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Ion Exchange Equilibria Data for Systems Involving H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} Ions

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Extensive ion exchange equilibrium data is presented for all binary, ternary, and quaternary systems as well as for the five-component system involving the ions H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} on the gel-type Amberjet 1200H resin manufactured by Rohm and Hass. Solution concentrations studied are 0.10 mol L^{-1}, 0.20 mol L^{-1}, 0.50 mol L^{-1}, and 1.00 mol L^{-1}. All experiments are conducted with Cl^- as the nonexchanging anion at (25.0 ± 0.1) °C. This extensive data set is used to test the predictions of a published ion exchange equilibrium model.

Introduction

For over half a century, a range of models have been proposed with varying degrees of accuracy to predict binary and multicomponent ion exchange equilibrium behavior. One approach to modeling multicomponent ion exchange systems is to predict the system behavior based upon the experimental data developed for the constitutive binary systems. Thus, when three or more ions are exchanging with one another between the two phases the system is considered to be made up of a number of competing binary equilibria. Therefore, if a system involves the exchange between three ions, A−B−C, it may be represented by the three binary equilibria A−B, A−C, and B−C, whereas a four-component system may be represented by its six constitutive binary systems A−B, A−C, A−D, B−C, B−D, and C−D. It is usually assumed that the binary model parameters that may include the equilibrium constant for a binary system will be independent of the presence of any other ionic species. Thus, the equilibrium constant for the A−B system will be assumed to be independent of the presence or absence of ions C and D.

Even in simple binary systems involving the exchange of just two ions, some models that have been proposed fail even the most simple of tests, such as ensuring that the equilibrium constant calculated from experimental data is independent of the solution-phase concentration. No fully theoretical model has been developed to date that allows equilibrium behavior to be predicted without at least some experimental data. Much work has been conducted to develop semitheoretical models that allow multicomponent behavior to be predicted upon the basis of the experimental data of the constitutive binary systems.

Workers who propose their own models for ion exchange equilibrium system behavior often test their models on very limited data collected by them. Models proposed to predict binary systems might be tested on only two or three binary systems. Such limiting testing does not allow the consistency of the model predictions to be verified or validated. This paper presents extensive equilibrium data for all the constitutive systems involving cation exchange between five different ions. The 10 binary systems presented include 1−1, 1−2, and 2−2 valance systems. The 10 ternary systems presented include 1−1−1, 1−1−2, and 1−2−2 valance systems, whereas the five quaternary systems represent 1−1−1−2 and 1−1−2−2 systems. By making this extensive data available, future workers will be able to test their models thoroughly.

The data set is used to test the ion exchange equilibrium model of Mehablia et al.[1] This model accounts for the nonideal behavior of the solution and exchanger phases by applying Pitzer's electrolyte solution theory[2,3] and the Wilson model,[4] respectively.

Modeling Ion Exchange Equilibria

The exchange of two cations between a solution phase and an exchanger phase may be represented by the reversible stoichiometric equation of the type

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

where z_a and z_b are the valencies of ionic species A and B, respectively, and the underline denotes that the ion is in the exchanger rather than the solution phase. The equilibrium constant for such an exchange may be written in terms of the activities of the ions in the two phases

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

where a_i and a'_i are the activities of ionic species i, either A or B, in the solution and exchanger phases, respectively.

The equilibrium constant, K_{AB}, is defined in eq 2 in terms of activities rather than concentrations because of the nonideal behavior usually exhibited in both the solution and the exchanger phases. Early workers[5,6] assumed that both phases behaved ideally. They made use of the selectivity coefficients, which for a binary system is defined as

$$K^T_{AB} = \left(\frac{q_A}{C_A}\right)^{z_b} \times \left(\frac{C_B}{q_B}\right)^{z_a} \qquad (3)$$

where q_i is the concentration of species i in the exchanger phase and C_i is the normality in the liquid phase. Although the equilibrium constant of an ion exchange process should be a function of temperature only, the selectivity coefficient

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is also a function of the total concentration and the composition of the solution phase.[7]

The early models developed to predict the equilibrium behavior of ternary systems were based upon binary system data and assumed that the presence of other counterions would not appreciably affect the equilibrium relationships between two particular ions.[5,6] These workers assumed that the selectivity coefficient values obtained from the data of the constitutive binary systems could be used to predict ternary system behavior.

Elprince and Babcock[8] proposed the use of the Wilson model[4] to estimate the exchanger-phase activity coefficients. The Wilson equation applied to the exchanger phase to calculate the activity coefficients is

$$\ln \gamma_i = 1 - \ln\{\sum_{j=1}^{M} y_{mi}\Lambda_{ij}\} - \sum_{k=1}^{M}\left\{\frac{y_{mk}\Lambda_{ki}}{\sum_{j=1}^{M} y_{mi}\Lambda_{kj}}\right\} \tag{4}$$

where y_{mi} is the mole fraction of component i in the exchanger phase, M is the number of counterion species in the exchanger phase, and Λ_{ij} is the Wilson binary interaction parameter defined such that $\Lambda_{ij} = 1$ when $i = j$ and $\Lambda_{ij} > 0$ when $i \neq j$. For an ideal exchanger phase, $\Lambda_{ij} = 1 = \Lambda_{ji}$ for all i and j. For a binary system, only two parameters, Λ_{AB} and Λ_{BA}, are required to calculate the activity coefficient. Once determined for a binary system, these values may be used to calculate the exchanger-phase activity coefficients in a multicomponent system.

In 1978, Smith and Woodburn[9] proposed the use of the extended Debye−Hückel equation to calculate the activity coefficients in the aqueous solution phase. Like Elprince and Babcock, they applied the Wilson model to estimate the exchanger-phase activity coefficients. Using data for the three constitutive binary systems, they were able to predict the equilibrium behavior of the $SO_4^{2-}-NO_3^{-}-Cl^{-}$ ternary system successfully. The model of Smith and Woodburn requires values for three parameters for each constitutive binary system to be known in order that the ternary equilibrium behavior may be predicted. The parameters are the equilibrium constant, K_{AB}, and the two Wilson binary interaction parameters, Λ_{AB} and Λ_{BA}.

Allen et al.[10] suggested the use of the Hála[11] constraint in an effort to reduce the number of parameters required to characterize the system adequately. In its simplest form when applied to a binary system, the Hála constraint is

$$\Lambda_{AB}\Lambda_{BA} = 1 \tag{5}$$

When incorporated into the Smith and Woodburn model,[9] only two parameters are required to be regressed from the data of each constitutive binary system, namely, K_{AB} and Λ_{AB}. Allen et al.[10] applied their modified version of the Smith and Woodburn[9] model to data from other workers. Although on first inspection the model appears to fit the data adequately, it is disturbing to note that both the equilibrium constants and the Wilson binary interaction parameters are seen to vary significantly with solution concentration. This should not occur and suggests that the model is fundamentally flawed.

In calculating the solution-phase activity coefficients, it was found that the Debye−Hückel equation does not take into account the effect that the presence of other ions in the system may have on the activity coefficient values. Recognizing this, Shallcross et al.[12] proposed a model in which the Pitzer electrolyte solution theory[2,3] is used to predict the aqueous-phase activity coefficients. In all other respects, the model was identical to the Smith and Woodburn model.[9] Both the models of Smith and Woodburn and Shallcross et al. require three parameters (K_{AB}, Λ_{AB}, and Λ_{BA}) for each binary system to be regressed from the binary equilibrium data simultaneously. Because the three parameters are highly interdependent, the calculated value for K is highly sensitive to slight changes in the values of Λ_{AB} and Λ_{BA}. Mehablia et al.[1,13] developed an ion exchange equilibrium model in which the equilibrium constant is regressed separately before Λ_{AB} and Λ_{BA}. By decoupling these parameters, the model yields values for K that are independent of the solution concentration.

A completely different approach to predicting multicomponent equilibria was adopted by Melis et al.[14] In considering synthetic resin-type exchangers, they considered that the resin consisted of two different types of exchange sites, each having its own equilibrium constant for a binary system. The sites were present on the exchanger in equal amounts. They assumed that the solution phase behaved ideally and that all the nonideal behavior of the resin phase was accounted for by the use of the two-site model. The Melis model requires two parameters—the two equilibrium constants—to be fitted to the data of each binary system. More recently, the Melis model was extended by Vo and Shallcross[15] by accounting for nonideal behavior in the solution phase by applying Pitzer's electrolyte solution theory.[2,3] Melis et al.[14] noted that there was no physical evidence to support the concept that the resin consisted of only two different types of exchanger sites existing in equal numbers. They merely used the concept to model any and all nonideal behavior of the system.

An alternative model for exchanger-phase nonidealities was presented by de Kock and van Deventer[16] and later refined by Lukey et al.[17,18] This model is based upon the Metropolis Monte Carlo method for statistical thermodynamics and was initially applied to complex multicomponent sorption in hydrometallurgical processes. Recently, Provis et al.[19] combined this model with a more rigorous description of solution-phase behavior. Their model requires just one parameter to be fitted to the data of each binary system.

Experimental Material, Apparatus, and Procedures

Many of the models proposed in the literature to predict multicomponent ion exchange behavior have only ever been tested for three exchanging ions. The purpose of this paper is to present extensive equilibrium data for all of the cation exchange systems involving H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} ions. This includes the 10 constitutive binary systems, the 10 ternary systems, the 5 quaternary systems, and the 1 system in which all 5 ions are available for exchange.

The ion exchange equilibrium data were collected using a simple batch technique. In all systems, Cl^- was the only nonexchanging anion present. All experiments were conducted at (25.0 ± 1.0) °C.

The ion exchanger used in the experiments was the commercial gel-type Amberjet 1200H manufactured by Rohm and Hass. The spherical beads had a mean diameter of (650 ± 50) μm. Before the first use, the resin was subjected to a preconditioning process that washed it of any water-soluble residues or undesired cations and left them in the desired form.

The cation exchange capacity of the resin was determined for several of its forms. To determine the H^+-form capacity, a sample of the resin of known mass and moisture

Table 1. Summary of the Number of Equilibrium Data Points in the Equilibrium Data Set

	concentration				
system	0.10 mol L^{-1}	0.20 mol L^{-1}	0.50 mol L^{-1}	1.00 mol L^{-1}	table
Na^+-H^+	21	20	15	15	A1
Na^+-K^+	18	16	15	11	A2
K^+-H^+	18	18	15	14	A3
H^+-Ca^{2+}	19	18	15	13	A4
Na^+-Ca^{2+}	21	11	14	12	A5
K^+-Ca^{2+}	16	17	12	14	A6
$Ca^{2+}-Mg^{2+}$	18	15	14	12	A7
H^+-Mg^{2+}	15	14	13	12	A8
Na^+-Mg^{2+}	19	16	18	19	A9
K^+-Mg^{2+}	19	15	15	17	A10
$K^+-Na^+-H^+$	19	19	19	19	A11
$K^+-Na^+-Ca^{2+}$	19	19	19	11	A12
$K^+-Na^+-Mg^{2+}$	19	19	19	17	A13
$Na^+-H^+-Ca^{2+}$	19	19	19	11	A14
$Na^+-H^+-Mg^{2+}$	19	19	19	11	A15
$Na^+-Ca^{2+}-Mg^{2+}$	17	19	19	12	A16
$K^+-H^+-Ca^{2+}$	19	19	19	12	A17
$K^+-H^+-Mg^{2+}$	19	19	19	11	A18
$K^+-Ca^{2+}-Mg^{2+}$	17	19	19	10	A19
$H^+-Ca^{2+}-Mg^{2+}$	17	18	19	11	A20
$K^+-Na^+-H^+-Ca^{2+}$	15	14	18	16	A21
$K^+-Na^+-H^+-Mg^{2+}$	19	16	15	15	A22
$K^+-Na^+-Ca^{2+}-Mg^{2+}$	13	15	16	16	A23
$K^+-H^+-Ca^{2+}-Mg^{2+}$	15	17	16	14	A24
$Na^+-H^+-Ca^{2+}-Mg^{2+}$	17	17	18	14	A25
$K^+-Na^+-H^+-Ca^{2+}-Mg^{2+}$	15	23	20	19	A26

content was placed into a dry, clean flask. A known amount of the deionized and distilled water was then added to the flask. At this point, analytical-grade NaCl was introduced into the flask under stirring. The salt immediately went into solution, forming a concentrated solution of Na^+ ions that, it was assumed, displaced all of the H^+ ions from the resin. Thus, the resin was completely converted to the Na^+ form. The number of H^+ ions in the solution was then determined using a standard titration technique. A standard NaOH solution was titrated directly into the flask still containing the resin, under stirring action. When this process was repeated several times, the cation exchange capacity of the H^+ form of the resin was found to be (5.05 ± 0.03) mmol/g of dry resin.

The equilibrium experiments were performed in the following manner. A previously unused sample of resin of known form and mass was placed into a 250 mL Erlenmeyer flask with precisely 100.0 mL of a solution of known composition and concentration. Preliminary tests had confirmed that 3 days was sufficient to ensure that equilibrium was attained. At the conclusion of this period, the solution was separated from the resin, and its concentration was determined using appropriate analytical techniques including titration, inductively coupled plasma, and atomic adsorption spectrophotometry. The uncertainty associated with the analysis of the solution was $\pm{}^3/_4\%$ for inductively coupled plasma spectrophotometry and ±2% for atomic adsorption spectrophotometry and manual titration. Once the equilibrium composition of the solution phase was determined, the equilibrium composition of the exchanger or resin phase could be inferred by use of a simple material balance.

The amount of the resin used and the composition and concentration of the solution phases were varied to ensure that a wide range of equilibrated compositions were measured. All systems were studied at four solution-phase concentrations, namely, 0.10 mol L^{-1}, 0.20 mol L^{-1}, 0.50 mol L^{-1}, and 1.00 mol L^{-1}. Approximately 70 data points were collected for each binary system.

Table 2. Single Salt Pitzer Parameters[3]

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

Table 3. Binary Salt Pitzer Parameters[3]

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

Table 4. Salt Dissociation Constants[22] for Use in Equation 16

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

For most systems the equilibrium states were approached from at least two different directions. As an example, for the $Ca^{2+}-H^+$ binary system, some experiments were performed with the resin initially in the H^+ form in contact with a $CaCl_2$ solution, whereas other experiments started with the resin in the Ca^{2+} form in contact with a solution of HCl. Data gained from approaching the equilibrium state in either direction were in good agreement with one another, supporting the notion that the equilibrium data may be accurately calculated by material balance.

The experimental equivalent ionic fraction data presented in the Accompanying Data have an uncertainty of $2^1/_2\%$.

Because of the hydrophilic nature of the resin, all samples used in the equilibrium experiments were divided into two portions immediately prior to the experiments, with one portion being used for the equilibrium experiments and the other retained for moisture analysis. The moisture content sample of the resin was weighed and placed inside an oven at 110 °C for 24 h. This process drove off all of the interstitial as well as some of the structural moisture. The resin was then reweighed immediately upon removal from the oven. The moisture content was then determined from the difference in mass before and after heating. This technique allowed the content to be determined to within ±0.1%. Because heating the resin samples to 110 °C leads to irreversible changes in its properties, all samples that had been heated in this way were discarded once they had been reweighed.

The experimental material, equipment, and procedures are presented more fully elsewhere.[20]

The extent of the experimental program is summarized in Table 1. The number of data points for each solution concentration for each system is presented. Also listed is the Table in the Accompanying Data in which the actual experimental data may be found.

Mehablia Model Extended to Five Components

To illustrate the usefulness of the data set, it will be used to test the model predictions of the ion exchange equilibrium model proposed by Mehablia et al.[1] Heretofore, this model has only ever been applied up to a single, limited four-component system.[13]

We begin with a brief summary of the Mehablia model, but extended for the first time here to a system of five exchanging ions.

The model proposed by Mehablia et al. for multicomponent ion exchange equilibrium has the following key features:

- the equilibrium constants are calculated from the constitutive binary equilibrium empirical data using the approach of Gaines and Thomas;[21]
- the Wilson model[4] is applied to the nonidealities of the exchanger phase;
- the Pitzer model[3] is used to predict the activity coefficients of the solution phase; and
- the nonavailability for ion exchange of some of the ions due to the existence of ion pairs is considered.

We first must recognize that not all the ions of a species will be available for exchange onto the resin. When a salt M_xX_m is introduced into an aqueous solution, not all of the molecules will immediately dissociate into the separate ions. An equilibrium will be established corresponding to the equation

$$M_xX_m \leftrightarrow xM^{m+} + mX^{x-} \tag{6}$$

having a stability constant defined as

$$K_S^{MX} = \frac{[M_xX_m]}{[M^{m+}]_f^x\,[X^{x-}]_f^m} \tag{7}$$

where $[M]_f$ is the free ion concentration of species M and m and x are the valences of cation M and anion X, respectively.

Some of the ions present in the solution will not be available for ion exchange because they are not present as free ions but rather as ion pairs. Thus, for the five-component system of Na^+, K^+, H^+, Ca^{2+}, and Mg^{2+} ions with Cl^- ions as the nonexchanging anions some of the ions will be present as NaCl, KCl, HCl, $MgCl^+$, and $CaCl^+$ ion pairs. We assume that all $CaCl_2$ dissociates to at least $CaCl^+$ and Cl^-. Similarly, it is assumed that the $MgCl_2$ dissociates to $MgCl^+$ and Cl^-.

To calculate the free ion concentrations of each of the species, we use the method of Kester and Pytkowicz[22]. Thus, for our five-component system, because sodium is present as either Na^+ or NaCl, we have

$$[Na]_t = [Na^+]_f + [NaCl] \tag{8}$$

where $[Na]_t$ is the total concentration of sodium present in whatever form. According to the definition of the stability constant, we may write

$$[NaCl] = K_S^{NaCl}[Na^+]_f[Cl^-]_f \tag{9}$$

Substitution into eq 8 yields upon rearrangement

$$[Na^+]_f = \frac{[Na]_t}{1 + [Cl^-]_f K_S^{NaCl}} \tag{10}$$

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

$$[K]_f = \frac{[K]_t}{1 + [Cl^-]_f K_S^{KCl}} \tag{11}$$

$$[H^+]_f = \frac{[H]_t}{1 + [Cl^-]_f K_S^{HCl}} \tag{12}$$

$$[Ca^{2+}]_f = \frac{[Ca]_t}{1 + [Cl^-]_f K_S^{CaCl^+}} \tag{13}$$

$$[Mg^{2+}]_f = \frac{[Mg]_t}{1 + [Cl^-]_f K_S^{MgCl^+}} \tag{14}$$

$$[Cl^-]_f = \frac{[Cl]_t}{1 + [Na^+]_f K_S^{NaCl} + [K^+]_f K_S^{KCl} + [H^+]_f K_S^{HCl} + [Ca^{2+}]_f K_S^{CaCl^+} + [Mg^{2+}]_f K_S^{MgCl^+}} \tag{15}$$

Because the total concentrations of the ionic species present are known and values for the stability constants are tabulated for many ion pairs, eqs 11 to 15 may be solved to determine the concentrations of free ions available for ion exchange for the five-component system with Cl^-.

Kester and Pytkowicz[22] proposed that the stability constant K_S^{MX} may be related to the solution ionic strength I through an equation of the form

$$\ln(K_S^{MX}) = A' + B'I \tag{16}$$

where A' and B' are constants whose values are tabulated for a range of salts.[22]

Horvath[23] and Khoo[24] conducted extensive surveys of estimation and correlation methods for the activity coefficients of electrolytes. They recommend the use of an estimation method originally proposed by Pitzer[2] and subsequently updated.[3] The method may be used to determine the activity coefficients of ionic species in an aqueous solution of any number of ions. What follows is an abridged description of the application of the Pitzer model to activity coefficient calculations. A more thorough treatment is presented by Harvie and Weare[26] and Meijer and van Rosmalen.[27]

The nonideal behavior of the solution phase is accounted for by applying Pitzer's electrolyte solution theory.[2,3] The estimation model developed by Pitzer for single ions in aqueous solutions incorporates terms that relate to both binary and ternary interaction between the ions as well as incorporating a Debye–Hückel electrostatic term. The expression for the activity coefficient of the single cation M in an aqueous solution of *c* cations and *a* anions is given by Pitzer[3] as

$$\ln \gamma_M = {z_M}^2 f^{\gamma} + 2\sum_a m_a[B_{Ma} + (\sum_c m_c z_c)C_{Ma}] + 2\sum_c m_c \theta_{Mc} + \sum_c\sum_a [{z_M}^2 B'_{ca} + z_M C_{ca} + \psi_{Mca}] + \left(\frac{1}{2}\right)\sum_a\sum_{a'} m_a m_{a'}\,[{z_M}^2\theta_{a'a'} + \psi_{Maa'}] + \frac{{z_M}^2}{2}\sum_c\sum_{c'} m_c m_{c'}\theta'_{cc'} \quad (17)$$

where

$$f^{\gamma} = -A_{\phi}\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{\ln(1 + 1.2\sqrt{I})}{0.6}\right] \quad (18)$$

$$B_{Ma} = \beta^{(0)}_{Ma} + \frac{2\beta^{(1)}_{Ma}}{\alpha^2 I}[1 - (1 + \alpha\sqrt{I})\exp(-\alpha\sqrt{I})] \quad (19)$$

$$B'_{Ma} = \frac{2\beta^{(1)}_{Ma}}{\alpha^2 I^2}\left[-1 + \left(1 + \alpha\sqrt{I} + \frac{\alpha^2 I}{2}\right)\exp(-\alpha\sqrt{I})\right] \quad (20)$$

$$C_{Ma} = \frac{C^{(0)}_{Ma}}{2|z_M z_a|^{0.5}} \quad (21)$$

The above equations are valid for 1–1, 1–2, and 2–1 electrolytes. In these equations, z_i is the charge of ionic species *i*, and *I* is the ionic strength. A_{φ} is temperature-dependent, being defined as

$$A_{\phi} = \frac{1}{3}\frac{2\pi N_o \rho_w^{0.5}}{1000}\left(\frac{e^2}{\epsilon k T}\right)^{1.5} \quad (22)$$

where N_o is Avogardo's number, ρ_w and ϵ are the density and the static dielectric constant of the pure solvent, respectively, *k* is Boltzmann's constant, *T* is the absolute temperature, and *e* is the electron charge. At 25 °C, $A_{\varphi} = 0.392$ for water. A value of 2.0 for α is recommended by Pitzer.[3]

The β and θ terms in the above equations represent measurable combinations of the second virial coefficients and may be derived from single-electrolyte data. The *C* and ψ terms are measurable combinations of the virial coefficients and may be derived from data of two-salt systems. Values for $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and $C^{(0)}_{MX}$ are species-dependent and are tabulated in the literature[28,29] for over 250 electrolytes. The values of θ and ψ are known for 69 binary electrolyte mixtures.[29,30] For 2–2 electrolytes, eqs 19 and 20 are replaced by expanded equations.[28]

The Wilson[4] (1964) model is used to estimate the exchanger-phase activity coefficients. For a single binary system, eq 4 reduces to

$$\ln \bar{\gamma}_1 = 1 - \ln(y_{m1} + y_{m2}\Lambda_{12}) - \left[\frac{y_{m1}}{y_{m1} + y_{m2}\Lambda_{12}} + \frac{y_{m2}\Lambda_{21}}{y_{m1}\Lambda_{21} + y_{m2}}\right] \quad (23)$$

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

Thus, following Wilson's model, values for the two binary interaction parameters, namely, Λ_{12} and Λ_{21}, must be known before the resin-phase activity coefficients can be calculated. Once these values are determined, they may be used together with their counterparts from the other binary systems (e.g., Λ_{13} and Λ_{31}; Λ_{23} and Λ_{32}) to predict the activity coefficients in a multicomponent system. Thus, for a three-component system eq 4 would become

$$\ln \bar{\gamma}_1 = 1 - \ln(y_{m1} + y_{m2}\Lambda_{12} + y_{m3}\Lambda_{13} + y_{m4}\Lambda_{14} + y_{m5}\Lambda_{15}) - \frac{y_{m1}}{y_{m1} + y_{m2}\Lambda_{12} + y_{m3}\Lambda_{13} + y_{m4}\Lambda_{14} + y_{m5}\Lambda_{15}} - \frac{y_{m2}\Lambda_{21}}{y_{m1}\Lambda_{21} + y_{m2} + y_{m3}\Lambda_{23} + y_{m4}\Lambda_{24} + y_{m5}\Lambda_{25}} - \frac{y_{m3}\Lambda_{31}}{y_{m1}\Lambda_{31} + y_{m2}\Lambda_{32} + y_{m3} + y_{m4}\Lambda_{34} + y_{m5}\Lambda_{35}} - \frac{y_{m4}\Lambda_{41}}{y_{m1}\Lambda_{41} + y_{m2}\Lambda_{42} + y_{m3}\Lambda_{43} + y_{m4} + y_{m5}\Lambda_{45}} - \frac{y_{m5}\Lambda_{51}}{y_{m1}\Lambda_{51} + y_{m2}\Lambda_{52} + y_{m3}\Lambda_{53} + y_{m4}\Lambda_{54} + y_{m5}} \quad (24)$$

Smith and Woodburn[9] proposed that values for the Wilson binary interaction parameters may be calculated along with the equilibrium constant using equilibrium data from a single binary system. They achieved this by first defining an equilibrium quotient, λ, for each ion exchange reaction as

$$\lambda_{AB} = \left(\frac{\gamma_B C_B}{y_B}\right)^{z_a}\left(\frac{y_A}{\gamma_A C_A}\right)^{z_b} \quad (25)$$

This equilibrium quotient is related to the equilibrium constant by

$$\lambda_{AB} = K_{AB}\frac{{\bar{\gamma}_B}^{z_a}}{{\gamma_A}^{z_b}} \quad (26)$$

Thus, the equilibrium quotient would be equal to the equilibrium constant if the resin phase were ideal. Smith and Woodburn[9] chose to use the equilibrium quotient because it is a quantity that can be determined from experimental binary equilibrium data if the solution-phase activity coefficients are known.

Substitution of eq 4 into eq 26 yields upon rearrangement the equation

$$\ln \lambda_{AB} = \ln K_{AB} - \sum_{k=1}^{M}\omega_k\left[1 - \ln(\sum_{l=1}^{M} y_{ml}\Lambda_{kl}) - \sum_{n=1}^{M}\left(\frac{y_{mn}\Lambda_{nk}}{\sum_{l=1}^{M} y_{ml}\Lambda_{nl}}\right)\right] \quad (27)$$

Table 5. Thermodynamic Equilibrium Constant and Wilson Binary Interaction Parameters for the Mehablia et al. Model[1]

system (A–B)	concentration (mol L^{-1})	K_{AB}^{T}	Λ_{AB}	Λ_{BA}	system (A–B)	concentration (mol L^{-1})	K_{AB}^{T}	Λ_{AB}	Λ_{BA}
Na–H	0.1	2.65	2.75	0.501	Ca–K	0.1	12.4	0.831	1.82
	0.2	2.56	2.44	0.690		0.2	12.7	1.05	1.51
	0.5	2.59	2.68	0.544		0.5	12.9	1.10	1.38
	1.0	2.73	2.12	0.651		1.0	11.6	1.02	1.18
	all	2.61	2.01	0.603		all	12.4	1.14	1.07
K–H	0.1	3.55	1.91	1.64	Mg–K	0.1	7.05	2.74	0.122
	0.2	3.76	1.90	2.05		0.2	6.97	2.42	0.014
	0.5	3.78	1.43	2.03		0.5	6.66	1.95	0.302
	1.0	4.39	1.27	1.72		1.0	7.36	1.82	0.484
	all	3.84	1.09	1.66		all	7.01	2.23	0.677
Ca–H	0.1	97.1	0.980	0.831	Ca–Na	0.1	36.8	5.18	0.378
	0.2	106	1.43	0.791		0.2	36.3	5.24	0.410
	0.5	99.2	1.73	0.715		0.5	33.6	5.25	0.384
	1.0	89.7	1.80	0.734		1.0	39.9	3.98	0.404
	all	98.0	1.42	1.07		all	36.5	4.11	0.422
Mg–H	0.1	79.7	1.27	1.23	Mg–Na	0.1	20.0	0.692	2.21
	0.2	83.5	1.44	1.19		0.2	20.6	0.591	2.26
	0.5	86.3	1.48	1.04		0.5	21.5	0.504	2.02
	1.0	78.3	1.49	0.951		1.0	21.0	0.482	2.79
	all	82.0	1.80	0.744		all	20.8	0.421	2.30
K–Na	0.1	1.26	1.51	0.426	Ca–Mg	0.1	1.96	4.76	0.241
	0.2	1.16	1.81	0.645		0.2	2.00	4.47	0.391
	0.5	1.14	1.06	0.612		0.5	2.03	3.84	0.425
	1.0	1.32	1.75	0.601		1.0	1.63	4.94	0.453
	all	1.22	1.98	0.648		all	1.92	4.27	0.363

Table 6. Relative Residues and Average Absolute Errors for Each of the Equilibrium Systems[a]

system	relative residue *R*	av absolute error AAE	system	relative residue *R*	av absolute error AAE
Na^+–H^+	0.000079	0.00237	Na^+–H^+–Ca^{2+}	0.00271	0.00623
Na^+–K^+	0.000061	0.00122	Na^+–H^+–Mg^{2+}	0.00215	0.00449
K^+–H^+	0.000057	0.00065	Na^+–Ca^{2+}–Mg^{2+}	0.00315	0.00414
H^+–Ca^{2+}	0.000059	0.00014	K^+–H^+–Ca^{2+}	0.00318	0.00747
Na^+–Ca^{2+}	0.000075	0.00052	K^+–H^+–Mg^{2+}	0.00308	0.00672
K^+–Ca^{2+}	0.000088	0.00027	K^+–Ca^{2+}–Mg^{2+}	0.00338	0.00874
Ca^{2+}–Mg^{2+}	0.000167	0.00299	H^+–Ca^{2+}–Mg^{2+}	0.00268	0.00241
H^+–Mg^{2+}	0.000065	0.00072	K^+–Na^+–H^+–Ca^{2+}	0.00271	0.00322
Na^+–Mg^{2+}	0.000050	0.00011	K^+–Na^+–H^+–Mg^{2+}	0.00324	0.00274
K^+–Mg^{2+}	0.000076	0.00048	K^+–Na^+–Ca^{2+}–Mg^{2+}	0.00306	0.00479
K^+–Na^+–H^+	0.00250	0.00258	K^+–H^+–Ca^{2+}–Mg^{2+}	0.00287	0.00471
K^+–Na^+–Ca^{2+}	0.00226	0.00750	Na^+–H^+–Ca^{2+}–Mg^{2+}	0.00298	0.00386
K^+–Na^+–Mg^{2+}	0.00239	0.00871	K^+–Na^+–H^+–Ca^{2+}–Mg^{2+}	0.00841	0.00467

[a] The model was fitted to the binary system data only.

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

Mehablia et al.[1] proposed the use of the Gaines and Thomas[21] approach to first calculate the equilibrium constant. Then, a two-parameter regression is performed to determine the Wilson binary interaction parameters. This has the advantage of decoupling the effect of variations of the equilibrium constant from variations of the Wilson binary interaction parameters. The equilibrium constant is linked to the equilibrium quotient by the equation

$$\ln K_{AB} = (z_B - z_A) + \int_0^1 \ln(\lambda_{AB})\, dy_A \tag{28}$$

Because the equilibrium quotient is readily determined from simple binary batch equilibrium tests, a value for the equilibrium constant may be estimated by integrating the area under a plot of $\ln(\lambda_{AB})$ against the resin equivalent ionic fraction.

Once the equilibrium constant for a binary system is known, eq 26 is used to regress the values for the two binary interaction parameters.

The model of Mehablia et al.[1] requires values for three parameters to be determined for each binary system. The parameters are the equilibrium constant and the two Wilson binary interaction parameters.

The values used for the Pitzer parameters are presented in Tables 2 and 3. Values for θ_{MN} and ψ_{MNX} for systems other than those listed in Table 3 are assumed to be zero. Table 4 presents the parameters required in eq 16 to calculate the stability constants K_S^{MX}.

Analysis of Binary System Data

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

$$R = \frac{\displaystyle\sum_{i=1}^{N}\left[\sum_{j=1}^{M}\left(\frac{\chi_{model} - \chi_{expt}}{\chi_{expt}}\right)_j^2\right]_i}{NM - 1} \tag{29}$$

Here, *M* is the number of the set of equilibrium data, *N* is

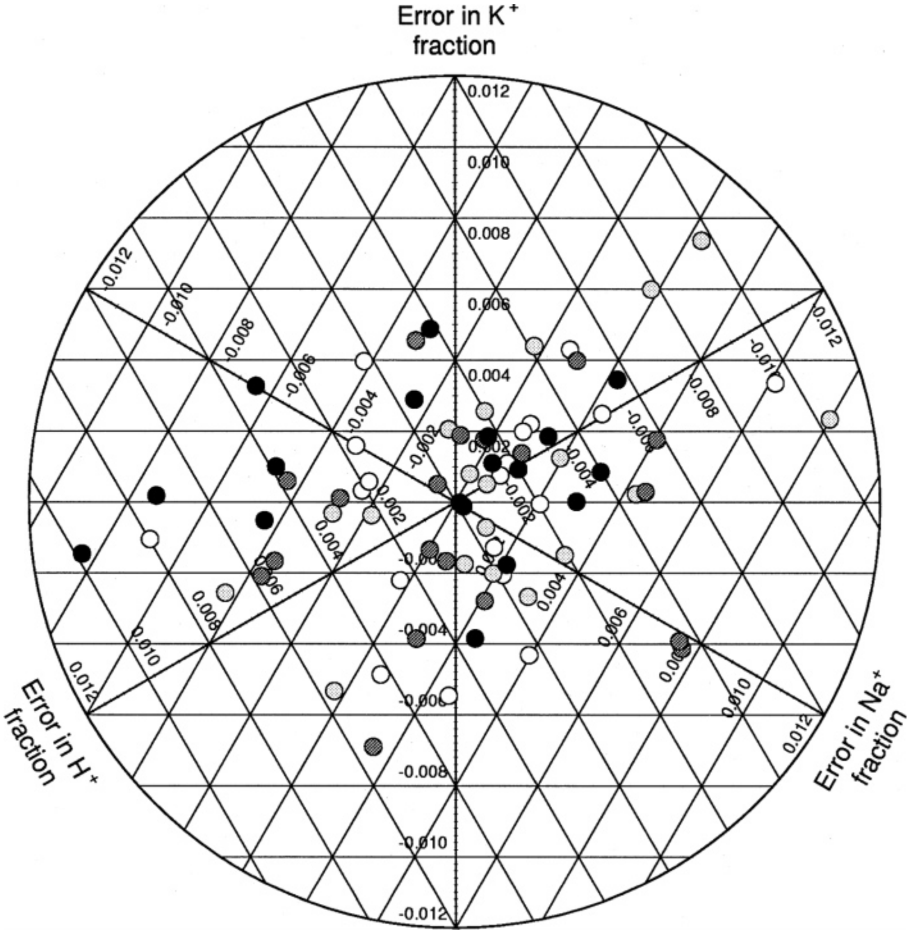

Figure 1. Ternary error diagram for the prediction of the exchanger-phase equilibrium composition for the $K^+-Na^+-H^+$ system at four solution concentrations: ○, 0.10 mol L^{-1}; light-gray ○, 0.20 mol L^{-1}; dark-gray ○, 0.50 mol L^{-1}; and ●, 1.00 mol L^{-1}.

the number of cationic species, and χ is the quantity of interest, either the equivalent ionic fraction in the solution phase or that in the exchanger phase. For the same systems, the model that yields the lowest value for the relative residue R will be the one that agrees most closely with the observed experimental equilibrium data. We also use the average absolute error, AAE:

$$\mathrm{AAE} = \frac{\sum_{i=1}^{N}[\sum_{j=1}^{M}\mathrm{abs}(\chi_{\mathrm{model}} - \chi_{\mathrm{expt}})_j]_i}{NM} \qquad (30)$$

The ion exchange model of Mehablia et al.[1] was fitted to each of the 10 constitutive binary systems. Table 5 presents the values for the three fitted parameters for each of the binary systems. The parameters were separately calculated for each of the four solution concentrations and then were calculated for each entire data set. The values for each binary system show no significant trend with varying solution concentration. This suggests that the model of Mehablia et al. is able to adequately account for the nonidealities that may be present within the solution and exchanger phases. The relative residue and average absolute error values as defined in eqs 29 and 30 for the binary systems are presented in Table 6.

Prediction of Multicomponent Equilibrium Behavior

Using the model parameters determined for the 10 constitutive binary systems as presented in Table 5, the model of Mehablia et al.[1] was used to predict the equilibrium behavior of the 10 ternary and 5 quaternary systems and 1 quinternary system. Table 6 presents the values for the relative residues and absolute average errors for the multicomponent systems. As expected, these values increase with the number of components in the system.

Figures 1 and 2 present the ternary error diagrams for the $K^+-Na^+-H^+$ and $K^+-Ca^{2+}-Mg^{2+}$ ternary systems, respectively. Each point on these diagrams represents the error in the exchange-phase equilibrium composition predicted by the model compared with the actual experimentally determined composition. The better the agreement between the model predictions and the experimental data, the closer the data point will be to the diagram's origin. The data in Figure 1 represents the 76 sets of equilibrium exchanger-phase compositions for the four different solution concentrations ranging from 01.0 to 1.00 N. The diagram allows visual confirmation that the model predicts the exchanger-phase equilibrium compositions equally accurately for all four solution concentrations. Although this is also true for Figure 2, we see that the model more accurately predicts the K^+ equivalent ionic fraction in the exchanger phases than for the other two divalent ions. Table 7 represents the equilibrium data and model predictions for the $K^+-Ca^{2+}-Mg^{2+}$ ternary system at 25 °C.

Because the ternary error diagram is applicable only to ternary systems, the data for the $K^+-Na^+-Ca^{2+}-Mg^{2+}$ and the $K^+-Na^+-H^+-Ca^{2+}-Mg^{2+}$ multicomponent systems are presented in a different form. Figures 3 and 4 present the errors in the exchanger-phase model predictions for these two systems. In Figure 3, each predicted exchanger-

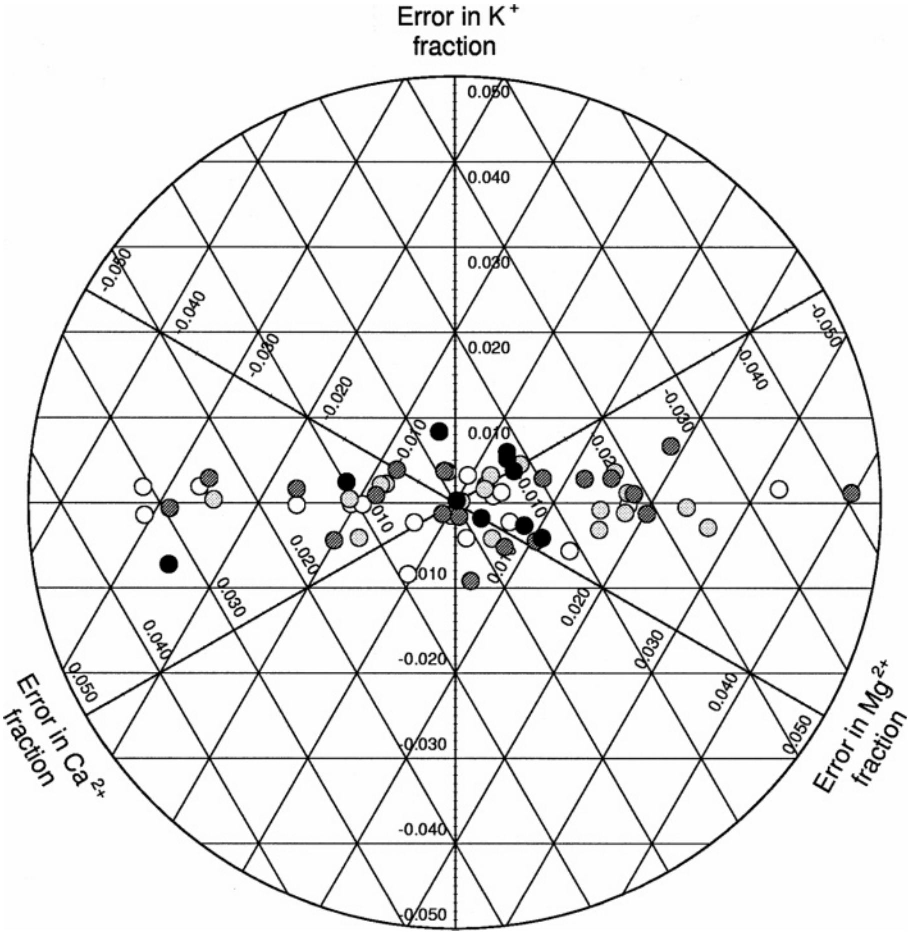

Figure 2. Ternary error diagram for the prediction of the exchanger-phase equilibrium composition for the K$^+$–Ca^{2+}–Mg^{2+} system at four solution concentrations: ○, 0.10 mol L^{-1}; light-gray ○, 0.20 mol L^{-1}; dark-gray ○, 0.50 mol L^{-1}; and ●, 1.00 mol L^{-1}.

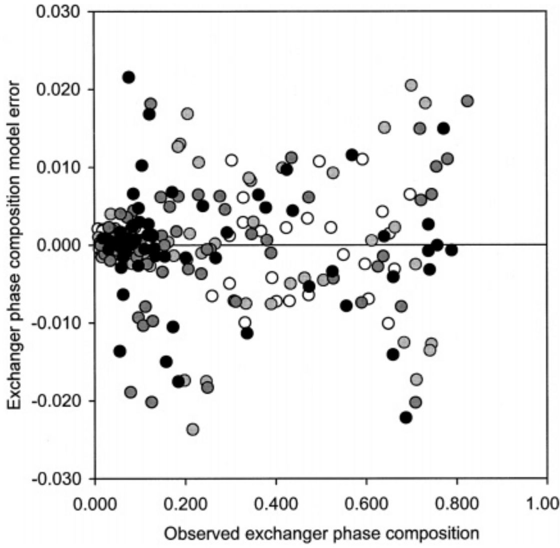

Figure 3. Errors in the predictions for the equilibrium exchanger-phase compositions for the three models for the K$^+$–Na$^+$–Ca^{2+}–Mg^{2+} quaternary system: ○, 0.10 mol L^{-1}; light-gray ○, 0.20 mol L^{-1}; dark-gray ○, 0.50 mol L^{-1}, and ●, 1.00 mol L^{-1}.

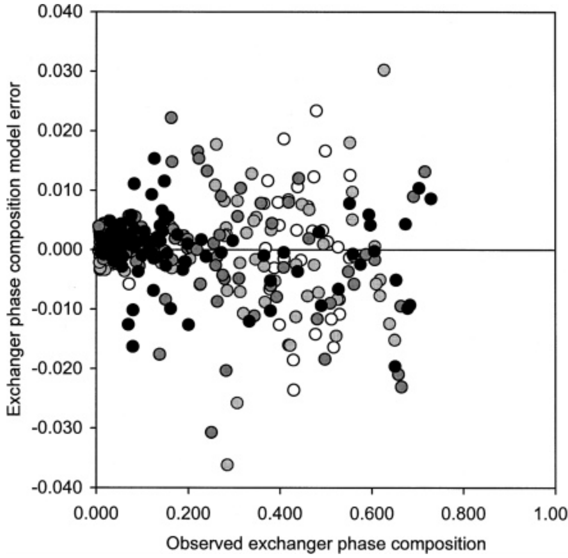

Figure 4. Errors in the predictions for the equilibrium exchanger-phase compositions for the three models for the K$^+$–Na$^+$–H$^+$–Ca^{2+}–Mg^{2+} quinternary system: ○, 0.10 mol L^{-1}; light-gray ○, 0.20 mol L^{-1}; dark-gray ○, 0.50 mol L^{-1}; and ●, 1.00 mol L^{-1}.

phase composition is represented by four points, one for each of the four exchanging ions. Similarly, in Figure 4, each predicted exchanger-phase composition is represented by five points. In both diagrams, the solution concentrations for each point are identified. As for the ternary systems, the model predicts the exchanger-phase compositions equally accurately at all four solution concentrations. Tables 8 and 9 present the equilibrium data and model predictions for the quaternary and quinternary systems, respectively.

Table 7. Observed and Predicted Equilibrium Compositions for the K^+−Ca^{2+}−Mg^{2+} Ternary System at 25 °C[a]

solution-phase concentration mol L^{-1}	experimental equilibrium solution-phase composition			experimental equilibrium exchanger-phase composition			predicted equilibrium exchanger-phase composition		
	x_K	x_{Mg}	x_{Ca}	y_K	y_{Mg}	y_{Ca}	y_K	y_{Mg}	y_{Ca}
0.10	0.0483	0.7915	0.1602	0.0064	0.6250	0.3685	0.0083	0.5924	0.3993
0.10	0.0971	0.7445	0.1585	0.0121	0.6296	0.3584	0.0137	0.6617	0.3246
0.10	0.1454	0.6978	0.1568	0.0192	0.5796	0.4012	0.0200	0.5830	0.3969
0.10	0.1944	0.6506	0.1551	0.0231	0.6003	0.3766	0.0217	0.5695	0.4089
0.10	0.2435	0.6034	0.1531	0.0318	0.5845	0.3837	0.0295	0.5815	0.3890
0.10	0.2919	0.5571	0.1511	0.0336	0.5796	0.3868	0.0373	0.5770	0.3858
0.10	0.3393	0.5119	0.1489	0.0388	0.5715	0.3897	0.0387	0.5610	0.4004
0.10	0.3896	0.4641	0.1463	0.0459	0.5737	0.3804	0.0478	0.5468	0.4054
0.10	0.4375	0.4187	0.1439	0.0543	0.4984	0.4473	0.0541	0.5162	0.4298
0.10	0.4874	0.3718	0.1408	0.0517	0.5192	0.4291	0.0549	0.5189	0.4262
0.10	0.5342	0.3281	0.1377	0.0676	0.4782	0.4542	0.0674	0.4622	0.4704
0.10	0.5809	0.2849	0.1341	0.0645	0.4902	0.4454	0.0623	0.4968	0.4409
0.10	0.6327	0.2379	0.1294	0.0803	0.4306	0.4892	0.0801	0.4213	0.4986
0.10	0.6797	0.1957	0.1246	0.0828	0.4106	0.5066	0.0787	0.4138	0.5075
0.10	0.7263	0.1544	0.1194	0.0922	0.3966	0.5112	0.0934	0.4007	0.5059
0.10	0.7784	0.1101	0.1115	0.0991	0.3558	0.5451	0.0935	0.3703	0.5363
0.10	0.8228	0.0739	0.1033	0.1117	0.2845	0.6039	0.1033	0.2839	0.6128
0.20	0.0487	0.8575	0.0937	0.0100	0.7425	0.2476	0.0121	0.7446	0.2434
0.20	0.0978	0.8090	0.0933	0.0183	0.7344	0.2473	0.0154	0.7616	0.2230
0.20	0.1461	0.7613	0.0926	0.0278	0.6864	0.2858	0.0280	0.6869	0.2851
0.20	0.1950	0.7131	0.0919	0.0355	0.7079	0.2566	0.0350	0.7317	0.2333
0.20	0.2435	0.6654	0.0912	0.0415	0.6821	0.2763	0.0419	0.6574	0.3007
0.20	0.2937	0.6160	0.0903	0.0472	0.6913	0.2616	0.0464	0.7065	0.2472
0.20	0.3429	0.5677	0.0894	0.0610	0.6727	0.2663	0.0568	0.6785	0.2647
0.20	0.3909	0.5208	0.0884	0.0731	0.6528	0.2742	0.0719	0.6707	0.2574
0.20	0.4397	0.4731	0.0872	0.0734	0.6264	0.3002	0.0766	0.6284	0.2950
0.20	0.4890	0.4252	0.0858	0.0780	0.6102	0.3118	0.0765	0.6106	0.3129
0.20	0.5365	0.3790	0.0844	0.0941	0.5870	0.3189	0.0963	0.5788	0.3248
0.20	0.5886	0.3287	0.0827	0.0974	0.5773	0.3253	0.0995	0.5687	0.3318
0.20	0.6373	0.2819	0.0808	0.1054	0.5297	0.3649	0.1023	0.5459	0.3518
0.20	0.6852	0.2362	0.0786	0.1100	0.5161	0.3738	0.1136	0.5306	0.3558
0.20	0.7334	0.1904	0.0762	0.1336	0.4990	0.3674	0.1348	0.5160	0.3493
0.20	0.7841	0.1430	0.0729	0.1456	0.4435	0.4109	0.1501	0.4478	0.4020
0.20	0.8333	0.0982	0.0685	0.1657	0.3851	0.4491	0.1616	0.3774	0.4610
0.20	0.8790	0.0579	0.0631	0.1937	0.3096	0.4967	0.1942	0.2986	0.5072
0.20	0.9210	0.0236	0.0554	0.2189	0.2406	0.5405	0.2205	0.2428	0.5367
0.50	0.0493	0.9075	0.0432	0.0156	0.8532	0.1312	0.0168	0.8929	0.0903
0.50	0.0984	0.8587	0.0430	0.0296	0.8384	0.1321	0.0334	0.8354	0.1313
0.50	0.1477	0.8095	0.0428	0.0461	0.8119	0.1420	0.0490	0.8264	0.1246
0.50	0.1977	0.7596	0.0427	0.0548	0.8034	0.1419	0.0504	0.7933	0.1563
0.50	0.2459	0.7116	0.0425	0.0682	0.7987	0.1331	0.0691	0.7902	0.1407
0.50	0.2963	0.6614	0.0423	0.0922	0.7387	0.1691	0.0916	0.7100	0.1984
0.50	0.3461	0.6119	0.0420	0.0941	0.7380	0.1679	0.0970	0.7454	0.1576
0.50	0.3954	0.5628	0.0418	0.1046	0.7451	0.1503	0.1075	0.7187	0.1738
0.50	0.4439	0.5145	0.0416	0.1230	0.6916	0.1854	0.1240	0.7093	0.1667
0.50	0.4924	0.4664	0.0412	0.1278	0.7086	0.1636	0.1317	0.7007	0.1676
0.50	0.5416	0.4176	0.0409	0.1468	0.6791	0.1742	0.1535	0.6977	0.1488
0.50	0.5922	0.3674	0.0404	0.1696	0.6272	0.2033	0.1683	0.6265	0.2052
0.50	0.6408	0.3192	0.0399	0.1677	0.6317	0.2006	0.1694	0.6148	0.2159
0.50	0.6874	0.2732	0.0394	0.1760	0.6104	0.2137	0.1788	0.6222	0.1990
0.50	0.7392	0.2221	0.0386	0.2063	0.5776	0.2161	0.2047	0.5788	0.2165
0.50	0.7863	0.1760	0.0377	0.2188	0.5320	0.2491	0.2175	0.5522	0.2303
0.50	0.8386	0.1249	0.0364	0.2756	0.4456	0.2788	0.2664	0.4517	0.2818
0.50	0.8857	0.0794	0.0348	0.2806	0.4254	0.2940	0.2754	0.4330	0.2916
0.50	0.9318	0.0360	0.0323	0.3527	0.3007	0.3467	0.3482	0.3111	0.3407
1.00	0.0490	0.9084	0.0426	0.0264	0.8182	0.1553	0.0267	0.8182	0.1551
1.00	0.4430	0.5154	0.0416	0.1553	0.6908	0.1539	0.1526	0.6991	0.1482
1.00	0.4914	0.4672	0.0414	0.1950	0.6331	0.1718	0.2002	0.6358	0.1640
1.00	0.5411	0.4178	0.0411	0.1934	0.6339	0.1726	0.1971	0.6380	0.1648
1.00	0.5899	0.3693	0.0408	0.2168	0.5942	0.1890	0.2096	0.5687	0.2217
1.00	0.6370	0.3226	0.0404	0.2268	0.5704	0.2027	0.2293	0.5581	0.2126
1.00	0.6848	0.2752	0.0400	0.2537	0.5491	0.1972	0.2596	0.5514	0.1890
1.00	0.7377	0.2229	0.0394	0.2525	0.5318	0.2157	0.2484	0.5427	0.2090
1.00	0.8347	0.1275	0.0378	0.3332	0.4213	0.2455	0.3314	0.4248	0.2437
1.00	0.8788	0.0845	0.0367	0.3845	0.3514	0.2641	0.3929	0.3456	0.2615

[a] Compositions expressed as equivalent ionic fractions.

Table 8. Observed and Predicted Equilibrium Compositions for the K^+–Na^+–Ca^{2+}–Mg^{2+} Quaternary System at 25 °C[a]

solution-phase concentration mol L^{-1}	experimental equilibrium solution-phase composition				experimental equilibrium exchanger-phase composition				predicted equilibrium exchanger-phase composition			
	x_K	x_{Na}	x_{Ca}	x_{Mg}	y_K	y_{Na}	y_{Ca}	y_{Mg}	y_K	y_{Na}	y_{Ca}	y_{Mg}
0.10	0.0485	0.4674	0.3029	0.1811	0.0055	0.0331	0.6628	0.2986	0.0076	0.0329	0.6597	0.2998
0.10	0.0972	0.4493	0.2749	0.1786	0.0113	0.0319	0.6975	0.2592	0.0109	0.0324	0.7040	0.2527
0.10	0.1456	0.4174	0.2601	0.1769	0.0171	0.0331	0.6515	0.2983	0.0191	0.0345	0.6530	0.2934
0.10	0.1944	0.3870	0.2437	0.1749	0.0212	0.0265	0.6488	0.3035	0.0199	0.0270	0.6387	0.3144
0.10	0.2426	0.3697	0.2162	0.1715	0.0290	0.0265	0.6365	0.3080	0.0313	0.0270	0.6408	0.3009
0.10	0.2915	0.3426	0.1971	0.1688	0.0347	0.0308	0.6054	0.3290	0.0348	0.0315	0.5985	0.3351
0.10	0.3385	0.3180	0.1773	0.1662	0.0461	0.0293	0.5925	0.3321	0.0445	0.0298	0.6035	0.3221
0.10	0.3880	0.2936	0.1560	0.1624	0.0501	0.0242	0.5974	0.3284	0.0489	0.0248	0.5949	0.3313
0.10	0.4362	0.2741	0.1319	0.1579	0.0576	0.0250	0.5496	0.3679	0.0558	0.0261	0.5484	0.3697
0.10	0.4840	0.2476	0.1147	0.1537	0.0647	0.0209	0.5223	0.3921	0.0663	0.0212	0.5246	0.3879
0.10	0.5321	0.2214	0.0975	0.1490	0.0780	0.0232	0.4970	0.4018	0.0757	0.0220	0.5078	0.3946
0.10	0.5790	0.1971	0.0801	0.1438	0.0800	0.0192	0.4705	0.4303	0.0823	0.0206	0.4739	0.4231
0.10	0.6254	0.1699	0.0662	0.1385	0.0863	0.0174	0.4239	0.4724	0.0886	0.0193	0.4262	0.4660
0.20	0.0492	0.4664	0.3818	0.1026	0.0080	0.0586	0.7442	0.1892	0.0091	0.0573	0.7315	0.2022
0.20	0.0980	0.4425	0.3578	0.1018	0.0156	0.0544	0.7320	0.1980	0.0157	0.0534	0.7502	0.1806
0.20	0.1480	0.4136	0.3375	0.1009	0.0223	0.0523	0.7406	0.1848	0.0221	0.0534	0.7270	0.1975
0.20	0.1968	0.3870	0.3162	0.1000	0.0294	0.0504	0.7097	0.2105	0.0301	0.0506	0.7072	0.2120
0.20	0.2447	0.3669	0.2894	0.0990	0.0380	0.0452	0.7010	0.2159	0.0389	0.0474	0.7215	0.1922
0.20	0.2942	0.3457	0.2623	0.0978	0.0406	0.0426	0.7106	0.2062	0.0401	0.0435	0.6933	0.2231
0.20	0.3439	0.3153	0.2441	0.0968	0.0482	0.0381	0.6834	0.2304	0.0479	0.0401	0.6709	0.2410
0.20	0.3916	0.2980	0.2151	0.0953	0.0592	0.0408	0.6636	0.2364	0.0590	0.0397	0.6659	0.2354
0.20	0.4404	0.2707	0.1948	0.0940	0.0760	0.0361	0.6417	0.2462	0.0744	0.0401	0.6568	0.2287
0.20	0.4903	0.2447	0.1726	0.0924	0.0861	0.0351	0.6123	0.2665	0.0837	0.0367	0.6129	0.2667
0.20	0.6338	0.1713	0.1082	0.0866	0.1098	0.0285	0.5272	0.3345	0.1088	0.0277	0.5365	0.3270
0.20	0.6828	0.1479	0.0856	0.0836	0.1253	0.0280	0.5049	0.3418	0.1226	0.0266	0.5004	0.3504
0.20	0.7316	0.1226	0.0654	0.0804	0.1620	0.0233	0.4635	0.3512	0.1624	0.0242	0.4593	0.3542
0.20	0.7783	0.0965	0.0486	0.0766	0.1764	0.0177	0.4158	0.3901	0.1751	0.0167	0.4257	0.3825
0.20	0.8259	0.0727	0.0303	0.0711	0.2057	0.0162	0.3455	0.4326	0.2039	0.0147	0.3538	0.4277
0.50	0.0495	0.4663	0.4386	0.0455	0.0108	0.0848	0.8255	0.0789	0.0111	0.0849	0.8439	0.0600
0.50	0.0986	0.4404	0.4158	0.0453	0.0230	0.1001	0.7806	0.0964	0.0219	0.0994	0.7916	0.0871
0.50	0.1485	0.4241	0.3825	0.0449	0.0352	0.1017	0.7560	0.1070	0.0349	0.1024	0.7661	0.0967
0.50	0.2478	0.3669	0.3410	0.0444	0.0545	0.0883	0.7454	0.1118	0.0551	0.0890	0.7519	0.1039
0.50	0.2971	0.3484	0.3105	0.0440	0.0642	0.0862	0.7218	0.1278	0.0637	0.0907	0.7276	0.1180
0.50	0.3461	0.3198	0.2903	0.0438	0.0760	0.0794	0.7195	0.1252	0.0797	0.0809	0.7344	0.1050
0.50	0.3948	0.2989	0.2629	0.0434	0.0945	0.0720	0.7087	0.1248	0.0930	0.0756	0.6885	0.1430
0.50	0.4957	0.2471	0.2145	0.0426	0.1183	0.0575	0.6777	0.1466	0.1159	0.0615	0.6698	0.1528
0.50	0.5414	0.2219	0.1945	0.0423	0.1471	0.0606	0.6379	0.1543	0.1483	0.0609	0.6365	0.1543
0.50	0.5926	0.1987	0.1670	0.0417	0.1530	0.0549	0.6262	0.1659	0.1496	0.0562	0.6234	0.1709
0.50	0.6417	0.1745	0.1427	0.0411	0.1787	0.0508	0.5898	0.1807	0.1850	0.0501	0.5824	0.1825
0.50	0.7425	0.1197	0.0981	0.0397	0.2230	0.0427	0.5272	0.2070	0.2295	0.0436	0.5229	0.2039
0.50	0.7885	0.0980	0.0747	0.0387	0.2567	0.0345	0.4731	0.2357	0.2562	0.0325	0.4793	0.2320
0.50	0.8355	0.0742	0.0529	0.0374	0.2838	0.0316	0.4358	0.2489	0.2884	0.0339	0.4470	0.2306
0.50	0.8826	0.0492	0.0325	0.0358	0.3190	0.0223	0.3812	0.2774	0.3117	0.0227	0.3819	0.2837
0.50	0.9282	0.0245	0.0141	0.0332	0.3909	0.0136	0.2485	0.3471	0.3899	0.0136	0.2480	0.3485
1.00	0.0995	0.4535	0.4232	0.0238	0.0287	0.1318	0.7894	0.0502	0.0294	0.1314	0.7887	0.0504
1.00	0.1493	0.4251	0.4019	0.0237	0.0381	0.1346	0.7721	0.0552	0.0382	0.1332	0.7870	0.0416
1.00	0.1988	0.3989	0.3787	0.0236	0.0552	0.1286	0.7575	0.0587	0.0569	0.1298	0.7575	0.0558
1.00	0.2476	0.3725	0.3564	0.0235	0.0719	0.1271	0.7381	0.0629	0.0728	0.1284	0.7373	0.0614
1.00	0.2981	0.3487	0.3298	0.0234	0.0821	0.1171	0.7379	0.0629	0.0845	0.1184	0.7405	0.0566
1.00	0.3478	0.3215	0.3074	0.0233	0.0990	0.0971	0.7408	0.0631	0.0964	0.1019	0.7376	0.0642
1.00	0.3966	0.2985	0.2817	0.0232	0.1258	0.1103	0.6873	0.0766	0.1269	0.1098	0.6651	0.0982
1.00	0.4965	0.2449	0.2356	0.0230	0.1562	0.0996	0.6603	0.0839	0.1548	0.1026	0.6562	0.0865
1.00	0.5475	0.2239	0.2058	0.0228	0.1647	0.0904	0.6589	0.0859	0.1715	0.0911	0.6448	0.0925
1.00	0.5967	0.1980	0.1826	0.0227	0.2030	0.0729	0.6400	0.0841	0.2014	0.0732	0.6411	0.0843
1.00	0.6958	0.1478	0.1341	0.0223	0.2691	0.0701	0.5558	0.1051	0.2675	0.0692	0.5480	0.1154
1.00	0.7440	0.1216	0.1123	0.0221	0.2913	0.0643	0.5254	0.1190	0.2929	0.0633	0.5220	0.1217
1.00	0.7924	0.0983	0.0874	0.0218	0.3481	0.0565	0.4736	0.1218	0.3368	0.0563	0.4683	0.1386
1.00	0.8424	0.0723	0.0639	0.0215	0.3738	0.0434	0.4254	0.1574	0.3786	0.0438	0.4351	0.1424
1.00	0.8925	0.0475	0.0391	0.0209	0.4339	0.0308	0.3629	0.1725	0.4383	0.0303	0.3694	0.1620
1.00	0.9382	0.0234	0.0182	0.0202	0.5581	0.0184	0.2394	0.1841	0.5697	0.0193	0.2445	0.1666

[a] Compositions expressed as equivalent ionic fractions.

Table 9. Observed and Predicted Equilibrium Compositions for the K^+−Na^+−H^+−Ca^{2+}−Mg^{2+} Quinternary System at 25 °C[a]

solution-phase concentration mol L^{-1}	experimental equilibrium solutio-phase composition					experimental equilibrium exchanger-phase composition					predicted equilibrium exchanger-phase composition				
	x_K	x_{Na}	x_H	x_{Ca}	x_{Mg}	y_K	y_{Na}	y_H	y_{Ca}	y_{Mg}	y_K	y_{Na}	y_H	y_{Ca}	y_{Mg}
0.10	0.0287	0.3184	0.3192	0.1802	0.1536	0.0054	0.0318	0.0124	0.5521	0.3983	0.0052	0.0304	0.0141	0.5647	0.3857
0.10	0.0860	0.2981	0.2946	0.1696	0.1517	0.0157	0.0343	0.0117	0.5507	0.3876	0.0201	0.0342	0.0118	0.5493	0.3846
0.10	0.1148	0.2923	0.2902	0.1536	0.1491	0.0196	0.0336	0.0124	0.5260	0.4084	0.0218	0.0311	0.0137	0.5265	0.4069
0.10	0.1433	0.2720	0.2784	0.1567	0.1496	0.0266	0.0346	0.0114	0.5294	0.3980	0.0297	0.0375	0.0121	0.5186	0.4021
0.10	0.1719	0.2680	0.2699	0.1431	0.1470	0.0302	0.0340	0.0116	0.5285	0.3957	0.0306	0.0318	0.0137	0.5202	0.4037
0.10	0.2013	0.2599	0.2602	0.1336	0.1451	0.0331	0.0321	0.0104	0.5161	0.4083	0.0314	0.0304	0.0115	0.4997	0.4270
0.10	0.2301	0.2466	0.2535	0.1264	0.1434	0.0406	0.0326	0.0116	0.4702	0.4451	0.0414	0.0309	0.0110	0.4734	0.4434
0.10	0.2589	0.2345	0.2455	0.1193	0.1418	0.0467	0.0265	0.0099	0.4982	0.4187	0.0458	0.0275	0.0091	0.5149	0.4027
0.10	0.2874	0.2220	0.2323	0.1172	0.1412	0.0498	0.0251	0.0104	0.4766	0.4381	0.0507	0.0265	0.0116	0.4624	0.4487
0.10	0.3159	0.2142	0.2211	0.1097	0.1391	0.0544	0.0274	0.0099	0.4790	0.4293	0.0562	0.0286	0.0071	0.5024	0.4057
0.10	0.3450	0.2060	0.2098	0.1020	0.1373	0.0607	0.0279	0.0093	0.4735	0.4286	0.0630	0.0311	0.0100	0.4858	0.4101
0.10	0.4035	0.1887	0.1885	0.0868	0.1326	0.0707	0.0250	0.0081	0.4359	0.4604	0.0649	0.0234	0.0047	0.4392	0.4677
0.10	0.4584	0.1648	0.1710	0.0763	0.1294	0.0861	0.0210	0.0083	0.3734	0.5112	0.0891	0.0192	0.0071	0.3850	0.4996
0.10	0.4872	0.1572	0.1623	0.0672	0.1261	0.0982	0.0240	0.0077	0.3778	0.4924	0.0982	0.0246	0.0103	0.3712	0.4957
0.10	0.5160	0.1470	0.1486	0.0640	0.1245	0.0972	0.0234	0.0081	0.3684	0.5028	0.0961	0.0227	0.0083	0.3687	0.5042
0.20	0.0291	0.3161	0.3157	0.2468	0.0923	0.0078	0.0609	0.0204	0.6497	0.2611	0.0082	0.0573	0.0211	0.6345	0.2789
0.20	0.0580	0.3085	0.3070	0.2349	0.0916	0.0137	0.0546	0.0196	0.6269	0.2852	0.0142	0.0558	0.0238	0.6571	0.2491
0.20	0.0876	0.2996	0.2999	0.2221	0.0908	0.0222	0.0573	0.0201	0.6178	0.2826	0.0215	0.0597	0.0198	0.6128	0.2863
0.20	0.1165	0.2866	0.2946	0.2122	0.0901	0.0280	0.0561	0.0185	0.6385	0.2589	0.0305	0.0585	0.0151	0.6261	0.2698
0.20	0.1751	0.2691	0.2679	0.1988	0.0891	0.0410	0.0461	0.0165	0.6177	0.2787	0.0421	0.0437	0.0173	0.6100	0.2869
0.20	0.2038	0.2592	0.2601	0.1885	0.0884	0.0475	0.0467	0.0163	0.6063	0.2832	0.0481	0.0449	0.0143	0.6069	0.2858
0.20	0.2337	0.2461	0.2506	0.1818	0.0878	0.0494	0.0463	0.0158	0.6093	0.2793	0.0484	0.0483	0.0181	0.6036	0.2817
0.20	0.2623	0.2340	0.2445	0.1721	0.0871	0.0595	0.0467	0.0159	0.5575	0.3204	0.0587	0.0478	0.0165	0.5673	0.3097
0.20	0.2907	0.2290	0.2299	0.1639	0.0864	0.0677	0.0441	0.0148	0.5605	0.3127	0.0694	0.0449	0.0159	0.5594	0.3105
0.20	0.3197	0.2213	0.2257	0.1481	0.0851	0.0729	0.0415	0.0150	0.5574	0.3131	0.0745	0.0421	0.0148	0.5625	0.3061
0.20	0.3503	0.2063	0.2067	0.1513	0.0853	0.0827	0.0455	0.0135	0.5517	0.3067	0.0849	0.0492	0.0152	0.5697	0.2810
0.20	0.3787	0.1967	0.2043	0.1363	0.0839	0.0869	0.0397	0.0129	0.5217	0.3387	0.0855	0.0431	0.0126	0.5072	0.3515
0.20	0.4090	0.1896	0.1896	0.1286	0.0832	0.0963	0.0405	0.0117	0.5242	0.3274	0.0973	0.0438	0.0128	0.5159	0.3303
0.20	0.4663	0.1713	0.1707	0.1103	0.0814	0.1118	0.0350	0.0122	0.4938	0.3472	0.1137	0.0346	0.0114	0.4948	0.3456
0.20	0.4944	0.1593	0.1634	0.1025	0.0803	0.1261	0.0360	0.0117	0.4830	0.3432	0.1273	0.0372	0.0117	0.4758	0.3481
0.20	0.5259	0.1484	0.1512	0.0950	0.0794	0.1190	0.0317	0.0100	0.4738	0.3655	0.1185	0.0358	0.0118	0.4712	0.3627
0.20	0.5507	0.1390	0.1466	0.0856	0.0781	0.1410	0.0329	0.0115	0.4474	0.3671	0.1387	0.0341	0.0137	0.4551	0.3583
0.20	0.6097	0.1196	0.1240	0.0708	0.0758	0.1537	0.0296	0.0099	0.4181	0.3887	0.1515	0.0305	0.0080	0.4266	0.3835
0.20	0.6403	0.1108	0.1130	0.0618	0.0741	0.1610	0.0279	0.0090	0.3806	0.4215	0.1649	0.0328	0.0129	0.3840	0.4054
0.20	0.6689	0.1013	0.1032	0.0540	0.0725	0.1635	0.0286	0.0085	0.3648	0.4346	0.1604	0.0295	0.0054	0.3726	0.4322
0.20	0.6962	0.0906	0.0922	0.0494	0.0716	0.1843	0.0252	0.0081	0.3483	0.4340	0.1860	0.0281	0.0094	0.3538	0.4227
0.20	0.7231	0.0811	0.0832	0.0427	0.0700	0.2032	0.0229	0.0071	0.3074	0.4594	0.2017	0.0261	0.0049	0.3156	0.4516
0.20	0.7829	0.0602	0.0620	0.0292	0.0658	0.2254	0.0202	0.0065	0.2849	0.4630	0.2196	0.0229	0.0097	0.2781	0.4698
0.50	0.0295	0.3142	0.3227	0.2906	0.0430	0.0101	0.1040	0.0329	0.7160	0.1370	0.0129	0.1042	0.0342	0.7292	0.1194
0.50	0.0884	0.3018	0.2996	0.2677	0.0426	0.0320	0.1068	0.0340	0.6647	0.1626	0.0320	0.1085	0.0330	0.6417	0.1848
0.50	0.1180	0.2866	0.2897	0.2633	0.0424	0.0346	0.0930	0.0313	0.6910	0.1501	0.0380	0.0903	0.0300	0.7000	0.1417
0.50	0.1476	0.2802	0.2817	0.2484	0.0421	0.0480	0.0977	0.0322	0.6581	0.1641	0.0506	0.1015	0.0318	0.6371	0.1789
0.50	0.1767	0.2666	0.2721	0.2426	0.0420	0.0537	0.0862	0.0302	0.6634	0.1665	0.0581	0.0842	0.0338	0.6539	0.1699
0.50	0.2649	0.2455	0.2455	0.2029	0.0412	0.0871	0.0842	0.0289	0.6064	0.1934	0.0857	0.0898	0.0284	0.6047	0.1914
0.50	0.4123	0.1905	0.1942	0.1627	0.0402	0.1243	0.0732	0.0242	0.5867	0.1916	0.1240	0.0776	0.0229	0.5860	0.1896
0.50	0.4713	0.1670	0.1717	0.1501	0.0398	0.1490	0.0704	0.0217	0.5607	0.1981	0.1488	0.0761	0.0218	0.5549	0.1983
0.50	0.5015	0.1592	0.1633	0.1364	0.0395	0.1645	0.0618	0.0196	0.5483	0.2058	0.1628	0.0651	0.0213	0.5446	0.2062
0.50	0.5286	0.1515	0.1524	0.1282	0.0393	0.1896	0.0625	0.0204	0.5090	0.2185	0.1920	0.0647	0.0248	0.5000	0.2185
0.50	0.5592	0.1375	0.1450	0.1194	0.0390	0.1984	0.0638	0.0201	0.4972	0.2205	0.2002	0.0632	0.0207	0.4788	0.2371
0.50	0.6190	0.1201	0.1218	0.1008	0.0383	0.2263	0.0534	0.0169	0.4803	0.2230	0.2205	0.0558	0.0166	0.4687	0.2384
0.50	0.6470	0.1102	0.1123	0.0925	0.0380	0.2408	0.0528	0.0158	0.4405	0.2502	0.2541	0.0564	0.0175	0.4525	0.2195
0.50	0.6773	0.0996	0.1041	0.0814	0.0375	0.2555	0.0479	0.0150	0.4185	0.2631	0.2566	0.0490	0.0134	0.4265	0.2544
0.50	0.7065	0.0893	0.0935	0.0735	0.0372	0.2687	0.0444	0.0161	0.4076	0.2632	0.2712	0.0468	0.0153	0.4046	0.2621
0.50	0.7363	0.0821	0.0834	0.0616	0.0366	0.2792	0.0431	0.0135	0.3926	0.2716	0.2743	0.0459	0.0145	0.3847	0.2806
0.50	0.7636	0.0711	0.0729	0.0561	0.0363	0.3080	0.0403	0.0126	0.3796	0.2596	0.3137	0.0419	0.0139	0.3736	0.2570
0.50	0.7921	0.0609	0.0635	0.0478	0.0358	0.3143	0.0327	0.0115	0.3589	0.2825	0.3247	0.0340	0.0123	0.3667	0.2622
0.50	0.8527	0.0420	0.0410	0.0300	0.0343	0.3823	0.0242	0.0078	0.2753	0.3105	0.3868	0.0259	0.0107	0.2710	0.3057
0.50	0.9053	0.0233	0.0240	0.0148	0.0326	0.4624	0.0175	0.0056	0.1705	0.3440	0.4643	0.0208	0.0095	0.1724	0.3329
1.00	0.0298	0.3206	0.3176	0.3088	0.0232	0.0127	0.1385	0.0508	0.7290	0.0690	0.0137	0.1399	0.0523	0.7376	0.0564
1.00	0.0596	0.3126	0.3062	0.2984	0.0232	0.0272	0.1384	0.0527	0.7029	0.0789	0.0277	0.1425	0.0539	0.7133	0.0626
1.00	0.0889	0.3023	0.3040	0.2817	0.0231	0.0358	0.1485	0.0552	0.6781	0.0824	0.0343	0.1536	0.0581	0.6683	0.0858
1.00	0.1184	0.2940	0.2964	0.2682	0.0230	0.0487	0.1428	0.0557	0.6735	0.0793	0.0508	0.1494	0.0528	0.6779	0.0691
1.00	0.1483	0.2832	0.2842	0.2615	0.0229	0.0574	0.1318	0.0517	0.6833	0.0758	0.0563	0.1339	0.0542	0.6740	0.0816
1.00	0.1779	0.2694	0.2749	0.2549	0.0229	0.0720	0.1433	0.0521	0.6505	0.0821	0.0770	0.1464	0.0524	0.6309	0.0932
1.00	0.2081	0.2604	0.2628	0.2458	0.0228	0.0810	0.1330	0.0500	0.6531	0.0829	0.0817	0.1318	0.0542	0.6480	0.0843
1.00	0.2968	0.2351	0.2296	0.2159	0.0226	0.1208	0.1249	0.0446	0.6056	0.1042	0.1202	0.1234	0.0436	0.6054	0.1073
1.00	0.3562	0.2081	0.2118	0.2015	0.0224	0.1508	0.1141	0.0403	0.5964	0.0984	0.1481	0.1145	0.0393	0.6006	0.0975
1.00	0.4139	0.1882	0.1966	0.1791	0.0223	0.1936	0.1037	0.0399	0.5580	0.1048	0.1915	0.1067	0.0379	0.5573	0.1066
1.00	0.5029	0.1610	0.1595	0.1545	0.0221	0.2283	0.0904	0.0345	0.5266	0.1202	0.2300	0.0867	0.0338	0.5200	0.1295
1.00	0.5625	0.1411	0.1464	0.1281	0.0219	0.2719	0.0883	0.0317	0.4843	0.1239	0.2714	0.0895	0.0346	0.4873	0.1171
1.00	0.6492	0.1125	0.1106	0.1060	0.0216	0.3329	0.0750	0.0283	0.4379	0.1258	0.3209	0.0758	0.0280	0.4342	0.1411
1.00	0.7119	0.0937	0.0941	0.0790	0.0213	0.3791	0.0699	0.0237	0.3795	0.1478	0.3688	0.0716	0.0259	0.3743	0.1594
1.00	0.7685	0.0719	0.0723	0.0661	0.0211	0.4079	0.0548	0.0188	0.3650	0.1535	0.4075	0.0565	0.0191	0.3640	0.1529
1.00	0.8282	0.0523	0.0519	0.0467	0.0208	0.4895	0.0415	0.0163	0.2970	0.1556	0.4801	0.0446	0.0156	0.2985	0.1611
1.00	0.8586	0.0413	0.0431	0.0364	0.0206	0.5511	0.0352	0.0144	0.2385	0.1608	0.5589	0.0375	0.0154	0.2374	0.1509
1.00	0.8896	0.0310	0.0320	0.0270	0.0204	0.5747	0.0294	0.0103	0.1980	0.1876	0.5723	0.0343	0.0102	0.1990	0.1842
1.00	0.9154	0.0224	0.0230	0.0190	0.0202	0.5934	0.0223	0.0082	0.1758	0.2003	0.5994	0.0242	0.0104	0.1784	0.1877

[a] Compositions expressed as equivalent ionic fractions.

Concluding Remarks

An extensive set of equilibrium data is presented for the exchange of H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} ions on a commercial resin. This data set will allow the rigorous testing of ion exchange equilibrium behavior predictions models. To illustrate this point, the multicomponent ion exchange equilibrium model proposed by Mehablia et al.[1] has been extensively tested using the data set. The model is able to reliably predict the equilibrium behavior of systems of up to five components using parameters determined from the constitutive binary systems.

Supporting Information Available:

Equilibrium data for all binary, ternary, quaternary, and quinternary systems involving H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} ions. All composition data is reported as equivalent ionic fractions. This material is available free of charge via the Internet at http://pubs.acs.org.

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