Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Ion-Exchange Equilibrium of Ca^{2}, Mg^{2}, K, Na, and H Ions on Amberlite IR-120: Experimental Determination and Theoretical Prediction of the Ternary and Quaternary Equilibrium Data

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To cite this Article De Lucas, Antonio , Zarca, Jacinto and Caizares, Pablo(1992) 'Ion-Exchange Equilibrium of Ca^{2}, Mg^{2}, K, Na, and H Ions on Amberlite IR-120: Experimental Determination and Theoretical Prediction of the Ternary and Quaternary Equilibrium Data', Separation Science and Technology, 27: 6, 823 — 841
To link to this Article: DOI: 10.1080/01496399208019727
URL: http://dx.doi.org/10.1080/01496399208019727

SEPARATION SCIENCE AND TECHNOLOGY, 27(6), pp. 823–841, 1992

Ion-Exchange Equilibrium of Ca^{2+}, Mg^{2+}, K^+, Na^+, and H^+ Ions on Amberlite IR-120: Experimental Determination and Theoretical Prediction of the Ternary and Quaternary Equilibrium Data

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Abstract

A study of the cation-exchange equilibria between Amberlite IR-120 resin and aqueous solutions of calcium, magnesium, potassium, and sodium chlorides and hydrochloric acid has been made. Experiments were carried out at 283, 303, and 323 K with solutions having total cation concentrations of approximately 0.1, 0.3, and 0.5 *N*. Experimental data for the ion-exchange equilibria of the ternary and quaternary systems are reported. These systems exhibit nonideal characteristics in both phases. The predictions have been based on the reaction equilibrium constants and correlations for the activity coefficients in both phases. A model which allows the prediction of multicomponent ion-exchange equilibria from binary data has been developed. Predictions of ternary and quaternary systems based solely on the binary data are in good agreement with the experimental results.

Key Words: Ion exchange; Equilibrium; Multicomponent systems

INTRODUCTION

One of the controlling factors governing the use of ion-exchange separations is the equilibrium distribution of ions between the resin and solution phases which can be achieved in any given system. For this reason, ion-exchange equilibria have been widely studied.

Nearly all practical and important ion-exchange processes deal with more than two exchangeable ions. However, most of our knowledge of the behavior of ion exchange comes from investigations of binary systems. Few

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systematic studies have been done on multicomponent ion exchange because of the complexity of both experimental and theoretical multi-ionic systems.

Prediction of multicomponent ion-exchange equilibrium is needed for the design of exchangers which operate over a wide range of conditions. A theoretical model that allows the equilibrium behavior of multicomponent systems to be predicted would therefore be extremely useful. This was the main goal of many works published about these separation processes. Little attention has been paid to the problem of the influence of resin composition on the affinity of ions in a multi-ionic resin.

Methods for the prediction of multicomponent ion-exchange equilibria can be classified in four main groups.

1. Models (*1–4*) based on the assumption of ideality of the exchange equilibria with a constant separation factor and activity coefficients of all components in the solid phase equal to unity.
2. Models (*2*, *5–8*) based on the assumption of regular systems with a linear transformation between the separation factor and the composition in the solid phase.
3. In the third group (*9*, *10*), the ion exchange is treated as a phase equilibrium using standard procedures developed for solution thermodynamics. Surface effects are taken into account by introducing surface excess variables similar to those used to study adsorption from liquid mixtures on solids.
4. The fourth group (*11–21*) includes models which consider nonideal or real systems, so they should be more accurate in predicting equilibrium behavior.

Among the different models available in the literature for the prediction of the ion-exchange equilibria, a model based on the mass action law, chosen in a previous paper (*20*), has been applied in this study.

The equilibrium experimental data of ternary systems combining Ca^{2+}, Mg^{2+}, K^+, Na^+, and H^+ ions and a quaternary system constituted by Ca^{2+}, K^+, Na^+, and H^+ ions on the same resin at different total ionic concentrations (0.1–0.5 *N*) and temperatures (283–323 K) are presented.

These systems exhibit nonideal characteristics in both phases. The experimental characterization has been based on the reaction equilibrium constants and correlations for the activity coefficients in both phases. The exchanger phase activity coefficients are obtained from the well-known Wilson model (*22*).

EXPERIMENTAL

The experimental set was constituted by seven 1-L Pyrex containers, hermetically sealed and mechanically agitated, submerged in a temperature-

TABLE 1
Physical Properties of Amberlite IR-120

Standard ionic form	Na^+
Shape	Spherical particles
Matrix type	Styrene–DVB
Functional structure	$—SO_3^+$
Density	0.717 g/cm³ (wet)
Effective size	0.47–0.62 mm
Moisture content	44–48%
Operating pH range	0–14
Maximum operating temperature	120°C
Uniformity coefficient	1.8 maximum
Total exchange capacity	5.05 meq/g dry

controlled thermostatic bath (*20*). The temperature was kept constant with maximum deviations of 0.5 K.

The analyses of the ionic solutions were done by titration (H^+), complexometry (Ca^{2+}, Mg^{2+}), and isotachophoresis (K^+, Na^+, Ca^{2+}, Mg^{2+}). The resin phase composition was determined by mass balance from the initial and equilibrium compositions of the aqueous phase.

All cations in the solutions were simultaneously analyzed in every experiment. Taking into account that the variations of the total cation concentration was always lower than 2%, electrolyte adsorption can be considered to be negligible.

The ion exchanger used was a commercial resin, Amberlite IR-120, supplied by Rohm and Haas, previously used in other ion-exchange studies (*20, 23–25*). The resin was conventionally treated (*23, 26*) in order to obtain normalized conditions of capacity and ionic form. The physical properties of the resin are summarized in Table 1.

The electrolytes used were $CaCl_2 \cdot 2H_2O$ (>99.5%), $MgCl_2 \cdot 6H_2O$ (>99.0%), KCl (>99.5%), NaCl (>99.5%), and $HCl_{aq.}$ (37%, impurities < 0.009%), purchased from Merck. The water used was conventionally treated in our laboratories (conductivity less than 1 μS/cm).

RESULTS AND DISCUSSION

Predictions of Ternary Systems

Calculation of the composition of one of the phases at a chosen composition of the other phase for real ternary systems is achieved by solving the following system of equations:

$$K_{AB}(T) = \frac{[\bar{x}_B \cdot \bar{\gamma}_B]^\alpha [(1 - x_B) \cdot C_T \cdot \gamma_{ACl_\alpha}^{(\alpha+1)}]^\beta}{[(1 - \bar{x}_B) \cdot \bar{\gamma}_A]^\beta [x_B \cdot C_T \cdot \gamma_{BCl_\beta}^{(\beta+1)}]^\alpha}$$

$$K_{AC}(T) = \frac{[\bar{x}_C \cdot \bar{\gamma}_C]^{\alpha}[(1 - x_C)\cdot C_T \cdot \gamma_{ACl_{\alpha}}^{(\alpha+1)}]^{\delta}}{[(1 - \bar{x}_C)\cdot \bar{\gamma}_A]^{\delta}[x_C \cdot C_T \cdot \gamma_{CCl_{\delta}}^{(\delta+1)}]^{\alpha}} \quad (1)$$

$$\bar{x}_A + \bar{x}_B + \bar{x}_C = 1$$

where $K_{AB}(T)$ and $K_{AC}(T)$ are the thermodynamic equilibrium constants for two independent binary reactions at temperature T.

Among the different models available in the literature for the characterization of the binary system equilibria, a model based on the mass action law, chosen in a previous paper (*20*), has been applied. The model is basically constituted by the equations summarized in Table 2.

The equilibrium constants and the Wilson parameters were reported in a previous paper (*27*). These values are summarized in Table 3, along with the average deviations of the solid composition between the experimental and the calculated data.

For the five ternary systems investigated, the three binary thermodynamic equilibrium constants are related as summarized in Table 4. It can be seen that the triangle rule for the equilibrium constants is obeyed to within less than 20% over the temperature range investigated.

The activity coefficients in the liquid phase may be calculated easily be using the Meissner and Kusik method (*28*) for a chosen set of compositions, total normality in the liquid phase, and the temperature and pressure of the system:

$$\log \gamma_{ACl_\alpha} = \frac{\alpha \cdot 1}{2}\left[\frac{(Y_{Cl} + X_A)}{\alpha \cdot 1}\log \gamma^{\circ}_{ACl_\alpha} + \frac{X_B}{\beta \cdot 1}\log \gamma^{\circ}_{BCl_\beta} + \frac{X_C}{\delta \cdot 1}\log \gamma^{\circ}_{CCl_\delta}\right]$$

$$\log \gamma_{BCl_\beta} = \frac{\beta \cdot 1}{2}\left[\frac{X_A}{\alpha \cdot 1}\log \gamma^{\circ}_{ACl_\alpha} + \frac{(Y_{Cl} + X_B)}{\beta \cdot 1}\log \gamma^{\circ}_{BCl_\beta} + \frac{X_C}{\delta \cdot 1}\log \gamma^{\circ}_{CCl_\delta}\right]$$

$$\log \gamma_{CCl_\delta} = \frac{\delta \cdot 1}{2}\left[\frac{X_A}{\alpha \cdot 1}\log \gamma^{\circ}_{ACl_\alpha} + \frac{X_B}{\beta \cdot 1}\log \gamma^{\circ}_{BCl_\beta} + \frac{(Y_{Cl} + X_C)}{\delta \cdot 1}\log \gamma^{\circ}_{CCl_\delta}\right]$$

$$(2)$$

where A, B, and C are the three cations of the ternary system and α, β, and δ are their respective valences.

The ionic strength fraction (X) of each cation can be expressed as follows:

$$X_A = \frac{m_A\alpha^2}{m_A\alpha^2 + m_B\beta^2 + m_C\delta^2}$$

TABLE 2
Model Equations for Characterization of Binary Systems

$$\boxed{\beta(\mathrm{R}_\alpha \mathrm{A}) + \alpha \mathrm{B}^{\beta+} \rightleftarrows \alpha(\mathrm{R}_\beta \mathrm{B}) + \beta \mathrm{A}^{\alpha+}}$$

Equilibrium constant:

$$K_{\mathrm{AB}}(T) = \frac{[\bar{x}_{\mathrm{B}} \cdot \bar{\gamma}_{\mathrm{B}}]^{\alpha}[(1 - x_{\mathrm{B}}) \cdot C_T \cdot \gamma_{\mathrm{ACl}_\alpha}^{(\alpha+1)}]^{\beta}}{[(1 - \bar{x}_{\mathrm{B}}) \cdot \bar{\gamma}_{\mathrm{A}}]^{\beta}[x_{\mathrm{B}} \cdot C_T \cdot \gamma_{\mathrm{BCl}_\beta}^{(\beta+1)}]^{\alpha}}$$

Activity coefficients in the solution phase:

$$\log \gamma_{\mathrm{ACl}_\alpha} = \frac{\alpha \cdot 1}{2}\left[\frac{\log \gamma^{\circ}_{\mathrm{ACl}_\alpha}}{\alpha \cdot 1}(1 + X_{\mathrm{A}}) + \frac{X_{\mathrm{B}}}{\beta \cdot 1} \log \gamma^{\circ}_{\mathrm{BCl}_\beta}\right]$$

$$\log \gamma_{\mathrm{BCl}_\beta} = \frac{\beta \cdot 1}{2}\left[\frac{\log \gamma^{\circ}_{\mathrm{BCl}_\beta}}{\beta \cdot 1}(1 + X_{\mathrm{B}}) + \frac{X_{\mathrm{A}}}{\alpha \cdot 1} \log \gamma^{\circ}_{\mathrm{ACl}_\alpha}\right]$$

$$X_{\mathrm{A}} = \frac{m_{\mathrm{A}} \cdot \alpha^2}{m_{\mathrm{A}} \cdot \alpha^2 + m_{\mathrm{B}} \cdot \beta^2}; \qquad x_{\mathrm{B}} = \frac{m_{\mathrm{B}} \cdot \beta^2}{m_{\mathrm{A}} \cdot \alpha^2 + m_{\mathrm{B}} \cdot \beta^2}$$

$$\log \gamma^{\circ}_{\mathrm{ACl}_\alpha} = -\mathrm{A} \cdot \alpha \cdot \mu^{0.5}/(1 + d \cdot \mathrm{B} \cdot \mu^{0.5}) - (1/2.303 \cdot v)k \cdot h_e^{*}(a_b - 1.0)$$

$$- \log [1 + 0.018 \cdot (v - k \cdot h_e^{*} \cdot a_b) \cdot m_{\mathrm{ACl}_\alpha}]$$

$$\log \gamma^{\circ}_{\mathrm{BCl}_\beta} = -\mathrm{A} \cdot \beta \cdot \mu^{0.5}/(1 + d \cdot \mathrm{B} \cdot \mu^{0.5}) - (1/2.303 \cdot v)k \cdot h_e^{*}(a_b - 1.0)$$

$$- \log [1 + 0.018 \cdot (v - k \cdot h_e^{*} \cdot a_b) \cdot m_{\mathrm{BCl}_\beta}]$$

Activity coefficients in the resin phase:

$$\ln \bar{\gamma}_{\mathrm{A}} = 1 - \ln(\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}}) - \frac{\bar{x}_{\mathrm{A}}}{\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}}} - \frac{\bar{x}_{\mathrm{B}}\Lambda_{\mathrm{BA}}}{\bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}}}$$

$$\ln \bar{\gamma}_{\mathrm{B}} = 1 - \ln(\bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}}) - \frac{\bar{x}_{\mathrm{B}}}{\bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}}} - \frac{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{AB}}}{\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}}}$$

$$T(1 - \ln \Lambda_{\mathrm{AB}} - \Lambda_{\mathrm{BA}}) \approx C^{\mathrm{A}}_{\mathrm{AB}}$$

$$T(1 - \ln \Lambda_{\mathrm{BA}} - \Lambda_{\mathrm{AB}}) \approx C^{\mathrm{B}}_{\mathrm{AB}}$$

Standard thermodynamic properties:

$$\Delta G^{\circ}_{\mathrm{AB}} = -\frac{R \cdot T}{\alpha \cdot \beta} \ln K_{\mathrm{AB}}$$

$$\Delta H^{\circ}_{\mathrm{AB}} = \frac{R \cdot T^2}{\alpha \cdot \beta} \frac{d(\ln K_{\mathrm{AB}})}{dT}$$

$$\Delta S^{\circ}_{\mathrm{AB}} = \frac{\Delta H^{\circ}_{\mathrm{AB}} - \Delta G^{\circ}_{\mathrm{AB}}}{T}$$

TABLE 3
Equilibrum Constants and Wilson Parameters Determined from Binary Experimental Data

A/B	K_{AB} (N)	Λ_{BA}	Λ_{AB}	T (K)	$\bar{\epsilon}$ (%)
H^+/Na^+	1.760	1	1	283	7.3
	1.674	1	1	303	
	1.510	1	1	323	
H^+/K^+	2.810	2.274	0.542	283	4.2
	2.360	2.301	0.489	303	
	2.060	2.439	0.411	323	
Na^+/K^+	1.553	1.947	0.578	283	5.9
	1.394	1.972	0.549	303	
	1.154	2.078	0.483	323	
Mg^{2+}/Ca^{2+}	2.537	0.742	1.104	283	4.1
	2.643	0.747	1.108	303	
	2.740	0.752	1.115	323	
H^+/Mg^{2+}	8.757	0.486	1.811	283	7.5
	10.188	0.502	1.773	303	
	11.634	0.516	1.741	323	
H^+/Ca^{2+}	25.70	0.785	0.728	283	6.2
	29.04	0.800	0.742	303	
	31.32	0.813	0.756	323	
Na^+/Mg^{2+}	3.468	0.120	1.900	283	6.5
	4.022	0.128	1.912	303	
	4.583	0.136	1.922	323	
Na^+/Ca^{2+}	9.121	1.070	0.796	283	2.6
	10.866	1.075	0.800	303	
	12.200	1.079	0.805	323	
K^+/Mg^{2+}	1.250	0.743	1.751	283	5.1
	2.256	0.730	1.738	303	
	2.530	0.718	1.728	323	
K^+/Ca^{2+}	3.860	0.192	1.900	283	7.9
	5.810	0.200	1.906	303	
	8.310	0.209	1.906	323	

TABLE 4
Triangle Rule for Equilibrium Constants

System	283 K	303 K	323 K
$K_{\mathrm{NaCa}} \cdot K^2_{\mathrm{HNa}} \cdot K_{\mathrm{CaH}} = 1$	1.10	1.05	0.89
$K_{\mathrm{KCa}} \cdot K^2_{\mathrm{HK}} \cdot K_{\mathrm{CaH}} = 1$	1.19	1.11	1.12
$K_{\mathrm{NaK}} \cdot K_{\mathrm{HNa}} \cdot K_{\mathrm{KH}} = 1$	0.97	0.99	0.85
$K_{\mathrm{KCa}} \cdot K^2_{\mathrm{NaK}} \cdot K_{\mathrm{CaNa}} = 1$	1.02	1.04	0.91
$K_{\mathrm{HMg}} \cdot K_{\mathrm{MgCa}} \cdot K_{\mathrm{CaH}} = 1$	0.88	0.93	1.02

$$X_{\mathrm{B}} = \frac{m_{\mathrm{B}}\beta^2}{m_{\mathrm{A}}\alpha^2 + m_{\mathrm{B}}\beta^2 + m_{\mathrm{C}}\delta^2}$$

$$X_{\mathrm{C}} = \frac{m_{\mathrm{C}}\delta^2}{m_{\mathrm{A}}\alpha^2 + m_{\mathrm{B}}\beta^2 + m_{\mathrm{C}}\delta^2} \tag{3}$$

where m_{A}, m_{B}, and m_{C} are the molalities of each cation in the ternary system.

The activity coefficients of each pure salt in the solution, γ°_{ij}, at the same total ionic strength as the mixture are estimated by the Nesbitt correlation in the same way as for binary systems (*27, 29*).

The activity coefficients in the solid phase are estimated by using the Wilson equation with two adjustable parameters obtained by characterization of binary systems (Table 3).

$$\ln \bar{\gamma}_A = 1 - \ln (\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{AC}}) - \left[\frac{\bar{x}_{\mathrm{A}}}{\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{AC}}} + \frac{\bar{x}_{\mathrm{B}}\Lambda_{\mathrm{BA}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}} + \bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{BC}}} + \frac{\bar{x}_{\mathrm{C}}\Lambda_{\mathrm{CA}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{CA}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{CB}} + \bar{x}_{\mathrm{C}}}\right]$$

$$\ln \bar{\gamma}_{\mathrm{B}} = 1 - \ln (\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}} + \bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{BC}}) - \left[\frac{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{AB}}}{\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{AC}}} + \frac{\bar{x}_{\mathrm{B}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}} + \bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{BC}}} + \frac{\bar{x}_{\mathrm{C}}\Lambda_{\mathrm{CB}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{CA}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{CB}} + \bar{x}_{\mathrm{C}}}\right]$$

$$\ln \bar{\gamma}_C = 1 - \ln(\bar{x}_A\Lambda_{CA} + \bar{x}_B\Lambda_{CB} + \bar{x}_C) - \left[\frac{\bar{x}_A\Lambda_{AC}}{\bar{x}_A + \bar{x}_B\Lambda_{AB} + \bar{x}_C\Lambda_{AC}} + \frac{\bar{x}_B\Lambda_{BC}}{\bar{x}_A\Lambda_{BA} + \bar{x}_B + \bar{x}_C\Lambda_{BC}} + \frac{\bar{x}_C}{\bar{x}_A\Lambda_{CA} + \bar{x}_B\Lambda_{CB} + \bar{x}_C}\right] \quad (4)$$

where Λ_{ij} and Λ_{ji} are the Wilson parameters at each temperature.

Since the three equilibrium constants and all the required activity coefficients in both phases are known, the model equations may be solved to yield the unknown phase composition at each temperature, pressure, and total normality of the liquid phase.

Figures 1 to 7 show predicted and experimental compositions (equivalent ionic fraction) in the resin phase for several ternary systems studied. These figures show good agreement between the model predictions and the experimental data over the entire range of liquid phase normalities and temperatures. Deviations higher than 10% are related to equivalent ionic

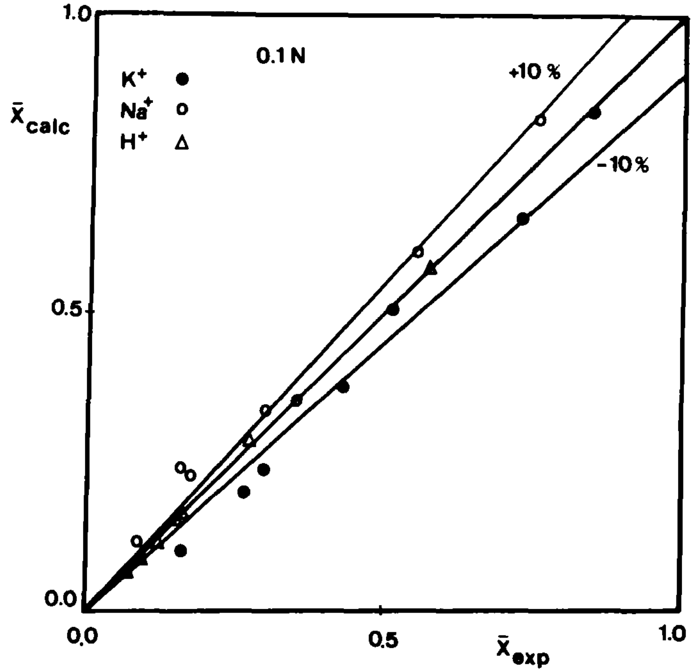

FIG. 1. Comparison of predicted and experimental compositions in the resin phase for the ternary system K^+-Na^+-H^+ at $C_T = 0.1\ N$ and $T = 323$ K.

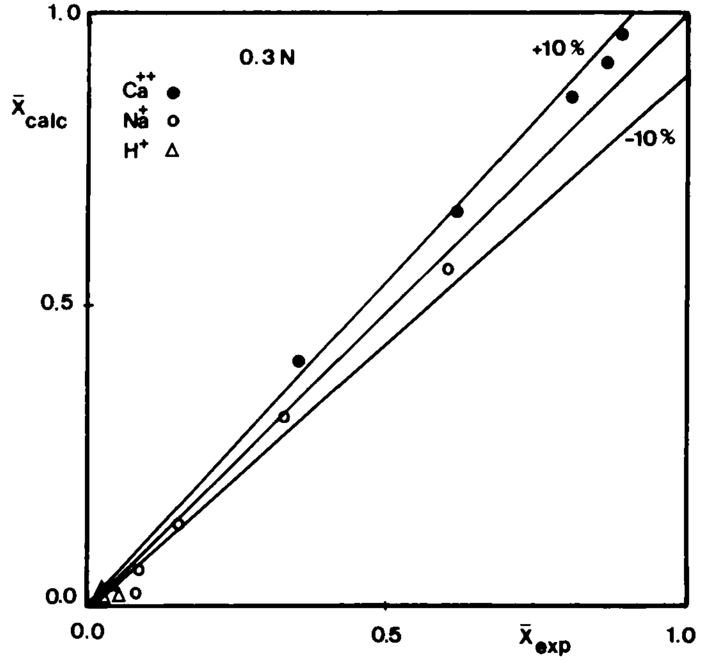

FIG. 2. Comparison of predicted and experimental compositions in the resin phase for the ternary system Ca^{2+}–Na^{+}–H^{+} at $C_T = 0.3$ N and $T = 303$ K.

fractions lower than 0.1. Since the experimental resin composition is determined by material balance, higher deviations can be expected at low concentrations due to experimental data scatter.

As an example, Fig. 8 shows the agreement between the experimental data and the predicted contour lines for the ternary system constituted by calcium and magnesium chlorides and hydrochloric acid at constant x_{Ca}/x_{Mg} ratios and 0.5 N total ionic concentration.

Prediction of a Quaternary System

Similarly to ternary systems, calculation for one of the phases at a chosen composition of the other phase for real systems is achieved by solving the following system of equations:

$$K_{AB}(T) = \frac{[\bar{x}_B \cdot \bar{\gamma}_B]^{\alpha}[(1 - x_B) \cdot C_T \cdot \gamma_{ACl_\alpha}^{(\alpha+1)}]^{\beta}}{[(1 - \bar{x}_B) \cdot \bar{\gamma}_A]^{\beta}[x_B \cdot C_T \cdot \gamma_{BCl_\beta}^{(\beta+1)}]^{\alpha}}$$

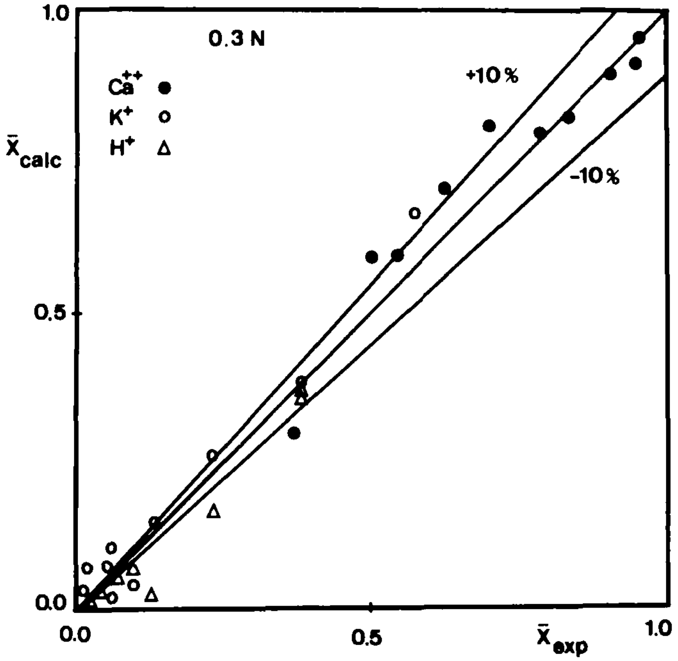

FIG. 3. Comparison of predicted and experimental compositions in the resin phase for the ternary system Ca^{2+}-K^+-H^+ at C_T = 0.3 N and T = 303 K.

$$K_{AC}(T) = \frac{[\bar{x}_C \cdot \bar{\gamma}_C]^{\alpha}[(1 - x_C) \cdot C_T \cdot \gamma_{ACl_\alpha}^{(\alpha+1)}]^{\delta}}{[(1 - \bar{x}_C) \cdot \bar{\gamma}_A]^{\delta}[x_C \cdot C_T \cdot \gamma_{CCl_\delta}^{(\delta+1)}]^{\alpha}}$$

$$K_{AD}(T) = \frac{[\bar{x}_D \cdot \bar{\gamma}_D]^{\alpha}[(1 - x_D) \cdot C_T \cdot \gamma_{ACl_\alpha}^{(\alpha+1)}]^{\epsilon}}{[(1 - \bar{x}_D) \cdot \bar{\gamma}_A]^{\epsilon}[x_D \cdot C_T \cdot \gamma_{DCl_\epsilon}^{(\epsilon+1)}]^{\alpha}}$$

$$\bar{x}_A + \bar{x}_B + \bar{x}_C + \bar{x}_D = 1 \qquad (5)$$

where $K_{AB}(T)$, $K_{AC}(T)$, and $K_{AD}(T)$ are the thermodynamic equilibrium constants for three independent binary reactions at temperture T. The fourth ionic exchange reaction is related to the others, and its equilibrium constant may be obtained by the triangle rule.

The activity coefficients in the liquid phase can be calculated by using the Meissner and Kusik method (*28*) for a chosen set of composition and

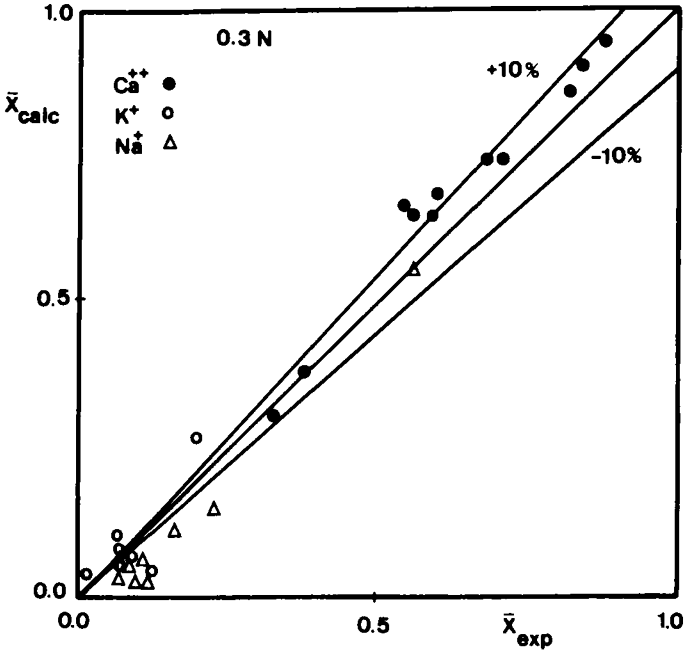

FIG. 4. Comparison of predicted and experimental compositions in the resin phase for the ternary system Ca^{2+}–K^+–Na^+ at $C_T = 0.3\ N$ and $T = 303$ K.

total normality in the liquid phase, temperature, and pressure of the system:

$$\log \gamma_{ACl_\alpha} = \frac{\alpha \cdot 1}{2}$$

$$\times \left[\frac{(Y_{Cl} + X_A)}{\alpha \cdot 1} \log \gamma^\circ_{ACl_\alpha} + \frac{X_B}{\beta \cdot 1} \log \gamma^\circ_{BCl_\beta} + \frac{X_C}{\delta \cdot 1} \log \gamma^\circ_{CCl_\delta} + \frac{X_D}{\epsilon \cdot 1} \log \gamma^\circ_{DCl_\epsilon} \right]$$

$$\log \gamma_{BCl_\beta} = \frac{\beta \cdot 1}{2}$$

$$\times \left[\frac{X_A}{\alpha \cdot 1} \log \gamma^\circ_{ACl_\alpha} + \frac{(Y_{Cl} + X_B)}{\beta \cdot 1} \log \gamma^\circ_{BCl_\beta} + \frac{X_C}{\delta \cdot 1} \log \gamma^\circ_{CCl_\delta} + \frac{X_D}{\epsilon \cdot 1} \log \gamma^\circ_{DCl_\epsilon} \right]$$

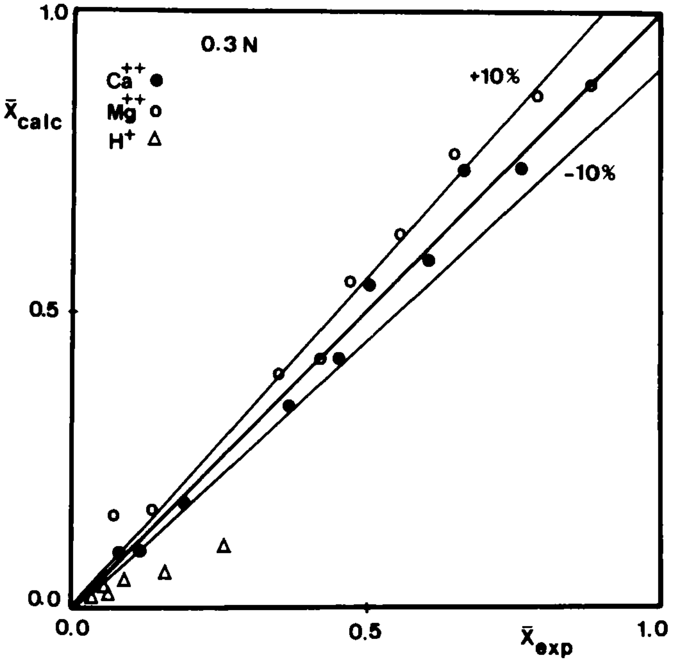

FIG. 5. Comparison of predicted and experimental compositions in the resin phase for the ternary system Ca^{2+}–Mg^{2+}–H^+ at $C_T = 0.3\ N$ and $T = 303$ K.

$$\log \gamma_{CCl_\delta} = \frac{\delta \cdot 1}{2}$$

$$\times \left[\frac{X_A}{\alpha \cdot 1} \log \gamma^\circ_{ACl_\alpha} + \frac{X_B}{\beta \cdot 1} \log \gamma^\circ_{BCl_\beta} + \frac{(Y_{Cl} + X_C)}{\delta \cdot 1} \log \gamma^\circ_{CCl_\delta} + \frac{X_D}{\epsilon \cdot 1} \log \gamma^\circ_{DCl_\epsilon} \right]$$

$$\log \gamma_{DCl_\epsilon} = \frac{\epsilon \cdot 1}{2}$$

$$\times \left[\frac{X_A}{\alpha \cdot 1} \log \gamma^\circ_{ACl_\alpha} + \frac{X_B}{\beta \cdot 1} \log \gamma^\circ_{BCl_\beta} + \frac{X_C}{\delta \cdot 1} \log \gamma^\circ_{CCl_\delta} + \frac{(Y_{Cl} + X_D)}{\epsilon \cdot 1} \log \gamma^\circ_{DCl_\epsilon} \right] \qquad (6)$$

where A, B, C, and D are the four cations of the quaternary system and α, β, δ, and ε are their respective valences.

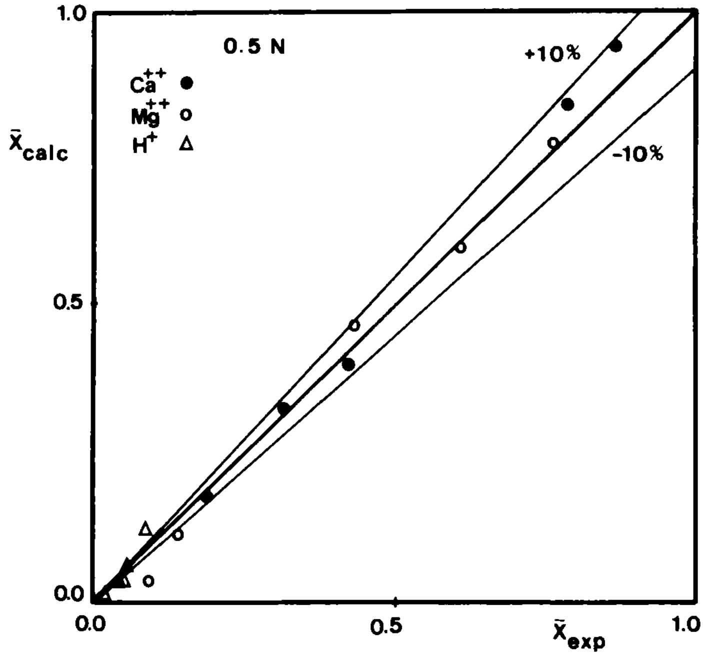

FIG. 6. Comparison of predicted and experimental compositions in the resin phase for the ternary system Ca^{2+}–Mg^{2+}–H^+ at C_T = 0.5 N and T = 283 K.

The ionic strength fraction (X) of each cation can be expressed as follows:

$$X_A = \frac{m_A\alpha^2}{m_A\alpha^2 + m_B\beta^2 + m_C\delta^2 + m_D\epsilon^2}$$

$$X_B = \frac{m_B\beta^2}{m_A\alpha^2 + m_B\beta^2 + m_C\delta^2 + m_D\epsilon^2}$$

$$X_C = \frac{m_C\delta^2}{m_A\alpha^2 + m_B\beta^2 + m_C\delta^2 + m_D\epsilon^2}$$

$$X_D = \frac{m_D\epsilon^2}{m_A\alpha^2 + m_B\beta^2 + m_C\delta^2 + m_D\epsilon^2} \qquad (7)$$

where m_A, m_B, m_C, and m_D are the molalities of each cation in the quaternary system.

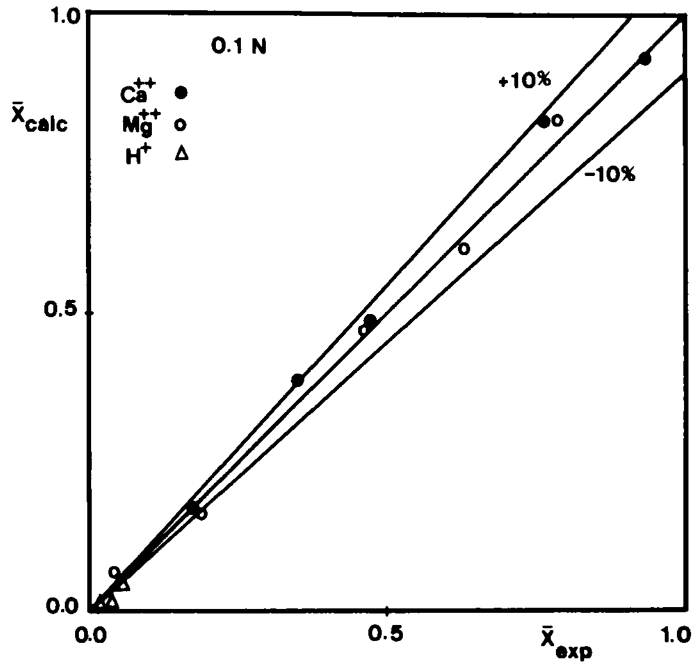

FIG. 7. Comparison of predicted and experimental compositions in the resin phase for the ternary system Ca^{2+}–Mg^{2+}–H^+ at $C_T = 0.1$ N and $T = 323$ K.

The activity coefficients of each pure salt in the solution, γ_{ij}°, at the same total ionic strength as the mixture are estimated by the Nesbitt correlation in the same way as for binary systems (*27, 29*).

The activity coefficients in the solid phase may be estimated by using the Wilson equation with two adjustable parameters obtained by nonlinear regression of experimental binary data (Table 3).

$$\ln \bar{\gamma}_A = 1 - \ln(\bar{x}_A + \bar{x}_B\Lambda_{AB} + \bar{x}_C\Lambda_{AC} + \bar{x}_D\Lambda_{AD})$$

$$- \left[\frac{\bar{x}_A}{\bar{x}_A + \bar{x}_B\Lambda_{AB} + \bar{x}_C\Lambda_{AC} + \bar{x}_D\Lambda_{AD}} + \frac{\bar{x}_B\Lambda_{BA}}{\bar{x}_A\Lambda_{BA} + \bar{x}_B + \bar{x}_C\Lambda_{BC} + \bar{x}_D\Lambda_{BD}}\right.$$

$$\left. + \frac{\bar{x}_C\Lambda_{CA}}{\bar{x}_A\Lambda_{CA} + \bar{x}_B\Lambda_{CB} + \bar{x}_C + \bar{x}_D\Lambda_{CD}} + \frac{\bar{x}_D\Lambda_{DA}}{\bar{x}_A\Lambda_{DA} + \bar{x}_B\Lambda_{DB} + \bar{x}_C\Lambda_{DC} + \bar{x}_D}\right]$$

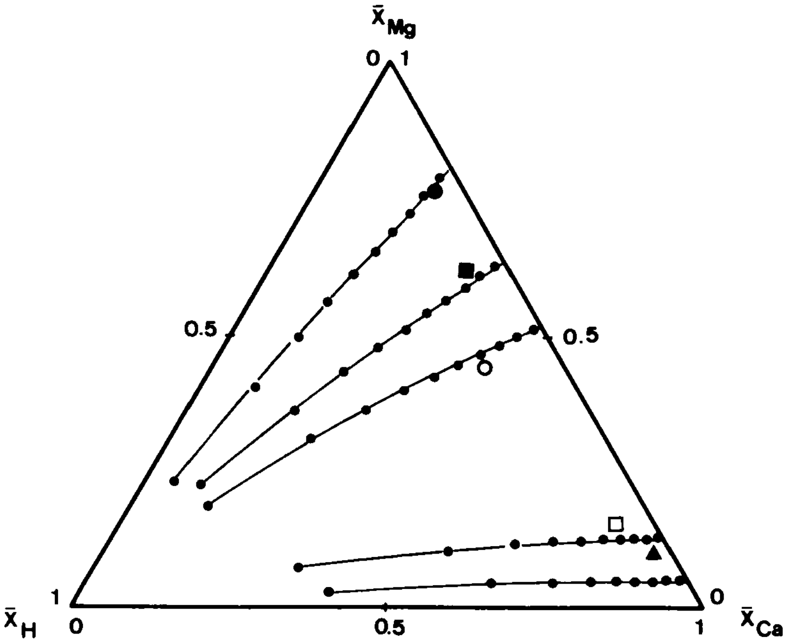

FIG. 8. Experimental data and predicted contour lines for the ternary system Ca^{2+}–Mg^{2+}–H^+ at $C_T = 0.5$ N and $T = 283$ K with constant x_{Ca}/x_{Mg} ratios. The symbols identify experimental data.

$$\ln \bar{\gamma}_B = 1 - \ln (\bar{x}_A\Lambda_{BA} + \bar{x}_B + \bar{x}_C\Lambda_{BC} + \bar{x}_D\Lambda_{BD}) - \left[\frac{\bar{x}_A\Lambda_{AB}}{\bar{x}_A + \bar{x}_B\Lambda_{AB} + \bar{x}_C\Lambda_{AC} + \bar{x}_D\Lambda_{AD}} + \frac{\bar{x}_B}{\bar{x}_A\Lambda_{BA} + \bar{x}_B + \bar{x}_C\Lambda_{BC} + \bar{x}_D\Lambda_{BD}} + \frac{\bar{x}_C\Lambda_{CB}}{\bar{x}_A\Lambda_{CA} + \bar{x}_B\Lambda_{CB} + \bar{x}_C + \bar{x}_D\Lambda_{CD}} + \frac{\bar{x}_D\Lambda_{DB}}{\bar{x}_A\Lambda_{DA} + \bar{x}_B\Lambda_{DB} + \bar{x}_C\Lambda_{DC} + \bar{x}_D}\right]$$

$$\ln \bar{\gamma}_C = 1 - \ln (\bar{x}_A\Lambda_{CA} + \bar{x}_B\Lambda_{CB} + \bar{x}_C + \bar{x}_D\Lambda_{CD}) - \left[\frac{\bar{x}_A\Lambda_{AC}}{\bar{x}_A + \bar{x}_B\Lambda_{AB} + \bar{x}_C\Lambda_{AC} + \bar{x}_D\Lambda_{AD}} + \frac{\bar{x}_B\Lambda_{BC}}{\bar{x}_A\Lambda_{BA} + \bar{x}_B + \bar{x}_C\Lambda_{BC} + \bar{x}_D\Lambda_{BD}} + \frac{\bar{x}_C}{\bar{x}_A\Lambda_{CA} + \bar{x}_B\Lambda_{CB} + \bar{x}_C + \bar{x}_D\Lambda_{CD}} + \frac{\bar{x}_D\Lambda_{DC}}{\bar{x}_A\Lambda_{DA} + \bar{x}_B\Lambda_{DB} + \bar{x}_C\Lambda_{DC} + \bar{x}_D}\right]$$

TABLE 5
Comparison between Calculated and Experimental Compositions of Each Cation in the Resin Phase at $C_T = 0.3\ N$ and $T = 303\ K$ on Amberlite IR-120

x(Ca)	x(K)	x(Na)	x(H)	$\bar{x}_{exp}$(Ca)	$\bar{x}_{cal}$(Ca)	$\bar{x}_{exp}$(K)	$\bar{x}_{cal}$(K)	$\bar{x}_{exp}$(Na)	$\bar{x}_{cal}$(Na)	$\bar{x}_{exp}$(H)	$\bar{x}_{cal}$(H)
0.053	0.291	0.342	0.313	0.390	0.386	0.289	0.262	0.181	0.232	0.138	0.118
0.232	0.258	0.249	0.259	0.650	0.644	0.161	0.130	0.146	0.102	0.041	0.102
0.451	0.187	0.184	0.176	0.757	0.772	0.104	0.071	0.091	0.051	0.047	0.103
0.674	0.109	0.113	0.103	0.861	0.835	0.067	0.034	0.033	0.025	0.036	0.104
0.558	0.174	0.169	0.097	0.829	0.809	0.064	0.060	0.057	0.026	0.048	0.104
0.052	0.442	0.098	0.406	0.368	0.354	0.362	0.401	0.108	0.072	0.160	0.171
0.244	0.342	0.103	0.310	0.677	0.720	0.183	0.175	0.087	0.041	0.052	0.062
0.451	0.225	0.107	0.216	0.779	0.795	0.112	0.084	0.061	0.063	0.046	0.057
0.050	0.105	0.738	0.105	0.392	0.376	0.110	0.101	0.448	0.482	0.048	0.039
0.090	0.159	0.645	0.104	0.505	0.489	0.140	0.123	0.311	0.355	0.042	0.031
0.055	0.109	0.410	0.423	0.439	0.451	0.107	0.107	0.287	0.281	0.164	0.160
0.229	0.096	0.354	0.319	0.685	0.722	0.116	0.051	0.107	0.126	0.089	0.099
0.444	0.110	0.229	0.215	0.793	0.793	0.076	0.042	0.083	0.063	0.047	0.100
0.049	0.774	0.075	0.099	0.331	0.297	0.454	0.601	0.169	0.057	0.044	0.043
0.092	0.658	0.147	0.101	0.447	0.446	0.372	0.434	0.142	0.087	0.038	0.032
0.082	0.403	0.404	0.108	0.458	0.440	0.311	0.293	0.189	0.231	0.040	0.034
0.223	0.217	0.456	0.102	0.750	0.791	0.132	0.114	0.072	0.042	0.043	0.051
0.334	0.222	0.336	0.106	0.733	0.774	0.148	0.096	0.090	0.111	0.027	0.017
0.052	0.109	0.104	0.732	0.455	0.493	0.119	0.118	0.113	0.081	0.312	0.306
0.091	0.109	0.180	0.619	0.560	0.597	0.123	0.092	0.080	0.110	0.236	0.198

$$\ln \bar{\gamma}_{\mathrm{D}} = 1 - \ln(\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{DA}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{DB}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{DC}} + \bar{x}_{\mathrm{D}}) - \left[\frac{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{AD}}}{\bar{x}_{\mathrm{A}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{AB}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{AC}} + \bar{x}_{\mathrm{D}}\Lambda_{\mathrm{AD}}} + \frac{\bar{x}_{\mathrm{B}}\Lambda_{\mathrm{BD}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{BA}} + \bar{x}_{\mathrm{B}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{BC}} + \bar{x}_{\mathrm{D}}\Lambda_{\mathrm{BD}}} + \frac{\bar{x}_{\mathrm{C}}\Lambda_{\mathrm{CB}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{CA}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{CB}} + \bar{x}_{\mathrm{C}} + \bar{x}_{\mathrm{D}}\Lambda_{\mathrm{CD}}} + \frac{\bar{x}_{\mathrm{D}}}{\bar{x}_{\mathrm{A}}\Lambda_{\mathrm{DA}} + \bar{x}_{\mathrm{B}}\Lambda_{\mathrm{DB}} + \bar{x}_{\mathrm{C}}\Lambda_{\mathrm{DC}} + \bar{x}_{\mathrm{D}}}\right] \tag{8}$$

Since the four equilibrium constants and all the required activity coefficients in both phases are known, the model equations may be solved to yield the unknown phase composition at each temperature, pressure, and total normality of the liquid phase.

Table 5 presents the calculated and experimental compositions of each cation in the resin phase for the Ca^{2+}–K^{+}–Na^{+}–H^{+} exchange in a chloride solution on Amberlite IR-120 at $C_T = 0.3$ N and $T = 303$ K. The predicted and experimental compositions (equivalent ionic fraction) in the resin phase are in good agreement for the investigated quaternary system. Deviations higher than 10% are related to equivalent ionic fractions lower than 0.1, where higher experimental errors are expected.

The above results confirm the validity of binary Wilson parameters and equilibrium constants deduced from binary systems, and the method proposed to predict the equilibrium behavior of multicomponent ion-exchange systems.

GLOSSARY

A	ionic species in solution
A	Debye–Hückel parameter
a_b	activity of water
B	ionic species in solution
B	Debye–Hückel parameter
C	ionic species in solution
C_T	total concentration in the liquid phase
C'_{AB}	constants of Gilliland's relation
D	ionic species in solution
d	equivalent diameter of ions contained in a salt
$\Delta G^{\circ}_{\mathrm{AB}}$	standard Gibbs free-enthalpy change
$\Delta H^{\circ}_{\mathrm{AB}}$	standard enthalpy change
$k \cdot h_e^*$	number of coordination ions contained in a salt
m_i	molality of ion i

m_{ij}	molality of salt *ij*
R^-	resinate
ΔS°_{AB}	standard entropy change
T	absolute temperature
v	number of ions formed by dissociation of an electrolyte
X_i	ionic strength fraction of cation *i* referred to the total ionic strength of cationic species
x_i	equivalent ionic fraction of ion *i* in the liquid phase
$\bar{x}_i$	equivalent ionic fraction of ion *i* in the solid phase
Y_j	ionic strength fraction of anion *j* referred to the total ionic strength of anionic species

Greek Letters

α	valence of ion A
α_{ij}	stoichiometric coefficient of salt *ij* in the liquid phase
$\bar{\alpha}_{ij}$	stoichiometric coefficient of salt *ij* in the solid phase
β	valence of ion B
γ_i	liquid phase activity coefficient of ion *i*
$\bar{\gamma}_i$	solid phase activity coefficient of ion *i*
γ°_{ij}	pure salt activity coefficient in the liquid phase for the same total ionic strength as the binary mixture
γ_{ij}	salt activity coefficient in the liquid phase
δ	valence of ion C
ϵ	valence of ion D
Λ_{ij}	Wilson binary interaction parameters
μ	ionic strength

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Received by editor March 13, 1991