Comparison between Heterogeneous and Homogeneous MASS Action Models in the Prediction of Ternary Ion Exchange Equilibria

Jose L. Valverde,* Antonio de Lucas, and Juan F. Rodríguez

Chemical Engineering Department, Faculty of Chemistry, University of Castilla-La Mancha, Campus Universitario s/n, 13004, Ciudad Real, Spain

In this paper two models for the prediction of multicomponent ion exchange equilibria were compared: one, a heterogeneous model, based on the mass action law in which ideal behavior for both the solution and the solid phase and the heterogeneity of ion exchange sites has been assumed, and the other a homogeneous model, based on the same mass action law in which nonideal behavior for both the solution and the solid phase has been taken into account. Considering counterions with different valences, the optimum value of the fraction of functional groups was obtained from binary systems data. It was shown that the energy distribution was practically symmetric. Likewise, a procedure for decreasing the number of adjustable parameters, based on the determination of the minimum linearly independent equilibria considering each equilibrium as a heterogeneous reaction, was developed. The adjustable parameters (namely, the equilibrium constants forced to satisfy the triangle rule) were used in the prediction of the ternary equilibrium data. In all cases the prediction of the heterogeneous model was in good agreement with experimental data. However, although the homogeneous model was somewhat superior to the heterogeneous model in the prediction of ternary systems, the comparison between both models did not allow us to distinguish statistically between them.

Introduction

Prediction of multicomponent ion exchange equilibrium is needed for the design of exchangers that operate over a wide range of conditions. A theoretical model that allows the prediction of equilibrium behavior of multicomponent systems would therefore be extremely useful. A test of an ion exchange model is that it be able to predict accurately the composition of one phase that is in equilibrium with the other phase of known composition. The typical approach is to develop thermodynamic models which, based on binary equilibrium data, can predict multicomponent equilibria. The models proposed in the literature can be divided in two main groups: those describing the ion exchange in terms of the law of mass action and those regarding the ion exchange as a phase equilibrium.

In early works, which belong to the first group, the ideality of the ion exchange equilibria was assumed with a constant separation factor and the activity coefficients of all components both in the solution and in the solid-phase equal to unity. This model assumes that the presence of other counterions does not affect the equilibrium exchange between two particular ions, which implies constant selectivities coefficients. However, the behavior of systems where the selectivity coefficients change with the resin composition cannot be described on the basis of these models. To solve this problem it was necessary to introduce models that consider nonideal or real systems. Smith and Woodburn successfully applied the Wilson equation to correlate the activity coefficients in the solid phase with the composition. To calculate the binary interaction parameter in the Wilson equation, these authors developed a computational method which consists of obtaining the set of values of the thermodynamic equilibrium constant and the two binary interaction constants in the Wilson equation which best fit the experimental equilibrium data. If the activity coefficients of the salts in the solution are known, the activity coefficient of each ion in the solid phase and the equilibrium constant can then be estimated from experimental data. Recently Vamos and Haas used the Margules equation to model the dependency of the resin phase activity coefficients with the resin composition. However, statistical analysis of data fits indicates that although the Wilson and Margules equations were able to model adequately the resin phase nonidealities, the Wilson model provided the superior data fits. Shallcross et al. on the basis of the model by Smith and Woodburn, proposed the use of the Pitzer equation to describe single ion activity coefficients in the liquid phase and the Wilson model for the activity coefficients in the solid phase. In previous works, de Lucas et al. developed a similar model which was used for the prediction of the ternary and quaternary equilibrium data. In this case, the activity coefficients in the liquid phase were calculated by using the Meissner and Kusik method. Likewise, a method to reduce the number of parameters was developed by Allen et al. and Allen and Addison and later used by de Lucas et al. by forcing the Wilson parameters to satisfy some constraints based on empirical relationships.

In the models of the second group, ion exchange is treated as an adsorption process. In this sense, the first attempts to explain and to predict ion exchange equilibria were based on the phenomena of adsorption and ion exchange, using the Freundlich and Langmuir isotherms for the characterization of equilibrium. More recently, Novosad and Myers and Myers and Byington suggested that the ion exchange should be treated in a similar way as the phenomenon of adsorption.

* Author to whom correspondence should be addressed. E-mail: jvalver@nqu-crc.udm.es.
These authors defined a thermodynamic variable, namely, the excess surface, which can be experimentally determined solely from measurements in the bulk liquid phase, thereby eliminating the ambiguity between adsorbed and exchanged ions.

In a previous paper\(^{10}\) different models for characterizing the ion exchange equilibrium in binary mixtures were compared. Three models were used: the Langmuir model, that proposed by Novosad and Myers\(^ {15}\) and Myers and Byington,\(^ {16}\) and one based on the law of mass action. It was observed that the model based on the law of mass action, which takes into account the effects of temperature, the total ionic concentration of the external solution, and the activity coefficients of the two phases in addition to the equilibrium constant, was the model which best represented the experimental binary equilibrium isotherms in all of the systems studied. Likewise, predictions of multicomponent ion exchange equilibria with the law of the mass action are more accurate than those made with the other models.\(^ {17}\)

Recently, Melis et al.\(^ {18}\) developed a new model based on the mass action law. This new model differs from all models of the first group discussed above in that it assumes that both the fluid and the solid-phase behave according to the law of mass action. By assuming that the effect of mixture nonidealities is smaller than that due to the resin heterogeneity and can be neglected. This corresponds to introducing the idea of Myers and Byington\(^ {16}\) accounting for the heterogeneous nature of the solid in the framework of the equilibrium models based on the law of mass action. These authors introduced the heterogeneity of ion exchange functional groups by assuming a given distribution for the standard free-energy change of the ion exchange process. Assuming the simplest situation in order to diminish the number of adjustable parameter, they consider that the resin could be characterized by using only two types of equally abundant functional groups. Accordingly, the total resin capacity is given by the sum of the capacity of the resin with respect to the functional groups of each type. Representing \(p_1\) and \(p_2\) as the fraction of functional groups of type 1 and 2, respectively, it is clear that

\[ p_1 + p_2 = 1 \]  

(1)

The values of the parameters \(p_1\) and \(p_2\) should be, for a given resin, the same for all binary and multicomponent systems. The reliability of the proposed model in describing binary uptake data as well as in predicting the behavior of multicomponent systems was tested by comparison with experimental data available in the literature.

The aim of this paper is to compare between a heterogeneous model and a homogeneous mass action model in the prediction of ion exchange equilibria. On the basis of the binary and ternary experimental data of \(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+,\) and \(\text{H}^+\) obtained in previous works,\(^ {8,10,17}\) in this paper we discuss the influence of the fraction of functional groups \((p_1 \text{ and } p_2)\) on describing experimental binary data where counterions with different valences are involved. Likewise, a procedure for decreasing the number of adjustable parameters, based on the determination of the minimum linearly independent equilibria when considering each equilibrium as a heterogeneous reaction, was developed. In this way, the adjustable parameters (namely, the equilibrium constants forced to satisfy the triple rule) were used in the prediction of the ternary equilibrium data. The results obtained with this model were compared to those of the homogeneous one based on the law of mass action described in previous papers in order to verify which model is more accurate to predict multicomponention exchange equilibria.

**Mathematical Formulation of the Heterogeneous MASS Action Model**

The following mathematical formulation is based on the previous one by Melis et al.\(^ {18}\)

**Binary Systems.** For a given binary system

\[ \beta A^a_{r} + \alpha B^b_{s} \leftrightarrow \beta A^a_{r} + \alpha B^b_{s} \]  

(2)

where \(A^a\) and \(B^b\) are the two exchanging ions and \(r\) and \(s\) indicate the resin and the solution phases, respectively. The thermodynamic equilibrium constant for such a reaction is given by

\[ K(T) = \frac{(A^a_r)^{\beta}(B^b_s)^{\alpha}}{(A^a_r)^{\alpha}(B^b_s)^{\beta}} \]  

(3)

in terms of the activities of the involved ionic species. This quantity is defined by the thermodynamic relationship

\[ \Delta G^\circ(T) = -RT \ln K(T) \]  

(4)

where \(\Delta G^\circ\) is the standard free-energy change associated with the ion exchange process. By assuming that the ion exchange equilibria is ideal and neglecting the effects due to the swelling and hydration of the resin, the equilibrium constant can be written as

\[ K(T) = \frac{(A^a_r)^{\beta}(B^b_s)^{\alpha}}{(A^a_r)^{\alpha}(B^b_s)^{\beta}} \]  

(5)

where \(q_a\) and \(C_i\) are the concentrations in the resin and in the solution phase, respectively. Introducing the ionic fraction of the generic ith ionic species

\[ X_i = \frac{n_i C_i}{N} \]  

(6)

\[ \sum_{k=1}^{N_c} n_i C_k \]

\[ Y_i = \frac{n_i q_i}{q_0} \]  

(7)

where \(C_i\) represents the concentration of ith ionic species in solution and \(n_i\) its charge. \(N_c\) is the total number of counterion species. \(N\) is the total ionic concentration in the solution phase or the solution normality, \(q_i\) is the solute concentration in the solid phase and \(q_0\) is the total capacity of the resin. Upon substituting in eq 5 the equilibrium constant becomes

\[ K(T) = \frac{Y_1^\beta X_1 A^a_r B^b_s (q_0)^{\beta - \alpha}}{X_1 A^a_r Y_1 B^b_s (N)} \]  

(8)
If we assumed that the resin is characterized by two type of functional groups, the total resin capacity is given by

$$q_0 = q_{0,1} + q_{0,2}$$  \hspace{1cm} (9)$$

where $q_{0,1}$ and $q_{0,2}$ represent the capacity of the resin with respect to the functional groups of type 1 and 2, respectively.

The fractions of functional groups of type 1 and 2, $p_1$ and $p_2$, are defined by

$$p_i = \frac{q_{0,i}}{q_0} \hspace{1cm} i = 1, 2$$  \hspace{1cm} (10)$$

being

$$\sum_{i=1}^{2} p_i = 1$$  \hspace{1cm} (11)$$

The ionic fraction of the generic $i$th ionic species on the $j$th functional group is given by

$$Y_{ji} = \frac{\nu_i q_{ij}}{q_{0,j}} \hspace{1cm} j = 1, 2$$  \hspace{1cm} (12)$$

and the equilibrium constant of the exchange process occurring on the same functional groups is

$$K_j(T) = \frac{Y_{ji}^{\alpha} X_{iB^+}^{\beta} \left( \frac{q_{0,j}}{N} \right)^{\beta-\alpha}}{X_{sB^+}^{\alpha} Y_{j,B^+}^{\beta}} \hspace{1cm} j = 1, 2$$  \hspace{1cm} (13)$$

where

$$K_j(T) = \exp \left( -\frac{\Delta G_j(T)}{RT} \right)$$  \hspace{1cm} (14)$$

The overall resin composition is obtained by considering for each component the quantities present on each type of functional group:

$$Y_{sA^{i+}} = \sum_{j=1}^{N=2} p_j Y_{j,sA^{i+}} \hspace{1cm} (15)$$

$$Y_{sB^{i+}} = \sum_{j=1}^{N=2} p_j Y_{j,sB^{i+}}$$

On the other hand, the following stoichiometric condition has to be satisfied:

$$Y_{j,A^{i+}} + Y_{j,B^{i+}} = 1$$  \hspace{1cm} (16)$$

**Multicomponent Systems.** Let us consider a multicomponent system containing $N_c$ counterions. Selecting a reference one, say the $N_{th}$ ion, we must consider the $(N_c - 1)$ equilibrium relations between this and each one of the other counterions.

$$K_{ji}(T) = \frac{(Y_{j,i+})^{\nu_i} (X_{j,N_{j=2}N_{j=2}})^{\nu_i} (q_{0,j})^{\nu_i}}{(X_{i+1})^{\nu_i} (Y_{j,N_{j=2}N_{j=2}})^{\nu_i} (N)} \hspace{1cm} (17)$$

for $j = 1, 2$ and $i = 1, 2, ..., (N_c - 1)$.

<table>
<thead>
<tr>
<th>Table 1. Matrix of Stoichiometric Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. of binary system</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>H^+</td>
</tr>
<tr>
<td>Na^+</td>
</tr>
<tr>
<td>K^+</td>
</tr>
<tr>
<td>Mg^{2+}</td>
</tr>
<tr>
<td>Ca^{2+}</td>
</tr>
<tr>
<td>H^+</td>
</tr>
<tr>
<td>Na^+</td>
</tr>
<tr>
<td>K^+</td>
</tr>
<tr>
<td>Mg^{2+}</td>
</tr>
<tr>
<td>Ca^{2+}</td>
</tr>
</tbody>
</table>

where $R^2$ is the coefficient of determination.

Table 1 is shown the matrix of stoichiometric coefficients. In this way, the following relationships between the standard Gibbs free energy for the equilibrium constants are positive for the products, negative for the reactants, and zero for the inert components. By applying the Gaussian algorithm to the matrix of stoichiometric coefficients yields the matrix

$$
\begin{align*}
\begin{bmatrix}
+1 & -1 & 0 & 0 & -1 & +1 & 0 & 0 \\
0 & +1 & -1 & 0 & 0 & -1 & +1 & 0 \\
0 & 0 & +2 & -1 & 0 & 0 & -2 & +1 \\
0 & 0 & 0 & +1 & -1 & 0 & 0 & -1 & +1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\end{align*}
$$

In general

$$
\beta^n_i A^n_{R_1} + \alpha^n_i B^n_{R_1} \leftrightarrow \beta^n_i A^n_{R_2} + \alpha^n_i B^n_{R_2}
$$

where $R = 1, 10$.

In this way, the following species occur: $H_2^+, Na_2^+, K^+, Mg^{2+}, Ca^{2+}, H_2^+, Na^+, K^+, Mg^{2+}$, and $Ca^{2+}$. In Table 1 is shown the matrix of stoichiometric coefficients.

In other words, four key equilibria were found, namely systems A–D. In this way, the following relationships between the standard Gibbs free energy corresponding to functional groups of type 1 and 2 may be established:

$$
\begin{align*}
\Delta G(T)_A + \Delta G(T)_B - \Delta G(T)_C \\
\Delta G(T)_A + \Delta G(T)_B - \Delta G(T)_D \\
\Delta G(T)_A + \Delta G(T)_B - \Delta G(T)_C \\
\Delta G(T)_A + \Delta G(T)_B - \Delta G(T)_D
\end{align*}
$$

where $j = 1, 2$ and $T = 283, 303, 323 \text{ K}$.

Those relationships are equivalent to assume the triangle rule for the equilibrium constants. This thermodynamic constraint allows us to diminish the number of parameters from 61 to 25 and ensures the thermodynamic consistency of the equilibrium parameters thus obtained.

As mentioned above, all of data (606) corresponding to the 10 binary systems were simultaneously fitted.

According to eq 20, the objective function to be minimized is given by the following equation:

$$
\chi^2 = \sum_{k=1}^{606} \left\{ (Y_{A,exp} - Y_{A,th})^2 + (Y_{B,exp} - Y_{B,th})^2 \right\}
$$

The results obtained for the free energy change on each functional group are shown in Table 2. The fraction of functional groups of type 1, $p_1$, is equal to 0.477. This value is close to 0.5, as assumed by Melis et al. In fact, the confidence interval of $p_1$ evaluated in the same way as in a previous work is 0.313 < $p_1$ < 0.640 with a significance of 0.05.

In Figure 1 is shown the influence of $p_1$ on $\chi^2$. As seen, the trend observed corroborates the previous statistical analysis. This result would indicate that the energy distribution is practically symmetric.

In Figures 2–4 are compared the HMAM and LAM models. It can be seen that the accuracy of the HMAM model in reproducing experimental data is comparable to that of LAM. Likewise, by means of an example, in Figures 5 and 6 are shown the ionic fraction of different species in the resin phase on functional groups of type 1 and 2. The capability of HMAM in describing the experimental data where counterions with different valences are involved can be also verified (Figure 3). It clearly appears that the effect of the solution normality, which increases the equilibrium uptake as the solution becomes more dilute, is properly accounted for by the model. However, it can be observed that the experimental data is just better reproduced with the LAM model than with the HMAM model. From the mathematical viewpoint, this result is expected. In the LAM model, each binary data at a given temperature were interpreted by fitting three parameters, namely, the equilibrium constant and the two binary interaction parameters of the Wilson model. As previously reported by Shallcross et al., the regression procedure does not imply that the triangle rule for the equilibrium constants has to be completely obeyed. In fact, the deviations of this rule are, in some cases, higher than 15% in the temperature range investigated (Table 3). According to Shallcross et al., these differences could be also attributed to the experimental error.

On the contrary, the HMAM model here used is forced in the fitting procedure of all binary data to satisfy the triangle rule for the equilibrium constants. Furthermore, the experimental error, in addition to the assumption that considers the behavior of the aqueous solution to be ideal, could have a clear negative effect on the quality of the fit. In this way the slight differences in the prediction of experimental data by both models could be justified.

The heterogeneity of the resin may be explained attending to different factors. Polymeric supports, such as ion exchange resins, are semi-rigid because their structure is influenced by molecules present in the bulk phase. In most cases swelling provides accessibility to new active groups. Therefore, one may distinguish between two types of accessibility, one related to the morphology in the inert bulk environment (noninterac-
tion accessibility) and another reflecting the influence of the solvent and adsorbed molecules (interaction accessibility). According to Buttersack,23 the corresponding fraction of accessible functional groups cannot be considered as a statistical distribution of groups since the degree of cross-linking should be lower in the surface region, which should in turn result in higher degrees of surface sulfonation. On the other hand, the interaction accessibility appears to be related to the ratio of styrene to DVB. These types of accessibility could explain the observed heterogeneous distribution of ion exchange centers.

On the other hand, if the surface were not heterogeneous, one would expect the relative separation to be approximately constant. Nonidealities in the bulk and surface phase would produce only minor deviations from this rule. But if the surface contains high- and low-energy sites, then the separation factor for the preferentially adsorbed species should decrease with its ionic

<table>
<thead>
<tr>
<th>(K)</th>
<th>(J/mol)</th>
<th>HNa</th>
<th>HK</th>
<th>H Mg</th>
<th>H Ca</th>
<th>NaK</th>
<th>Na Mg</th>
<th>Na Ca</th>
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<th>KCa</th>
<th>Mg Ca</th>
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<tbody>
<tr>
<td>283</td>
<td>ΔG°1</td>
<td>-2597.8</td>
<td>-5130.0</td>
<td>-6814.8</td>
<td>-6465.5</td>
<td>-2532.2</td>
<td>-1619.1</td>
<td>-1269.8</td>
<td>3445.3</td>
<td>3794.6</td>
<td>349.3</td>
</tr>
<tr>
<td>303</td>
<td>ΔG°1</td>
<td>-81.0</td>
<td>370.5</td>
<td>1219.2</td>
<td>4081.2</td>
<td>451.5</td>
<td>1381.1</td>
<td>3919.2</td>
<td>478.1</td>
<td>4822.2</td>
<td>-5300.3</td>
</tr>
<tr>
<td>323</td>
<td>ΔG°1</td>
<td>-1825.8</td>
<td>-4107.0</td>
<td>-3489.9</td>
<td>-6756.9</td>
<td>-2281.2</td>
<td>-161.7</td>
<td>-3105.3</td>
<td>4724.2</td>
<td>1457.2</td>
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<tr>
<td></td>
<td>ΔG°2</td>
<td>-136.4</td>
<td>316.8</td>
<td>-1750.3</td>
<td>-5165.9</td>
<td>453.2</td>
<td>-1477.6</td>
<td>-4893.2</td>
<td>-2383.9</td>
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<td>-3450.4</td>
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<td>-7446.2</td>
<td>-1775.7</td>
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<tr>
<td></td>
<td>ΔG°2</td>
<td>-849.8</td>
<td>-278.2</td>
<td>-4172.2</td>
<td>-8489.0</td>
<td>571.6</td>
<td>-2472.5</td>
<td>-4149.3</td>
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</tr>
</tbody>
</table>

In this table, for example, HNa corresponds to the binary equilibrium Na⁺ + H⁺ ↔ Na⁺ + H⁺.
The equilibrium experimental data of the ternary system combining \(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+, \text{Na}^+, \) and \(\text{H}^+\) on the same resin (Amberlite IR-120) at different total ionic concentrations (0.1, 0.3, and 0.5 N) and three temperatures (283, 303, and 323 K) have been reported in previous works. The resin composition of the ternary systems has been predicted from the parameters obtained in the above section by solving the set of nonlinear equations constituted by eqs 17–19 using Marquardt's algorithm in a similar way as done in previous works.

In Figures 7 and 8 are compared the capability of both models in predicting ternary experimental equilibrium data. It can be seen that the accuracy of the two models is approximately the same. Deviations higher than 10% are mainly related to the equivalent ionic fractions with values lower than 0.2. According to de Lucas et al., since the experimental resin composition is determined by material balance, higher deviations can be expected at low concentration values, due to experimental data scatter. To establish a better comparison between both models, a given ternary system constituted by the ions A, B, and C was defined by the following objective function:

\[
E = \frac{1}{N_E} \sum_{k=1}^{N_E} \left( (Y_{A,\text{exp}} - Y_{A,\text{th}})_k^2 + (Y_{B,\text{exp}} - Y_{B,\text{th}})_k^2 + (Y_{C,\text{exp}} - Y_{C,\text{th}})_k^2 \right) \quad (24)
\]

In Table 4 are shown the results reached with the HMAM and LAM models. It can be proven that the accuracy of the two models is similar. However, in the same way as in the binary systems where counterions with different valences are involved, the prediction of ternary systems with the LAM model is just better than that with the HMAM model. A perusal of those tables indicates that for the full \(\text{K}^+\)–\(\text{Na}^+\)–\(\text{H}^+\) ternary data set the objective function for the HMAM model is, in value, lower than that of the LAM model. In the case of the \(\text{Ca}^{2+}\)–\(\text{Na}^+\)–\(\text{H}^+\) and \(\text{Ca}^{2+}\)–\(\text{Mg}^{2+}\)–\(\text{H}^+\) ternary systems, the ratio of objective functions \(E_{\text{HMAM}}/E_{\text{LAM}}\) is higher than 2 in practically all cases.

The quality of the prediction achieved with the HMAM and LAM models also can be determined by using the F-test in a similar way as Allen et al. If it is assumed that eq 24 is a measurement of the variance, the following F-statistic could be defined:

\[
F_0 = \frac{E_{\text{HMAM}}}{E_{\text{LAM}}} \quad \text{if} \quad E_{\text{HMAM}} > E_{\text{LAM}}
\]

\[
F_0 = \frac{E_{\text{LAM}}}{E_{\text{HMAM}}} \quad \text{if} \quad E_{\text{HMAM}} \leq E_{\text{LAM}}
\]

In Table 4 is also shown the random variable \(F(v_1,v_2)\), where the degree of freedom, \(v_1\) and \(v_2\), are in this case equal to \(N_E\). The results of these computations show that there is not a statistically significant reduction in the quality of the prediction with both models. The systems for which there is a significant lessening (at 0.25 level) are those in which counterions with different valences are present. In any case, the differences in the objective functions for the two models are not statistically significant. In other words, the only conclusion to be drawn in comparing the two models by their minimized objective function is that the model which provides the objective functions smaller in value is superior to the other for a given data set.

Summarizing, although the LAM model is just superior to the HMAM model in the prediction of the ternary systems, the comparison between both models does not allow us to distinguish statistically between them. In all cases, however, the HMAM model predicts values to be in good agreement with experimental data. These results clearly demonstrate that the potential of the
Figure 7. Comparison between calculated and experimental values of the ionic fraction in the resin phase for the ion exchange equilibrium $K^+ / Na^+ / H^+$ at 283, 303, and 323 K: (a) $K^+$, (b) $Na^+$, and (c) $H^+$.

Figure 8. Comparison between calculated and experimental values of the ionic fraction in the resin phase for the ion exchange equilibrium $Ca^{2+} / Mg^{2+} / H^+$ at 283, 303, and 323 K: (a) $Ca^{2+}$, (b) $Mg^{2+}$, and (c) $H^+$.
HMAM model in predicting the equilibrium ion exchange data for binary and ternary systems is similar to that of LAM model. On the other hand, the HMAM model has a clear advantage with respect to LAM model. The procedure for decreasing the number of adjustable parameters, based on the determination of the minimum linearly independent equilibria considering each equilibrium as a heterogeneous reaction, allows us to predict the equilibrium constants for the two functional groups of a new binary equilibrium system. As above-mentioned, this prediction is, from the thermodynamic point of view, more consistent than that carried out with the LAM model. Consider, for example, the system A/D different from the 10 here studied, where A is Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, or H$^+$. The resulting equilibrium constants for the two functional groups of the binary system constituted by D and another ion different from A, could be predicted by applying the triangle rule.

On the other hand, the programming effort for the prediction of the equilibrium experimental data of the ternary system is similar in both models. In this situation, either model could be equally used for the prediction of multicomponent ion exchange equilibria. However, as concluded in the previous section, the programming effort for the HMAM model in the evaluation of the standard Gibbs free energy corresponding to functional groups of type 1 and 2 from binary systems is always greater than that for the LAM model with no restrictions. The computational effort would moreover increase if the nonideality of the aqueous phase was considered.

**Conclusions**

In this paper heterogeneous and homogeneous models (HMAM and LAM, respectively) based on the mass action law have been compared. The influence of the distribution of functional groups on the prediction of the binary equilibria, where counterions with different valences are involved, has been studied. The best fit is obtained when the energy distribution is practically symmetric. Likewise, a procedure for decreasing the number of adjustable parameters, based on determination of the minimum linearly independent equilibria considering each equilibrium as a heterogeneous reaction, has been developed. The adjustable parameters (namely, the equilibrium constants forced to satisfy the triangle rule) have been used in the prediction of the ternary equilibrium data. The quality of the prediction achieved with the heterogeneous and homogeneous models has been determined by using the F-test. In all cases the heterogeneous model predicted values to be in good agreement with experimental data. However, in the same way as in the binary systems, where counterions with different valences are involved, the prediction of ternary ones with the homogeneous model is slightly better than that with the heterogeneous model. Although the homogeneous model is somewhat superior to the heterogeneous model in the prediction of ternary systems, the comparison between both models does not in general distinguish statistically between them. This result clearly demonstrates the potential of the heterogeneous model in predicting the equilibrium ion exchange data for binary and ternary systems. Finally, if the programming effort is considered, either model could be equally used to predict the multicomponent ion exchange equilibria.

**Nomenclature**

- $a_i$ = activity of $i$th ion
- $C_i$ = concentration of $i$th ion in the solution phase, mol/L
- $F = F$-test value
- $F_0$ = function defined by eq 25
- $\Delta G^\circ$ = standard Gibbs free energy change, J/mol
- $\Delta G^\circ = \Delta G^\circ$ = standard Gibbs free energy change corresponding to functional groups of type $j$
- $K$ = thermodynamic equilibrium constant
- $K_j$ = thermodynamic equilibrium constant for functional groups of type $j$
- $N$ = total concentration or normality of the solution phase
- $N_i$ = number of counterions in the system
- $N_j$ = number of types of functional groups
- $N_e$ = number of experiments carried out with a given ternary system
- $\rho_j$ = fraction of functional groups of type $j$
\( q_i \) = concentration of ith ion in the resin phase, mol/L
\( q_{ij} \) = concentration of ith ion in the resin phase on functional groups of type j, mol/L
\( q_{R} \) = total ion exchange capacity, mol/L
\( q_{ij,R} \) = ion exchange capacity of functional groups of type j, mol/L

\( R \) = ideal gas constant
\( T \) = temperature
\( X_i \) = ionic fraction of ith ion in the solution phase
\( Y_i \) = ionic fraction of ith ion in the resin phase
\( Y_{ij} \) = ionic fraction of ith ion in the resin phase on functional groups of type j

Greek Letters
\( \alpha, \beta, \nu \) = stoichiometric coefficients or ion charge
\( \nu \) = stoichiometric coefficients or ion charge, degrees of freedom
\( E \) = function defined by eq 24
\( \chi \) = objective function defined by eq 23

Subscripts
\( \exp \) = experimental
\( r \) = resin phase
\( s \) = solution phase
\( th \) = predicted

Literature Cited

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