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# Effect of Added Complexing Anions on Cation Exchange of Cu(II) and Zn(II) with a Strong-Acid Resin

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Ion exchange is widely used for the recovery and separation of metals from process and waste streams in chemical process industries. The effect of added complexing anions such as EDTA, NTA, and citrate on the cation exchange of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with strong-acid Purolite NRW100 resin was studied at 298 K, with the metals in solution in excess over the complexing anions. Experiments were performed as a function of solution pH (1.0–6.0), concentration of metals (4.5–22.5 mol/m<sup>3</sup>), and concentration ratio of complexing anions to metals (0–1). It was shown that the rate of metal exchange decreased when the complexing anions were present. The addition of EDTA and NTA decreased the amount of metal exchange throughout the entire pH range studied, but it was the case for the citrate system only at high pH (>4). In the absence of complexing anions, the Langmuir equation could be used to correlate the exchange isotherms at a given pH on a macroscopic basis. However, a proposed chemical model that takes into account possible solid–liquid exchange reactions and solution chemistry could be used to describe the metal exchange equilibria in the presence of complexing anions.

## Introduction

Water-soluble complexing agents are often applied in chemical process industries because of their three-fold function: to keep metals in solution, to dissolve metal compounds, and to affect the chemical reactivity of metal ions.<sup>1</sup> Thus, the effluents discharged from relevant industries, such as the manufacturing of printed circuit boards, metal finishing, and chemical cleaning for power plant boilers, contain various complexing agents.<sup>2–5</sup> The most widely encountered complexing agents are aminopolycarboxylic acids including ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid, and nitrilo-triacetic acid (NTA). This is mainly because these materials offer greater complex stability than polycarboxylic acids, such as citrate, oxalate, and tartrate acids, as well as phosphoric acids.

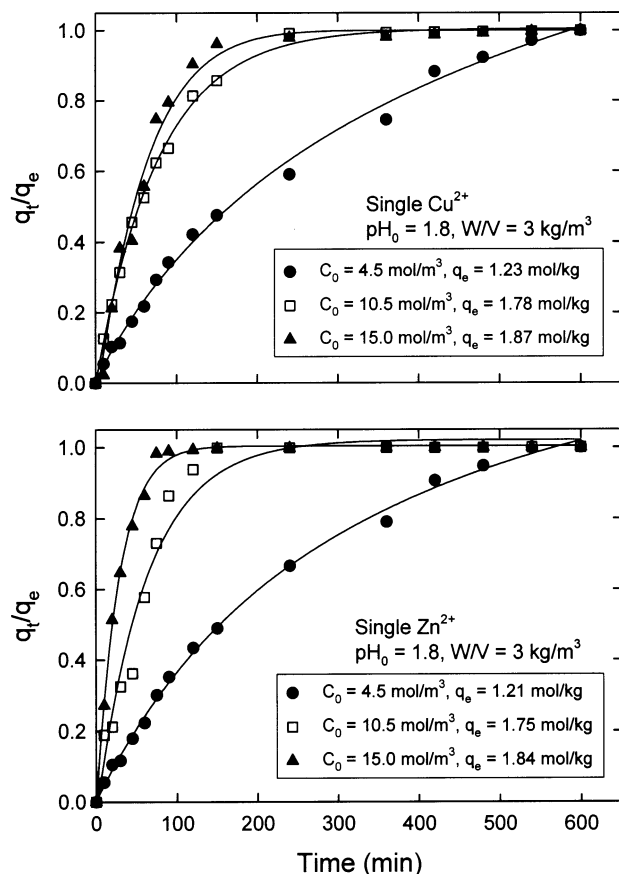
For the treatment of metal-bearing solutions, the presence of complexing agents can make conventional chemical such as hydroxide and sulfide precipitation less effective because of the formation of stable negatively charged complexes.<sup>5,6</sup> The high buffer capacity provided by these complexing agents requires excessive amounts of chemicals to neutralize the alkalinity. Alternative treatment methods are highly desired, depending strongly on the particular agents and metal ions as well as their concentrations. For dilute solutions, reverse osmosis, adsorption, and ion exchange could be applied.<sup>2,3,7,8</sup> In general, reverse osmosis has high operating and maintenance costs and is subject to fouling. Activated carbon adsorption is not effective for this application, although it has been widely used for the removal of organic contaminants.<sup>7</sup> Thus, ion exchange appears to be a promising candidate for the treatment of such streams in chemical process industry and drinking water applications.

When the complexing anions are in excess of the metal ions in solution, anion-exchange resins<sup>8–10</sup> or chelating exchangers<sup>2,11</sup> can be used because the complexes are negatively charged. If the metals are in excess, commercial cation-exchange resins are the alternative of choice. The goal of this paper was to investigate the cation exchange of metal ions in the presence of smaller amounts of the complexing anions EDTA, NTA, and citrate. In this work, Cu(II) was selected as the target ion because of its wide use in many electroplating and electroless plating industries. Among the first-row transition metals, Zn(II), rather than Ni(II), was adopted for comparison because Zn(II) has formation constants with the three complexing anions that are 1–2 log units smaller than those of Cu(II).<sup>12</sup> Experiments were performed as a function of the initial aqueous pH (1.0–6.0), metal concentration (4.5–22.5 mol/m<sup>3</sup>), and concentration ratio of complexing anions to metals (0–1). The Langmuir equation is proposed to describe the isotherm data on a macroscopic basis, and the chemical equilibria of the exchange reactions are also discussed.

## Experimental Details

**Resin and Solutions.** The strong-acid cation-exchange resin Purolite NRW100 [with the sulfonic acid ( $-\text{SO}_3\text{H}$ ) group] was used in this work. The resin was made of poly(styrene) and cross-linked with divinyl benzene. The physical and chemical properties of the resin are listed in Table 1. Prior to use, the resin was washed with NaOH (1 mol/dm<sup>3</sup>), HCl (1 mol/dm<sup>3</sup>), and *n*-hexane in sequence to remove possible organic and inorganic impurities; it was then washed with deionized water (Millipore Milli-Q) three times. The resin was converted to  $\text{Na}^+$  form by flushing the column with 1 mol/dm<sup>3</sup> NaCl solution for 12 h. It was finally washed with deionized water and dried in a vacuum oven at 333 K overnight.

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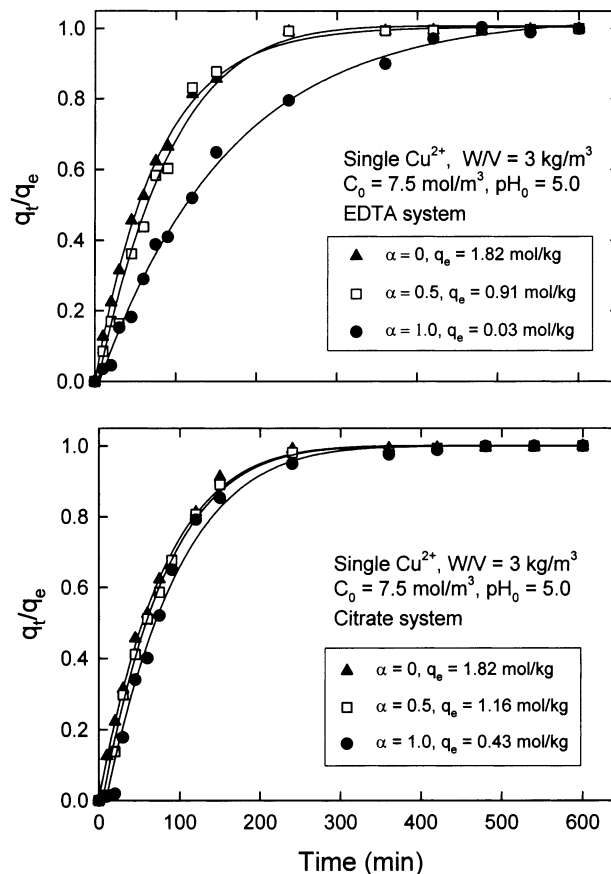
**Figure 1.** Effect of the initial metal concentration on the rate of cation exchange of metal ions in the absence of complexing anions at 298 K.

**Table 1. Physical and Chemical Properties of the Resin Purolite NRW100**

property	description or value
matrix	polystyrene DVB, gel type
degree of cross-linking	not available
functional group	sulfonic acid ( $-\text{SO}_3^-$ )
ionic form	$\text{H}^+$ (>99.9%)
exchange capacity (equiv/kg of dry resin)	4.5
moisture content (%)	50–55
particle size (mm)	0.425–1.2
specific gravity	1.20

Analytical reagent grade disodium salt of EDTA, trisodium salt of NTA, citric acid, and other inorganic chemicals were obtained from Merck Co. Aqueous solutions were prepared by dissolving metal sulfate and different amounts of EDTA, NTA, or citrate in deionized water. The initial solution pH was adjusted to be in the range of 1.0–6.0 by adding small amounts of HCl or NaOH. The initial concentration of metals ranged from 4.5 to 22.5 mol/m<sup>3</sup>. The temperature of the water bath was controlled at 298 K.

**Experimental Procedures.** In exchange experiments, an aliquot of dry resin (0.3 g) and 100 cm<sup>3</sup> of aqueous solution were placed in a 125-cm<sup>3</sup> glass-stoppered flask and shaken at 120 rpm for 12 h using a temperature-controlled shaker (Firstek model B603, Taiwan). Preliminary tests showed that the exchange reactions studied were complete after 6 h. After equilibrium, the aqueous-phase concentrations of metals and Na<sup>+</sup> were determined using a Varian atomic absorption spectrophotometer (model 220FS). The solution pH was measured with a pH meter (Horiba model F22, Japan).



**Figure 2.** Effect of added EDTA and citrate on the rate of cation exchange of Cu<sup>2+</sup> at 298 K.

The resin-phase concentrations of the metals at equilibrium,  $q_e$  (mol/kg), were obtained according to

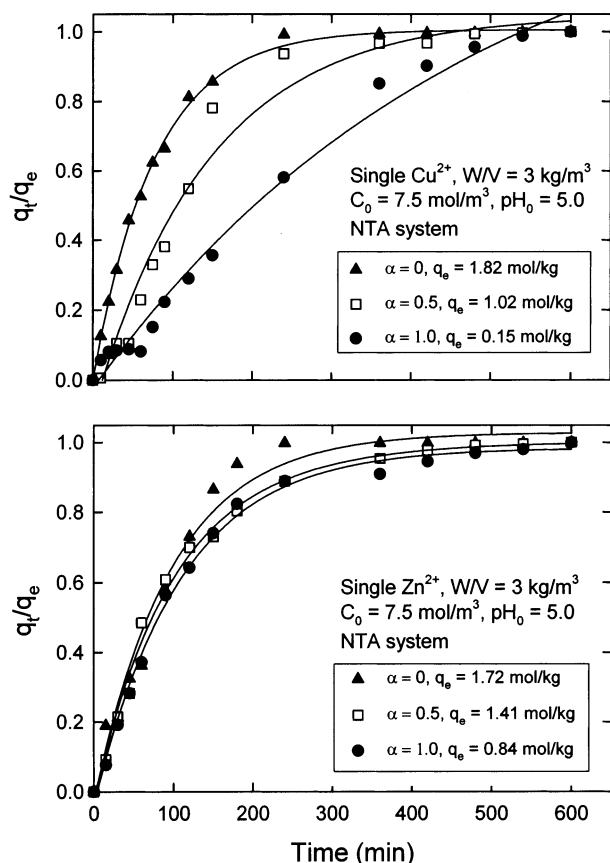
$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium liquid-phase concentrations of the metal ions, respectively (mol/m<sup>3</sup>) and  $W/V$  is the dose of dry resin (3 kg/m<sup>3</sup>).

For contact-time experiments, the procedure was essentially the same except that aqueous samples were taken at preset time intervals. The concentrations of the metals were measured similarly. Each experiment was at least duplicated under identical conditions. The reproducibility of the measurements was within 6% (mostly 3%).

## Results and Discussion

**Rate of Ion-Exchange Process.** Figures 1–3 show typical time profiles for the cation exchange of Cu<sup>2+</sup> and Zn<sup>2+</sup>. To compare the rate of cation exchange on a quantitative basis, the half-life, defined as the time where  $q_t/q_e = 0.5$ , was obtained and is compiled in Table 2. The exchange rate generally increased with increasing initial metal concentration  $C_0$ . In the absence of complexing anions, the exchange of Zn<sup>2+</sup> was slightly faster than that of Cu<sup>2+</sup> under comparable conditions. This might be caused by the equilibrium limitation of reversible exchange, rather than by the diffusivity difference ( $1.696 \times 10^{-9}$  for Zn<sup>2+</sup> vs  $1.715 \times 10^{-9}$  m<sup>2</sup>/s for Cu<sup>2+</sup> in infinitely dilute solution).



**Figure 3.** Effect of added NTA on the rate of cation exchange of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  at 298 K.

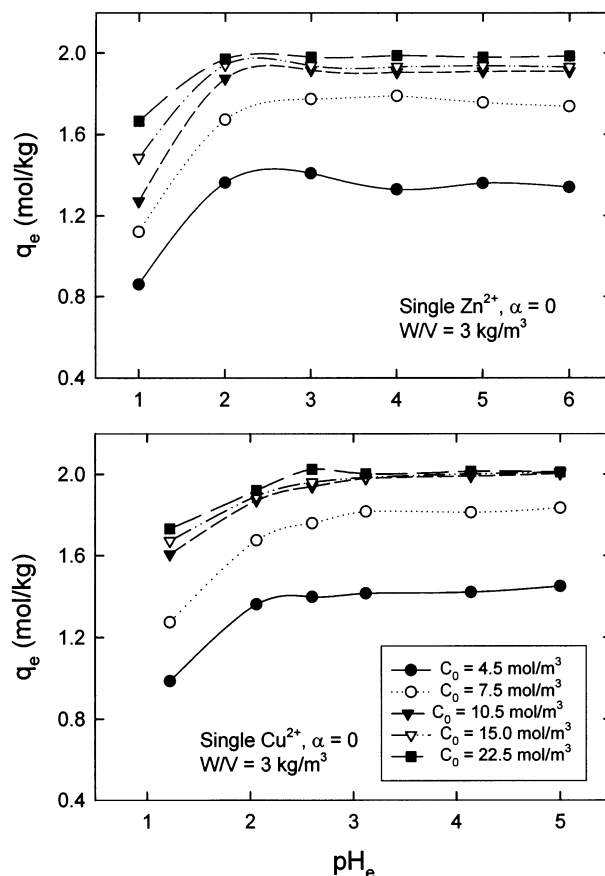
**Table 2.** Half-Lives of Cation Exchange of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  under Different Conditions<sup>a</sup>

metal	solution		complexing anion	$q_e$ (mol/kg)	half-life (min)
	$C_0$ (mol/m <sup>3</sup> )	pH <sub>0</sub>			
$\text{Zn}^{2+}$	4.5	1.8	none ( $\alpha = 0$ )	1.21	154.7
	10.5			1.75	44.5
	15.0			1.84	20.4
$\text{Cu}^{2+}$	4.5	1.8	none ( $\alpha = 0$ )	1.23	166.4
	10.5			1.78	53.9
	15.0			1.87	46.9
$\text{Zn}^{2+}$	7.5	5.0	EDTA ( $\alpha = 0.5$ )	1.12	49.6
			NTA ( $\alpha = 0.5$ )	1.41	81.2
			citrate ( $\alpha = 0.5$ )	1.63	42.7
$\text{Cu}^{2+}$	7.5	5.0	EDTA ( $\alpha = 0.5$ )	0.91	63.3
			NTA ( $\alpha = 0.5$ )	1.02	105.5
			citrate ( $\alpha = 0.5$ )	1.16	58.6
			EDTA ( $\alpha = 1.0$ )	0.03	112.5
			NTA ( $\alpha = 1.0$ )	0.15	201.6
			citrate ( $\alpha = 1.0$ )	0.43	69.2

<sup>a</sup> Dose of the dried resin = 3 kg/m<sup>3</sup>.

The addition of complexing anions always retards the exchange of metal ions because of the resulting decrease in amount of free metal ion in solution. However, the case of NTA is abnormal (Table 2) because the metal-complexing ability decreases in the order EDTA > NTA > citrate.<sup>12</sup> This can possibly be attributed to the use of the trisodium salt for NTA. A higher Na<sup>+</sup> concentration in the solution does not favor the exchange of metal ions with the Na form of the resin.

Tare et al.<sup>11</sup> used an ion exchanger with iminodiacetic acid groups, Chelex-100, to recover  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  from synthetic water containing a total metal concentration of 4.2 mol/m<sup>3</sup> and mixtures of EDTA, citrate, and tartrate (at a total concentration of 7.3 mol/m<sup>3</sup>). The



**Figure 4.** Effect of equilibrium pH and initial metal concentration on the amount of exchange of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in the absence of complexing anions.

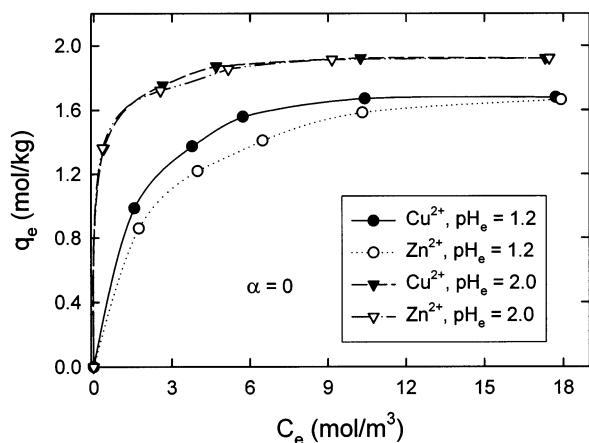
half-life for metal exchange ranged from 1 min to 10 h. They found that the rate of metal exchange depended not only on the rate-limiting step (film diffusion, particle diffusion, or chemical reaction), but also strongly on the rate of complex formation or destruction in solution and the competition for soluble ligands or exchange sites among various metal ions. This might partially account for the faster exchange of  $\text{Zn}^{2+}$  than  $\text{Cu}^{2+}$  under comparable conditions, as shown in Table 2.

**Ion-Exchange Equilibria in the Absence of Complexing Anions.** Figure 4 shows the effect of equilibrium pH ( $\text{pH}_e$ ) on the amount of exchange ( $q_e$ ) in the absence of complexing anions. It was found that  $q_e$  increases with increasing  $\text{pH}_e$  and reaches a plateau at  $\text{pH}_e$  beyond  $\sim 2$ . The low  $q_e$  obtained at low  $\text{pH}_e$  is caused by the competitive exchange of  $\text{H}^+$  and the Na form of the resin with the metal cations.<sup>13</sup>

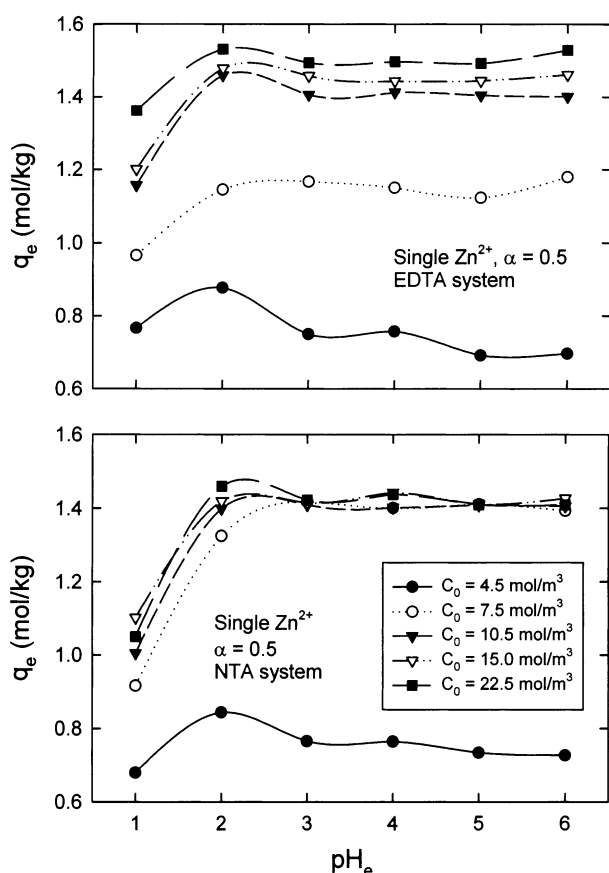
Figure 5 shows the exchange isotherms obtained at different  $\text{pH}_e$  values, which were directly determined from Figure 4. It is expected that the common two-parameter Langmuir equation can correlate these data; this equation is given by

$$q_e = \frac{q_{\text{sat}} K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $K_L$  is the Langmuir constant and  $q_{\text{sat}}$  is the amount of metal exchanged at saturation at a given equilibrium pH. The parameters  $K_L$  and  $q_{\text{sat}}$  can be obtained from a plot of  $1/q_e$  vs  $1/C_e$  (Table 3). The solid and dashed curves in Figure 5 were calculated from the Langmuir equation (correlation coefficient  $r^2 > 0.998$ ).



**Figure 5.** Exchange isotherms of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in the absence of complexing anions at 298 K. (The solid curves are predicted by the Langmuir equation.)

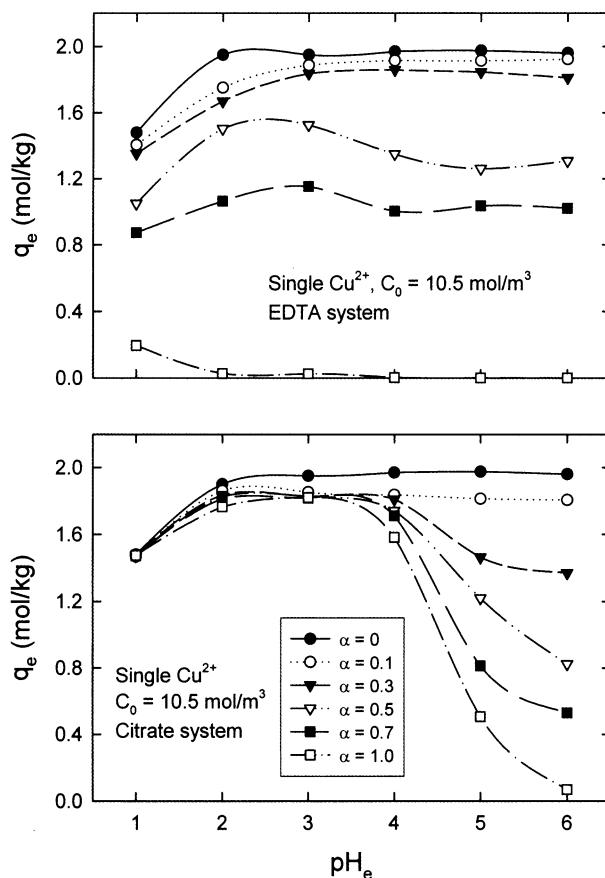


**Figure 6.** Effect of equilibrium pH and initial metal concentration on the amount of exchange of  $\text{Zn}^{2+}$  in the presence of EDTA or NTA.

**Table 3. Parameters of the Langmuir Equation for Cation Exchange of Metals on Na-Form Purolite NRW100 at 298 K**

system	$\text{pH}_e$	$q_{\text{sat}}$ (mol/kg)	$K_L$ ( $\text{m}^3/\text{mol}$ )
$\text{Cu}^{2+}$ ( $\alpha = 0$ )	1.2	1.854	$1.21 \times 10^{-2}$
$\text{Cu}^{2+}$ ( $\alpha = 0$ )	2.0	1.927	$9.48 \times 10^{-2}$
$\text{Zn}^{2+}$ ( $\alpha = 0$ )	1.2	1.847	$7.41 \times 10^{-3}$
$\text{Zn}^{2+}$ ( $\alpha = 0$ )	2.0	1.905	$1.08 \times 10^{-1}$

It can be seen that  $K_L$  and  $q_{\text{sat}}$  increase with increasing  $\text{pH}_e$ . Under comparable conditions,  $q_{\text{sat}}$  decreases in the order  $\text{Cu}^{2+} > \text{Zn}^{2+}$ . For example, the values are 1.927 and 1.905 mol/kg at  $\text{pH}_e$  2.0 for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively, which are both less than the resin capacity



**Figure 7.** Effect of equilibrium pH and concentration ratio on the amount of exchange of  $\text{Cu}^{2+}$  in the presence of EDTA or citrate.

(4.5 equiv/kg). The remaining exchange sites on the resin are mostly occupied by  $\text{Na}^+$  ions.

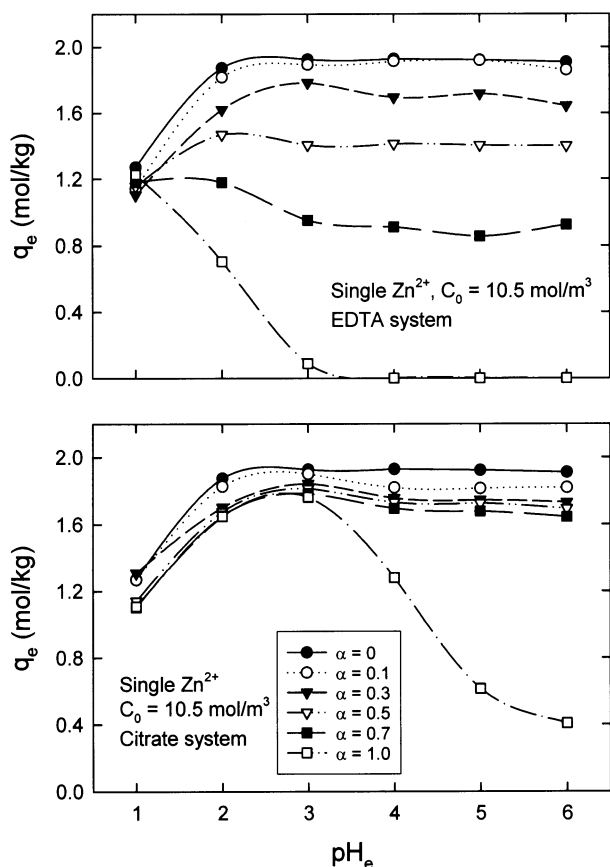
**Effect of Added Complexing Anions on Exchange Equilibria.** The effects of equilibrium pH on the amount of exchange,  $q_e$ , at different initial metal concentrations  $C_0$  and concentration ratios of complexing anions to metals ( $\alpha$ ) are shown in Figures 6–8. Because of different complexing affinities, discrepancies in the pH trends of  $q_e$  are apparent between the EDTA and citrate systems, as shown in Figures 7 and 8, particularly at  $\alpha > 0.3$ . Similar trends are found at high  $C_0$  ( $> 10.5 \text{ mol/m}^3$ ) in the case of EDTA and NTA (Figure 6,  $\alpha = 0.5$ ), possibly because of the sufficiently large ( $> 10^{12}$ ) and/or rather comparable overall formation constants,  $K_f$ , of their complexes with metal ions, as shown in Table 4. At lower  $C_0$  ( $< 7.5 \text{ mol/m}^3$ ), however,  $q_e$  is affected more significantly by the stronger complexing anion EDTA than by NTA. In the absence of complexing anions, a metal concentration of  $10.5 \text{ mol/m}^3$  is roughly enough for saturated exchange under the conditions investigated (Figure 4). This might imply that the free metal ion at concentrations below 50% of that required for saturated exchange cannot compete with  $\text{H}^+$  for effective exchange.

Evidently, the amount of metal exchanged,  $q_e$ , decreases with increasing amount of EDTA (i.e.,  $\alpha$ ) throughout the entire pH range studied, although this decrease is less pronounced at low enough  $\text{pH}_e$ . On the other hand, the presence of citrate has little effect on  $q_e$  if  $\text{pH}_e < 3$ , even for  $\alpha = 1$ . Generally speaking, the cation exchange of  $\text{Cu}^{2+}$  is affected to a larger extent than that of  $\text{Zn}^{2+}$  by the addition of complexing anions.



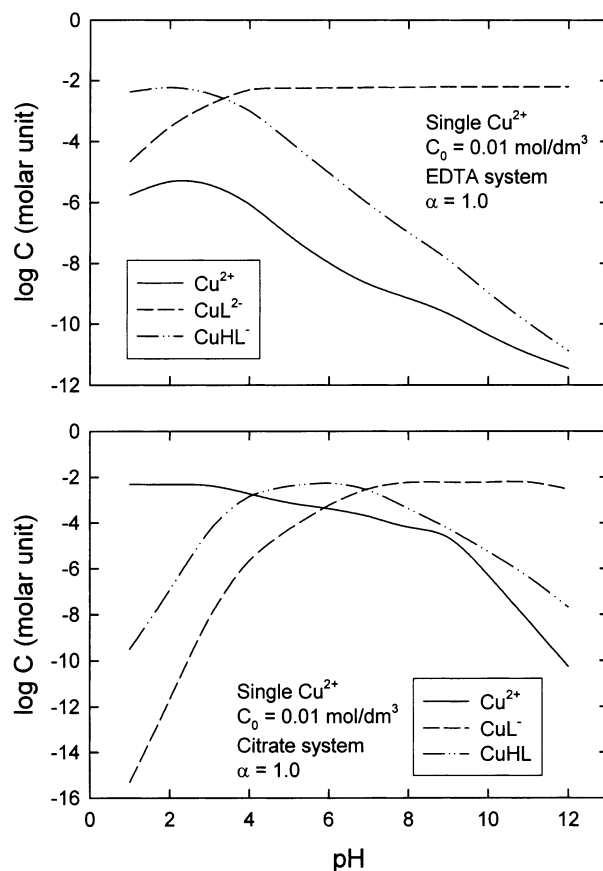
**Table 4.** Overall Formation Constants ( $\log K_f$ )<sup>a</sup> for Complexes of Metals and Anionic Ligands (L) at 298 K and Zero Ionic Strength<sup>12</sup>

cation	ligands (L)				
	OH <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	citrate <sup>3-</sup>	NTA <sup>3-</sup>	EDTA <sup>4-</sup>
H <sup>+</sup>	HL (14.00)	HL (1.99)	HL (6.40) H <sub>2</sub> L (11.16) H <sub>3</sub> L (14.29)	HL (10.33) H <sub>2</sub> L (13.27) H <sub>3</sub> L (14.92) H <sub>4</sub> L (16.02)	HL (11.12) H <sub>2</sub> L (17.80) H <sub>3</sub> L (21.04) H <sub>4</sub> L (23.76) H <sub>5</sub> L (24.76)
Na <sup>+</sup>		NaL (1.06)	NaL (1.4)	NaL (1.9)	NaL (2.5)
Cu <sup>2+</sup>	CuL (6.3) CuL <sub>2</sub> (11.8) CuL <sub>4</sub> (16.4)	CuL (2.4)	CuL (7.2) CuHL (10.7) CuOHL (16.4)	CuL (14.2) CuL <sub>2</sub> (18.1) CuOHL (18.6)	CuL (20.5) CuHL (23.9) CuOHL (22.6)
Zn <sup>2+</sup>	ZnL (5.0) ZnL <sub>2</sub> (11.1) ZnL <sub>3</sub> (13.6)	ZnL (2.1) ZnL <sub>2</sub> (3.1)	ZnL (6.1) ZnL <sub>2</sub> (6.8) ZnHL (10.3)	ZnL (12.0) ZnL <sub>2</sub> (14.9) ZnOHL (15.5)	ZnL (18.3) ZnHL (21.7) ZnOHL (19.9)

<sup>a</sup> Unit of solution-phase concentration used for calculating  $K_f$  is mol/dm<sup>3</sup>.**Figure 8.** Effect of equilibrium pH and concentration ratio on the amount of exchange of Zn<sup>2+</sup> in the presence of EDTA or citrate.

The presence of equimolar EDTA ( $\alpha = 1$ ) thus provides a possibility for the exchange separation of Zn<sup>2+</sup> and Cu<sup>2+</sup> from solutions at  $pH_e < 2$ , as is clearly shown in Figures 7 and 8.

It is known that EDTA, NTA, and citrate can exist in a number of protonated forms in aqueous solution.<sup>12</sup> They readily form stable complexes with most metals in a 1:1 molar ratio. Table 4 lists the overall formation constants ( $K_f$ ) at 298 K and zero ionic strength. The distribution of species at different solution pH values can basically be calculated from a set of mass-balance equations. Figure 9 shows typical results for equimolar solutions of the Cu<sup>2+</sup>–EDTA and Cu<sup>2+</sup>–citrate systems. Results for the Cu<sup>2+</sup>–NTA system are not shown because they are very similar to those for the Cu<sup>2+</sup>–EDTA system.

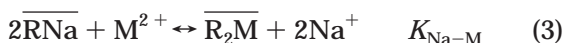
**Figure 9.** Typical pH trends of species distributions in equimolar solutions of Cu<sup>2+</sup>–EDTA and Cu<sup>2+</sup>–citrate at 298 K ( $C_0 = 0.01$  mol/dm<sup>3</sup>,  $\alpha = 1$ ).

In this figure, only the three most abundant species are shown. In the EDTA system, the divalent CuL<sup>2-</sup> predominates at  $pH > 3.2$  and the univalent CuHL<sup>-</sup> at  $pH < 3.2$ . Free Cu<sup>2+</sup> ions are essentially absent in the pH range tested. On the other hand, the dominant species are the exchangeable Cu<sup>2+</sup> at  $pH < 4.0$  and the univalent CuL<sup>-</sup> at  $pH > 6.8$  in the citrate system. Between pH 4.0 and 6.8, the neutral species CuHL dominates. Such distribution diagrams can explain the above trends of  $q_e$  with pH in the presence of complexing anions.

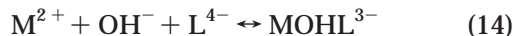
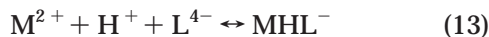
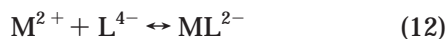
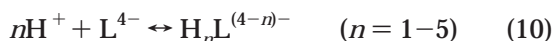
Korngold et al.<sup>14</sup> removed Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, and Cd<sup>2+</sup> from tap water containing small amounts of salts of carboxylic acid by a chelating resin having the imino-diacetic group, Purolite S930. From column test results, they found that the presence of salts of two or four

carboxylic groups such as tartrate and EDTA dramatically decreased the efficiency of metal exchange, even to zero. In addition, Haas and Tare applied the chelating resin Chelex-100 to recover  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  from synthetic solutions containing EDTA, citrate, and tartrate (at a total concentration of  $7.3 \text{ mol/m}^3$ ).<sup>11</sup> In a slightly different way, a plot of  $q_e/C_e$  vs  $\text{pH}_e$  revealed a maximum for each metal studied. Some of the present results in the citrate system also show similar trends.

**Microscopic Exchange Equilibrium Model.** As can be seen in Figure 6, the Langmuir equation cannot describe the exchange equilibria when strong complexing anions are present. Such data were therefore treated in terms of concentration-based equilibrium relationships. Whether or not the complexing anions were present, the following reactions were considered



where the overbar refers to the resin phase and R denotes the skeleton of the resin. In the presence of EDTA, for example, the following additional reactions must also be covered



At equilibrium, the following mass balance equations are obtained

$$[\text{M}^{2+}]_{\text{tot}} = [\text{M}^{2+}] + [\text{MOH}^+] + [\text{M(OH)}_2] + [\text{MSO}_4] + [\text{ML}^{2-}] + [\text{MHL}^-] + [\text{MOHL}^{3-}] + (W/V)\overline{[\text{R}_2\text{M}]} \quad (15)$$

$$[\text{L}^{4-}]_{\text{tot}} = [\text{L}^{4-}] + \sum [\text{H}_n\text{L}^{(4-n)-}] + [\text{NaL}^{3-}] + [\text{ML}^{2-}] + [\text{MHL}^-] + [\text{MOHL}^{3-}] \quad (16)$$

$$[\text{Na}^+]_{\text{tot}} = [\text{Na}^+] + [\text{NaSO}_4^-] + [\text{NaL}^{3-}] \quad (17)$$

$$[\text{SO}_4^{2-}]_{\text{tot}} = [\text{SO}_4^{2-}] + [\text{HSO}_4^-] + [\text{NaSO}_4^-] + [\text{MSO}_4] \quad (18)$$

Four unknowns ( $[\text{M}^{2+}]$ ,  $[\text{L}^{4-}]$ ,  $[\text{Na}^+]$ , and  $[\text{SO}_4^{2-}]$ ) were determined simultaneously by solving the system of eqs 15–18 using Mathematica, version 3.0. These terms

**Table 5. Thermodynamics-Based Equilibrium Constant for Cation Exchange of Metals on Na Form of Purolite NRW100 at 298 K<sup>a</sup>**

metal	solution	$\log K_{\text{Na-H}}^0$	$\log$
$\text{Cu}^{2+}$	$\alpha = 0$	3.22 (pH 1–5)	0.81 (pH < 3)
$\text{Cu}^{2+}$	EDTA ( $\alpha = 0.5$ )	3.14 (pH 1–5)	0.76 (pH < 3)
$\text{Zn}^{2+}$	$\alpha = 0$	2.83 (pH 1–5)	0.79 (pH < 3)
$\text{Zn}^{2+}$	EDTA ( $\alpha = 0.5$ )	2.79 (pH 1–5)	0.73 (pH < 3)

<sup>a</sup> Concentration units used for calculating  $K$  are mol/kg (resin) and mol/dm<sup>3</sup> (solution).

enabled the first value of the ionic strength  $I$  of the solution to be calculated

$$I = \frac{1}{2} \sum C_i z_i^2 \quad (19)$$

where  $C_i$  is the molar concentration of species  $i$  and  $z_i$  is its valence.

The thermodynamics-based equilibrium constant of the exchange reaction in eq 3, for example, can be written as

$$K_{\text{Na-M}}^0 = \frac{\overline{a_{\text{R}_2\text{M}}} a_{\text{Na}^+}^2}{a_{\text{M}^{2+}} \overline{a_{\text{RNa}}}^2} = \left( \frac{\overline{[\text{R}_2\text{M}]} [\text{Na}^+]^2}{[\text{M}^{2+}] \overline{[\text{RNa}]}^2} \right) \left( \frac{\gamma_{\text{R}_2\text{M}} \gamma_{\text{Na}^+}^2}{\gamma_{\text{M}^{2+}} \gamma_{\text{RNa}}^2} \right) = K_{\text{Na-M}} \Gamma_{\text{Na-M}} \quad (20)$$

where  $a_i$  and  $\gamma_i$  refer to the activity and activity coefficient, respectively, of species  $i$  and  $K_{\text{Na-M}}$  represents the concentration-based equilibrium constant.

Although  $K_{\text{Na-M}}^0$  is a true “constant” that can be compared with literature results, it requires the activity coefficients of the species in both phases. Simplification of the expression in eq 20 might make it more suitable for practical use. As a reasonable assumption, the resin-phase activity coefficients can be considered to remain essentially constant as long as the variations in the resin-phase concentration are small.<sup>10</sup> This is roughly the case under the conditions selected here,  $C_0 = 10.5 \text{ mol/m}^3$ ,  $\alpha = 0$ , and  $0.5$ .

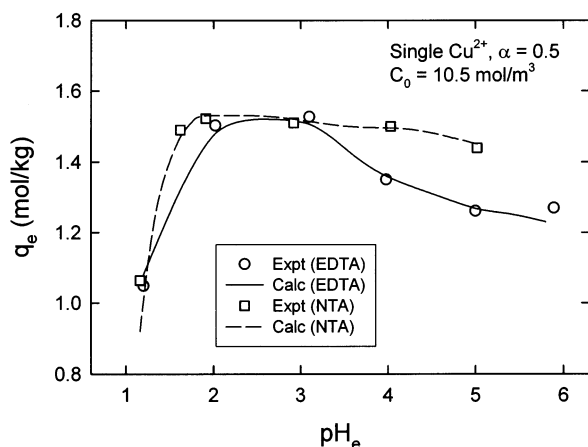
The aqueous-phase activity coefficient of a single ion is correlated here by the Davis equation, which is given at 298 K by<sup>15</sup>

$$\log \gamma_i = - \frac{0.511 z_i^2 \sqrt{I}}{1 + \sqrt{I}} + 0.102 z_i^2 I \quad (21)$$

It should be noted that eq 21 provides reasonable estimates at molalities up to  $0.1 \text{ mol/kg}$ . The formation constants of all aqueous-phase complexes (eqs 5–14) are also correlated. For the reaction in eq 12, for example, the following relationship holds

$$\frac{K_f^0}{K_f} = \frac{\gamma_{\text{ML}^{2-}}}{\gamma_{\text{M}^{2+}} \gamma_{\text{L}^{4-}}} \quad (22)$$

Table 5 lists the calculated results. The value of  $K_{\text{Na-M}}^0$  is nearly constant regardless of whether the complexing anions are present. It is difficult to compare the results with literature values because few data for the same resin are available.<sup>13</sup> Figure 10 provides a typical comparison of the measured and calculated values of  $q_e$  at different  $\text{pH}_e$  values in the EDTA and



**Figure 10.** Comparison of experimental and calculated results in the presence of EDTA and NTA.

NTA systems. The close agreement implies that these complexing anions play an important role only in the solution phases, i.e., in the solution chemistry.

### Conclusions

The effects of added EDTA, NTA, and citrate on the rates and equilibria of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  cation exchange by the strong-acid Purolite NRW100 resin were examined at 298 K. In the absence of complexing anions, the exchange of  $\text{Zn}^{2+}$  was slightly faster than that of  $\text{Cu}^{2+}$ . The isotherm data at a given equilibrium pH ( $\text{pH}_e$ ) could be correlated by the Langmuir equation. The saturated amount of exchange,  $q_{\text{sat}}$ , decreased in the order  $\text{Cu}^{2+} > \text{Zn}^{2+}$ . For example, the  $q_{\text{sat}}$  values at  $\text{pH}_e$  2.0 were 1.927 and 1.905 mol/kg, respectively.

The presence of complexing anions decreased the rate and amount of exchange because of the decrease of in the concentration of free metal ions in solution. Generally speaking, the amount of exchange of  $\text{Cu}^{2+}$  was affected to a larger extent than that of  $\text{Zn}^{2+}$  by the addition of complexing anions. The amount of metal exchange,  $q_e$ , showed a larger difference between the EDTA and citrate systems under comparable conditions than between the EDTA and NTA systems. Moreover,  $q_e$  significantly decreased with increasing amount of EDTA (i.e.,  $\alpha$ ) throughout the entire pH range studied, but the presence of citrate had little effect on  $q_e$  at  $\text{pH}_e < 3$ , even for  $\alpha = 1$ . Such a pH effect on  $q_e$  could be satisfactorily explained with the distribution diagram for each species the solution. The close agreement between the experimental  $q_e$  values and the results calculated using a chemical equilibrium model indicated the predominant role of strong complexing anions only in the solution phase.

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### Nomenclature

$a_i$  = activity of species  $i$

$C_e$  = liquid-phase metal concentration at equilibrium (mol/ $\text{m}^3$ )

$C_0$  = initial liquid-phase metal concentration (mol/ $\text{m}^3$ )

$\text{H}_n\text{L}$  = complexing agent ( $n = 4$  for EDTA and 3 for NTA and citric acid)

$I$  = ionic strength of the solution (mol/kg)

$K_L$  = Langmuir constant ( $\text{m}^3/\text{mol}$ )

$q_e$  = amount of metal exchange at equilibrium (mol/kg)

$q_{\text{sat}}$  = saturated amount of metal exchange at a given equilibrium pH (mol/kg)

$q_t$  = amount of metal exchange at any time  $t$  (mol/kg)

$V$  = volume of the solution ( $\text{m}^3$ )

$W$  = weight of dry resin (kg)

$z_i$  = valence of species  $i$

### Greek Letters

$\alpha$  = initial concentration ratio of complexing anions to metal

$\gamma_i$  = activity coefficient of species  $i$

### Superscript

0 = thermodynamic basis

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