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Equilibrium Data for the Exchange of Cu^{2+}, Cd^{2+}, and Zn^{2+} Ions for H^+ on the Cationic Exchanger Amberlite IR-120

José L. Valverde, Antonio de Lucas, Marcela González, and Juan F. Rodríguez*

Department of Chemical Engineering, University of Castilla-La Mancha, Avenida de Camilo José Cela 10,
13004 Ciudad Real, Spain

Equilibrium ion-exchange isotherms of H^+/Cu^{2+}, H^+/Cd^{2+}, and H^+/Zn^{2+} on a strong acid resin, Amberlite IR-120, in an aqueous medium at (283 and 303) K have been determined in order to assess the possibility of using ion exchange to eliminate heavy-metal ions from industrial aqueous liquid streams. The experimental equilibrium data have been satisfactorily correlated using the homogeneous mass action law model (LAM). This model assumes nonideal behavior for both the solution and solid phases. Wilson and Pitzer equations have been used to calculate activity coefficients in the resin and liquid phases, respectively. The values of the thermodynamic equilibrium constants show a temperature dependence.

Introduction

Disposal of hazardous ions in aqueous waste streams is a significant industrial problem. Basic metals such as aluminum, cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, and zinc have been classified as the 10 metals of primary importance for recovery from industrial waste streams.[1] The main drawback of the treatment of the mentioned waste effluents charged with toxic metals is the generation of a concentrated reject or regeneration stream using whatever removal procedures (precipitation, ion exchange, solvent extraction, adsorption, osmosis, etc.). This concentrated effluent must be minimized and reduced in order to reach the ideal objective of "zero discharge".[1] In this way, the regeneration process must be optimized to minimize the volume of the concentrated residual stream.

The affinity of the strong acid resins for metallic ions is not as high as that of the chelating resins. Even so, it has been found that the affinity of those resins for such ions could be suitable for its use in the removal of these metallic ions from water streams,[2] with its advantages being easier regeneration and simpler working conditions. In this work, equilibrium data of the systems H^+/Cu^{2+}, H^+/Cd^{2+}, and H^+/Zn^{2+} are obtained and used to evaluate the behavior of the systems if an acid is used for regeneration.

Experimental Section

Chemicals. Zinc, copper, and cadmium nitrates were PRS grade (99%), and nitric acid (65%, w/w) was PA grade, supplied by Panreac. Demineralized water was used with a conductivity value lower than 5 μS/cm. The cationic resin Amberlite IR-120, supplied by Rhom & Haas, was used as the ion exchanger. The resin was pretreated and regenerated to convert it to the H^+ form, as described by de Lucas et al.[3]

Procedure. The experimental set consisted of nine 0.25 L Pyrex containers, hermetically sealed and submerged in a temperature-controlled thermostatic bath. The temperature was kept constant within ±0.1 K. The suspension formed by the resin and solution was vigorously agitated by means of a multipoint magnetic stirrer.

Equilibrium resin loading data were generated for H^+/Cu^{2+}, H^+/Cd^{2+}, and H^+/Zn^{2+} systems. To obtain these data, samples of 0.1 L of an ionic solution of known composition were weighed and added into each of several flasks.[4] Different known masses of resin, in H^+ form, had previously been added to each flask. The accuracy of weighing was ±0.0001 g. The solution and resin were maintained at a fixed temperature (±0.1 K) under vigorous stirring, until equilibrium was achieved (24 h).[4] At the end of this period, the mixtures were filtered to remove the ion-exchange resin and the filtrate was analyzed for the metal content. The resin-phase composition was determined by mass balance from initial and equilibrium compositions of the liquid phase, according to eq 1, where c_0 and c^* are

$$q^* = \frac{V}{m}(c_0 - c^*) \tag{1}$$

the metal ion initial concentration and the metal ion equilibrium concentration in the liquid phase, respectively, and q^* denotes the resin-phase equilibrium concentration of metal. V and m are the volume of solution and the mass of the dry ion-exchange resin, respectively.

The solutions were analyzed for their metal content by atomic absorption spectrophotometry in a Varian 220 AS spectrophotometer. The standard uncertainty and reproducibility of measurements was found to be ±0.1%. To improve the reproducibility of the results, the resin was preconditioned (several regeneration cycles and finally treated with a 1 mol·L^{-1} solution of clorhidric acid).

Model and Prediction

Ion-exchange equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a counterion which is different from that in the ion exchanger. Consider the ion exchanger (r) initially in the A form and the counterion in the solution (s) is B. Counterion exchange occurs, and the ion A in the ion exchanger is partially replaced by B:

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* To whom correspondence should be addressed. E-mail: juanfran@inqu-cr.uclm.es. Fax: 3426295318.

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$$\beta \mathrm{A}_{\mathrm{r}}^{\alpha+} + \alpha \mathrm{B}_{\mathrm{s}}^{\beta+} \leftrightarrow \beta \mathrm{A}_{\mathrm{s}}^{\alpha+} + \alpha \mathrm{B}_{\mathrm{r}}^{\beta+} \tag{2}$$

In equilibrium, both the ion exchanger and the solution contain both competing counterion species, A and B.

The ionic fraction for a binary system can be introduced as

$$x_{\mathrm{A}} = c_{\mathrm{A}}/N; \quad x_{\mathrm{B}} = c_{\mathrm{B}}/N \tag{3}$$

$$y_{\mathrm{A}} = q_{\mathrm{A}}/q_0; \quad y_{\mathrm{B}} = q_{\mathrm{B}}/q_0 \tag{4}$$

where C_i represents the normality concentration of the ith ionic species in solution. N is the total ionic concentration in the solution phase, q_i is the solute concentration in the solid phase, and q_0 is the useful capacity of the resin in the system studied.

The equilibrium constant for the exchange reaction (eq 2) assuming real behavior for both phases could be calculated from the following equation:

$$K_{\mathrm{AB}}(T) = \frac{(y_{\mathrm{B}}\bar{\gamma}_{\mathrm{B}})^{\alpha}[(1 - x_{\mathrm{B}})N\gamma_{\mathrm{A}}]^{\beta}}{[(1 - y_{\mathrm{B}})\bar{\gamma}_{\mathrm{A}}]^{\beta}[x_{\mathrm{B}}\gamma_{\mathrm{B}}N]^{\alpha}} \tag{5}$$

where $\bar{\gamma}$ and γ are the activity coefficients of each ion in the ion exchanger and in the solution and y_{B} and x_{B} are the ionic fraction of ion B in the solid phase and in the solution.

The activity coefficients in the resin phase were calculated using the Wilson equations:

$$\bar{\gamma}_{\mathrm{A}} = \exp[1 - \ln(y_{\mathrm{A}} + (1 - y_{\mathrm{A}})\Lambda_{\mathrm{AB}})] - \left(\frac{y_{\mathrm{A}}}{y_{\mathrm{A}} + (1 - y_{\mathrm{A}})\Lambda_{\mathrm{AB}}}\right) - \left(\frac{(1 - y_{\mathrm{A}})\Lambda_{\mathrm{BA}}}{(1 - y_{\mathrm{A}}) + y_{\mathrm{A}}\Lambda_{\mathrm{BA}}}\right) \tag{6}$$

$$\bar{\gamma}_{\mathrm{B}} = \exp[1 - \ln[(1 - y_{\mathrm{A}}) + y_{\mathrm{A}}\Lambda_{\mathrm{BA}}]] - \left(\frac{1 - y_{\mathrm{A}}}{(1 - y_{\mathrm{A}}) + y_{\mathrm{A}}\Lambda_{\mathrm{BA}}}\right) - \left(\frac{y_{\mathrm{A}}\Lambda_{\mathrm{AB}}}{y_{\mathrm{A}} + (1 - y_{\mathrm{A}})\Lambda_{\mathrm{AB}}}\right) \tag{7}$$

$$T(1 - \ln \Lambda_{\mathrm{AB}} - \Lambda_{\mathrm{BA}}) = C_{\mathrm{AB}}^{\mathrm{A}} \tag{8}$$

$$T(1 - \ln \Lambda_{\mathrm{BA}} - \Lambda_{\mathrm{AB}}) = C_{\mathrm{AB}}^{\mathrm{B}} \tag{9}$$

where Λ_{AB} and Λ_{BA} are the Wilson coefficients, T is the absolute temperature, and $C_{\mathrm{AB}}^{\mathrm{A}}$ and $C_{\mathrm{AB}}^{\mathrm{B}}$ are the constants of the Robinson and Gilliland relationship.[5]

The activity coefficients in the liquid phase were determined from the Pitzer limiting law:[6]

$$\ln \bar{\gamma}_{\mathrm{M}} = z_{\mathrm{M}}^{2}F + \sum_{\mathrm{a}} m_{\mathrm{a}}(2B_{M\mathrm{a}} + ZC_{M\mathrm{a}}) + \sum_{\mathrm{c}} m_{\mathrm{c}}(2\Phi_{M\mathrm{c}} + \sum_{\mathrm{a}} m_{\mathrm{a}}\psi_{M\mathrm{ca}}) + \sum_{\mathrm{a}}\sum_{\mathrm{a}'} m_{\mathrm{a}}m_{\mathrm{a}'}\psi_{M\mathrm{aa}'} + |z_M|\sum_{\mathrm{c}}\sum_{\mathrm{a}} m_{\mathrm{c}}m_{\mathrm{a}}C_{\mathrm{ca}} \tag{10}$$

where the subscript M refers to the ions A or B. c is the cation, a and a′ are anions, and m_i is the molality of ion i. The charge is indicated by z_M. The quantity F includes the Debye−Hückel term and other terms as follows:

$$F = -A_{\phi}[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] + \sum_{\mathrm{c}}\sum_{\mathrm{a}} m_{\mathrm{c}}m_{\mathrm{a}}B'_{\mathrm{ca}} + \sum_{\mathrm{c}}\sum_{\mathrm{c}'} m_{\mathrm{c}}m_{\mathrm{c}'}\Phi'_{\mathrm{cc}'} + \sum_{\mathrm{a}}\sum_{\mathrm{a}'} m_{\mathrm{a}}m_{\mathrm{a}'}\Phi'_{\mathrm{aa}'}$$

Table 1. Parameters of the Pitzer Limiting Law, $\beta^{(0)}$, $\beta^{(1)}$, and C_{MX}, for HNO_3, $Cd(NO_3)_2$, $Zn(NO_3)_2$, and $Cu(NO_3)_2$

species	$\beta^{(0)}$	$\beta^{(1)}$	C_{MX}
HNO_3	0.1168	0.355	−0.002 69
$Cd(NO_3)_2$	0.3820	1.668	−0.009 07
$Zn(NO_3)_2$	0.4641	1.691	−0.005 54
$Cu(NO_3)_2$	0.4224	1.430	−0.007 76

Table 2. Ion Fraction of Cd^{2+} in the Liquid Phase, $x_{Cd^{2+}}$, and Experimental and Theoretical Ionic Fractions of Cd^{2+} in the Resin Phase, $y_{Cd^{2+}}$, of the Ion-Exchange Equilibrium H^+/Cd^{2+}

exp		theor	exp		theor
$x_{Cd^{2+}}$	$y_{Cd^{2+}}$	$y_{Cd^{2+}}$	$x_{Cd^{2+}}$	$y_{Cd^{2+}}$	$y_{Cd^{2+}}$
$c_t = 0.05$ mol·L^{-1}, $T = 283$ K					
0.0023	0.2802	0.1729	0.6441	0.9482	0.9662
0.0085	0.3828	0.3544	0.7685	0.9724	0.9874
0.0616	0.6097	0.6429	0.8026	0.9847	0.9906
0.2710	0.8383	0.8348	0.8200	0.9845	0.9920
0.2863	0.8562	0.8422	0.8468	0.9882	0.9938
0.3673	0.8682	0.8771	0.8572	0.9970	0.9944
0.4946	0.9122	0.9228	0.8604	0.9987	0.9946
$c_t = 0.05$ mol·L^{-1}, $T = 303$ K					
0.0060	0.2770	0.3335	0.4772	0.9243	0.9327
0.0120	0.3767	0.4395	0.5763	0.9576	0.9597
0.0640	0.6752	0.6755	0.6932	0.9858	0.9813
0.1650	0.7985	0.7934	0.7123	0.9955	0.9837
0.2840	0.8924	0.8422	0.7127	0.9994	0.9837
0.3474	0.9073	0.8880	0.8202	0.9990	0.9929
0.4745	0.9351	0.9318	0.8742	0.9998	0.9957

Table 3. Ion Fraction of Cu^{2+} in the Liquid Phase, $x_{Cu^{2+}}$, and Experimental and Theoretical Ionic Fractions of Cu^{2+} in the Resin Phase, $y_{Cu^{2+}}$, of the Ion-Exchange Equilibrium H^+/Cu^{2+}

exp		theor	exp		theor
$x_{Cu^{2+}}$	$y_{Cu^{2+}}$	$y_{Cu^{2+}}$	$x_{Cu^{2+}}$	$y_{Cu^{2+}}$	$y_{Cu^{2+}}$
$c_t = 0.05$ mol·L^{-1}, $T = 283$ K					
0.0076	0.3856	0.3599	0.4292	0.9919	0.9986
0.0730	0.8238	0.8468	0.4836	0.9931	0.9989
0.1123	0.9363	0.9397	0.5146	0.9958	0.9990
0.1461	0.9856	0.9832	0.5800	0.9941	0.9992
0.1826	0.9951	0.9929	0.5830	0.9959	0.9993
0.2052	0.9871	0.9947	0.6691	0.9991	0.9995
0.2643	0.9882	0.9968	0.8295	0.9996	0.9998
0.3065	0.9894	0.9975	0.9221	0.9997	0.9999
0.3767	0.9909	0.9983			
$c_t = 0.05$ mol·L^{-1}, $T = 303$ K					
0.0072	0.3840	0.4047	0.4561	0.9979	0.9986
0.0708	0.8772	0.8802	0.5115	0.9960	0.9989
0.0902	0.9529	0.9282	0.5429	0.9991	0.9990
0.1250	0.9885	0.9796	0.5640	0.9966	0.9991
0.1701	0.9904	0.9924	0.5890	0.9991	0.9992
0.2073	0.9917	0.9949	0.6480	0.9967	0.9993
0.2977	0.9948	0.9972	0.7290	0.9985	0.9995
0.3317	0.9999	0.9977	0.8040	0.9922	0.9997
0.3870	0.9967	0.9982	0.9130	0.9971	0.9999

$$Z = \sum_i m_i|z_i| \tag{11}$$

$$B_{\mathrm{ca}}^{\phi} = B_{\mathrm{ca}} + IB'_{\mathrm{ca}} \tag{12}$$

$$\Phi_{\mathrm{cc}'}^{\phi} = \Phi_{\mathrm{cc}'} + I\Phi'_{\mathrm{cc}'} \tag{13}$$

where I is the ionic strength in the bulk phase in molal units, B is the short-range interaction parameter, Φ is the interaction between ions of like sign parameter, and B' and Φ' are the ionic strength derivatives of B and Φ. The sums over i include all solute species; uncharged species do not contribute to I or Z. The double summation indices, c < c′ and a < a′, denote the sum over all distinguishable pairs

Table 4. Ion Fraction of Zn^{2+} in the Liquid Phase, $x_{Zn^{2+}}$, and Experimental and Theoretical Ionic Fractions of Zn^{2+} in the Resin Phase, $y_{Zn^{2+}}$, of the Ion-Exchange Equilibrium H^+/Zn^{2+}

exp		theor	exp		theor
$x_{Zn^{2+}}$	$y_{Zn^{2+}}$	$y_{Zn^{2+}}$	$x_{Zn^{2+}}$	$y_{Zn^{2+}}$	$y_{Zn^{2+}}$
$c_t = 0.05$ mol·L^{-1}, $T = 283$ K					
0.0074	0.3855	0.3447	0.4542	0.9905	0.9933
0.0383	0.7198	0.7494	0.4642	0.9922	0.9936
0.1117	0.9032	0.9533	0.5201	0.9946	0.9947
0.1245	0.9935	0.9606	0.5509	0.9936	0.9953
0.1687	0.9884	0.9745	0.5658	0.9924	0.9955
0.2173	0.9814	0.9817	0.6700	0.9917	0.9970
0.2972	0.9885	0.9878	0.7400	0.9996	0.9978
0.3451	0.9923	0.9900	0.8700	0.9992	0.9990
$c_t = 0.05$ mol·L^{-1}, $T = 303$ K					
0.0064	0.3577	0.4176	0.4790	0.9877	0.9945
0.0212	0.7601	0.7054	0.5133	0.9974	0.9951
0.1117	0.9413	0.9673	0.5301	0.9997	0.9954
0.1258	0.9926	0.9717	0.5575	0.9943	0.9958
0.1642	0.9968	0.9792	0.5688	0.9940	0.9960
0.2109	0.9976	0.9843	0.5759	0.9978	0.9961
0.2940	0.9930	0.9893	0.6800	0.9975	0.9974
0.3546	0.9982	0.9915	0.7200	0.9972	0.9978
0.4467	0.9969	0.9939	0.8300	0.9993	0.9988

Table 5. Ion-Exchange Equilibrium Constant, K_{AB}, Wilson's Coefficients, Λ_{AB} and Λ_{BA}, Average Deviation of the Calculated Values, Av. Dev., and Constants of the Robinson and Gilliland Relation, C_{AB}^{A} and C_{AB}^{B}, for the Binary Systems H^+/Cd^{2+}, H^+/Cu^{2+}, and H^+/Zn^{2+} at (283 and 303) K

system (A/B)	T/K	K_{AB}	$10^2\Lambda_{AB}$	Λ_{BA}	Av. Dev. (%)	$10^{-2}C_{AB}^{A}$	$10^{-2}C_{AB}^{B}$
H^+/Cu^{2+}	283	50.41	6.58	1.770	9.42	12.17	1.27
H^+/Cu^{2+}	303	67.79	8.33	1.770	6.86	12.17	1.27
H^+/Cd^{2+}	283	31.02	2.48	3.294	4.39	3.97	−0.61
H^+/Cd^{2+}	303	38.01	2.89	3.233	3.50	3.97	−0.61
H^+/Zn^{2+}	283	46.93	5.24	1.474	1.68	7.14	1.68
H^+/Zn^{2+}	303	76.74	5.90	1.474	1.96	7.14	1.68

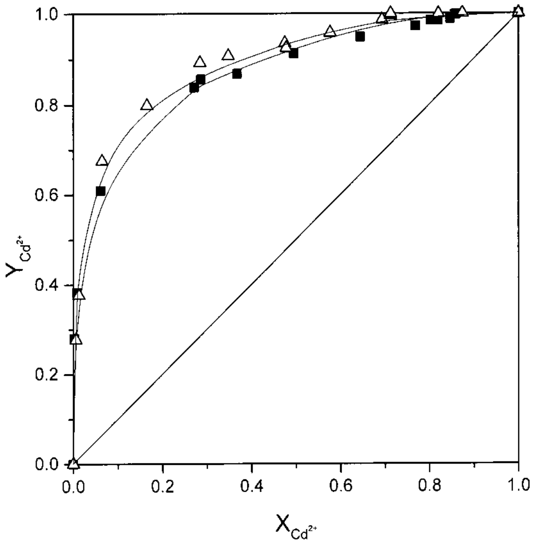

Figure 1. Isotherms for the system H^+/Cd^{2+}, $c_t = 0.05$ mol·L^{-1}: ■, exp with $T = 283$ K; △, exp with $T = 303$ K; —, model.

of different cations or anions. The constant b has the value of 1.2 kg$^{1/2}$·mol$^{-1/2}$, and the constant A_ϕ has the values of 0.3821 and 0.3949 at 283 K and 303 K, respectively. The parameter C_{MX} is related to the commonly tabulated parameter C_{MX}^{ϕ} by the equation

$$C_{MX} = C_{MX}^{\phi}/(2|Z_M Z_X|^{1/2}) \tag{14}$$

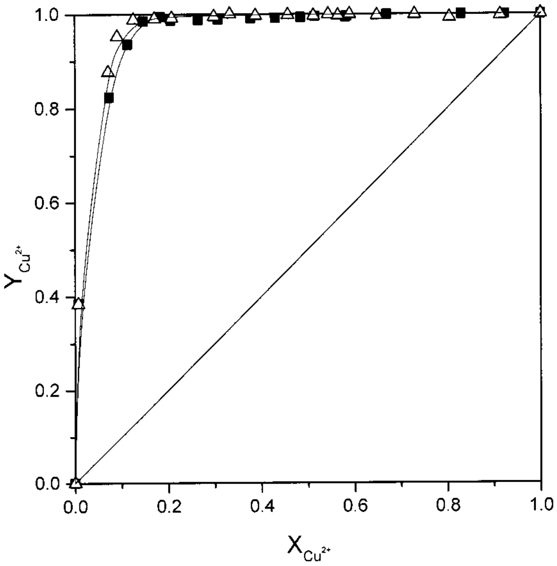

Figure 2. Isotherms for the system H^+/Cu^{2+}, $c_t = 0.05$ mol·L^{-1}: ■, exp with $T = 283$ K; △, exp with $T = 303$ K; —, model.

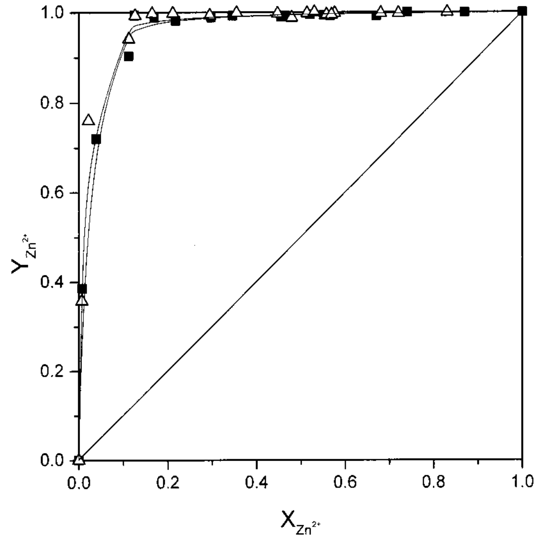

Figure 3. Isotherms for the system H^+/Zn^{2+}, $c_t = 0.05$ mol·L^{-1}: ■, exp with $T = 283$ K; △, exp with $T = 303$ K; —, model.

The ionic strength dependence of the B terms is shown by the following equations:

$$B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \exp(-\alpha_2 I^{1/2}) \tag{15}$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g(\alpha_2 I^{1/2}) \tag{16}$$

$$B'_{MX} = [\beta_{MX}^{(1)} g'(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} g'(\alpha_2 I^{1/2})]/I \tag{17}$$

where the functions g and g' are given by

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \tag{18}$$

$$g'(x) = -2[1 - (1 + x + x^2/2)\exp(-x)]/x^2 \tag{19}$$

The above equations (eqs 10−19) are valid for 1−1, 1−2, and 2−1 electrolytes. Values for $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and $C_{MX}^{(0)}$ are species-dependent and are tabulated by Pitzer.[7] $\beta_{MX}^{(2)}$ is important only for 2−2 or higher valence electrolytes that show a tendency toward electrostatic ion pairing. A value of 2.0 kg$^{1/2}$·mol$^{-1/2}$ for α is recommended by Pitzer.[6] The values of θ and ψ are known for 69 binary electrolyte

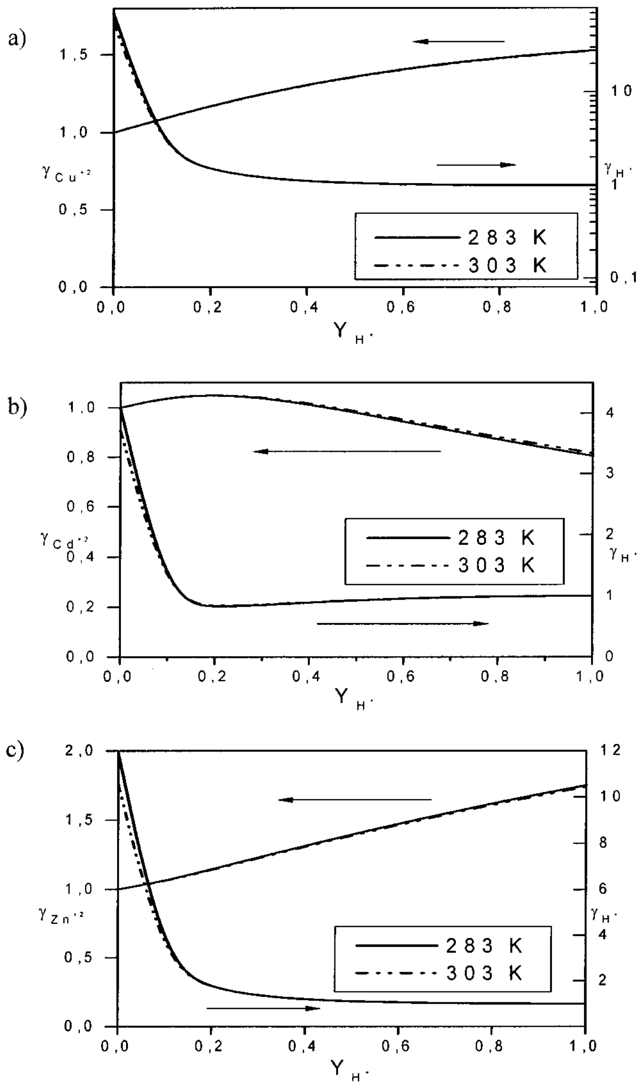

Figure 4. Activity coefficients in the resin phase: (a) $\bar{\gamma}_{Cu^{2+}}$ and $\bar{\gamma}_{H^+}$ for the system H^+/Cu^{2+}; (b) $\bar{\gamma}_{Cd^{2+}}$ and $\bar{\gamma}_{H^+}$ for the system H^+/Cd^{2+}; (c) $\bar{\gamma}_{Zn^{2+}}$ and $\bar{\gamma}_{H^+}$ for the system H^+/Zn^{2+}.

mixtures.[8] θ' is evaluated using a series of equations presented by Pitzer.[7]

The Φ terms can be calculated by using the equations

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{20}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \tag{21}$$

where ${}^{E}\theta(I)$ and ${}^{E}\theta'(I)$ account for electrostatic unsymmetrical mixing effects and depend only on the charges of the ions i and j, the total strength, and the density and dielectric constant of the solvent (hence, on the temperature and pressure). The values of these terms are graphically represented behind the ionic strength by Pitzer.[7]

Table 1 contains the values of the parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and $C^{(0)}_{MX}$ used in this work.

Results and Discussion

The capacity of the resin was obtained in a previous work,[9] and it was used to calculate the corresponding ionic fractions. It is 5 mmol/g of dry resin. In the set of equations presented above (eqs 5−10), the three unknown parameters (the equilibrium constant, K_{AB}, and the Wilson parameters Λ_{AB} and Λ_{BA}) were obtained by fitting of the experimental data to the model. A nonlinear regression method based on the Marquardt algorithm, described in previous works,[10,11] has been used to obtain the mentioned parameters. The experimental data and the values from the model are shown in Tables 2−4. Likewise, Table 5 contains the equilibrium constant (K_{AB}) and the binary interaction parameters of the Wilson equations (Λ_{AB} and Λ_{BA}). These values were used to plot the theoretical isotherms (Figures 1−3). Theoretical results for the ionic fraction of the metal ion in the resin phase are in good agreement with experimental values. The activity coefficients in the resin and liquid phases are shown in Figures 4−7. The activity coefficients in the liquid phase for the hydrogen cation are higher than those for metal cations.

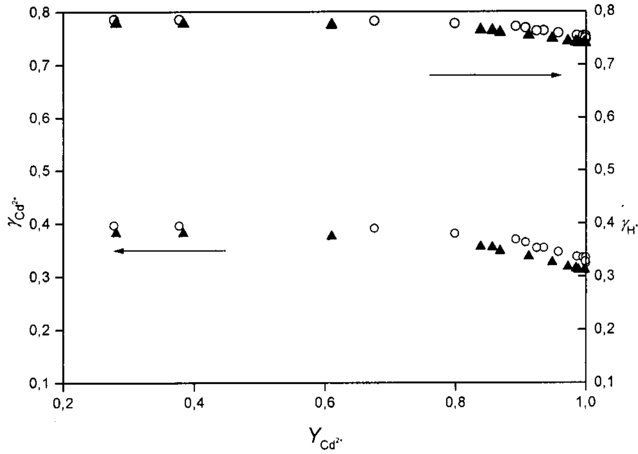

Figure 5. Activity coefficients in the liquid phase for the system H^+/Cd^{2+}, $c_t = 0.05\ mol{\cdot}L^{-1}$: ○, $T = 283$ K; ▲, $T = 303$ K.

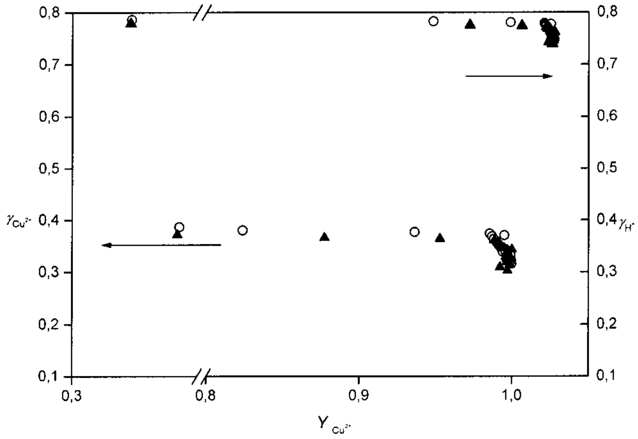

Figure 6. Activity coefficients in the liquid phase for the system H^+/Cu^{2+}, $c_t = 0.05\ mol{\cdot}L^{-1}$: ○, $T = 283$ K; ▲, $T = 303$ K.

The average deviation was calculated from the difference, in absolute value (ABS), between the experimental concentration of the metal ion in the resin and that predicted by the model, according to the following formula:

$$\text{Av. Dev. (\%)} = \frac{\sum_{i=1}^{n} \text{ABS}\left(\frac{y^{\text{exp}}_{M^{2+}} - y^{\text{theor}}_{M^{2+}}}{y^{\text{exp}}_{M^{2+}}}\right) \times 100}{n} \tag{22}$$

The average deviation is lower than 10% in most cases.

As expected, the value of the ion-exchange equilibrium constants, K_{AB}, increases with temperature, as shown in Table 5. Besides, calculated values of the equilibrium constants, K_{AB}, show that Amberlite IR-120 is more selec-

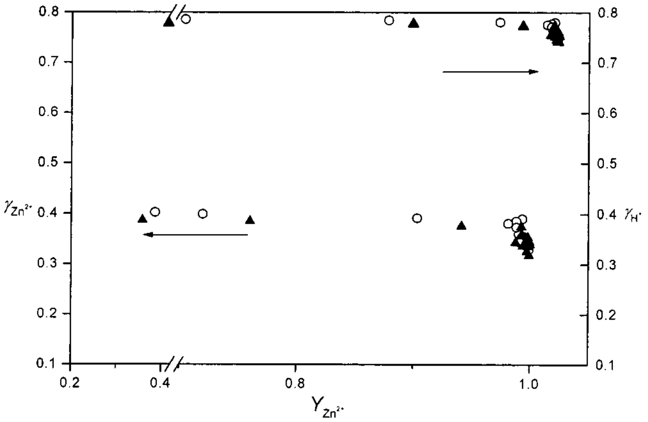

Figure 7. Activity coefficients in the liquid phase for the system H^+/Zn^{2+}, $c_t = 0.05$ mol·L^{-1}: ○, $T = 283$ K; ▲, $T = 303$ K.

Table 6. Ion-Exchange Equilibrium Constant, K_{AB}, Standard Gibbs Free Energy Change, $\Delta G°_{AB}$, Standard Enthalpy Change, $\Delta H°_{AB}$, and Standard Entropy Change, $\Delta S°_{AB}$, of the Binary Systems H^+/Cd^{2+}, H^+/Cu^{2+}, and H^+/Zn^{2+} at (283 and 303) K

system (A/B)	T/K	K_{AB}	$\Delta G°_{AB}$/(kJ·mol^{-1})	$\Delta H°_{AB}$/(kJ·mol^{-1})	$\Delta S°_{AB}$/(kJ·kmol^{-1})
H^+/Cu^{2+}	283	50.41	−9.22	−10.56	−4.71
H^+/Cu^{2+}	303	67.78	−10.62	−10.56	0.2178
H^+/Cd^{2+}	283	31.02	−8.08	−17.53	−33.39
H^+/Cd^{2+}	303	38.01	−9.16	−17.53	−27.61
H^+/Zn^{2+}	283	46.93	−9.05	−7.26	6.35
H^+/Zn^{2+}	303	76.74	−10.93	−7.26	12.13

tive for Cu^{2+}, Cd^{2+}, and Zn^{2+} than for H^+ and Mg^{2+}, whose values were calculated in previous works.[3] Furthermore, Amberlite IR-120 exhibits different orders of selectivity at (283 and 303) K, being $Cu^{2+} > Zn^{2+} > Cd^{2+} > Ca^{2+}$ at 283 K and $Zn^{2+} > Cu^{2+} > Cd^{2+} > Ca^{2+}$ at 303 K.[3]

In addition, the standard thermodynamic properties of the binary systems constituted by H^+/Cu^{2+}, H^+/Cd^{2+}, and H^+/Zn^{2+} and Amberlite IR-120 could be evaluated from the thermodynamic constant, K_{AB}, and the temperature:[10]

$$\Delta G°_{AB} = -RT \ln K_{AB} \tag{23}$$

$$\Delta H°_{AB} = (RT^2/\alpha\beta)\, \mathrm{d}(\ln K_{AB})/\mathrm{d}T \tag{24}$$

$$\Delta S°_{AB} = (\Delta H°_{AB} - \Delta G°_{AB})/T \tag{25}$$

Assuming a linear variation of ln K_{AB} with $1/T$, a negative slope is obtained. Table 6 contains these thermodynamic properties at (283 and 303) K.

The negative standard free energy would indicate that metal cations would be preferably bound to the resin as compared to the hydrogen cation, and this preference would increase at higher temperature. Furthermore, the exchange process is exothermic, as the negative enthalpy indicates.

Conclusions

Ion-exchange equilibrium H^+/Cu^{2+}, H^+/Cd^{2+}, and H^+/Zn^{2+} systems using the cationic exchanger Amberlite IR-120 have been measured at (283 and 303) K. Experimental equilibrium data can be satisfactorily correlated using the LAM using the Wilson and Pitzer limiting law equations to calculate activity coefficients in the solid and liquid phases, respectively. Theoretical results are in good agreement with experimental ones. As expected, the affinity of the resin for the metal ions increases with increasing temperature.

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