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Ion-exchange equilibria of Cu(II) and Zn(II) from aqueous solutions with Chelex 100 and Amberlite IRC 748 resins

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Abstract

Two chelating ion exchange resins Chelex 100 and Amberlite IRC 748 (formerly, IRC 718), both which have iminodiacetic acid (IDA) function group, were used to exchange Cu(II) and Zn(II) from aqueous solutions. Batch experiments were performed using the Na-form resins by varying the initial concentration of metals (0.8–10.5 mol/m^3), initial aqueous pH (1.0–5.0), and temperature (15–45 °C). It was shown that the amount of Cu(II) and Zn(II) exchanged increased with increasing the pH value and temperature. In addition, the amount of metals exchanged using IRC 748 resin was greater than Chelex 100 resin under comparable conditions. The equilibrium data were treated and compared by the conventional Langmuir adsorption isotherm and by the mass-action law that takes into account the activity corrections of the ions in the aqueous phase. The enthalpy changes for the present ion-exchange processes were also evaluated and discussed.

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Keywords: Ion exchange; Cu(II); Zn(II); Chelating resins; Equilibrium studies

1. Introduction

Ion exchange now is a well-established technology, particularly in water purification and the concentration and removal of hazardous substances at very low concentrations in chemical process industries [1]. For example, it has been applied for the recovery of copper from rayon spinning wastewater and the recovery of gold from cyanide solution in metallurgical industries. Besides, many studies presented covered applications in the wine industry, the separation of amino acids and nucleic acids, and therapeutic uses. However, selective removal of one or more metal ions from multi-metal mixtures using common organic cation exchange resins is generally not feasible, especially for those ions with the same valence [2]. Ion exchange resins with specific functional groups such as iminodiacetic acid, aminophosphonic acid, and amidoxime, as commonly referred to the chelating resins, can meet such requirements, although their high manufacturing costs make them rather limited for practical applications [3].

In the past, the use of chelating resins for selective removal of heavy metals from process and waste streams has been extensively studied [1,3–18]. Of these studies, the resins with iminodiacetic acid (IDA) functional group such as Chelex 100, Amberlite IRC 748 (formerly, IRC 718), Purolite S930, and Lewatit TP 207 were mainly applied due to their high selectivity and low manufacturing cost [3]. The IDA group could provide electron pairs so that the binding forces for alkaline earth metals is 5000 times than those for alkali metals like Na^+, which can react with divalent metals to form a stable coordination covalent bond. For example, the resins Chelex 100 and IRC 718 have been used to treat the waste effluents discharged from printed circuit board manufacturing, which contain Cu^{2+}, Ni^{2+}, Na^+, and some strong complexing agents such as EDTA and citrate [2,5,6]. Moreover, Korngold et al. [8] removed Cu^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+} from tap water containing small amounts of salts of carboxylic acid using Purolite S930 resin. They indicated that the presence of one carboxylic group salts such as acetate has little effect on exchange performance. The presence of salts with two or four carboxylic groups such as tartrate and EDTA dramatically decreases the column exchange efficiency.

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Nomenclature

a_i	activity of species i
C_e	aqueous-phase metal concentration at equilibrium (mol/m^3)
C_0	initial aqueous-phase metal concentration (mol/m^3)
ΔH°	standard enthalpy change of exchange reaction (kJ/mol)
I	ionic strength of the solution (mol/kg)
K_L	Langmuir constant (m^3/mol)
$K_{M\text{–}Na}$	exchange reaction constant (mol/kg)
m_i	molality of species i (mol/kg)
q_e	amount of metal exchanged at equilibrium (mol/kg)
q_{sat}	saturated amount of metal exchanged under specified conditions (mol/kg)
V	volume of the solution (m^3)
W	weight of dry resins (kg)
z_i	valance of the ion i

Greek letter

γ_i	activity coefficient of species i

Subscript

0	initial

Superscript

0	thermodynamic basis

In general, the exchange equilibrium can be represented either by "adsorption" isotherms such as the Langmuir equation (macroscopic basis) [10–14] or by the mass-action law (microscopic basis) [15–18]. To our knowledge, little attention has been paid to comparing both two types of data treatment with respect to the same system. In this work, the exchange equilibria of Cu^{2+} and Zn^{2+} with Chelex 100 and Amberlite IRC 748 resins were systematically studied in a batch mode. Experiments were performed at different initial concentrations of metals (0.8–10.5 mol/m^3), initial aqueous pH values (1.0–5.0), and temperatures (15–45 °C). The common two-parameter Langmuir equation and the mass-action law considering activity corrections and ion strength effect in the aqueous phase were used to describe the exchange equilibrium phenomena.

2. Materials and methods

2.1. Resins and solutions

In this work, two chelating resins Chelex 100 (Sigma Co.) and Amberlite IRC 748 (Rohm Haas Co.) were used because they both contain IDA functional groups. The physical properties and specifications as reported by the suppliers are listed in Table 1. Prior to use, these resins were washed with NaOH (1 mol/dm^3), HCl (1 mol/dm^3), and *n*-hexane to remove possible organic and inorganic impurities. They were then washed with deionized water (Millipore Milli-Q) three times, and were converted to Na^+ form by column flushing with 1 mol/dm^3 NaCl for 12 h [16]. These resins were finally washed with deionized water and dried in vacuum oven at 60 °C.

Table 1
Physical and chemical properties of the chelating resins used

Properties	Chelex 100	Amberlite IRC 748
Grade	Laboratory grade	Industrial grade
Physical form	Small, white beads	Opaque, beige beads
Functional group	Iminodiacetic acid	Iminodiacetic acid
Matrix	Styrene-divinylbenzene	Styrene-divinylbenzene
Structure	Macroporous	Macroporous
Particle size (mm, dry)	0.15–0.30 (50–100 mesh)	0.50–0.65
Capacity (eq/dm^3 of resin)	0.7	1.25
Bulk density (g/cm^3)	0.9681	0.6872
pH range	0–14	1.5–14
Maximum operating temperature	75 °C (Na^+ form)	90 °C (Na^+ form)

Analytical-reagent grade of $Cu(NO_3)_2$, $Zn(NO_3)_2$, and other inorganic chemicals including NaCl, HCl, NaOH, and HNO_3 were purchased from Merck Co. The aqueous phase was prepared by dissolving metal nitrate in deionized water (Millipore, Milli-Q), and the initial concentrations were in the range 0.8–10.5 mol/m^3. The initial aqueous pH was adjusted to be in the range 1.0–5.0 by adding a small amount of 0.1 mol/dm^3 HNO_3 or 0.1 mol/dm^3 NaOH.

2.2. Experimental procedures

In the exchange experiments, an aliquot of dry resin (0.3 g) and 100 cm^3 of the aqueous phase were placed in a 125 cm^3 glass-stoppered flask and shaken at 120 rpm for 48 h in a shaker (Firstek B603, Taiwan). The shaker bath was controlled at several fixed temperatures (15–45 °C). After equilibrium, the concentrations of metals in the aqueous phase were analyzed by a Perkin-Elmer atomic absorption spectrophotometer (AA-100). In addition, the solution pH was measured with a digital pH meter (Mettler MP 220). The amount of metal exchanged at equilibrium, q_e (mol/kg), was thus calculated by

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ions in the aqueous phase, respectively (mol/m^3), and W/V is the dose of dry resin (3 kg/m^3). Each experiment was at least duplicated under identical conditions. The reproducibility of the measurements was within 4%.

3. Results and discussion

3.1. Effect of aqueous pH

Figs. 1–3 show the typical time profiles for exchange of metal ions with Na-form chelating resins. It is found that the concentrations of Cu^{2+} and Zn^{2+} in the solution decrease rapidly within 200 min and the exchange is virtually completed within 600–800 min. Thus, an equilibrium time of 48 h was selected in all experiments as described in the above section.

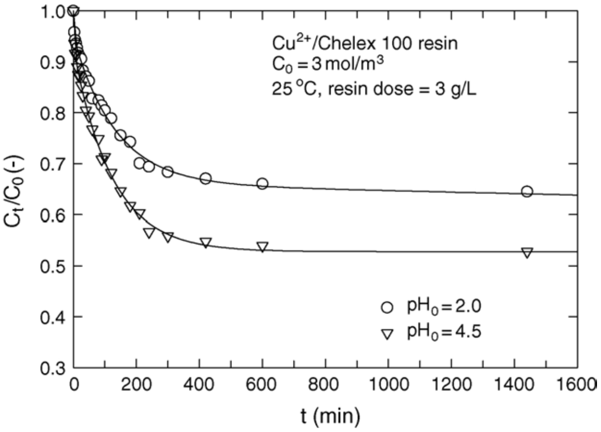

Fig. 1. Time profiles for the exchange of Cu^{2+} with Na-form Chelex 100 resin at 25 °C.

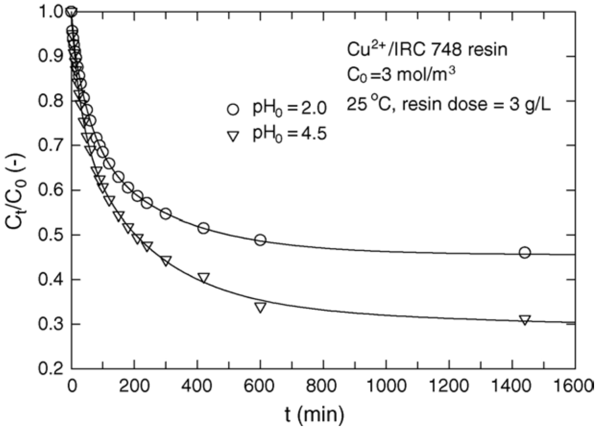

Fig. 2. Time profiles for the exchange of Cu^{2+} with Na-form IRC 748 resin at 25 °C.

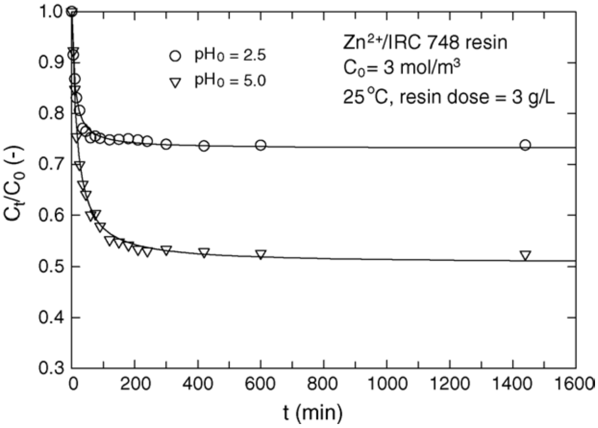

Fig. 3. Time profiles for the exchange of Zn^{2+} with Na-form IRC 748 resin at 25 °C.

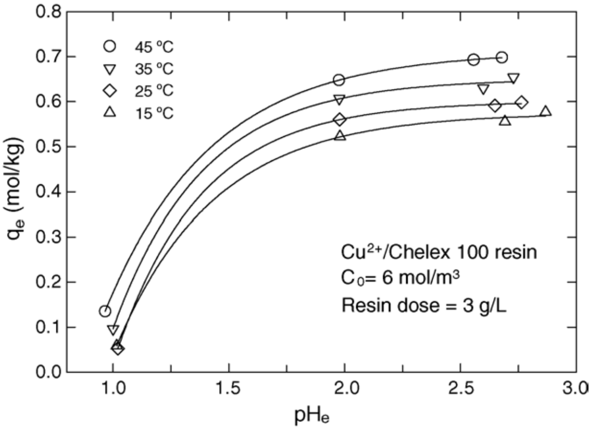

Fig. 4. Effect of equilibrium pH on the amount of Cu^{2+} exchanged with Na-form Chelex 100 resin at 25 °C.

The influence of equilibrium aqueous pH (pH_e) on the amount of metals exchanged (q_e) using the Na-form chelating resins are shown in Figs. 4–6. It is seen that the q_e value increases sharply with increasing pH_e, and finally levels off [13,14]. This trend is likely ascribed to the competitive binding between Cu^{2+} or Zn^{2+} and H^+ ions for the binding sides on the resin surface [16]. When the initial pH value is below 2, an excess of H^+ ions compete effectively with Cu^{2+} or Zn^{2+} for binding sites, to result in a lower level of metal uptake, so the final pH becomes higher after exchange. But at an initial pH of 4–5, the final pH becomes lower after exchange.

Equilibrium isotherm, the relationship between the amount of exchange (q_e) and the remaining concentration in the aqueous phase (C_e), is important to describe how metal ions interact with the resins and so critical in optimizing the use of the resins. Figs. 7–9 illustrate typical exchange isotherms of Cu^{2+} and Zn^{2+} ions onto Chelex 100 and IRC

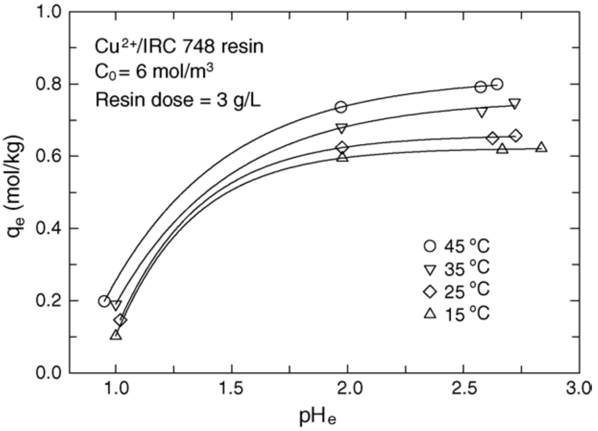

Fig. 5. Effect of equilibrium pH on the amount of Cu^{2+} exchanged with Na-form IRC 748 resin at 25 °C.

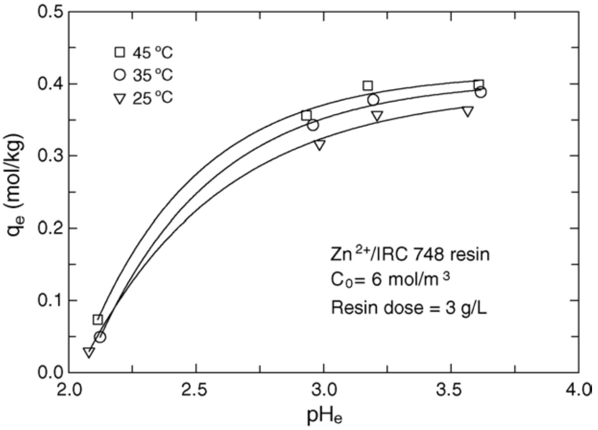

Fig. 6. Effect of equilibrium pH on the amount of Zn^{2+} exchanged with Na-form IRC 748 resin at 25 °C.

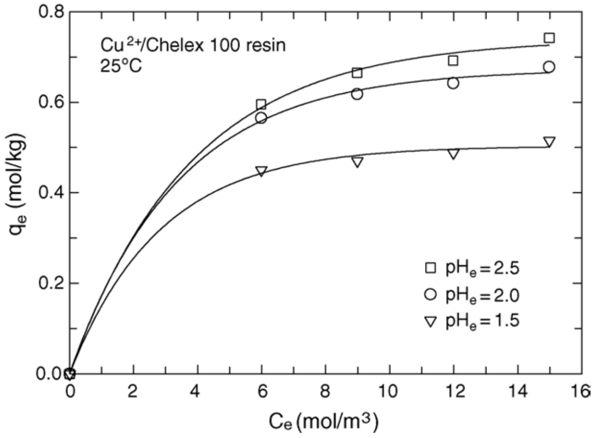

Fig. 7. Exchange isotherms of Cu^{2+} onto Na-form Chelex 100 resin at different equilibrium pH values (the solid curves are calculated by the Langmuir equation).

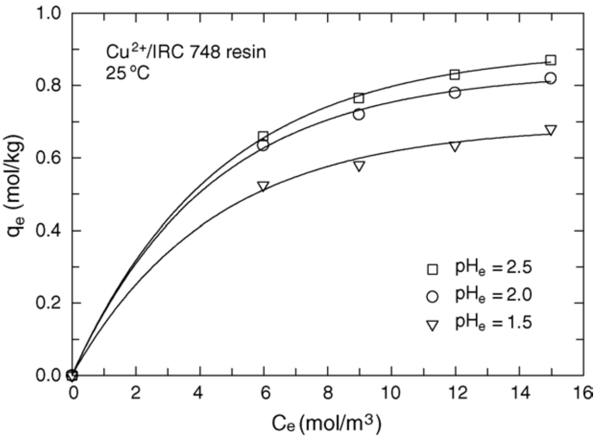

Fig. 8. Exchange isotherms of Cu^{2+} onto Na-form IRC 748 resin at different equilibrium pH values (the solid curves are calculated by the Langmuir equation).

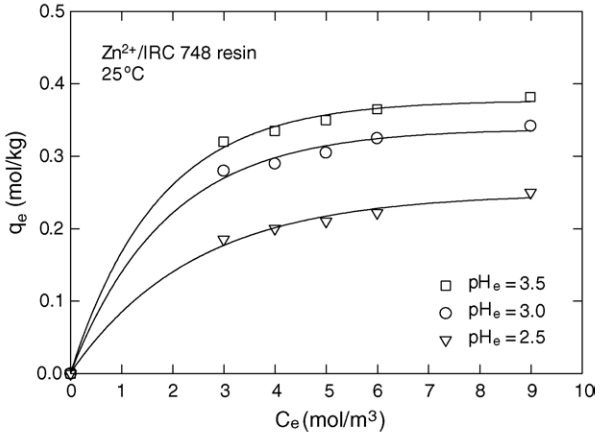

Fig. 9. Exchange isotherms of Zn^{2+} onto Na-form IRC 748 resin at different equilibrium pH values (the solid curves are calculated by the Langmuir equation).

748 resins at three fixed equilibrium pH and 25 °C. It is found that the exchange isotherm eventually reaches the plateau, which represents the saturated amount for the metals of interest on chelating resins under the specified conditions.

3.2. *Macroscopic equilibrium studies—isotherm modeling*

If ion exchange resin is thought as a charged adsorbent, the adsorption isotherm equations can be thus applicable. Of these equations, Langmuir equation is widely adopted because the exchange reaction is essentially a kind of chemical reaction [10–14,19–22]. The Langmuir equation applies to the ion exchange process with specific assumption, viz: that (i) maximum adsorption depends on the saturation level of a monolayer of solute molecules on the adsorbent surface, (ii) the solid surface is provided with distribution uniform on the site adsorption, (iii) each adsorbed matter on the site adsorption has the same affinity, and (iv) for homovalent and heterovalent exchange, the concentration of one of the ions or of the total solution is constant [10,14,21].

The common two-parameter Langmuir equation is given by

$$q_e = \frac{q_{sat} K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_{sat} is the saturated amount of metal exchanged at given solution conditions (mol/kg) and K_L the Langmuir constant (m^3/mol). Eq. (2) can be rewritten by

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{sat} K_L}\right) + \left(\frac{1}{q_{sat}}\right) C_e \tag{3}$$

Table 2 lists the values of q_{sat} and K_L, which are graphically determined from the plot of C_e/q_e versus C_e. Basically, the Langmuir fit is good (correlation coefficient, $R^2 > 0.992$). In fact, the Freundlich equation is also tried here but the fit is slightly worse ($R^2 > 0.974$). In this work, the maximum q_{sat} values at 25 °C are found to be 0.88 mol/kg (pH_e

Table 2
Parameters of the Langmuir equation for the exchange of Cu^{2+} and Zn^{2+} with Na-form chelating resins at different temperatures[a]

System	pH_e	15 °C		25 °C		35 °C		45 °C	
		q_{sat}	K_L	q_{sat}	K_L	q_{sat}	K_L	q_{sat}	K_L
Cu–Chelex 100	1.5	0.53	0.585	0.57	0.577	0.65	0.527	0.70	0.516
	2.0	0.70	0.505	0.78	0.498	0.82	0.464	0.86	0.435
	2.5	0.78	0.441	0.88	0.423	0.91	0.378	0.94	0.345
Cu–IRC 748	1.5	0.74	0.337	0.85	0.264	0.89	0.255	1.00	0.231
	2.0	0.91	0.359	1.02	0.319	1.07	0.284	1.08	0.273
	2.5	0.96	0.353	1.10	0.314	1.12	0.299	1.15	0.250
Zn–IRC 748	2.5			0.31	1.090	0.33	0.972	0.35	0.958
	3.0			0.39	0.768	0.43	0.714	0.45	0.702
	3.5			0.43	0.503	0.44	0.472	0.46	0.458

[a] Units: q_{sat} (mol/kg) and K_L (m^3/mol).

2.5), 1.10 mol/kg (pH_e 2.5), and 0.43 mol/kg (pH_e 3.5) in the Cu–Chelex 100, Cu–IRC 748, and Zn–IRC 748 systems, respectively.

Rao et al. [13] have also used the Duolite ES-467 resin with aminophosphonic acid group to treat the wastewater containing Cu(II) and Zn(II). On the basis of the Langmuir equation, they found comparable maximum exchange capacity for Cu^{2+} and Zn^{2+}, i.e., 1.18 mol/dm^3 of resin at pH 5 and 0.49 mol/dm^3 of resin at pH 3.5, respectively.

Although the representation of equilibrium data by “adsorption” isotherm equations is simple and excellent, their parameters such as q_{sat} and K_L obviously depend on the solution environment particularly on the pH in this case. This makes the expression complicated. Consequently, more unified treatment based on the mass-action law is required.

3.3. Microscopic equilibrium studies—mass action law

The exchange reaction of divalent metals (M^{2+}) using the Na-form Chelex 100 and IRC 748 resins can be represented by [4,10,15]

$$\mathrm{RNa_2 + M^{2+} \Leftrightarrow RM + 2Na^+}, \quad \mathrm{K_{M\text{–}Na}} \tag{4}$$

where R refers to the resin matrix.

Considering the ionic strength effect of aqueous phase and the non-ideal phenomena, we write the thermodynamic equilibrium constant $K^0_{\text{M–Na}}$ as [23,24]

$$K^0_{\text{M–Na}} = \frac{a_{\mathrm{RM}}a^2_{\mathrm{Na}}}{a_{\mathrm{RNa_2}}a_{\mathrm{M}}} = \left(\frac{m_{\mathrm{RM}}m^2_{\mathrm{Na}}}{m_{\mathrm{RNa_2}}m_{\mathrm{M}}}\right)\left(\frac{\gamma_{\mathrm{RM}}\gamma^2_{\mathrm{Na}}}{\gamma_{\mathrm{RNa_2}}\gamma_{\mathrm{M}}}\right) \tag{5}$$

where a_i is the activity of species i, γ the activity coefficient, and m the molality (mol/kg).

Because the activity of species in the resin phase is rather difficult to accurately determine [23], the concentration instead of the activity is used for simplicity. That is, the non-ideality corrections are not made with respect to the resin phase, and the ratio $(\gamma_{RM}/\gamma_{RNA_2})$ is assumed to be kept nearly constant under the conditions studied.

In this work, the extended Debye–Huckel limiting law, Davies equation, and Pitzer method are adopted to calculate the activity coefficients of the cations in the aqueous phase [25,26].

(1) The extended Debye–Huckel limiting law [25]

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + Bd_i\sqrt{I}} \tag{6}$$

where z_i is the valance of ion i and I is the ionic strength which is defined as $I = 0.5\sum m_i z_i^2$. At 25 °C, the constants A and B are 0.51 (mol/kg)$^{1/2}$ and 3.3×10^9 (kg/mol)$^{1/2}$/m, respectively. Here, d_i is the effective diameter of the hydrated ion i ($d_{\mathrm{H}} = 0.6$ nm, $d_{\mathrm{Na}} = 0.5$ nm, and $d_{\mathrm{Cu}} = d_{\mathrm{Zn}} = 0.6$ nm) [25]. It is assumed that these constants are temperature-independent under the ranges studied. In general, this law gives a fair representation of γ_i’s of the solution up to $I = 0.1$ mol/kg.

(2) Davies equation [25]

$$\log \gamma_i = -A|z_+z_-|\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right) \tag{7}$$

This equation enables the activity coefficients to be calculated with an uncertainty not greatly exceeding 2% at a molality of 0.1 mol/kg at 25 °C.

(3) Pitzer method [26]

The equation for cation M in the mixed solution (with the anion X) is expressed as

$$\begin{aligned}\ln \gamma_{\mathrm{M}} &= z^2_{\mathrm{M}}F + \sum m_{\mathrm{A}}(2\beta_{\mathrm{MA}} + zC_{\mathrm{MA}}) \\ &\quad + z_{\mathrm{M}}\sum\sum m_{\mathrm{C}}m_{\mathrm{X}}C_{\mathrm{CX}}\end{aligned} \tag{8}$$

where

$$\begin{aligned}F &= -A_\phi\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \left(\frac{2}{b}\right)\ln(1+b\sqrt{I})\right] \\ &\quad + \sum\sum m_{\mathrm{C}}m_{\mathrm{A}}\beta'_{\mathrm{CA}}\end{aligned} \tag{9}$$

$$z = \sum m_i|z_i| = 2\sum m_{\mathrm{C}}z_{\mathrm{C}} \tag{10}$$

Table 3
Thermodynamic equilibrium constants for the exchange of Cu^{2+} and Zn^{2+} with Na-form chelating resins using different methods

System	Temperature (°C)	Debye–Huckel	Davies	Pitzer
Cu–Chelex 100	15	2.58×10^{-3}	3.54×10^{-3}	3.89×10^{-3}
	25	4.39×10^{-3}	6.02×10^{-3}	6.61×10^{-3}
	35	7.93×10^{-3}	1.08×10^{-2}	1.20×10^{-2}
	45	1.20×10^{-2}	1.64×10^{-2}	1.83×10^{-2}
Cu–IRC 748	15	2.83×10^{-3}	3.87×10^{-3}	4.24×10^{-3}
	25	4.94×10^{-3}	6.76×10^{-3}	7.43×10^{-3}
	35	8.33×10^{-3}	1.14×10^{-2}	1.26×10^{-2}
	45	1.42×10^{-2}	1.93×10^{-2}	2.18×10^{-2}
Zn–IRC 748	25	2.31×10^{-4}	2.97×10^{-4}	3.13×10^{-4}
	35	3.19×10^{-4}	4.11×10^{-4}	4.36×10^{-4}
	45	4.07×10^{-4}	5.24×10^{-4}	5.61×10^{-4}

$$C_{MX} = \frac{C^{\phi}_{MX}}{2|z_M z_X|^{1/2}} \tag{11}$$

and $A_\phi = 0.391$ and $b = 1.2$ at 25 °C.

For 1–1, 1–2, and 2–1 electrolytes, β_{MX} and β'_{MX} are given by

$$\beta_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} f(x) \tag{12}$$

$$\beta'_{MX} = \beta^{(1)}_{MX} \frac{f'(x)}{I} \tag{13}$$

where

$$f(x) = \frac{2}{x^2}[1 - (1 + x)\exp(-x)] \tag{14}$$

$$f'(x) = \frac{2}{x^2}\left[1 - \left(1 + x + \frac{x^2}{2}\right)\exp(-x)\right] \tag{15}$$

$$x = \alpha\sqrt{I} \tag{16}$$

and $\alpha = 2.0$ at 25 °C. It is also assumed that these constants are temperature-independent under the ranges studied [27]. The constants $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and C^{ϕ}_{MX} characteristic of the single electrolyte MX are taken from the literature [26].

Table 3 lists the calculated thermodynamic equilibrium constants, showing that they increase with increasing temperature for a given system. Moreover, the $K^0_{Cu–Na}$ values obtained with the two resins are considered to be acceptably consistent.

3.4. Thermodynamic parameters

The standard enthalpy change for exchange reaction, ΔH°, can be obtained by the following van't Hoff equation [17,22,24]

$$\left(\frac{d \ln K^0}{d(1/T)}\right)_P = \frac{-\Delta H^\circ}{R} \tag{17}$$

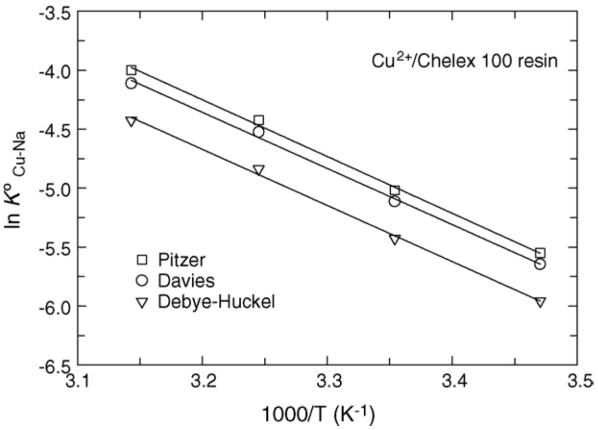

Fig. 10. The van't Hoff plot for the exchange of Cu^{2+} with Na-form Chelex 100 resin.

Figs. 10–12 show the good linearity for the plots of $\ln K^0$ versus $1/T$ ($R^2 > 0.995$), and the calculated ΔH° values are listed in Table 4.

The standard enthalpy changes in the Cu–Chelex 100, Cu–IRC 748 and Zn–IRC 748 systems are obtained to be 39.7, 43.1, and 22.6 kJ/mol, respectively. The reactions are

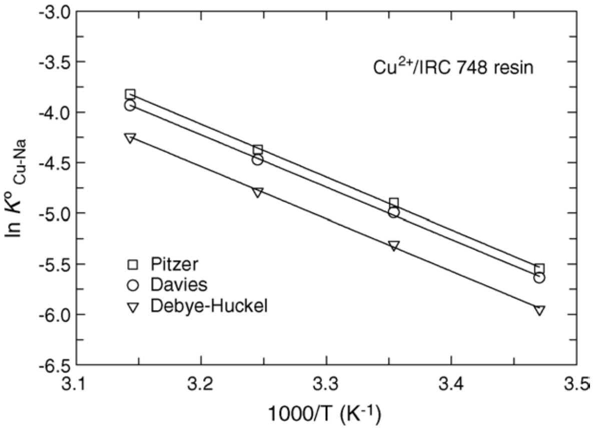

Fig. 11. The van't Hoff plot for the exchange of Cu^{2+} with Na-form IRC 748 resin.

Table 4
The standard enthalpy changes ΔH° (kJ/mol) for the exchange of Cu^{2+} and Zn^{2+} with Na-form chelating resins

Method	Cu–Chelex 100		Cu–IRC 748		Zn–IRC 748	
	ΔH°	R^2	ΔH°	R^2	ΔH°	R^2
Debye–Huckel	40.0	0.9976	43.4	0.9994	22.9	0.9961
Davies	39.6	0.9975	43.0	0.9993	22.4	0.9958
Pitzer	39.6	0.9973	42.9	0.9993	22.4	0.9956
Average	39.7		43.1		22.6	

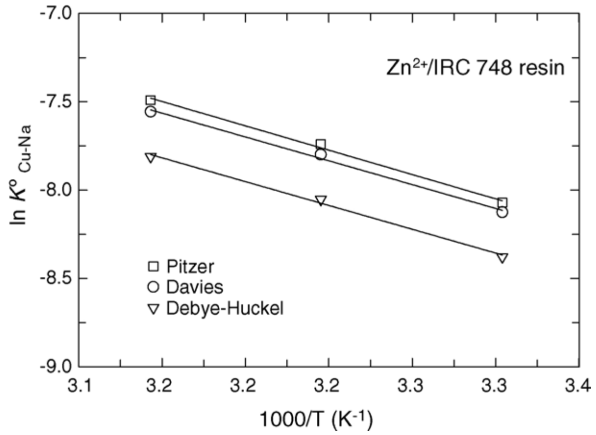

Fig. 12. The van’t Hoff plot for the exchange of Zn^{2+} with Na-form IRC 748 resin.

all endothermic. The similar ΔH° values obtained for the exchange reaction of RNa_2 and Cu^{2+} with the two resins used may prove the validity of the assumptions made in calculating the activity coefficients.

Zagorodni et al. [17] have studied the effect of temperature on the exchange reaction between RZn and Cu^{2+} in sulfate solution using the Amberlite IRC 718 chelating resin. They also obtained a positive enthalpy change of 2.32 kJ/mol in the temperature range 15–75 °C, according to the van’t Hoff plot of the equilibrium constants that consider the aqueous complexation reactions between metals and sulfate ions only.

On the other hand, in examining the exchange of Cr(III) from chloride solution using Chelex 100 resin, Gode and Pehlivan [14] obtained a negative enthalpy of −37.4 J/mol according to the van’t Hoff plot of an equilibrium constant K_c, which is defined as the ratio (q_e/C_e). The K_c value virtually equals the product of q_{sat} and K_L when C_e is low enough as shown in Eq. (2). The van’t Hoff plot of K_L is hence tested in this work (not shown) to yield the so-called isosteric enthalpy of adsorption [28]. Such enthalpies are found to be −4.5, −8.6, and −3.6 kJ/mol in the Cu–Chelex 100, Cu–IRC 748, and Zn–IRC 748 systems, respectively. Indeed, they are all negative. Based on these results, the present chelating ion exchange should be a type of physisorption because the enthalpy of physisorption is usually in the region of 20 kJ/mol and that of chemisorption is in the region of 200 kJ/mol [28]. This is obviously a mistake. Therefore, the treatment of ion-exchange equilibrium data based on the mass-action law is highly recommended.

4. Conclusions

The ion-exchange equilibria of Cu(II) and Zn(II) between the Na-form Chelex 100 or IRC 748 resins and aqueous phase have been investigated in the temperature range 15–45 °C. At 25 °C, for example, the maximum amounts of metal exchange were 0.88 mol/kg (pH_e 2.5), 1.10 mol/kg (pH_e 2.5), and 0.43 mol/kg of resin (pH_e 3.5) in the Cu–Chelex 100, Cu–IRC 748, and Zn–IRC 748 systems. Although the simple-to-follow Langmuir equation gave a good representation of the equilibrium data (correlation coefficient, $R^2 > 0.992$), their parameters such as q_{sat} and K_L changed with the pH and/or ionic strength of the aqueous phase. This makes the representation inconvenient to use. Moreover, the van’t Hoff plot of K_L would yield misleading enthalpy changes and the subsequent conclusions.

On the other hand, the description of the equilibrium data based on the mass-action law was recommended. Even though some assumptions were made to simplify the treatment during the activity corrections, the reasonably consistent results could be still obtained. By this way, the standard enthalpy changes in the Cu–Chelex 100, Cu–IRC 748 and Zn–IRC 748 systems were all positive and were 39.7, 43.1, and 22.6 kJ/mol, respectively.

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