(ord(i))
   25  CONTINUE
```

```
      RETURN
      END


      FUNCTION zriddr(pol,x1,x2,xacc,lam,ord,n,flag)
      IMPLICIT REAL*8(A-H,O-Z)
      INTEGER MAXIT
      REAL*8 zriddr,x1,x2,xacc,pol,lam(15),ord(15)
         PARAMETER (MAXIT=60,UNUSED=-1.11E30)
      INTEGER n,flag
      EXTERNAL pol
      INTEGER j
      REAL*8 fh,fl,fm,fnew,s,xh,xl,xm,xnew
      fl=pol(x1,lam,ord,n)
      fh=pol(x2,lam,ord,n)
      IF((fl.gt.0..and.fh.lt.0.).OR.(fl.lt.0..and.fh.gt.0.))THEN
       xl=x1
       xh=x2
       zriddr=UNUSED
       DO 11 j=1,MAXIT
        xm=0.5*(xl+xh)
        fm=pol(xm,lam,ord,n)
        s=sqrt(fm**2-fl*fh)
        IF(s.eq.0.)RETURN
          xnew=xm+(xm-xl)*(sign(1.,fl-fh)*fm/s)
        IF (abs(xnew-zriddr).le.xacc) RETURN
          zriddr=xnew
          fnew=pol(zriddr,lam,ord,n)
        IF(fnew.eq.0.) RETURN
        IF(sign(fm,fnew).ne.fm) THEN
         xl=xm
         fl=fm
         xh=zriddr
         fh=fnew
        ELSEIF(sign(fl,fnew).ne.fl) THEN
         xh=zriddr
         fh=fnew
        ELSEIF(sign(fh,fnew).ne.fh) THEN
         xl=zriddr
         fl=fnew
        ELSE
         WRITE(*,*) 'Ridder's method ineffective'
          flag = 1
        RETURN
        ENDIF
```

```fortran
      IF(abs(xh-xl).le.xacc) RETURN
11    CONTINUE
      WRITE(*,*)'Ridders' method exceed maximum number of iterations.'
        flag = 1
        RETURN
      ELSEIF(fl.eq.0.) THEN
       zriddr=x1
      ELSEIF(fh.eq.0.) THEN
       zriddr=x2
      ELSE
       WRITE (*,*)'root must be bracketed in zriddr'
       flag=1
       RETURN
      ENDIF
      RETURN
      END
```

VITA

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