INTERNALLY CONSISTENT REPRESENTATION OF

BINARY ION EXCHANGE EQUILIBRIA

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ABSTRACT

A model has been developed to obtain the thermodynamic parameters, equilibrium constant and solid phase activity coefficients, that describe binary ion exchange reactions. Based on the thermodynamic framework for adsorption exchange reactions presented in Gaines & Thomas (1953) we present a modified form of the Wilson’s activity coefficient for the adsorbed phase that takes into account the stoichiometry of the exchange reaction. The solution model’s parameters are regressed with a new data reduction technique, based on the use of the Vanselow selectivity coefficient taken at various points on the isotherm equilibrium surface. For the estimation of the selectivity coefficient the Bromley-Zemaitis model is used in calculating the activity coefficients in the electrolyte phase. The relationship between the selectivity and the equilibrium constant gives the value of the latter after substitution of the activity coefficients of the solid phase species. The data reduction of several binary pairs has shown to abide by the triangular rule consistency test. The aqueous speciation of the systems tested has been taken into account, to satisfactorily predict their uptake graphs.
Introduction

Ion exchange reactions are important at the water-mineral interface in natural systems where they implicitly regulate the fate of the pollutants to the environment (Dzombak and Hudson, 1995), as well as in the chemical process industries, as for example in the separation of aminoacids (Jones and Carta 1993, Melis et al. 1996) in the food and pharmaceutical industries. Applications of ion exchange have also shown in reverse-micellar phases, where the organic solvents are immiscible with water (Ashrafizadeh et al., 1993).

Modeling in ion exchange systems calls for an efficient and practical methodology of data reduction of the uptake graphs of binary systems. These graphs report the equivalent ionic fraction of the preferentially adsorbed species versus its equivalent fraction in the liquid phase, given at a specific ionic strength and temperature and at equilibrium conditions. As Gaines and Thomas (1953) showed this experimental information along with the exchange capacity of the solid surface is adequate to give the thermodynamic parameters of the system for exchange reactions on constant charge surfaces.

A significant aspect of the work of Gaines and Thomas (1953) is the ability it gives for an independent estimation of the equilibrium constant that describes the exchange reaction from the activity coefficients in the adsorbed phase. A particular model used extensively for describing the activity coefficients in the adsorbed phase is the Wilson solution model (1964) which was introduced in the ion exchange field by Smith and Woodburn (1978). Nonetheless, in the approach of Smith and Woodburn (1978) the
solution model parameters are estimated simultaneously with the equilibrium constant from data reduction of the selectivity coefficient. The same approach to parameter estimation has been used thereafter by other authors, as by Shallcross et al. (1988), and by Pabalan (1994). A somewhat different technique has been used by Perona (1993) to reduce experimental data given in a Langmuir type of an isotherm plot.

However, a particular problem of the simultaneous fitting of the solution parameters and the equilibrium constant, is the high degree of correlation of the two sets of parameters as Mehablia et al. (1994) explained. These authors, followed the approach of decoupling the two sets of parameters shown in Gaines and Thomas (1953) and they estimated the equilibrium constant independent of the solution model parameters. The authors showed that the values of the parameters remain fairly constant with solution normality for several 1-1, and 1-2 electrolyte systems. A second point shown in the work of Mehablia et al. (1994), is the importance of the aqueous phase reactions, which result in the unavailability of ions for exchange. This is a very important issue in ion exchange, since the value of the equilibrium constant derived is driven by the aqueous speciation. In our work we use the OLI System’s software package (OLI Systems, 1998) which provides a database with a detailed speciation in the aqueous phase. The particular software provides a framework for calculating the liquid phase activities based on an extended form of the Bromley model (Zemaitis et al. 1986, Anderko and Shuler 1997).

In this work we present a modified Wilson model that accounts for the stoichiometry of the exchange reaction, in a more convenient approach of introducing a solid phase solution model in the expressions for the chemical potential used by Gaines
and Thomas (1953). By following their approach we also introduce a somewhat different data reduction technique, good for cases where the data points of the uptake graph do not extend to the limits of the liquid phase mole fractions, or the data are inaccurate at those limits. Only a few data points from the uptake graph can be used with our approach. Thereafter, the value of the equilibrium constant is derived statistically from its relation to the selectivity coefficient. It is important to note that the value of the equilibrium constant as derived from our methodology has to be constant over the range of the equilibrium liquid phase composition. This can be considered as a consistency test in addition to the triangular rule test, which represents a major test in a model that does not impose this rule externally.

Our data reduction approach is different from that used in Mehablia et al. (1994), which has the particular problem of the need of accurate experimental information at the limits of the liquid phase composition. Nonetheless, there are not any known theoretical values of the selectivity coefficient imposed at those limits. By introducing the liquid phase activity coefficients into the selectivity coefficient, this coefficient can be regarded as the only experimental information we have at equilibrium conditions derived from an uptake graph. With our model a few data points of the selectivity coefficient can be used to derive the solution model parameters, in an independent way of the equilibrium constant. Then the equilibrium constant can be derived statistically, at the experimental points chosen for data reduction.
Thermodynamic Framework

For the reversible exchange of two ions between a solution and a solid matrix, where the A ion replaces ion B in the solid matrix we write the stoichiometry:

\[ z_{\text{st},A} A + z_{\text{st},B} \bar{B} \leftrightarrow z_{\text{st},A} \bar{A} + z_{\text{st},B} B \]  \hspace{1cm} (1)

where, \( z_{\text{st}} \) denotes the stoichiometric coefficient and the bar, ions in the solid phase. The solid phase species denote a complex of the ions with the solid surface. The stoichiometric coefficients for the binary reaction case are equal to the charges of the counterion. With a system of several reactions we can transform the stoichiometric coefficient of the species in the independent reactions in order to have a unique stoichiometric coefficient for each species in the mixture. Then the ratio of the largest of these coefficients to each transformed stoichiometric coefficient gives the charge of each species \( z_i \).

For the stoichiometry in equation (1) the chemical potentials are interrelated by:

\[ z_{\text{st},A} \mu_A + z_{\text{st},B} \mu_B = z_{\text{st},B} \mu_B + z_{\text{st},A} \mu_A \]  \hspace{1cm} (2)

Following Gaines and Thomas (1953), we write for the chemical potentials:
\[ \bar{\mu}_A = \bar{\mu}^0_A + RT \ln \bar{E}_A f_A \]  \hspace{1cm} (3)

and

\[ \mu_A = \mu^0_A + RT \ln M_A \gamma_A \]  \hspace{1cm} (4)

where \( \bar{\mu}^0 \) denotes the standard state, \( R \) the gas constant, \( T \) the temperature, \( \bar{E}_i \) is the amount of species \( i \) per equivalent exchange capacity of the solid matrix, \( M_i \) is the amount of species \( i \) in the solution on a molality basis and \( f_i \) and \( \gamma_i \) are the rational and conventional activity coefficients of species \( i \) in the solid and solution phase respectively. With the term rational we mean an activity coefficient written in terms of equivalent mole fractions and they refer to the combination of the ions with the specific exchanger. The asymmetric convention is used for the activity coefficients. These activity coefficients should be expressed in terms of the representing concentration units for the ions. The equivalent ionic fraction of species \( i \) in terms of the mole numbers \( n_i \) is:

\[ \bar{E}_i = \frac{z_i n_i}{\sum_j z_j n_j} \]  \hspace{1cm} (5)

The equilibrium constant for equation (2) is as follows:
\[ K_A^B = \frac{(E_A)^{z_{A,B}} (M_B)^{z_{A,B}} (f_A)^{z_{A,B}} (\gamma_B)^{z_{A,B}}}{(E_B)^{z_{A,B}} (M_A)^{z_{A,B}} (f_B)^{z_{A,B}} (\gamma_A)^{z_{A,B}}} \]

\[
\exp\left[\left( z_{st,B} \mu_B^0 + z_{st,B} \mu_A^0 - z_{st,B} \mu_A^0 - z_{st,B} \mu_B^0 \right) / RT \right]
\]

According to Gaines and Thomas (1953) we write for the Gibbs-Duhem equation in the adsorbed phase:

\[ n_A \, d\mu_A + n_B \, d\mu_B + n_s \, d\mu_S = 0 \]  

(7)

where \( n_s \) is the number of solvent imbibed in the resin, and \( \mu_S \) its chemical potential.

Equation (7) in terms of the ionic fractions can be written as:

\[ \bar{E}_A \, d \ln (E_A f_A)^{z_{A,B}} + \bar{E}_B \, d \ln (E_B f_B)^{z_{A,B}} + z_{st,A} \, z_{st,B} \, n_s \, d \ln a_S = 0 \]  

(8)

where we replaced the chemical potential of the solvent with its activity.

Equation (8) can be solved for \( f_B \) as:

\[ \bar{E}_B \, d \ln f_B^{z_{A,B}} = - \bar{E}_A \, d \ln (E_A f_A)^{z_{A,B}} - \bar{E}_B \, d \ln \bar{E}_B^{z_{A,B}} - z_{st,A} \, z_{st,B} \, n_s \, d \ln a_S \]  

(9)
We also split the equilibrium constant:

\[ \ln K_C = \ln K_A^B + \ln f_B^{Z_{a,B}} - \ln f_A^{Z_{a,A}} \]  
\[ (10) \]

so that,

\[ d \ln K_C - d \ln f_B^{Z_{a,B}} + d \ln f_A^{Z_{a,A}} = 0 \]
\[ (11) \]

or,

\[ \overline{E}_B d \ln f_B^{Z_{a,B}} = \overline{E}_B d \ln K_C + \overline{E}_A d \ln f_A^{Z_{a,A}} \]
\[ (12) \]

Equations (9) and (12) can be combined to eliminate \( f_B \):

\[ \overline{E}_A d \ln K_C + \overline{E}_A d \ln f_A^{Z_{a,A}} = -\overline{E}_A d \ln (\overline{E}_A f_A)^{Z_{a,A}} - \overline{E}_B d \ln \overline{E}_B^{Z_{a,A}} - Z_{st,A} Z_{st,B} n_S d \ln a_S \]
\[ (13) \]

and solved for \( f_A \):

\[ d \ln f_A^{Z_{a,A}} = - \overline{E}_B d \ln K_C - \overline{E}_A d \ln (\overline{E}_A f_A)^{Z_{a,A}} - \overline{E}_B d \ln \overline{E}_B^{Z_{a,A}} - Z_{st,A} Z_{st,B} n_S d \ln a_S \]
\[ (14) \]
With the same way we can derive the following equation:

\[ d \ln f_B^{ZA} = \bar{E}_A d \ln K_C - \bar{E}_B d \ln(\bar{E}_A)^{ZA} - \bar{E}_B d \ln \bar{E}_B^{ZA} - z_{st,A} z_{st,B} n_s d \ln a_s \] (15)

Integration of equation (14) from a mixture fraction at point \( Q_1 \) in the adsorption isotherm surface to a mixture fraction at a point \( Q_2 \) gives:

\[ \int_{Q_1}^{Q_2} d \ln f_A^{ZA} = - \int_{Q_1}^{Q_2} \bar{E}_B d \ln K_C - \int_{Q_1}^{Q_2} z_{st,A} \bar{E}_A d \ln \bar{E}_A - \int_{Q_1}^{Q_2} z_{st,B} \bar{E}_B d \ln \bar{E}_B - z_{st,A} z_{st,B} \int_{Q_1}^{Q_2} n_s d \ln a_s \] (16)

Equation (16) can be simplified by identifying the following relations along an isothermal path between points \( Q_1 \) and \( Q_2 \):

\[ \int_{Q_1}^{Q_2} E_B d \ln K_C = [E_B d \ln K_C]_{Q_1}^{Q_2} - \int_{Q_1}^{Q_2} \ln K_C d E_B \] (17)

\[ \int_{Q_1}^{Q_2} z_{st,A} \bar{E}_A d \ln \bar{E}_A = \int_{Q_1}^{Q_2} z_{st,A} d \bar{E}_A = - \int_{Q_1}^{Q_2} z_{st,A} d \bar{E}_B \] (18)
\[
\int_{Q_2}^{Q_1} z_{st,B} E_B d \ln E_B = \int_{Q_1}^{Q_2} z_{st,B} d E_B = -\int_{Q_1}^{Q_2} z_{st,B} d E_A
\]  

(19)

Equation (16) now turns as follows:

\[
\ln \frac{f_A^{z_{st,B}}(Q_2)}{f_A^{z_{st,B}}(Q_1)} = \\
- [E_B \ln K_c]_{Q_2}^{Q_1} + \int_{Q_1}^{Q_2} K_C d E_B + (z_{st,A} - z_{st,B}) \int_{Q_1}^{Q_2} d E_B - z_{st,A} z_{st,B} \int_{Q_1}^{Q_2} d \ln a_S
\]

(20)

We also integrate equation (15) from point \( Q_2 \) to point \( Q_1 \) to get:

\[
\int_{Q_2}^{Q_1} d \ln f_B^{z_{st,B}} = \\
\int_{Q_2}^{Q_1} E_A d \ln K_C - \int_{Q_2}^{Q_1} z_{st,A} E_A d \ln E_A - \int_{Q_2}^{Q_1} z_{st,B} E_B d \ln E_B - z_{st,A} z_{st,B} \int_{Q_2}^{Q_1} d \ln a_S
\]

(21)

which becomes:

\[
\ln \frac{f_B^{z_{st,B}}(Q_1)}{f_B^{z_{st,B}}(Q_2)} = \\
[E_A \ln K_c]_{Q_2}^{Q_1} - \int_{Q_2}^{Q_1} K_C d E_A - (z_{st,A} - z_{st,B}) \int_{Q_2}^{Q_1} d E_A - z_{st,A} z_{st,B} \int_{Q_2}^{Q_1} d \ln a_S
\]

(22)
With the addition of equations (20) and (22) we get the relationship:

\[
\ln \frac{f_A^{\nu_{x,y}}(Q_1)}{f_B^{\nu_{x,y}}(Q_1)} + \ln \frac{f_A^{\nu_{x,y}}(Q_2)}{f_B^{\nu_{x,y}}(Q_2)} = [\ln K_c]^{\nu_{x,y}}_{Q_1} = \ln K_c(Q_1) - \ln K_c(Q_2) \tag{23}
\]

As equation (23) implies with the introduction of a solid phase solution model, the parameters of the activity coefficient model can be obtained by data reduction of the right side of equation (23). Then, by equation (10) we can statistically derive the value of the equilibrium constant. Note that our approach of calculating the adsorbed phase thermodynamic parameters is different from that proposed in Gaines and Thomas (1953) where the solvent’s activity is involved in deriving the thermodynamic parameters.

Integration of equations (14) and (15) from a pure component A (point a) and a pure component B (point b) to a mixture point Q and the combination of the resulting equations, gives the following equation:

\[
\ln K = (z_{st,A} - z_{st,B}) + \ln \frac{f_A^{\nu_{x,y}}(a)}{f_B^{\nu_{x,y}}(b)} + \int_0^{z_{st,B}} \ln K_c d\bar{\bar{E}}_B - z_{st,A} z_{st,B} \int_a^b n_s d\ln a_s \tag{24}
\]

Under several assumptions, as Gaines and Thomas (1953) explained, equation (24) can be simplified to:
\[ \ln K = (z_{st,A} - z_{st,B}) + \int_0^1 \ln K_c d\bar{E}_B \] (25)

Equation (25) has been used by Mehablia et al. (1994) for the calculation of the equilibrium constant in an independent way from the solid phase solution model parameters. Nonetheless, the above equations require accurate experimental data in the limits of the integral, which are difficult to obtain. We can see the integral plot of equation (25) in the work of Sengupta and Paul (1985) for the binary exchanges of the ternary system Cd\(^{2+}\)/Zn\(^{2+}\)/H\(^+\). In contrast with our approach we can use data in the range of liquid fractions 0.2 to 0.8 where they are usually given.

**Solid Phase Solution Model**

Examples of solution models used in equation (4) are the extended Debye-Hückel model (Smith and Woodburn, 1978), the Meissner's and Kusik's method (De Lucas et al., 1992), the Pitzer's model (Mehablia et al. 1994, Pabalan, 1994), and Bromley's model (Zheng et al. 1997). All of the above models express the activity coefficient in terms of molality concentration units. For the adsorbed phase examples of solution models used are the Margules expression (Pabalan, 1994), and the Wilson's solution model (Mehablia et al., 1994).

To avoid the unnecessary recalculation of concentration units in the derivation of the equilibrium constant we decided to modify the Wilson model and express its
composition dependence in terms of equivalent mole fractions. Our modification is consistent with the ideal mixing state implied by equation (3).

As a starting point we write the probabilities $p$ of forming the local composition of the two fluids with central $i$ and $j$ molecules with respect to the equivalent mole fraction:

$$
\begin{align*}
    p_{ii} &= \frac{\bar{E}_i \exp(-\lambda_{ii} / RT)}{p_{ji} \bar{E}_j \exp(-\lambda_{ji} / RT)} \\
    p_{ji} &= \bar{E}_j \exp(-\lambda_{ji} / RT)
\end{align*}
$$

(26)

where, $\lambda_{ij}$ denotes the energy of interaction in an i-j pair of molecules. The lattice coordination number now becomes:

$$
q_i = \frac{1}{\sum_j p_{ji} v_j / v_i}
$$

(27)

where $v_i$ is the molar volume of species $i$. By substituting equation (26) into (27) we get:

$$
q_i = \frac{\bar{E}_i}{\sum_j \bar{E}_{ij} \Lambda_{ij}}
$$

(28)

where $\Lambda_{ij}$ and $\Lambda_{ji}$ are the binary pair parameters given by:
\[ \Lambda_{ij} = \frac{v_j}{v_i} \exp\left( \frac{\lambda_{ji} - \lambda_{ij}}{RT} \right) \]  

(29)

For a density independent solution model \( \Lambda_{ij} \) and \( \Lambda_{ji} \) are treated as constant model parameters. For the mixture total Gibbs energy we write:

\[ \frac{\Delta \overline{G}_m}{RT} = \sum_i n_i \ln q_i \]  

(30)

where the underscore denotes a total molar property. On the basis of equation (3) the mixture Gibbs energy can be also written as:

\[ \frac{\Delta \overline{G}_m}{RT} = \sum_i n_i \ln(\overline{E}_i f_i) \]  

(31)

For the ideal state of the mixture we have:

\[ \frac{\Delta \overline{G}^o}{RT} = \sum_i n_i \ln(\overline{E}_i) \]  

(32)

Equations (30) and (32) give for the total excess Gibbs energy:
\[
\frac{\overline{G}^e}{RT} = \sum_i n_i \ln \frac{\overline{q}_i}{\overline{E}_i}
\]  
(33)

or in terms of mole fractions,

\[
\frac{\overline{G}^e}{RT} = -\sum_i \overline{X}_i \ln (\sum_j \overline{E}_j \Lambda_{ij})
\]  
(34)

The activity coefficient for this model is given by:

\[
\ln f_k = -\ln (\sum_j \overline{E}_j \Lambda_{kj}) + z_k \sum_i \frac{\overline{E}_i}{z_i} \left(1 - \frac{\Lambda_k}{\sum_j \overline{E}_j \Lambda_{ij}}\right)
\]  
(35)

In the special case where the charges of the species are equal equation (35) reduces to the Wilson original model.

**Relationship Between Various Expressions of the Equilibrium Constant**

Various forms of equation (6) for the equilibrium constant have been used in the literature, depending on equations (3) and (4) that have been assumed. By keeping the liquid phase part of equation (6) constant \((A_0)\) we can write the equilibrium constant in terms of mole fractions in the solid phase as:
\[ K_X = (A_1) (\frac{f_{xA} X_A}{f_{xB} X_B})^{z_{u,A}} \]  

(36)

Many authors report the values of the equilibrium constant in terms of equation (36). In the approach that we have used we can write an equivalent to equation (6):

\[ K_E = (A_1) (\frac{f_{EA} E_A}{f_{EB} E_B})^{z_{u,A}} \]  

(37)

Now we write the chemical potential of component A under both formulations:

\[ \mu_1 = \mu_{i(x)} + RT \ln(f_{xA} X_A) \]  

(38)

and

\[ \mu_1 = \mu_{i(E)} + RT \ln(f_{EA} E_A) \]  

(39)

At the standard state of pure A both the activity coefficients will be one and so:

\[ \mu_{i(x)}^0 - \mu_{i(E)}^0 = RT \ln\left( \frac{E_A}{X_A} \right) = 0 \]  

(40)

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Equations (38) to (40) mean that the values of the two equilibrium constants given by equations (36) and (37) should be equal.

If composition of the solid phase in the equilibrium constant is written with respect to mole numbers, then the following relationship is established:

$$K_E = (A_1) \frac{(f_{EA} E_A)^{z_{u,A}}}{(f_{EB} E_B)^{z_{u,B}}} =$$

$$\left( \frac{f_{EA} n_A}{f_{EB} n_B} \right)^{z_{u,A}} \left( \frac{z_A}{z_B} \right)^{z_{u,A}} N_T^{z_{u,B} - z_{u,A}} = K_M \left( \frac{z_A}{z_B} \right)^{z_{u,A}} N_T^{z_{u,B} - z_{u,A}}$$

(41)

where $n$ denotes moles per gram of solid, $N_T$ is the exchange capacity of the solid and $K_M$ the equilibrium constant which is based on moles per gram of solid for the adsorbed phase. It is easy to show after defining an equilibrium constant written with respect to equivalent mole fractions in the adsorbed phase ($K_N$) that:

$$K_N = K_E (N_T)^{z_{u,A} - z_{u,B}}$$

(42)

and,

$$K_N = K_M \left( \frac{z_A}{z_B} \right)^{z_{u,A}}$$

(43)
The above relationships can help comparing various values of equilibrium constants reported in the literature.

Model Application

Several binary systems taken from the literature were chosen to test our model. Two of these systems are the K⁺/Na⁺ and Ca²⁺/Na⁺ exchange on clinoptilolite reported by Pabalan (1994) at three different solution normalities, at 25°C. The exchange capacity of the solid as reported is 2.04 meq/g. The Wilson parameters and the equilibrium constant for these two systems are reported in Table 1. The all-entries parameters represent the simultaneous fitting of data at all normalities. As we see in Table 1, the values of the parameters remain fairly constant with the variation of normality, except for the low normality case, more prominent for the Ca²⁺/Na⁺ system where the experimental data were more scattered. A way to minimize the variation of the solution model parameters along normality is to reduce the number of the model parameters. For example a reciprocal relationship of the Wilson parameters has been assumed by Allen and Addison (1989), which did not represent well all of the systems examined by Mehablia et al. (1994), as for example the K⁺/H⁺ system. In this work we decided to use an approach based to the use of ionic parameters to reduce the number of parameters of the modified Wilson model. The assumptions we use are the following:
\[
\Lambda_{12} = \left( \frac{r_{x2}}{r_{x1}} + \beta \right) \\
\Lambda_{21} = \left( \frac{r_{x1}}{r_{x2}} - \beta \right)
\]

where \( \beta \) denotes a single adjustable parameter, and \( r_{xi} \) is the crystallographic radius of the \( i^{th} \) ion, as reported by Shock and Helgesson (1988). Equations (44) and (45) can be seen as a first order perturbation of equation (29), where we require the exponent in equation (29) to be of opposite sign for the \( \Lambda_{12} \) and \( \Lambda_{21} \) parameters. This means that for species of equal crystallographic radiiuses the parameters \( \Lambda_{12} \) and \( \Lambda_{21} \) are both positive but one of them is greater than one whereas the other less the one. Thus their product can be freely adjusted to any number, instead to one as Allen and Addison (1989) required.

In Table 1 and under the reduced-parameter form heading we see that the above assumption reduced the variation of the Wilson parameters with normality for the \( \text{Ca}^{++}/\text{Na}^{+} \) case, though not for the equilibrium constant. The parameters from the all-entries of the reduced-parameter model are used further for predictions of the uptake graphs, solid phase excess Gibbs energy and activity coefficients. In Figure 1 we plot the value of the equilibrium constant for the \( \text{K}^{+}/\text{Na}^{+} \) exchange as derived from the substitution of the Wilson parameters to equation (10), and at each experimental datum. In Figure 2 we plot the predictions of the uptake graph along with the experimental points for the same system, and in Figure 3 we plot the experimental data and the predictions of the uptake graphs for the \( \text{Ca}^{++}/\text{Na}^{+} \) exchange with two different sets of parameters. We
note that the parameter set obtained from the data reduction of the 0.5 normality fits the experimental data better, though not with an excellent representation of the 0.5 normality data, since we do not fit the solid phase fractions to obtain the parameters. Figure 4 shows the activity coefficients and Figure 5 the excess Gibbs energy in the solid phase for both systems. The reported value for \( \ln K_x \) for the \( K^+/Na^- \) exchange by Pabalan (1994) is 3.22 and that for the \( Ca^{++}/Na^- \) exchange is \(-1.65\), though Ames (1964) reports a value of \(-0.161\) which is closer to our predicted value of the high normality data set.

In Table 2 we report the model parameters for the systems \( NO_3^-/Cl^- \), \( NO_3^-/SO_4^{2-} \), and \( Cl^-/SO_4^{2-} \) on the amberlite IRA 400 resin at 22°C, reported by Smith and Woodburn (1978). The model in its reduced-parameter form has been used to obtain the values in Table 2, though the two-parameter form gave fairly constant parameters as well. The triangular rule for these three systems requires that the product \((K_{NO_3}^{Cl^-})^2 K_{Cl^-}^{SO_4^{2-}} [K_{NO_3}^{SO_4^{2-}}]^{-1}\) equals one, which is close to the value we calculate 1.099. The value for \( \ln K_M \) for the \( NO_3^-/Cl^- \) exchange reported in the reference is 1.330, while those for the \( Cl^-/SO_4^{2-} \) and \( NO_3^-/SO_4^{2-} \) exchanges are 1.630 and 4.290. Note here that the above values for \( \ln K_M \) were obtained with the use of molarity basis for the liquid phase, but the difference from molality base units is negligible at the conditions used for the experiment. In order to compare the authors' estimates with the values in Table 2 and for the 1-2 electrolyte systems, we have to use equation (41). The exchange capacity of the resin is reported in Korngold (1973) as 2.075 meq/g, and so the \( K_M \) values reported translate to \( \ln K_x \) values of 0.207 and 2.867 for the \( Cl^-/SO_4^{2-} \) and \( NO_3^-/SO_4^{2-} \) exchanges respectively which satisfy
the triangular rule exactly. The authors used the extended Debye-Hückel model to calculate the activity coefficients of the species in the aqueous phase, and the total sulfate concentration in the solution phase. Our predictions though reveal that the sulfate ion is about 95% of the total sulfate concentration for both $\text{SO}_4^{2-}$ binary systems at 0.4 N, due to the presence of the $\text{NaSO}_4^-$ ion. This ion will affect not only the free concentration of the sulfate ion in the solution but the activity coefficient calculation in the solution phase as well. In our analysis of equation (6) we used the free sulfate concentration. In Figure 6 we plot the uptake graphs predictions for all three systems with the use of the all-parameter entries. With the experimental data reported for the ternary system we predicted the free sulfate ion concentration and then with the model parameters the resin phase composition, with a mean error of 14.4, 5.3, and 3.0% for the $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$ solid species respectively. Note that there is some uncertainty in the experimental data, since the authors deducted the nitrate ion mass balance from the chloride ion and the total sulfate analysis, at an assumed constant normality of the solution. For the application of equation (23) this assumption does not have to hold, but the experimental data are usually given under this assumption.

A second ternary system we chose for study is the $\text{Ca}^{2+}/\text{Mg}^{2+}/\text{Na}^+$ exchange system on an amberlite resin 252 reported by Shallcross et al. (1988) at 25 °C. For the binary pairs we report the values of the reduced parameter model in Table 3. As Table 3 shows the parameters vary about a mean with a small standard deviation. Values at one standard deviation around the mean are kept to derive the reported value for the
equilibrium constant. While the 2-2 electrolyte system shows negative deviations from Raoult’s law, the 2-1 electrolytes exhibit positive deviations. In a work on molecular adsorption by O’Brien and Myers (1987) the positive deviations have been explained with the existence of stronger lateral than vertical interactions in the adsorbed phase. Shallcross et al. (1988), report values for $\ln K_m$ 1.03, 2.682, and 1.466 for the Ca$^{++}$/Mg$^{++}$, Ca$^{++}$/Na$^+$, and Mg$^{++}$/Na$^+$ exchanges respectively, in the basis of molarity units in the liquid phase. With a cation exchange capacity of 2.38 meq/g the values for the Ca$^{++}$/Na$^+$ and Mg$^{++}$/Na$^+$ systems translate to $\ln K_e$ values of 4.244 and 3.026 respectively, according to equation (41). According to the triangular the quantity $K_{Ca^{++}}^{Na^+} / K_{Mg^{++}}^{Na^+} / K_{Ca^{++}}^{Mg^{++}}$ should equal one. From the work of Shallcross et al. (1988) we get a value of 1.207 and from our predictions a value of 1.031 for the above quotient. The predictions of the uptake graphs are shown in Figure 7 for all three systems, along with the experimental data at various normalities.

Another ternary system we have tested the model on, is the H$^+$/Na$^+$/Cu$^{++}$ system on a Dowex-50 resin. All three binary systems are reported in Pieroni and Dranoff (1963), while we have also tested the Cu$^{++}$/Na$^+$ system, which is reported in Rao and David (1957). The binary parameters for all three systems taken by Pieroni and Dranoff (1963) with the reduced parameter model are reported in Table 4. A particular experimental problem with the Cu$^{++}$ binaries is the presence of the CuNO$_3^-$ ion, which should be accounted for estimating the free Cu$^{++}$ ion concentration. In particular the concentration of the CuNO$_3^-$ ion becomes more important as the normality of the
solution increases. The ion chemical analysis shown by Pieroni and Dranoff (1963), does not indicate the existence of the CuNO$_3^-$ ion, since it incorporates dilution, which brings the equilibrium of Cu(NO$_3$)$_3$ to total dissociation. The correction in the assumed solution normality required is more pronounced for the Cu$^{++}$/H$^+$ case, where the Cu$^{++}$ ion is more strongly adsorbed than in the Cu$^{++}$/H$^+$ system onto the solid. These corrected normalities were used for the data reduction. Nevertheless, as Table 4 indicates the low normality system exhibits higher overall experimental error. Pieroni and Dranoff (1963), report the lnK$_M$ values of the Na$^+$/H$^+$, Cu$^{++}$/Na$^+$, and Cu$^{++}$/H$^+$ systems as 0.982, -0.620 and 1.345 respectively. With the exchange capacity reported 4.74 meq/g, we transform the last two values to lnK$_E$ values of 1.629 and 3.595 respectively. Now, according to the triangular rule we should have that the quotient $(K_{Na^+}^{H^+})^2 K_{Cu^{++}}^{Na^+} / K_{Cu^{++}}^{H^+}$ should equal to one. From the 0.05 N values reported in Table 4 we get a value of 1.14, and by changing to the 0.1 N entries for the Cu$^{++}$/Na$^+$, and Cu$^{++}$/H$^+$ systems a value of 0.938, while the parameters reported in Pieroni and Dranoff (1963) give a value of 1. The uptake graph predictions with the parameters taken at the 0.1 N parameter-entries are shown in Figure 8 along with the experimental data, while in Figure 9 we plot the activity coefficients in the solid phase for all three systems. We note in Figure 9 that high lateral interactions exist for dilute H$^+$ fractions in the Na$^+$/H$^+$ system.

As an alternative to the Cu$^{++}$/Na$^+$ system from Pieroni and Dranoff (1963) where the background ion is the nitrate ion we have the data of Rao & David (1957) on the same Dowex-50 resin with the chloride ion as the background ion. The data span a range of
solution normalities 0.01 N to 4.0 N. The aqueous speciation for this system reveals interference to the Cu$^{+2}$ balance in the solution from the CuCl$^-$ ion and to a lesser extent from the CuCl$_2^-$ ion. Besides, at high normalities there is a higher than 10% CuCl$_2$ of the initial amount added. Due to the fact that the mass balance on the experimental data was deduced by analyzing the eluant solution for the Cu$^{+2}$ ion, there is a high uncertainty in the solution normalities assumed in the experiment. The estimated solution normalities for each experimental datum are shown in Table 5. Due to the high uncertainties in the assumed normalities we have used only the data set at the lowest normality to estimate the $\Lambda_{12}$ and $\Lambda_{21}$ parameters. Their values are 2.408 and 0.326 for the pair Cu$^{+2}$(1)/Na$^+$(2), close enough to the values reported in Table 4. The estimated value of ln$K_E$ is 1.661.
Conclusion

As the model applications show we have developed a simple and practical way to identify the thermodynamic parameters in a binary ion exchange system based on the Gibbs-Duhem equation written for the adsorbed phase, and the definition of the selectivity coefficient. This two-phase binary exchange equilibrium problem can be easily extended to multicomponent systems once the equilibrium constants and solid phase activity coefficient parameters for the binary pairs are identified. Our model incorporates the Wilson activity coefficient model written in a suitable form that complies to the definition of an ideal mixture in the adsorbed phase chosen by Gaines and Thomas (1953). The assumption used in our derivation is that of a constant exchange capacity, or constant surface charge among all equilibrium points in the isotherm surface. The latter point can be easily understood when we see the derivation of equation (23) as a subtraction of equation (10) at two different equilibrium points. As we have shown in the model development part this is consistent with the Gibbs-Duhem equation written for the solid phase. Equation (10) should be changed accordingly if other energy fields are assumed to exist as for example shown in Jansen et al. (1996), and Rhee and Dzombak (1998), though with the addition of extra parameters in the model.

A major issue that should not be neglected in the ion exchange equilibria as the systems investigated revealed, is the effect of the aqueous speciation on the liquid phase activity coefficients and the equilibrium constant through the overall mass balance. Our methodology introduces an additional consistency test based on the invariance of the equilibrium constant with the variation of the liquid phase composition. A statistically
constant average value should result from the data reduction technique we have presented.


Sengupta, M., and T. B. Paul, "Multicomponent Ion Exchange Equilibria. I. Zn\(^2+\)-Cd\(^2+\)-H\(^+\)


Acknowledgment

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### Table 1. Model parameters for $K^+$/Na$^+$ and Ca$^{++}$/Na$^+$ exchange

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### Table 2. Model parameters for NO$_3^-$/Cl$^-$, NO$_3^-$/SO$_4^{2-}$, and Cl$^-$/SO$_4^{2-}$ exchange

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### Table 3. Model parameters for Ca$^{++}$/Mg$^{++}$, Ca$^{++}$/Na$^+$, and Mg$^{++}$/Na$^+$ exchange

<table>
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<tr>
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### Table 4. Model parameters for Na$^+$/$H^+$, Cu$^{+}$/Na$^+$, and Cu$^{+}$/H$^+$ exchange

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<th>Na$^+(1)/$H$^+(2)$</th>
<th>Cu$^{+}(1)/$Na$^+(2)$</th>
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Table 5. Estimated solution normalities in the Cu$^{2+}$/Na$^+$ exchange (Rao and David, 1957)

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FIGURE CAPTIONS

Figure 1. Equilibrium constant for the K⁺/Na⁺ exchange on clinoptilolite

Figure 2. Uptake graphs predictions and experimental points for the K⁺/Na⁺ exchange on clinoptilolite

Figure 3. Uptake graph predictions and experimental points for the Ca²⁺/Na⁺ exchange on clinoptilolite for two parameter sets

Figure 4. Activity coefficients in the solid phase for the K⁺/Na⁺ and Ca²⁺/Na⁺ exchange on clinoptilolite

Figure 5. Excess Gibbs energy in the solid phase for the K⁺/Na⁺ and Ca²⁺/Na⁺ exchange on clinoptilolite

Figure 6. Uptake graph predictions for the Cl⁻/NO₃⁻, Cl⁻/SO₄²⁻, and NO₃⁻/SO₄²⁻ exchanges on amberlite IRA 400 resin

Figure 7. Uptake graph predictions for the Ca²⁺/Mg²⁺, Ca²⁺/Na⁺, and Mg²⁺/Na⁺ exchanges on amberlite 252 resin

Figure 8. Uptake graph predictions for the Cu²⁺/Na⁺, Cu²⁺/H⁺, and Na⁺/H⁺ exchanges on dowex-50 resin

Figure 9. Activity coefficients in the solid phase for the Cu²⁺/Na⁺, Cu²⁺/H⁺, and Na⁺/H⁺ exchanges on dowex-50 resin
Figure 1
Figure 2
Figure 6

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Key:
- Plain
- Dotted
- Crosshair
Figure 9