J. Chem. Eng. Data **2010,** *55,* 1333–1341

Ion Exchange Equilibrium Prediction for the System $Cu^{2+}-Zn^{2+}-Na^{+}$

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In this work, ion exchange experimental data were obtained in batch operation for the binary systems $Cu^{2+}-Na^{+}$, $Zn^{2+}-Na^{+}$, and $Zn^{2+}-Cu^{2+}$ and for the ternary system $Cu^{2+}-Zn^{2+}-Na^{+}$. The ionic exchanger employed was the cationic resin Amberlite IR 120. The experimental data for the binary systems and the ternary system were obtained at total concentrations of (1, 3, and 5) $mEq \cdot L^{-1}$. The total exchange capacity of the Amberlite IR 120 resin was obtained by the column technique. All experiments were carried out at 25 °C. To model the ion exchange equilibrium, the Mass Action Law was used. The model considered both ideal and nonideal behavior to represent the experimental data. The nonideality in the solution phase and in the resin phase was described by Bromley's model and by Wilson's model. Wilson's model interaction parameters and the thermodynamic equilibrium constants were obtained from the experimental data for each binary system, from which ternary system ion exchange equilibrium was predicted. On the basis of the results obtained to represent the ion exchange equilibrium for the binary systems, a prediction was made using only the nonideal Mass Action Law. Good agreement was obtained between the calculated and measured values of the resin phase composition.

1. Introduction

The industrial treatment of wastewaters with low concentrations of heavy metals constitutes a major problem. An ordinary process to remove these heavy metals is by ion exchange.[1]

The equipment design to treat wastewaters by ion exchange demands the exact representation of the equilibrium either for one component or for multicomponent systems.[2,3] According to some investigators,[3,4] the major point preceding an ion exchange industrial operation is a detailed assessment of the equilibrium composition between the solution phase and the resin phase.

Mathematical modeling by means of the Mass Action Law is a powerful tool to evaluate the equilibrium composition of ionic species among phases. This mathematical approach enables one to predict the multicomponent ion exchange equilibrium, i.e., during modeling, starting with the Mass Action Law, and the experimental data obtained for the pairs of components present in a multicomponent system are used to determine the model parameters. Therefore, whenever a system involves the exchange of three ions A−B−C among the phases, it can be described from the information regarding estimates from the binary systems A−B, A−C, and B−C in equilibrium. In this case, the model parameters for the binary systems, which include the equilibrium constant for each pair of components, are independent from any other ionic species present.[5] This method has been successfully used by several authors.[4−7]

The Mass Action Law is based on the chemical equilibrium constant definition for the ion exchange reaction in which the stoichiometric coefficients are the charges of the species involved in the exchange.

The thermodynamic equilibrium constant is expressed as a function of activities due to the nonideal behavior present both in the solution phase and in the resin phase. When the resin phase and the solution phase exhibit ideal behavior, the ionic species activity coefficients are equal to one. Whenever nonideal behavior is present in both phases, the activity coefficients should be determined.

El Prince and Babcock[8] were one of the first to model nonideal equilibrium in both phases. They used Wilson's model for the resin phase. When the parameters of Wilson's model are available for a binary system, they are used to obtain the activity coefficients for a multicomponent system.[9]

Vamos and Haas[10] and Pabalan and Bertetti[11] compared the efficency of Wilson's and Margule's models to estimate the resin phase activity coefficients. They agreed that Wilson's model was slightly better. Several investigators[4−9,12−16] have successfully used Wilson's model to calculate the activity coefficient of the species in the resin phase.

For the solution phase, several models have been used. An overview of these models to calculate electrolyte activity coefficients is given by Zemaitis.[17] The first model to calculate the activity coefficient of an ionic species in solution was proposed by Debye and Hückel.[18] Several authors[4,9,19] have used variants of Debye and Hückel's model, in which empirical parameters have been added. Debye and Hückel's model is limited to dilute solutions with ionic strengths up to 0.1 *m*.[17]

The model proposed by Bromley,[20] according to some investigators,[17,21] is efficient to calculate the activity coefficient of strong electrolytes with ionic strengths up to 6 *m*. Petrus and Warchol[22] used successfully Bromley's model to calculate the activity coefficient in the solution phase for the ionic species Cu^{2+}, Cd^{2+}, Pd^{2+}, and Na^{+}.

One of the most used models to calculate the ionic species activity coefficients in the solution is the one based on the theory of electrolytic solutions developed by Pitzer.[23] Shallcross et al.[13] were among the first to use this model to calculate the activity

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10.1021/je900649e

coefficients of ions in solution to represent the equilibrium of ionic exchange processes by the Mass Action Law. Later, Pitzer's model was used by several authors[5,9,12,14,22] to calculate the activity coefficients in the solution phase.

After the work of El Prince and Babcock,[8] other investigators have used the Mass Action Law to predict the multicomponent ionic exchange equilibrium starting with the experimental data of binary systems of the species making up the mixture.

Smith and Woodburn[4] predicted the ionic exchange equilibrium of the system $SO_4^{2-}-Cl^{-}-NO_3^{-}$. Debye and Hückel's equation and Wilson's model were used to calculate the solution phase activities and the resin phase activities, respectively. Smith and Woodburn proposed the definition of an equilibrium coefficient to obtain, starting with the experimental data for the ionic exchange equilibrium of each binary system ($SO_4^{2-}-Cl^{-}$, $SO_4^{2-}-NO_3^{-}$, $Cl^{-}-NO_3^{-}$), the thermodynamic equilibrium constant (K_{AB}) as well as Wilson's model interaction parameters (Λ_{AB}, Λ_{BA}).

Mehablia et al.[12] modeled the system made up of ions $H^{+}-Na^{+}-K^{+}$. To calculate the activity coefficients in the solution phase and in the resin phase, Pitzer's model and Wilson's model was used, respectively. Wilson's model interaction parameters for each binary system were obtained by fitting the model to the experimental ionic exchange data, while the thermodynamic equilibrium constant was obtained by the approximation suggested by Gaines and Thomas.[24]

Vo and Shalcross[5,9] used, successfully, the model described by Mehablia et al.[12] to predict the equilibrium of ternary and quarternary systems and another one with five components starting with the experimental data for the binary systems.

On the basis of the possibility to predict the multicomponent ion exchange equilibrium condition for several systems, the objective of this work was to assess the capacity of the Mass Action Law to predict the ionic exchange equilibrium condition for the system $Cu^{2+}-Zn^{2+}-Na^{+}$ employing as an ionic exchanger the Amberlite IR 120 resin.

The novelty associated to this work is the acquisition of equilibrium data of ionic exchange of all the constitutive pairs ($Cu^{2+}-Na^{+}$, $Zn^{2+}-Na^{+}$, $Zn^{2+}-Cu^{2+}$) of the ternary system $Cu^{2+}-Zn^{2+}-Na^{+}$. Valverde et al.[25] obtained experimental data for the binary systems $Cu^{2+}-Na^{+}$ and $Zn^{2+}-Na^{+}$ using the Amberlite IR 120 resin but did not obtain equilibrium data for the binary system $Zn^{2+}-Cu^{2+}$ and the ternary system. The prediction of ionic exchange equilibrium of the ternary system $Cu^{2+}-Zn^{2+}-Na^{+}$, through the nonideal Mass Action Law, requires equilibrium data of all constitutive pairs of the ternary system to be known, and therefore the data obtained by Valverde et al.[25] are not enough. In addition, Valverde et al.[25] studied the ionic exchange in the following concentration range: (50 to 100) mEq·L^{-1}. This range is too high since the ionic exchange process for treatment of wastewater is usually applied for diluted systems.

2. Material and Methods

2.1. Chemicals. Only analytical grade (purity above 99 %) chemicals were used. Distilled/deionized water was used for the preparation of any solution. The reactants used were: dehydrated copper(II) chloride, from Vetec, zinc(II) chloride, from Vetec, sodium chloride, from Vetec, hydrochloric acid, from Synth, and hexane, from Synth.

The Amberlite IR 120 cationic resin produced by RohmHaas was used as an ionic exchanger. As mentioned by Juang et al.,[26] the resin was treated and converted to the Na^{+} form. Some physical properties and specifications of the Amberlite resin are presented in Table 1.

Table 1. Properties of Amberlite IR 120

functional group	$-SO_3H$
matrix	styrene divinylbenzene copolymer
ionic form	Na^{+}
physical form	Amber Beads
mean diameter	0.5 mm

2.2. Procedure. 2.2.1. Determination of Total Cationic Capacity (TCC). The column technique was used to determine the total cationic capacity of the resin. Three breakthrough curves were obtained for each monocomponent system (Zn^{2+} and Cu^{2+}). The feed concentrations were (1, 3, and 5) mEq·L^{-1}. A jacketed glass column was used with internal diameter of 0.9 cm and height of 30 cm. It was linked to a peristaltic pump and to a temperature control system. The column was packed with 1 g of the resin. The temperature was kept at 25 °C. The feed pH was kept at 4.

The ionic solution was fed to the bottom of the column, previously flooded with distilled/deionized water, by means of the peristaltic pump (Cole Palmer (6 to 600) rpm), at a constant flow rate of 6 mL·min^{-1}. Column effluent samples were collected at regular intervals, and the species concentrations were determined by atomic absorption spectrophotometry (Analitica GRC-32).

The amount of heavy metals present in the resin was calculated by eq 1 starting with the experimentally obtained breakthrough curves.

$$q_j^* = \frac{C_j^F \dot{Q}}{m_r} \int_0^t (1 - C_j|_{z=L}/C_j^F)dt - \frac{V_L \varepsilon_T C_j^F}{m_r} \qquad (1)$$

where $C_j|_{z=L}$ is the ion concentration at the column outlet; C_j^F is the ion concentration at the feed; $\dot{Q}$ is the feed flow rate; t is the bed saturation time; V_L is the bed volume; m_r is the resin dried mass; and ε_T is the total bed voidage.

2.2.2. Equilibrium Data. The experimental equilibrium data for the binary systems ($Cu^{2+}-Na^{+}$, $Zn^{2+}-Na^{+}$, $Zn^{2+}-Cu^{2+}$) and for the ternary system ($Cu^{2+}-Zn^{2+}-Na^{+}$) were obtained by batch operation at total concentrations of (1, 3, and 5) mEq·L^{-1}. The equipment used was an incubator provided with agitation (Tecnal - TE421). The temperature was kept at (25 ± 0.1) °C. Volumes of 0.1 L of an ionic solution with a known composition at pH 4 (adjusted with 1 M HCl) were added to 250 mL flasks, each with different mass of the cationic resin in the Na^{+} form. The weighing precision was ± 0.0001 g. The suspension remained under agitation for 24 h. Subsequently, the content was filtered, and the filtrate was analyzed for heavy metals and pH. The concentration of Cu^{2+} and Zn^{2+} was determined by atomic absorption spectrophotometry (Analitica GRC-32), while the concentration of Na^{+} was determined by a flame photometer (Digimed DM-61). The composition in the resin phase was obtained by mass balance, given by eqs 2 and 3. Equation 2 refers to the cation originally present in the solution, while eq 3 refers to the cation released by the resin.

$$q_j^* = \frac{(C_j^0 - C_j^*)V}{m_r} \qquad (2)$$

$$q_i^* = \mathrm{TCC} - \frac{(C_j^0 - C_j^*)V}{m_r} \qquad (3)$$

where q_j^* is the concentration at equilibrium of species j in the resin; C_j^0 is the initial concentration of species j in the solution;

C_j^* is the equilibrium concentration of species j in the solution; V is the solution volume; and m_r is the resin dried mass.

The ionic ratios of species j in solution and in the resin were calculated, respectively, by eqs 4 and 5.

$$x_j = \frac{C_j^*}{C_t} \tag{4}$$

$$y_j = \frac{q_j^*}{\mathrm{TCC}} \tag{5}$$

where x_j is the ionic ratio of species j in solution; y_j is the ionic ratio of species j in the resin; C_j is the total solution concentration; and TCC is the total ionic exchange capacity of the resin.

For each binary system, ion exchange experiments were carried out at total concentrations of (1, 3, and 5) $\mathrm{mEq \cdot L^{-1}}$ and for the ternary system at total concentrations of (1, 3, and 5) $\mathrm{mEq \cdot L^{-1}}$. All experiments were carried out in duplicate.

3. Mathematical Modeling

To represent the ion exchange equilibrium data for the binary systems $\mathrm{Cu^{2+}-Na^{+}}$, $\mathrm{Zn^{2+}-Na^{+}}$, and $\mathrm{Zn^{2+}-Cu^{2+}}$, the Mass Action Law was used, considering ideal and nonideal behavior. For the ternary system $\mathrm{Cu^{2+}-Zn^{2+}-Na^{+}}$, the Mass Action Law was used considering only nonideal behavior. To calculate the activity coefficients in the solution and in the resin, Bromley's model and Wilson's model were used.

3.1. Modeling Ion Exchange Equilibria: Binary System. The exchange of the cations A^{+z_A} and B^{+z_B} between the solution and the resin is given by the following reversible reaction

$$z_B A_S^{+z_A} + z_A B_R^{+z_B} \leftrightarrow z_B A_R^{+z_A} + z_A B_S^{+z_B} \tag{6}$$

The thermodynamic equilibrium constant (K_{AB}) for the ion exchange reaction between species A and B is defined by eq 7

$$K_{AB} = \left(\frac{y_A \gamma_{R_A}}{C_A \gamma_{S_A}}\right)^{z_B} \left(\frac{C_B \gamma_{S_B}}{y_B \gamma_{R_B}}\right)^{z_A} \tag{7}$$

where z_j is the valence of species j; y_j is the equivalence fraction of species j in the resin phase; C_j is the equivalent concentration of species j in the liquid phase; γ_{R_j} is the activity coefficient of species j in the resin phase; and γ_{S_j} is the activity coefficient of species j in the liquid phase.

If there is ideal behavior, then the activity coefficients for both phases are one, and eq 7 becomes

$$K_{AB} = \left(\frac{y_A}{C_A}\right)^{z_B} \left(\frac{C_B}{y_B}\right)^{z_A} \tag{8}$$

If nonideal behavior is present, then the activity coefficients should be calculated.

3.1.1. Activity Coefficients in the Solution Phase. To calculate the activity coefficients in the solution, Bromley's model was used, which considers the effect of all species (cations and anions) present. The expression proposed by Bromley is

$$\ln \gamma_{S_j} = \frac{-A_\phi z_j^2 \sqrt{I}}{1 + \sqrt{I}} + F_j \tag{9}$$

The ionic strength I is given in eq 10.

$$I = \frac{1}{2}\sum_{j=1}^{n} z_j^2 m_j \tag{10}$$

where n is the number of species in solution and m_j is the molality of species j in solution. The term F_j is the sum of the interaction parameters. For each cationic species j in a multicomponent solution, this term is given by eq 11.

$$F_j = \sum_i \dot{B}_{ji} Z_{ji}^2 m_i \tag{11}$$

where

$$Z_{ji} = \frac{z_i + z_j}{2} \tag{12}$$

$$\dot{B}_{ji} = \frac{(0,06 + 0,6B_{ji})|z_i z_j|}{\left(1 + \frac{1,5}{|z_i z_j|} I\right)^2} + B_{ji} \tag{13}$$

The subscripts i and j refer to the anions and cations in solution, respectively. The parameters A_ϕ and B_{ij} depend on temperature. Values for these parameters are given by Zemaitis et al.[17] for several components.

3.1.2. Activity Coefficient in the Exchange Phase. To estimate the activity coefficient in the resin phase, Wilson's model was used. Wilson's model equation for the calculation of the activity coefficients of species A and B is given by[27]

$$\ln \gamma_{R_i} = 1 - \ln\left(\sum_{j=1}^{n} y_j \Lambda_{ij}\right) - \sum_{k=1}^{n} \left[\frac{y_k \Lambda_{ki}}{\sum_{j=1}^{L} y_j \Lambda_{kj}}\right] \tag{14}$$

where n is the species number in the resin phase and Λ is the Wilson's model interaction parameter.

3.1.3. Parameter Identification Method. Equation 7, used to model the binary system A−B ionic exchange isotherm experimental data, demands Wilson's model interaction parameters as well as the thermodynamic equilibrium constant. On the other hand, eq 8 demands only the thermodynamic equilibrium constant.

In this work, the model parameters were estimated in the nonlinear identification procedure using the experimental data and the least-squares statistical method to form the objective function (criterion). The model parameter values (K_{AB}, Λ_{AB}, Λ_{BA}) were obtained during the search for a minimum of the following objective function

$$F_{OBJ} = \sum_{i=1}^{N} \left[\sum_{j=1}^{M} (y_{ji}^{\exp} - y_{ji}^{\mathrm{mod}})^2\right] \tag{15}$$

where M is the number of the set of equilibrium data and N is the number of cationic species.

In the search procedure, the optimization method of Nelder and Mead,[28] coded in Fortran, was used. This procedure was carried out for the binary systems $\mathrm{Cu^{2+}-Na^{+}}$, $\mathrm{Zn^{2+}-Na^{+}}$, and $\mathrm{Zn^{2+}-Cu^{2+}}$.

3.2. Prediction of Ion Exchange Equilibria: Ternary System. The ionic exchange reaction that occurs in the ternary system $\mathrm{Cu^{2+}-Zn^{2+}-Na^{+}}$ can be represented by the following stoichiometric equations

$$\mathrm{Cu_S^{2+} + 2Na_R^{+} \leftrightarrow Cu_R^{2+} + 2Na_S^{+}} \tag{16}$$

$$\mathrm{Zn_S^{2+} + 2Na_R^{+} \leftrightarrow Zn_R^{2+} + 2Na_S^{+}} \tag{17}$$

$$\mathrm{Zn_S^{2+} + Cu_R^{2+} \leftrightarrow Zn_R^{2+} + Cu_S^{2+}} \tag{18}$$

The thermodynamic equilibrium constants for the three ion exchange equations are given by

$$K_{\mathrm{CuNa}} = \left(\frac{\gamma_{S_{\mathrm{Na}}} C_{\mathrm{Na}}}{\gamma_{R_{\mathrm{Na}}} y_{\mathrm{Na}}}\right)^2 \left(\frac{\gamma_{R_{\mathrm{Cu}}} y_{\mathrm{Cu}}}{\gamma_{S_{\mathrm{Cu}}} C_{\mathrm{Cu}}}\right) \tag{19}$$

$$K_{\mathrm{ZnNa}} = \left(\frac{\gamma_{S_{\mathrm{Na}}} C_{\mathrm{Na}}}{\gamma_{R_{\mathrm{Na}}} y_{\mathrm{Na}}}\right)^2 \left(\frac{\gamma_{R_{\mathrm{Zn}}} y_{\mathrm{Zn}}}{\gamma_{S_{\mathrm{Zn}}} C_{\mathrm{Zn}}}\right) \tag{20}$$

$$K_{\mathrm{ZnCu}} = \left(\frac{\gamma_{S_{\mathrm{Cu}}} C_{\mathrm{Cu}}}{\gamma_{R_{\mathrm{Cu}}} y_{\mathrm{Cu}}}\right) \left(\frac{\gamma_{R_{\mathrm{Zn}}} y_{\mathrm{Zn}}}{\gamma_{S_{\mathrm{Zn}}} C_{\mathrm{Zn}}}\right) \tag{21}$$

Besides the equations, which define the equilibrium constant, it is also necessary to consider the ionic fractions in the resin, related by

$$y_{\mathrm{Cu}} + y_{\mathrm{Zn}} + y_{\mathrm{Na}} = 1 \tag{22}$$

For a given solution composition (C_{Cu}, C_{Zn}, C_{Na}), the ionic resin composition (y_{Cu}, y_{Zn}, y_{Na}) in equilibrium with the solution can be determined if the equilibrium constants are known and the activity coefficients for both phases can be determined.[12] The resin composition can be calculated starting with the solution composition, by solving a nonlinear system, given by eqs 19, 20, and 22, by eqs 19, 21, and 22 or by eqs 20, 21, and 22.

To calculate the ionic exchange ternary equilibrium, the thermodynamic equilibrium constants (K_{CuNa}, K_{ZnNa}, K_{ZnCu}) and the Wilson's interaction parameters (Λ_{CuNa}, Λ_{NaCu}, Λ_{ZnNa}, Λ_{NaZn}, Λ_{ZnCu}, Λ_{ZnCu}), obtained for the binary systems, were used.

4. Results and Discussion

4.1. pH Results. When a salt M_xX_m is dissolved in an aqueous solution, not all molecules would dissociate into ions. So, not all species in solution are under the form of free ions, available to participate in an ion exchange process. The amount of free ions in solution is dependent on pH.[5] In this work the initial pH was set to 4. At the end of each experiment, after equilibrium was reached, the pH was measured. In all experiments, the pH increased but less than 0.53 units.

To determine the ionic forms of copper, zinc, and sodium in solution, diagrams were simulated using the software HYDRA (Hydrochemical Equilibrium-Constant Database).[29] The diagrams were simulated for each binary system considering a concentration of 5 mEq·L^{-1} (2.5 mM for Cu^{2+} and Zn^{2+} and 5.0 mM for Na^+). This concentration corresponds to the maximum species concentration in solution. Figures 1 to 6 present the diagrams referent for each binary system.

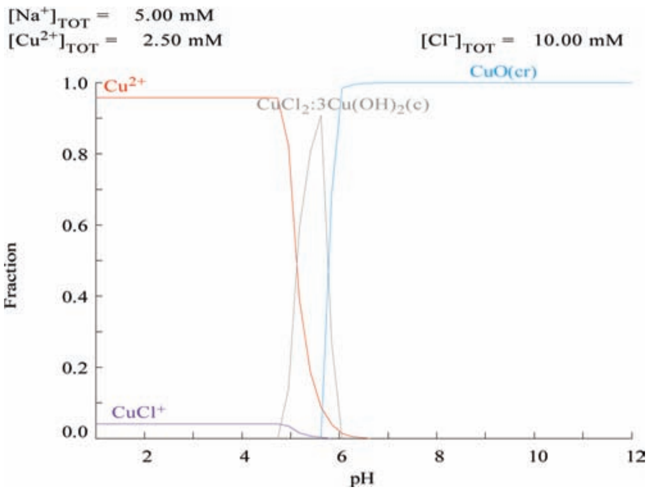

Figure 1. Speciation in ion exchange $Cu^{2+}-Na^+$ as a function of pH$-$copper.

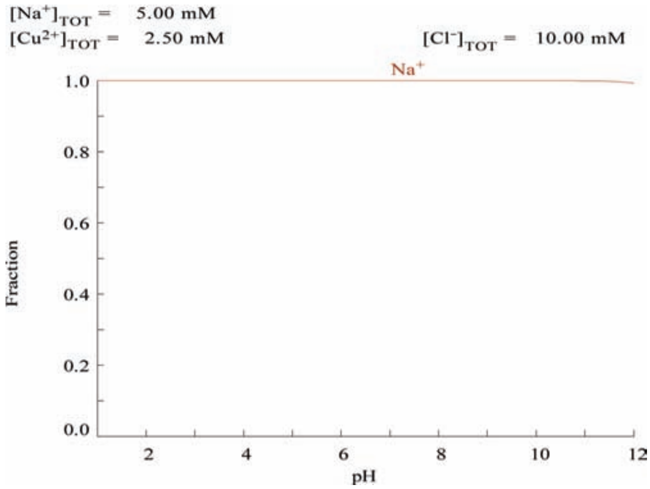

Figure 2. Speciation in ion exchange $Cu^{2+}-Na^+$ as a function of pH$-$sodium.

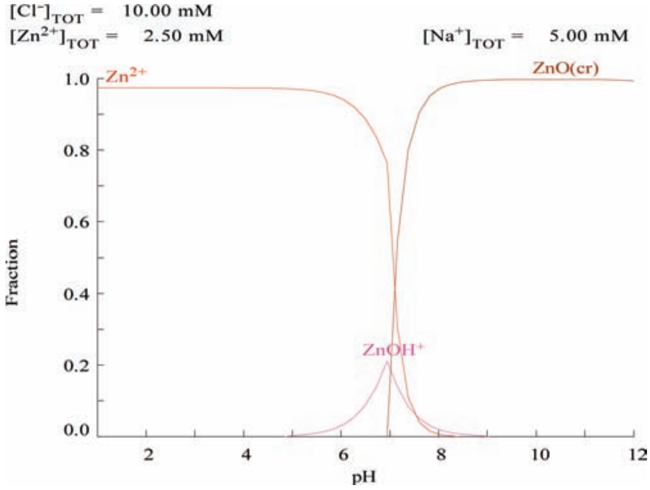

Figure 3. Speciation in ion exchange $Zn^{2+}-Na^+$ as a function of pH$-$zinc.

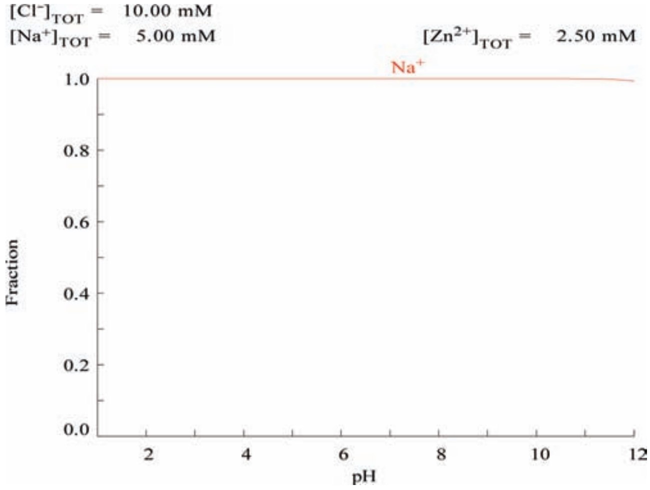

Figure 4. Speciation in ion exchange $Zn^{2+}-Na^+$ as a function of pH$-$sodium.

The diagrams in Figures 1 to 6 indicate that, in the pH range of 4.0 to 4.53, in which the experiments were carried out, the predominant ionic forms were Cu^{2+}, Zn^{2+}, and Na^+ (close to

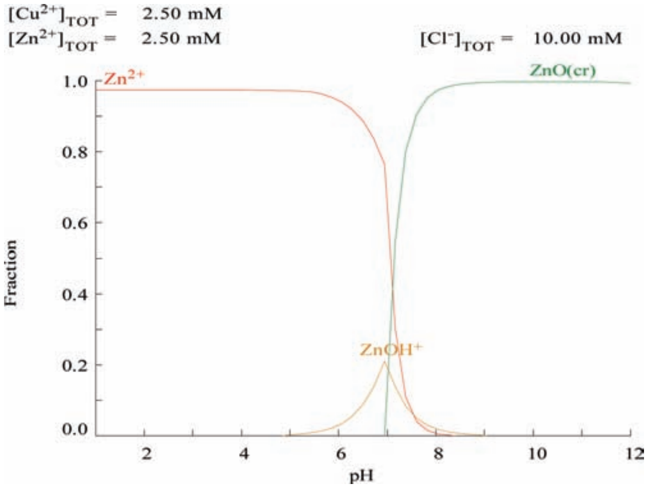

Figure 5. Speciation in ion exchange $Zn^{2+}-Cu^{2+}$ as a function of pH−zinc.

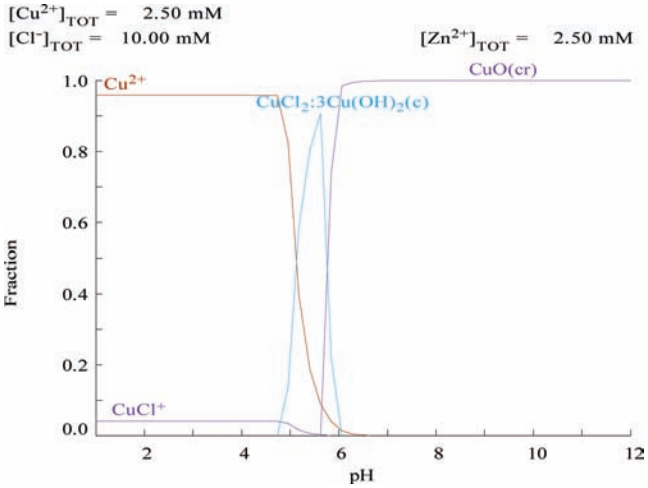

Figure 6. Speciation in ion exchange $Zn^{2+}-Cu^{2+}$ as a function of pH−copper.

Table 2. Total Cationic Capacity of Amberlite IR 120

	q_j^* (mEq·g^{-1})		
heavy metal in feed	$C_j^F = 1$ mEq·L^{-1}	$C_j^F = 3$ mEq·L^{-1}	$C_j^F = 5$ mEq·L^{-1}
Zn^{2+}	5.0029	5.1086	5.3016
Cu^{2+}	5.0325	5.2454	5.1189

Table 3. Bromley's Model Parameters at 25 °C

A_ϕ	B_{CuCl_2}	B_{ZnCl_2}	B_{NaCl}
0.5162	0.0654	0.0364	0.0574

100 %). Thus, the thermodynamic equilibrium constants can be written in terms of these species.

4.2. Total Cationic Capacity. In this work, experiments were carried out in a continuous column, feeding monocomponent solutions of Zn^{2+} and Cu^{2+} at concentrations of (1, 3, and 5) mEq·L^{-1} with the objective to determine the total cationic capacity of the Amberlite IR 120. Table 2 shows the values of total ionic capacity, calculated by eq 1, as a function of feed concentration. The total ionic capacity considered in this work was 5.13 mEq·g^{-1}, which is the average of the values in Table 2.

4.3. Ion Exchange Equilibria: Binary System. Experimental ion exchange equilibrium data were obtained for the binary systems at total concentrations of (1, 3, and 5) mEq·L^{-1}. The binary systems were modeled according to eq 7 and eq 8. When the system was considered nonideal, the activity coefficient in the solution phase was calculated by Bromley's model, whose parameters are presented in Table 3.

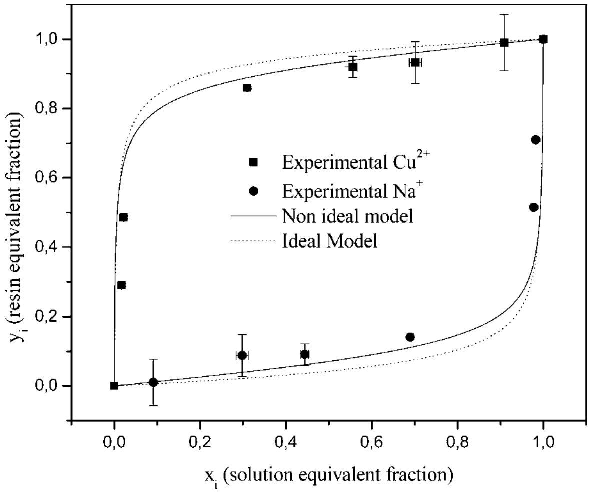

Figure 7. Isotherm for the system Cu^{2+}/Na^+: $C_t = 1$ mEq·L^{-1}, $T = 298$ K.

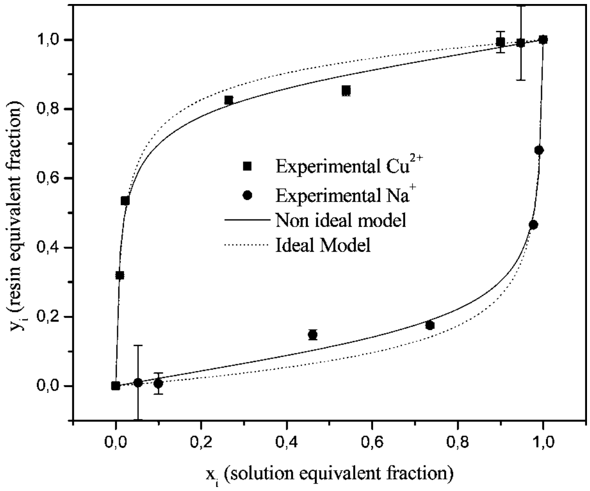

Figure 8. Isotherm for the system Cu^{2+}/Na^+: $C_t = 3$ mEq·L^{-1}, $T = 298$ K.

The activity coefficient for the resin was calculated by Wilson's model, given by eq 14. The thermodynamic equilib-

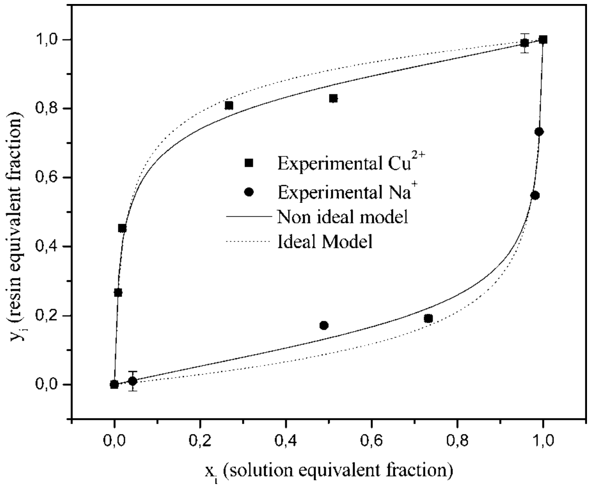

Figure 9. Isotherm for the system Cu^{2+}/Na^+: $C_t = 5$ mEq·L^{-1}, $T = 298$ K.

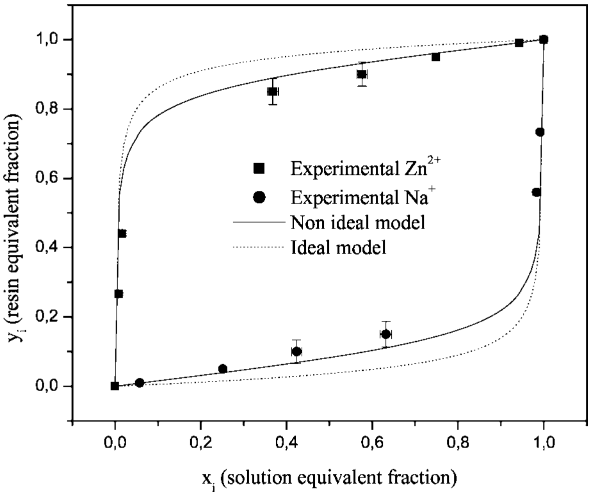

Figure 10. Isotherm for the system Zn^{2+}/Na^{+}: $C_t = 1$ mEq·L^{-1}, $T = 298$ K.

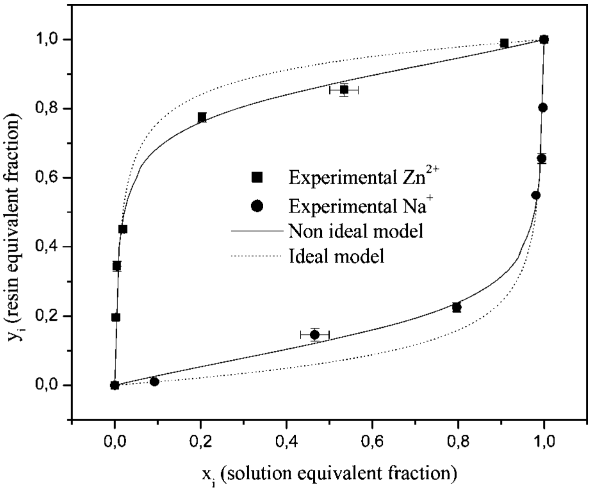

Figure 11. Isotherm for the system Zn^{2+}/Na^{+}: $C_t = 3$ mEq·L^{-1}, $T = 298$ K.

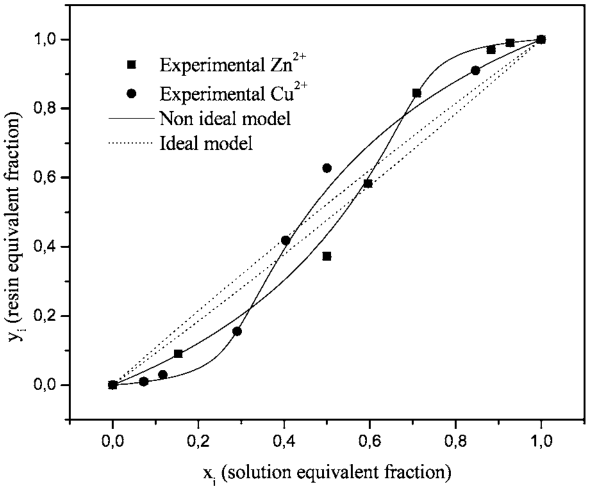

Figure 13. Isotherm for the system Zn^{2+}/Cu^{2+}: $C_t = 1$ mEq·L^{-1}, $T = 298$ K.

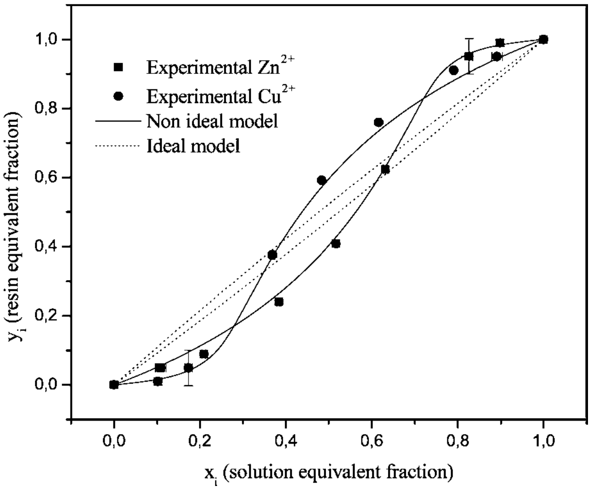

Figure 14. Isotherm for the system Zn^{2+}/Cu^{2+}: $C_t = 3$ mEq·L^{-1}, $T = 298$ K.

rium constant, as well as the interaction parameters of Wilson's model, were obtained by the experimental results for each binary system. Table 4 presents the estimated parameters for each binary system.

Valverde et al.[25] also obtained experimental data for the binary systems $Cu^{2+}-Na^{+}$ and $Zn^{2+}-Na^{+}$ using Amberlite IR 120. To represent this equilibrium, a nonideal Mass Action Law was used. The values of thermodynamic constants and of the interaction parameters of Wilson's model are different from those obtained in this work. This is probably due to the range of concentration and temperature studied by Valverde et al.,[25]

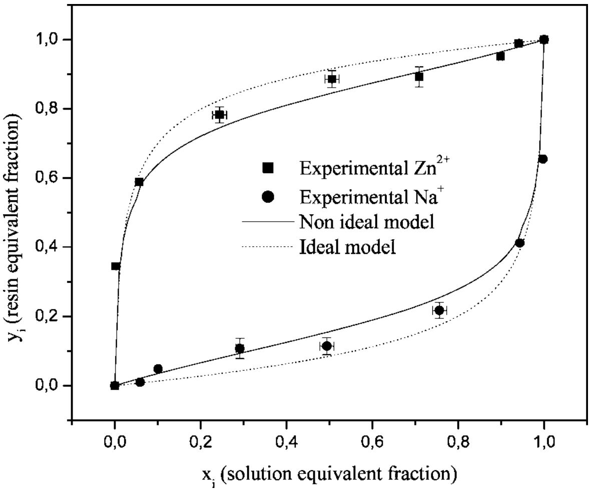

Figure 12. Isotherm for the system Zn^{2+}/Na^{+}: $C_t = 5$ mEq·L^{-1}, $T = 298$ K.

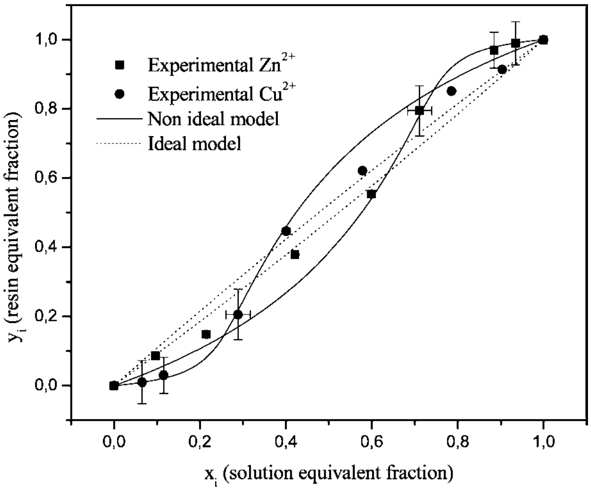

Figure 15. Isotherm for the system Zn^{2+}/Cu^{2+}: $C_t = 5$ mEq·L^{-1}, $T = 298$ K.

Table 4. Thermodynamic Equilibrium Constants, Wilson's Binary Interaction Parameters, and Objective Function[a]

system	K_{AB} IDM	K_{AB} NIDM	Λ_{AB}	Λ_{BA}	F_{OBJ} IDM	F_{OBJ} NIDM
$Cu^{2+}-Na^+$	0.2896	0.3258	2.7286	0.3666	0.0399	0.0242
$Zn^{2+}-Na^+$	0.3589	0.3782	2.0750	1.0485	0.0426	0.0076
$Zn^{2+}-Cu^{2+}$	0.9112	0.9817	1.1769	0.0896	0.2876	0.0264

[a] Ideal Model, IDM; Nonideal Model, NIDM.

Table 5. Mean Square Error and Coefficient of Determination for the Binary Systems

C_T	system $Cu^{2+}-Na^+$		system $Zn^{2+}-Na^+$		system $Zn^{2+}-Cu^{2+}$	
$(mEq\cdot L^{-1})$	ideal model	nonideal model	ideal model	nonideal model	ideal model	nonideal model
e_M	0.0204	0.0100	0.0259	0.0158	0.0145	0.0013
R^2	0.8539	0.9162	0.8900	0.9233	0.9200	0.9900

Table 6. Predicted and Experimentally Determined Exchanger Phase Composition in Equilibrium for the $Cu^{2+}-Zn^{2+}-Na^+$ System

experimental solution phase equivalent ionic fraction at equilibrium			experimental exchanger phase equivalent ionic fraction at equilibrium			predicted exchanger phase equivalent ionic fraction at equilibrium		
x_{Cu}	x_{Zn}	x_{Na}	y_{Cu}	y_{Zn}	y_{Na}	y_{Cu}	y_{Zn}	y_{Na}
				$C_t = 1$ $mEq\cdot L^{-1}$				
0.3162	0.3101	0.3737	0.4021	0.3590	0.2389	0.4348	0.4702	0.0951
0.0523	0.0386	0.9091	0.4434	0.4094	0.1472	0.4059	0.3565	0.2376
0.0172	0.0056	0.9772	0.4575	0.2269	0.3156	0.4915	0.1858	0.3227
0.4120	0.3914	0.1966	0.3867	0.4100	0.2033	0.4783	0.4617	0.0601
0.2109	0.4091	0.3800	0.2584	0.6583	0.0833	0.2137	0.6841	0.1022
0.0196	0.0146	0.9658	0.2531	0.4229	0.3240	0.3523	0.3335	0.3142
0.4398	0.2035	0.3567	0.6097	0.3026	0.0877	0.6716	0.2549	0.0736
0.0381	0.0081	0.9538	0.6136	0.1018	0.2846	0.6011	0.1342	0.2647
				$C_t = 3$ $mEq\cdot L^{-1}$				
0.3473	0.3582	0.2944	0.3919	0.4435	0.1646	0.4064	0.4834	0.1102
0.1166	0.1238	0.7596	0.3298	0.4602	0.2100	0.3240	0.4450	0.2310
0.0075	0.0061	0.9864	0.2627	0.2806	0.4567	0.2278	0.2654	0.5068
0.1504	0.5495	0.3001	0.1998	0.7054	0.0948	0.0954	0.8044	0.1002
0.0672	0.2985	0.6343	0.1345	0.6502	0.2153	0.0837	0.7312	0.1851
0.0034	0.0126	0.9840	0.1248	0.4288	0.4464	0.0736	0.4300	0.4964
0.2640	0.0626	0.6734	0.5882	0.2058	0.2060	0.6766	0.1478	0.1756
0.0140	0.0036	0.9824	0.3584	0.1312	0.5104	0.3811	0.1305	0.4884
				$C_t = 5$ $mEq\cdot L^{-1}$				
0.4951	0.4440	0.0609	0.4998	0.4313	0.0689	0.5171	0.4392	0.0437
0.4601	0.4191	0.1208	0.4573	0.4203	0.1224	0.4810	0.4467	0.0723
0.3751	0.3523	0.2726	0.4178	0.4538	0.1284	0.4250	0.4501	0.1250
0.1171	0.1107	0.7722	0.4103	0.3755	0.2142	0.3244	0.3968	0.2788
0.2801	0.5379	0.1820	0.2486	0.6410	0.1104	0.2167	0.6809	0.1024
0.1949	0.3995	0.4056	0.2888	0.5411	0.1701	0.1944	0.6397	0.1659
0.5490	0.2676	0.1834	0.6222	0.2672	0.1106	0.6505	0.2678	0.0817
0.4132	0.1981	0.3887	0.5225	0.2609	0.2166	0.5857	0.2688	0.1455

which is different from this work. Besides, the anion present in the systems studied by Valverde et al.[25] is different from the one used in this work which interposes in the calculus of the activity coefficient in solution and, consequently, the value of the equilibrium thermodynamic constant.

Figures 7 to 15 present the ionic exchange experimental data as well as the equilibrium curves estimated by the models (ideal Mass Action Law and nonideal Mass Action Law) for each binary system and for each total concentration. In Figures 7 to 9, which correspond to the binary system $Cu^{2+}-Na^+$, the shape of the curves indicates higher affinity of the ion Cu^{2+} with the resin. In Figures 10 to 12, which correspond to the binary system $Zn^{2+}-Na^+$, the shape of the curves indicates higher affinity of the ion Zn^{2+} with the resin. Both models describe the experimental isotherm shape of these systems. In Figures 13 to 15 are presented the experimental isotherms and the one calculated for the binary system $Zn^{2+}-Cu^{2+}$. The occurrence of points of azeotropy was verified by the experimental data, which had a systematic and well-defined tendency. Related to this system, only the nonideal Mass Action Law represented this phenomenon, which justifies the use of this model to represent the ionic exchange equilibrium of the ternary system $Cu^{2+}-Zn^{2+}-Na^+$.

Additionally, the values of thermodynamic equilibrium constants establish the selectivity of ionic exchanger. The systems $Cu^{2+}-Na^+$ and $Zn^{2+}-Na^+$ present close values for these parameters. This indicates little selectivity defined for the ions Cu^{2+} and Zn^{2+}, as can be seen in the equilibrium data presented in Figures 13 to 15. In the system $Cu^{2+}-Zn^{2+}$, the affinity changed with the ion equivalent fraction in solution.

To compare the adjustment degree of the models to the equilibrium experimental data of ion exchange, the mean square error (e_M) and the mean coefficient of determination (R^2) were calculated. In Table 5, these statistical parameters are presented for each binary system. The mean square errors and the coefficient of determination indicate that in all of the binary systems the nonideal Mass Action Law better represented the equilibrium experimental data.

4.4. Ion Exchange Equilibria: Ternary System. For the ternary system $Cu^{2+}-Zn^{2+}-Na^+$, experimental data were obtained for the concentrations (1, 3, and 5) $mEq\cdot L^{-1}$. On the basis of the representation of the ionic exchange equilibrium for the binary systems, the multicomponent equilibrium was undertaken regarding nonideal behavior. Using the Wilson's model interaction parameters and the equilibrium constant for

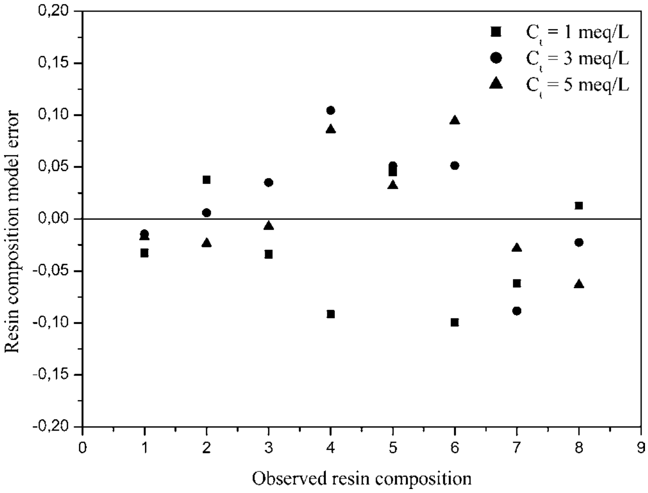

Figure 16. Cu^{2+} concentration in the resin phase error diagram related to the ternary system.

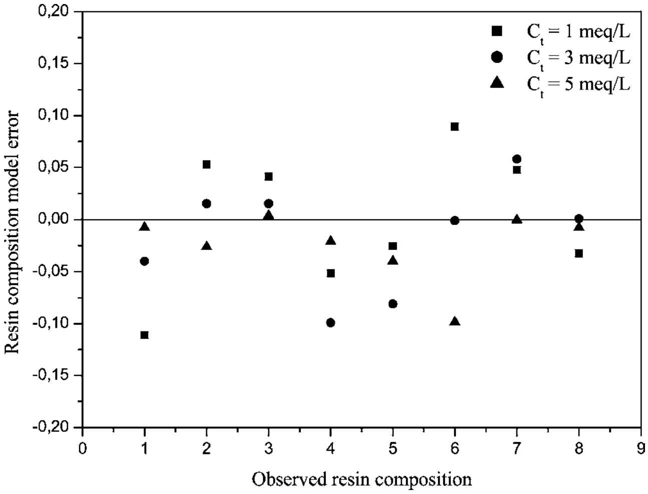

Figure 17. Zn^{2+} concentration in the resin phase error diagram related to the ternary system.

each binary system, the model described by eqs 19, 20, and 22 was used to predict the equilibrium of the ternary system. In Table 6 are presented the experimental equilibrium data and the one calculated through the model (nonideal Mass Action Law).

To check the consistency of the thermodynamic equilibrium constants, the "triangle rule" is applied

$$(K_{AB})^{z_C}(K_{BC})^{z_A}(K_{CA})^{z_B} = 1 \qquad (23)$$

In this work, a value of 0.73 was obtained. Although the equilibrium constants did not satisfy the triangle rule, the model was able to predict the ternary system ionic exchange equilibria. The same was experienced by several other investigations.[9,13]

Figures 16 to 18 present the error diagram related to the estimation of the composition in the resin for the ternary system. The diagrams indicate the residue is in the range of 0.10 to −0.10, for the cation Cu^{2+}, 0.10 to −0.12, for the cation Zn^{2+}, and 0.15 to −0.10, for the cation Na^{+}. It is important to highlight that the residue distribution was random. To evaluate the adjustment degree of the model to the equilibrium experimental data of ion exchange of the ternary system, the coefficient of determination and mean square error were calculated. The mean values obtained for these parameters were 0.8350 and 0.0724, respectively.

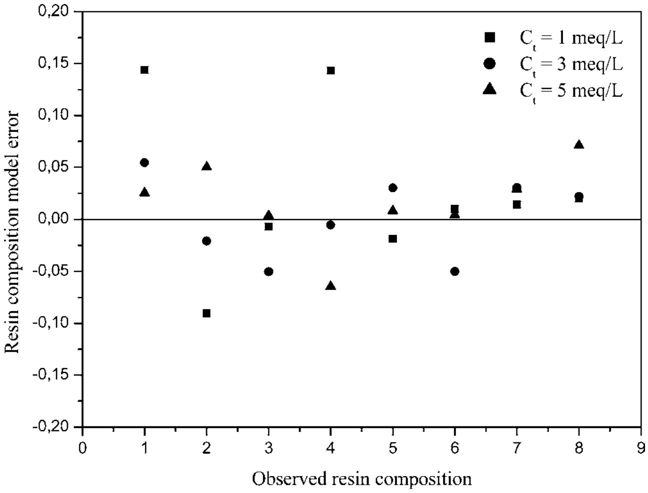

Figure 18. Na^{+} concentration in the resin phase error diagram related to the ternary system.

5. Conclusions

Ion exchange experimental equilibrium data were obtained for the ternary system $Cu^{2+}-Zn^{2+}-Na^{+}$ as well as for each binary system made up of the same constituents. The Mass Action Law was used to represent the equilibrium for the binary systems considering ideal and nonideal behavior. For the ternary system, the same law was used, but only the nonideal situation was considered. The conclusions of this work are following:

- In the pH range of 4.0 (initial) and 4.53 (end of experiments), approaching 100 %, the copper, zinc, and sodium were in the form of Cu^{2+}, Zn^{2+}, and Na^{+}.
- When ideal behavior is assumed in both phases, the ideal Mass Action Law represented satisfactorily the experimental data for the binary systems $Cu^{2+}-Na^{+}$ and $Zn^{2+}-Na^{+}$. When nonideal behavior in both phases was considered by activity coefficients of Wilson's and Bromley's models, the Mass Action Law mass described satisfactorily all binary systems.
- In the systems $Cu^{2+}-Na^{+}$ and $Zn^{2+}-Na^{+}$, the affinity changed with total concentration. In the system $Cu^{2+}-Zn^{2+}$, the affinity changed with the ion equivalent fraction and total concentration in solution.
- Starting with the parameters K_{AB}, Λ_{AB}, and Λ_{BA} for each binary system, it was possible to predict the equilibrium for the ternary system with a determination coefficient of 0.8350.
- The Mass Action Law proved to be a powerful tool to represent the ionic exchange equilibrium for binary and ternary systems.

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Received for review July 31, 2009. Accepted January 14, 2010.

JE900649E