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Ion-Exchange Equilibria of Cu^{2+}, Cd^{2+}, Zn^{2+}, and Na^{+} Ions 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, Avda. de Camilo José Cela s/n,
13004 Ciudad Real, Spain

Equilibrium ion-exchange isotherms of Na^+/Cu^{2+}, Na^+/Cd^{2+}, and Na^+/Zn^{2+} on a strong acid resin, Amberlite IR-120, in 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 the solid phase. Wilson and Pitzer equations have been used to calculate activity coefficients in the solid and liquid phases, respectively. The values of the thermodynamic equilibrium constant demonstrate temperature dependence.

Introduction

Disposal of hazardous ions in aqueous waste streams is a significant industrial waste 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] In this direction, a great effort has been made in the synthesis of new classes of extractants, exchangers, and adsorbers capable of improving significantly the efficiency and selectivity of a number of separation techniques for a wide range of chemical species.

Strong acid resins may be used for the recovery of toxic metals under certain conditions. Although ion-exchange processes with alkaline and alkaline-earth metals have been extensively studied and are well documented, there are not practical studies considering cations such as Cu^{2+}, Cd^{2+}, and Zn^{2+}. As a consequence, industrial removal of these ions is far from being able to be quantified.

In this paper, Na^+/Cu^{2+}, Na^+/Cd^{2+}, and Na^+/Zn^{2+} ion-exchange equilibrium data were obtained in aqueous medium at (283 and 303) K and total concentrations in the solution of 0.05 mol·L^{-1} and 0.1 mol·L^{-1}. The experimental data were fitted to the homogeneous mass action law model[2,3] in order to obtain the thermodynamic equilibrium constant and the binary interaction parameters. Wilson and Pitzer equations are used to calculate activity coefficients in the solid and liquid phases, respectively.

Experimental Section

Chemicals. Zinc, copper, cadmium, and sodium nitrates were PRS grade supplied by Panreac (99%). Demineralized water was used with a conductivity value lower than 1 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 Na^+-form, as described by Lucas et al.[4]

Table 1. Parameters of the Pitzer Limiting Law

species	$\beta^{(0)}$	$\beta^{(1)}$	C_{MX}
$Na(NO_3)$	0.0068	0.178	−0.000 36
$Cd(NO_3)_2$	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. Comparison among Experimental and Predicted Ion-Exchange Equilibrium Data for Cd^{2+} on Amberlite IR-120

exp		theor	exp		theor
$X_{Cd^{2+}}$	$Y_{Cd^{2+}}$	$Y_{Cd^{2+}}$	$X_{Cd^{2+}}$	$Y_{Cd^{2+}}$	$Y_{Cd^{2+}}$
(a) $c_t = 0.05$ mol·L^{-1}; $T = 283$ K			(c) $c_t = 0.1$ mol·L^{-1}; $T = 283$ K		
0.0138	0.1866	0.1711	0.0284	0.1717	0.1803
0.0665	0.4356	0.4121	0.1525	0.4465	0.4643
0.1039	0.4934	0.4936	0.2607	0.5391	0.5825
0.1971	0.6012	0.6166	0.5872	0.8217	0.8077
0.4140	0.8243	0.7758	0.6695	0.8612	0.8543
0.6658	0.9344	0.8984	0.8454	0.9095	0.9447
0.8579	0.9424	0.9670	0.9528	0.9941	0.9864
(b) $c_t = 0.05$ mol·L^{-1}; $T = 303$ K			(d) $c_t = 0.1$ mol·L^{-1}; $T = 303$ K		
0.0019	0.1616	0.0862	0.0100	0.1900	0.1819
0.0070	0.2391	0.2223	0.0259	0.2741	0.3189
0.0173	0.3122	0.3594	0.0404	0.3596	0.3931
0.0401	0.3753	0.4979	0.0649	0.4351	0.4750
0.0312	0.6468	0.4565	0.0974	0.5026	0.5466
0.0755	0.7175	0.6016	0.1381	0.5619	0.6088
0.2841	0.8782	0.8105	0.1817	0.6183	0.6560
0.3454	0.9036	0.8415	0.2865	0.7135	0.7366
0.6417	0.9587	0.9407	0.6426	0.9153	0.9107
0.8382	0.9619	0.9791	0.7683	0.9278	0.9506
0.9500	0.9750	0.9943	0.8533	0.9742	0.9721
0.9185	0.9816	0.9904	0.9693	0.9742	0.9951

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 with maximum deviations of ±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 Na^+/Cu^{2+}, Na^+/Cd^{2+}, and Na^+/Zn^{2+} systems. To obtain these data, 0.1 L of a known composition solution were weighed and added into each of several flasks. Different known masses of resin, in Na^+-form, had previously been added

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* To whom correspondence should be addressed. E-mail: juanfran@inqu-cr.uclm.es. Fax: 34926295318.

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Table 3. Comparison among Experimental and Predicted Ion-Exchange Equilibrium Data for Cu^{2+} on Amberlite IR-120

exp		theor	exp		theor
$X_{Cu^{2+}}$	$Y_{Cu^{2+}}$	$Y_{Cu^{2+}}$	$X_{Cu^{2+}}$	$Y_{Cu^{2+}}$	$Y_{Cu^{2+}}$
(a) $c_t = 0.05$ mol·L^{-1}; $T = 283$ K			(c) $c_t = 0.1$ mol·L^{-1}; $T = 283$ K		
0.0091	0.2282	0.1807	0.0233	0.1765	0.2086
0.0515	0.4119	0.3872	0.0657	0.3338	0.3350
0.1408	0.5538	0.5408	0.1389	0.4598	0.4493
0.2700	0.6395	0.6574	0.2511	0.5480	0.5590
0.8062	0.8938	0.9240	0.3694	0.6297	0.6453
0.8564	0.9432	0.9441	0.8468	0.9064	0.9167
0.9602	0.9899	0.9846	0.9303	0.9389	0.9619
			0.9646	0.9706	0.9805
(b) $c_t = 0.05$ mol·L^{-1}; $T = 303$ K			(d) $c_t = 0.1$ mol·L^{-1}; $T = 303$ K		
0.0064	0.1932	0.1855	0.0189	0.1811	0.2292
0.0279	0.3687	0.3604	0.0540	0.3460	0.3625
0.1526	0.6472	0.6131	0.1179	0.4821	0.4813
0.1980	0.6988	0.6563	0.2168	0.5833	0.5884
0.2667	0.7329	0.7078	0.3448	0.6549	0.6827
0.3954	0.8052	0.7808	0.4727	0.7039	0.7569
0.6576	0.9019	0.8891	0.8015	0.8946	0.9136
0.8419	0.9667	0.9512	0.8862	0.9504	0.9507
0.9255	0.9829	0.9773	0.9210	0.9572	0.9658
0.9157	0.9842	0.9743	0.9185	0.9703	0.9647
			0.9592	0.9817	0.9824

Table 4. Comparison among Experimental and Predicted Ion-Exchange Equilibrium Data for Zn^{2+} on Amberlite IR-120

exp		theor	exp		theor
$X_{Zn^{2+}}$	$Y_{Zn^{2+}}$	$Y_{Zn^{2+}}$	$X_{Zn^{2+}}$	$Y_{Zn^{2+}}$	$Y_{Zn^{2+}}$
(a) $c_t = 0.05$ mol·L^{-1}; $T = 283$ K			(c) $c_t = 0.1$ mol·L^{-1}; $T = 283$ K		
0.0230	0.3763	0.3397	0.0193	0.1811	0.2586
0.0813	0.5204	0.4921	0.0589	0.3388	0.3766
0.1691	0.6252	0.5982	0.1277	0.4743	0.4791
0.2951	0.7077	0.6919	0.2249	0.5745	0.5698
0.3936	0.8081	0.7475	0.3454	0.6540	0.6530
0.8692	0.9540	0.9503	0.4685	0.7081	0.7244
0.9259	0.9826	0.9719	0.6100	0.7795	0.7992
			0.9268	0.9632	0.9613
(b) $c_t = 0.05$ mol·L^{-1}; $T = 303$ K			(d) $c_t = 0.1$ mol·L^{-1}; $T = 303$ K		
0.0040	0.1814	0.2098	0.0038	0.1936	0.1552
0.0306	0.3639	0.4195	0.0364	0.3616	0.3658
0.0776	0.5414	0.5393	0.1020	0.4961	0.4989
0.1462	0.6393	0.6287	0.2025	0.6007	0.6043
0.2510	0.7328	0.7119	0.4305	0.7585	0.7483
0.3906	0.8038	0.7875	0.5656	0.8654	0.8138
0.5594	0.8789	0.8572	0.8510	0.9594	0.9375
0.6758	0.9249	0.8985	0.9341	0.9697	0.9724
0.8909	0.9670	0.9673			
0.9402	0.9800	0.9822			

Table 5. Equilibrium Parameters of the Binary Systems Na^+/Cd^{2+}, Na^+/Cu^{2+}, and Na^+/Zn^{2+}, on the Resin Amberlite IR-120 at (283 and 303) K

system (A/B)	T/K	K_{AB}	Λ_{AB}	Λ_{BA}	av dev %	$10^{-2}C_{AB}{}^{A}$	$10^{-2}C_{AB}{}^{B}$
Na^+/Cu^{2+}	283	5.65	3.965	0.106	4.58	−1.331	−1.663
Na^+/Cu^{2+}	303	8.92	3.793	0.106	3.39	−1.331	−1.663
Na^+/Cd^{2+}	283	4.65	0.124	2.670	3.80	1.046	−0.350
Na^+/Cd^{2+}	303	14.37	0.133	2.670	11.72	1.046	−0.350
Na^+/Zn^{2+}	283	9.85	5.572	0.039	5.62	−2.117	−3.064
Na^+/Zn^{2+}	303	14.92	5.259	0.039	4.28	−2.117	−3.064

to each flask. The accuracy of weighing was ±0.0001 g. Solution and resin were maintained at fixed temperature (±0.1 K) under vigorous stirring, until the equilibrium was achieved (24 h). 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:

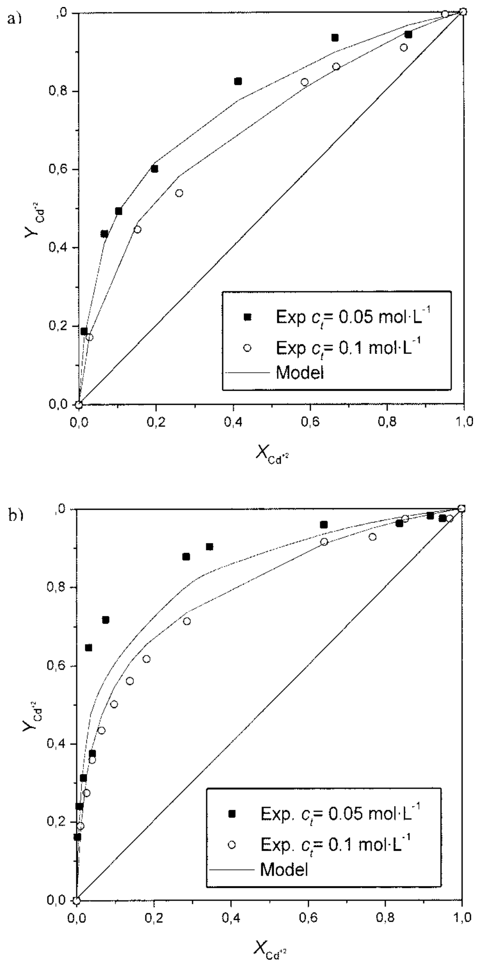

Figure 1. Equilibrium isotherms of Na^+/Cd^{2+} with Amberlite IR-120: (a) $c_t = 0.05$ mol·L^{-1} and $c_t = 0.1$ mol·L^{-1} at $T = 283$ K; (b) $c_t = 0.05$ mol·L^{-1} and $c_t = 0.1$ mol·L^{-1} at $T = 303$ K.

$$q^* = \frac{V}{W}(C_0 - C^*) \qquad (1)$$

where C_0 and C^* are the initial concentration and the equilibrium concentration of metal in the liquid phase (mol·L^{-1}), respectively, and q^* denotes the resin-phase equilibrium concentration of metal (mmol/g dry resin). V and W are the volume of solution and the mass of dry ion-exchange resin, respectively.

The solutions were analyzed for 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 sodium hydroxide).

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. Suppose that the ion exchanger (r) is initially in the A form and that the counterion in the solution (s) is B. Counterion exchange occurs, and the ion A in the ion

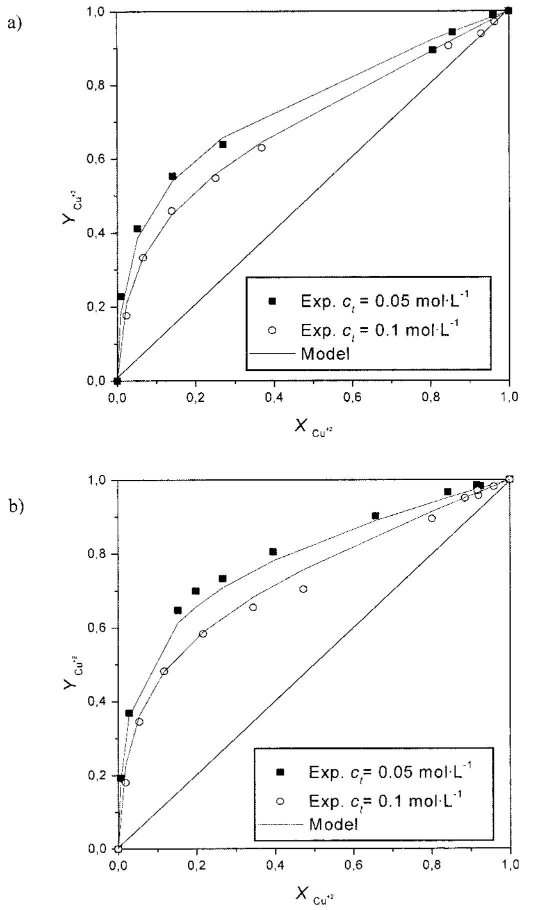

Figure 2. Equilibrium isotherms of Na^+/Cu^{2+} with Amberlite IR-120: (a) $c_t = 0.05$ mol·L^{-1} and $c_t = 0.1$ mol·L^{-1} at $T = 283$ K; (b) $c_t = 0.05$ mol·L^{-1} and $c_t = 0.1$ mol·L^{-1} at $T = 303$ K.

exchanger is partially replaced by B:

$$\beta \mathrm{A_r}^{\alpha+} + \alpha \mathrm{B_s}^{\beta+} \leftrightarrow \beta \mathrm{A_s}^{\alpha+} + \alpha \mathrm{B_r}^{\beta+} \tag{2}$$

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

$$x_\mathrm{A} = \frac{C_\mathrm{A}}{N}; \quad x_\mathrm{B} = \frac{C_\mathrm{B}}{N} \tag{3}$$

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

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.

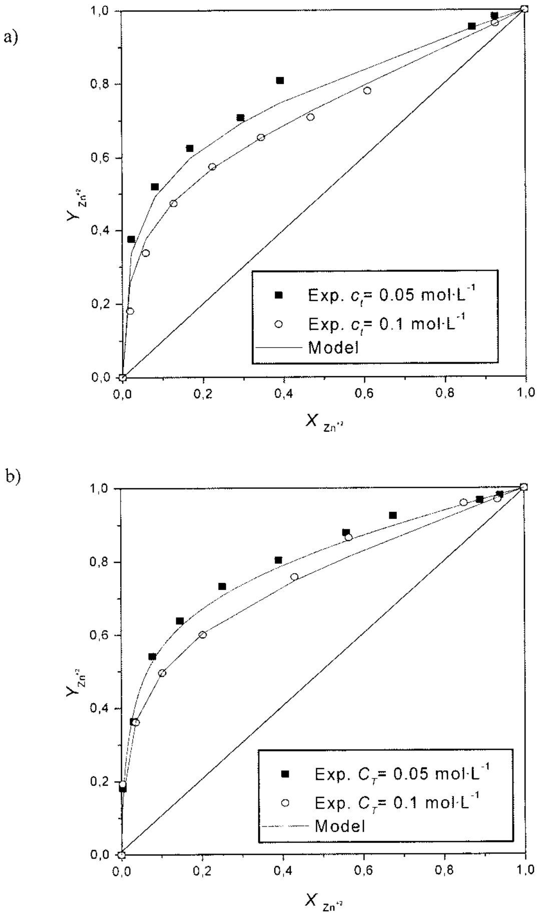

Figure 3. Equilibrium isotherms of Na^+/Zn^{2+} with Amberlite IR-120: (a) $c_t = 0.05$ mol·L^{-1} and $c_t = 0.1$ mol·L^{-1} at $T = 283$ K; (b) $c_t = 0.05$ mol·L^{-1} and $c_t = 0.1$ mol·L^{-1} at $T = 303$ K.

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

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

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

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

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

where Λ_AB and Λ_BA are the Wilson coefficients, T is the absolute temperature, and C_AB^A and C_AB^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]

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

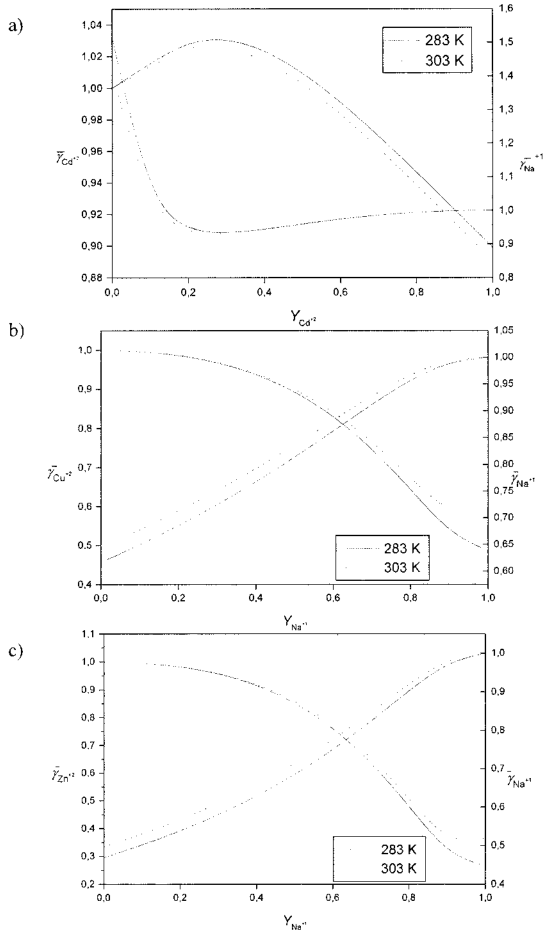

Figure 4. Activity coefficients in the resin phase: (a) $\bar{\gamma}_{Cd^{2+}}$ and $\bar{\gamma}_{Na^+}$ for the system Na^+/Cd^{2+} with Amberlite IR-120; (b) $\bar{\gamma}_{Cu^{2+}}$ and $\bar{\gamma}_{Na^+}$ for the system Na^+/Cu^{2+} with Amberlite IR-120; (c) $\bar{\gamma}_{Zn^{2+}}$ and $\bar{\gamma}_{Na^+}$ for the system Na/Zn^{2+} with Amberlite IR-120.

where c and c' are cations and a and a' are anions and m_i is the molality of the ion i. The charge is indicated by z_M. The quantity F includes the Debye−Hückel term and other terms as follows:

$$F = -A_\phi[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] + \sum_c\sum_a m_c m_a B_{ca}' + \sum_c\sum_{c'} m_c m_{c'} \Phi_{cc'}' + \sum_a\sum_{a'} m_a m_{a'} \Phi_{aa'}'$$

$$Z = \sum_i m_i|z_i| \qquad (11)$$

$$B_{ca}^{\phi} = B_{ca} + IB_{ca}' \qquad (12)$$

$$\Phi_{cc'}^{\phi} = \Phi_{cc'} + I\Phi_{cc'}' \qquad (13)$$

where I is the ionic strength in the bulk phase in molal units, 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 of different cations or anions. The constant b has the value 1.2 $kg^{1/2}\cdot mol^{-1/2}$, and the constant A_ϕ has the values 0.3821 and 0.3949 at 10 °C and 30 °C, respectively. The parameter C_{MX} is related to the commonly tabulated parameter C^{Φ}_{MX} by the equation

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

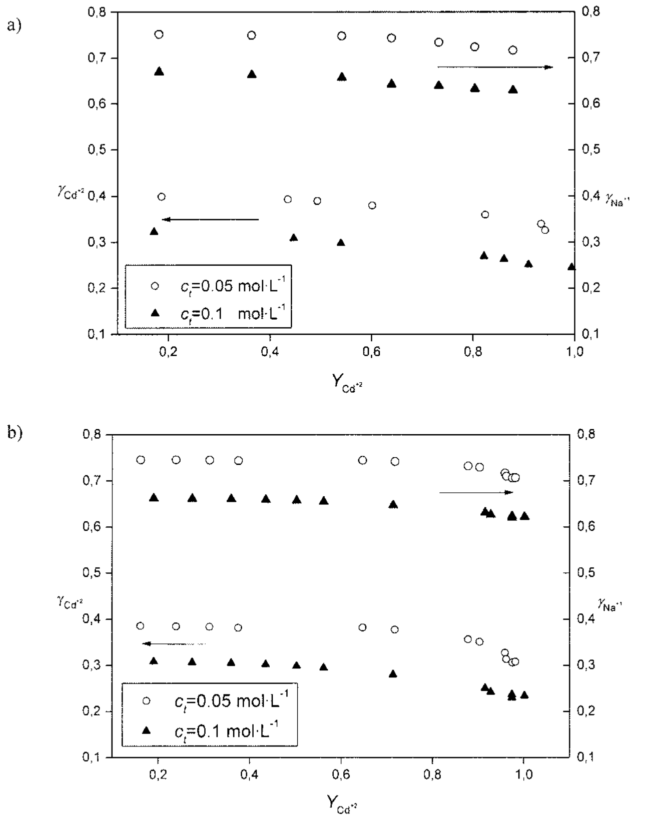

Figure 5. Activity coefficients in the liquid phase for the system Na^+/Cd^{2+}: (a) $\gamma_{Cd^{2+}}$ and γ_{Na^+} at T = 283 K; (b) $\gamma_{Cd^{2+}}$ and γ_{Na^+} at T = 303 K.

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

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

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

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

where the functions g and g' are given by

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

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

The above equations are valid for 1−1, 1−2, and 2−1 electrolytes. Values for $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and $C^{(0)}_{MX}$ are species-dependent and are tabulated by Pitzer et al.[6] $\beta^{(2)}_{MX}$ is important only for 2−2 or higher valence electrolytes that show a tendency toward electrostatic ion pairing. A value of 2.0 $kg^{1/2}\cdot mol^{-1/2}$ for α is recommended by Pitzer.[7] The values of θ' and ψ are known for 69 binary electrolyte mixtures.[8] θ' is evaluated using a series of equations presented by Pitzer et al.[6]

The Φ terms can be calculated by using the equations

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

$$\Phi_{ij}' = {}^{E}\theta_{ij}'(I) \qquad (21)$$

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, an the density and

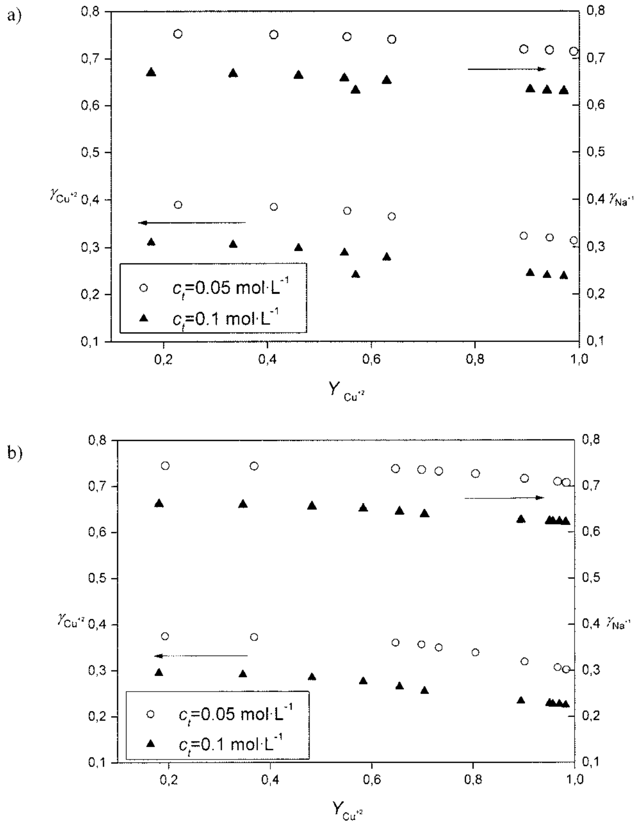

Figure 6. Activity coefficients in the liquid phase for the system Na^+/Cu^{2+}: (a) $\gamma_{Cu^{2+}}$ and γ_{Na^+} at T = 283 K; (b) $\gamma_{Cu^{2+}}$ and γ_{Na^+} at T = 303 K.

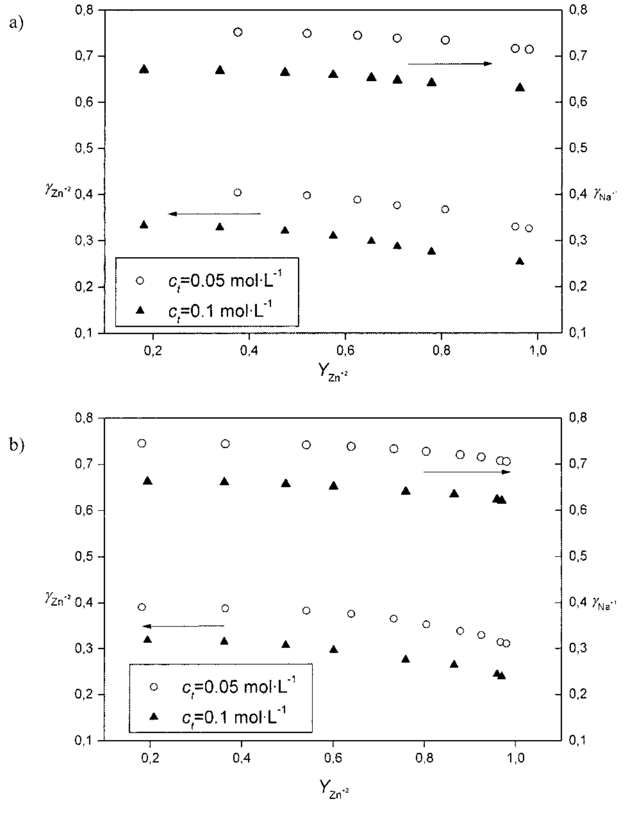

Figure 7. Activity coefficients in the liquid phase for the system Na^+/Zn^{2+}: (a) $\gamma_{Zn^{2+}}$ and γ_{Na^+} at T = 283 K; (b) $\gamma_{Zn^{2+}}$ and γ_{Na^+} at T = 303 K.

Table 6. Standard Thermodynamic Properties of the Binary Systems Na^+/Cd^{2+}, Na^+/Cu^{2+}, and Na^+/Zn^{2+}, on the Resin Amberlite IR-120 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}
Na^+/Cu^{2+}	283	5.65	−4.06	−16.28	−43.12
Na^+/Cu^{2+}	303	8.92	−5.52	−16.28	−35.52
Na^+/Cd^{2+}	283	4.65	−3.62	−40.22	−129.34
Na^+/Cd^{2+}	303	14.37	−6.72	−40.22	−110.58
Na^+/Zn^{2+}	283	9.85	−5.38	−14.80	−33.28
Na^+/Zn^{2+}	303	14.92	−6.80	−14.80	−26.38

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 et al.[6]

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

In this set of equations, the three unknown parameters (the equilibrium constant and the Wilson parameters) were obtained by fitting of the experimental data to the model. A nonlinear regression method based on the Marquardt algorithm, described in previous works,[9,10] has been used to obtain the mentioned parameters.

Results and Discussion

The capacity of the resin was obtained in order to calculate the corresponding ionic fractions, and was found to be 5 mmol/g of dry resin. The experimental data and the theoretical ones from the model are shown in Tables 2−4. Likewise, Table 5 contains the equilibrium constant (K_{AB}) and the binary interaction parameters of Wilson (Λ_{AB} and Λ_{BA}). These values were used to plot the theoretical equilibrium isotherms (Figures 1−3). Theoretical results are in good agreement with experimental ones. The activity coefficients in the solid and liquid phases are shown in Figures 4−7. As can be seen, activity coefficients in the liquid phase for the sodium cation are higher than those for the metal cations.

The average deviation from an experimental basis 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 models, according to the following formula:

$$\text{av dev (\%)} = \frac{\sum_{i=1}^{m} \text{ABS}\left(\frac{Y_{M^{2+}}^{\text{exp}} - Y_{M^{2+}}^{\text{theor}}}{Y_{M^{2+}}^{\text{exp}}}\right) \times 100}{m} \qquad (22)$$

The average deviation is lower than 12% in most cases.

As expected, ion-exchange equilibrium increases with temperature, as shown in Table 5. In addition, ion-exchange equilibrium curves for different metal ion concentrations in solution are not coincident, because concentrations in the resin phase are a parameter included in the equilibrium constant. Besides, the equilibrium constant and the selectivity do not change with concentration but the equilibrium curves move to the diagonal as the concentration increases.

Calculated values of the equilibrium constants, K_{AB}, show that Amberlite IR-120 is more selective for Cu^{2+}, Cd^{2+}, and Zn^{2+} than for Mg^{2+}, whose values were calculated in previous works.[2] Furthermore, Amberlite IR-120 exhibits different orders of selectivity at (283 and 303) K, being $Zn^{2+} > Ca^{2+} > Cu^{2+} > Cd^{2+}$ at 283 K and $Zn^{2+} > Cd^{2+} > Ca^{2+} > Cu^{2+}$ at 303 K.[2]

In addition, the standard thermodynamic properties of the binary systems constituted by Na^+/Cu^{2+}, Na^+/Cd^{2+}, and Na^+/Zn^{2+} and Amberlite IR-120 could be evaluated from the thermodynamic constant, K_{AB}, and the temperature:[9]

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

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

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

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 sodium cation and this preference would increase at higher temperature. On the other hand, the negative value of the standard entropy could suggest that metal cations would be more strongly bound to the resin than the sodium cation. Furthermore, the exchange process is exothermic, as the negative enthalpy indicates.

Conclusions

Ion-exchange equilibrium Na^+/Cu^{2+}, Na^+/Cd^{2+}, and Na^+/Zn^{2+} systems using cationic exchanger Amberlite IR-120 have been measured at (283 and 303) K. Experimental equilibrium data can be satisfactorily correlated using the homogeneous mass action model (LAM) using the Wilson and Pitzer limiting law equations to calculate activity coefficients in the solid phase and in the liquid phase, respectively. Theoretical results are in good agreement with experimental ones.

As expected, the temperature of the reaction has an influence on the equilibrium behavior. In addition, the selectivity of the resin changes with the metal ion concentration in solution.

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