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Synergistic Extraction of Zinc(II) with Mixtures of CA-100 and Cyanex 272

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ABSTRACT

The extraction of zinc(II) from an aqueous chloride medium has been studied using mixtures of sec-nonylphenoxy acetic acid (CA-100) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272). The results demonstrate that zinc ion is extracted into heptane as $ZnA_2 \cdot 2HA$ with CA-100, $ZnL_2 \cdot 2HL$ with Cyanex 272, and $ZnA_2L_2H_2$ with synergistic mixture. The equilibrium constants of the these species have been calculated and extraction mechanisms have been proposed. Thermodynamic parameters of the extraction process were determined by the temperature coefficient of extractability. The synergistic system enhances the extraction efficiency of zinc(II) and also improves the selectivity between zinc(II) and cadmium(II).

Key Words: Synergistic extraction; Zinc; CA-100; Cyanex 272.

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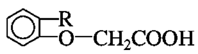
INTRODUCTION

The increased interest in extraction processes in recent years prompted the development of novel, highly selective extractants for the recovery of metal ions from their aqueous solutions. sec-Nonylphenoxy acetic acid (CA-100) is a novel carboxylic acid extractant developed by Shanghai Institute of Organic Chemistry, Chinese Academic of Science. Its molecular structure can be expressed as:



R:nonyl

Studies indicated that the extractant had several advantages, including, stable composition, easy preparation, low solubility, and strong acidity in an aqueous phase, hence, it may be superior to naphthenic acid. Previous research on the kinetics and thermodynamics extraction indicated that CA-100 was an effective extractant in extraction and separation of rare earth ions and Ga(III).[1–4] At present in China CA-100 has been used in the rare earth industry for the separation and purification of these metal ions. Nevertheless, the study of CA-100 has been limited to the extraction of trivalent ions, despite its advantages. We considered that it would be interesting to extend our studies to the extraction and separation of divalent ions, such as zinc(II) and cadmium(II).

Synergistic extraction systems have been applied to zinc(II) numerous times, with large effects on the extraction efficiency being observed.[5–10] Moreover, a few synergistic systems have shown improved separation between zinc(II) and divalent metal ions. Most of the work was concentrated on organic acid and organic base systems, and little was concentrated on organic acid and organic acid systems.

The present research deals with the synergistic extraction of zinc(II) from chloride medium with mixtures of CA-100 and Cyanex 272 in heptane. Distribution data were analyzed graphically and numerically to determine the composition of the extracted, complexes and their formation constants. The effects of aqueous acidity, extractant concentration, the ratio of two extractants and experimental temperature on the extraction behavior were examined. Furthermore, the separation of zinc(II) and cadmium(II) with mixtures of CA-100 and Cyanex 272 are discussed.

EXPERIMENTAL

Materials

CA-100 (purity $> 98\%$) was kindly donated by Tianjin Xiandai Factory of China and used without further purification. Cyanex 272 (supplied by CYTEC Canada, Inc.) has a content of bis(2,4,4-trimethylpentyl) phosphinic acid of about 85% and was used without purification. Organic phase solutions were prepared by dissolving the appropriate amount of extractant in heptane, then diluted to the required volume. Stock solutions of zinc(II) and cadmium(II) were prepared by dissolving 7.13 g of $ZnCl_2$ or 6.85 g of $CdCl_2$ in 100 mL of distilled water. NaCl was used to maintain the ionic strength constant. All other regents were of analytical grade.

Experimental Procedure

Extraction tests were carried out in a thermostated vessel (298K $\pm$ 0.2K) by shaking equal volumes (5 mL) of aqueous and organic phases in equilibrium tubes using a mechanical shaker for 30 min, the time experimentally found sufficient to reach equilibrium. After phase separation, the concentration of the Zn^{2+} or Cd^{2+} left in the aqueous phase was analyzed volumetrically using EDTA. The concentration of metal ions in the organic phase was obtained by mass balance, and the error is within 1% compared to the concentration obtained by stripping the organic phase. The concentration of extractants was determined by titrating with standard sodium hydroxide in an ethanol–water mixture using phenolphthalein as an indicator. A pHs-3C digital pH meter (Shanghai Rex Instruments Factory) was used for pH measurement by means of a combined glass-reference electrode. The distribution ratio, D, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase.

RESULTS AND DISCUSSION

Extraction of Zinc (II) with CA-100

The extraction of zinc (II) with CA-100 alone in heptane as a function of the hydrogen ion concentration and the extractant concentration, respectively, were studied. The plot of $\log D_1$ vs pH has a slope of 2 (Fig. 1). This, in conjunction with the slope of 2 observed for Zn^{2+} with extraction

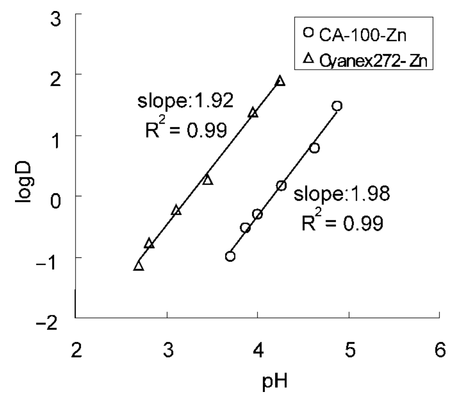


Figure 1. Effect of equilibrium pH on the extraction of Zn^{2+} with CA-100 and Cyanex 272. For CA-100-Zn: $C_{CA-100} = 0.025\,mol/L$, $C_{NaCl} = 0.6\,mol/L$, $C_{Zn}^{2+} = 3.2 \times 10^{-3}\,mol/L$. For Cyanex 272-Zn: $C_{272} = 0.025\,mol/L$, $C_{NaCl} = 0.6\,mol/L$, $C_{Zn}^{2+} = 3.2 \times 10^{-3}\,mol/L$.

concentration variation at constant pH value (Fig. 2), confirms that the extraction equilibrium may be expressed as:

$$Zn^{2+} + 2H_2A_{2,(o)} \overset{K_1}{\longleftrightarrow} ZnA_2{\cdot}2HA_{(o)} + 2H^+ \tag{1}$$

where H_2A_2 represents the dimeric species of CA-100 due to its larger dimerization constant in heptane[4]; K_1 denotes the equilibrium constant; "o" subscripted formulas and unsubscripted formulas stand for organic phase and aqueous phase species, respectively. The distribution ratio (D_1) is given by:

$$D_1 = \frac{[ZnA_2{\cdot}2HA]_{(O)}}{[Zn^{2+}]\left(1 + \sum_{i=1}^{4} \beta_i [Cl^-]_i\right)} \tag{2}$$

where $\beta_i (i = 1\text{–}4)$ are the complex formation constants of Zn^{2+} with chloride ions in the aqueous phase, and the values are 2.69, 4.07, 3.39, and 1.58, respectively.[11] Then K_1 can be written from Eqs. (1) and (2) as:

$$K_1 = \frac{D_1 [H^+]^2 \left(1 + \sum_{i=1}^{4} \beta_i [Cl]^i\right)}{[H_2A_2]^2_{(O)}} \tag{3}$$

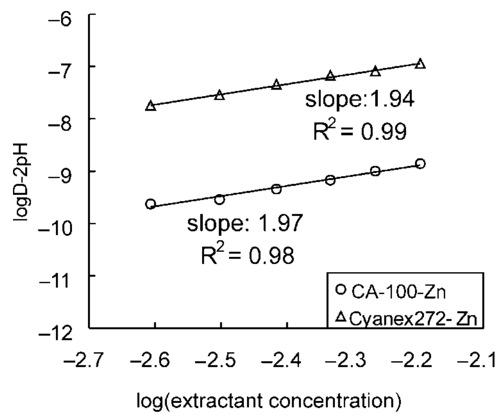


Figure 2. Effect of equilibrium extractant concentration on the extraction of Zn^{2+}. For CA-100-Zn: $C_{NaCl} = 0.6\,mol/L$, $C_{Zn}^{2+} = 3.2 \times 10^{-3}\,mol/L$, pH = 1.3. For Cyanex 272-Zn: $C_{NaCl} = 0.6\,mol/L$, $C_{Zn}^{2+} = 3.2 \times 10^{-3}\,mol/L$, pH = 3.0.

where $[H_2A_2]_{(o)} = C_{H_2A_2} - (2 \times C_{Zn^{2+}} \times D_1)/(1 + D_1)$; $C_{H_2}A_2$, and $C_{Zn^{2+}}$ represent the initial concentration of H_2A_2 in the organic phase and the initial concentration of Zn^{2+} in the aqueous phase, respectively. The value of $\log K_1$ was calculated and is shown in Table 1.

Extraction of Zinc(II) with Cyanex 272

It is clear from the plots (see Figs. 1 and 2) of $\log D_2$ vs pH and $\log D_2$-2pH vs $\log[H_2L_2]_{(O)}$ that two molecules of the Cyanex 272 are in involved in

Table 1. Species concentrations and equilibrium constants of Zn^{2+} extracted with CA-100 (ionic srength = 0.6 mol/L).

$C_{CA\text{-}100}$ (mol/L)	$\log([H_2A_2]_{(o)})$	Equilibrium pH	D_1	$\log K_1$	Average $\log K_1$
0.0197	−2.20	4.65	1.44	−3.72	
0.0175	−2.26	4.70	1.30	−3.70	
0.0153	−2.33	4.75	1.07	−3.73	− 3.70 ± 0.12
0.0131	−2.41	4.80	0.89	−3.73	
0.0109	−2.50	4.84	0.70	−3.72	
0.00874	−2.61	4.83	0.53	−3.58	

the extracted complex. Thus, the extraction of zinc(II) with Cyanex 272 from a chloride medium may be represented as:

$$Zn^{2+} + 2H_2L_{2(o)} \overset{K_2}{\longleftrightarrow} ZnL_2{\cdot}2HL_{(o)} + 2H^+ \tag{4}$$

where H_2L_2 represents the dimeric species of Cyanex 272. It has been reported elsewhere that Cyanex 272 exists as dimers in diluents.[12,13] The distribution ratio (D_2) and equilibrium constant (K_2) can be written as follows:

$$D_2 = \frac{[ZnL_2{\cdot}2HL]_{(O)}}{[Zn^{2+}]\left(1 + \sum_{i=1}^{4} \beta_i [Cl^-]_i\right)} \tag{5}$$

$$K_2 = \frac{D_2[H]^2\left(1 + \sum_{i=1}^{4} \beta_i [Cl]^i\right)}{[H_2L_2]^2_{(o)}} \tag{6}$$

where $[H_2L_2]_{(o)} = C_{H_2L_2} - (2 \times C_{Zn^{2+}} \times D_2)/(1 + D_2)$. $C_{H_2}L_2$ represents the initial concentration of H_2L_2 in the organic phase. The value of $\log K_2$ was calculated and is shown in Table 2.

Synergistic Extraction of Zinc(II) with Mixtures of CA-100 and Cyanex 272

The extraction of zinc (3.2×10^{-3} mol/L) from 0.6 mol/L sodium chloride solution of pH = 1.8 with 0.01 to 0.05 mol/L CA-100, 0.01 to

Table 2. Species concentrations and equilibrium constants of Zn^{2+} extracted with Cyanex 272 (ionic strength = 0.6 mol/L).

C_{272} (mol/L)	$\log([H_2L_2]_{(o)})$	Equilibrium pH	D_2	$\log K_2$	Average $\log K_2$
0.0197	−2.20	3.55	1.44	−1.80	−1.75 ± 0.07
0.0175	−2.26	3.60	1.30	−1.80	
0.0153	−2.33	3.60	1.07	−1.73	
0.0131	−2.41	3.65	0.89	−1.73	
0.0109	−2.50	3.70	0.70	−1.74	
0.00874	−2.61	3.73	0.53	−1.68	

0.05 mol/L Cyanex 272, and mixtures of CA-100 and Cyanex 272 was studied. At a variety of extractant concentrations the distribution ratio and synergistic enhancement factor, R, which is defined as $R = D_{12}/(D_1 + D_2)$,[14,15] are listed in Table 3. With mixtures of CA-100 and Cyanex 272, considerable synergistic enhancement in the extraction of Zn^{2+} was observed. Moreover, R was greatest with the mixtures of 0.025 mol/L CA-100 and 0.025 mol/L Cyanex 272, which suggests that at a ratio of CA-100 to Cyanex 272 of 1 to 1, the maximal synergistic enhancement could be obtained.

The extraction equilibrium of zinc(II) with mixtures of CA-100 and Cyanex 272 may be represented as:

$$Zn^{2+} + nH_2A_{2,(O)} + mH_2L_{2,(O)} \overset{K_{12}}{\longleftrightarrow} ZnA_{2n}L_{2m}H_{2n+2m-2,(O)} + 2H^+ \quad (7)$$

where n and m represent unknown coefficients. The equilibrium constant, K_{12}, of the synergistic extraction system is given as:

$$K_{12} = \frac{[ZnA_{2n}L_{2m}H_{2n+2m-2}]_{(O)}[H^+]^2}{[Zn^{2+}][H_2A_2]^n_{(O)}[H_2L_2]^m_{(O)}} \quad (8)$$

Table 3. Distribution ratios and synergistic enhancement factors of Zn^{2+} with mixtures of CA-100 and Cyanex 272 (pH = 1.8, ionic strength = 0.6 mol/L).

$C_{CA\text{-}100}$ (mol/L)	C_{272} (mol/L)	$C_{CA\text{-}100}:C_{272}$	D_1	D_2	D_{12}	R
0	0.05	0:0.05	0	0.056	0.056	1
0.005	0.045	0.005:0.045	0	0.046	0.092	2.00
0.01	0.04	0.010:0.040	0	0.037	0.12	3.24
0.015	0.035	0.015:0.035	0	0.030	0.15	5.00
0.02	0.03	0.020:0.030	0.015	0.010	0.28	11.02
0.025	0.025	0.025:0.025	0.019	0	0.49	25.79
0.03	0.02	0.030:0.020	0.21	0	0.84	4.00
0.035	0.015	0.035:0.015	0.27	0	1.37	3.70
0.04	0.01	0.040:0.010	0.44	0	2.36	5.36
0.045	0.005	0.045;0.005	1.91	0	3.58	1.87
0.05	0	0.05:0	4.27	0	4.27	1

The distribution ratio, D_{12}, of the synergistic extraction system is given by:

$$D_{12} = \frac{[ZnA_2(HA)_2]_{(o)} + [ZnL_2(HL)_2]_{(o)} + [ZnA_{2n}L_2mH_{2n+2m-2}]_{(o)}}{[Zn^{2+}]\left(1 + \sum_{i=1}^{4}(\beta_i[Cl]^i)\right)} \tag{9}$$

From Eqs. (2), (5), and (9):

$$K_{12} = \frac{(D_{12} - D_1 - D_2)[H^+]^2\left\{1 + \sum_{i=1}^{4}(\beta_i[Cl]^i)\right\}}{[H_2A_2]^n_{(o)}[H_2L_2]^m_{(o)}} \tag{10}$$

where

$$[H_2A_2]_{(o)} = C_{H_2L_2} - \frac{C_{Zn^{2+}} \times [2 \times D_1 + n \times (D_{12} - D_1 - D_2)]}{1 + D_{12}} \tag{11}$$

$$[H_2L_2]_{(o)} = C_{H_2L_2} - \frac{C_{Zn^{2+}} \times [2 \times D_2 + m \times (D_{12} - D_1 - D_2)]}{1 + D_{12}} \tag{12}$$

Taking logarithms:

$$\log K_{12} = \log(D_{12} - D_1 - D_2) - n\log[H_2A_2]_{(o)} - m\log[H_2L_2]_{(o)} - 2pH + \log\left\{1 + \sum_{i=1}^{4}(\beta_i[Cl]^i)\right\} \tag{13}$$

The coefficients, n and m, were determined by slope analysis. It is clear from the plot (Fig. 3) of $\log(D_{12} - D_1 - D_2)$ vs $\log[H_2A_2]_{(O)}$ that at a constant Cyanex 272 concentration and constant pH in aqueous phase, only one H_2A_2 molecule is attached to the synergistic species extracted into the organic phase. The slope of a plot of $\log(D_{12} - D_1 - D_2)$ vs $\log[H_2L_2]_{(O)}$ at constant CA-100 concentration indicates that 1 H_2L_2 molecule in the extracted species in the synergistic extraction reaction. This, in conjunction with the slope of 2 observed in Fig. 4 for the extraction of zinc(II) with pH variation experiment at constant extractant concentration, indicates that the synergistic extraction reaction can be written as:

$$Zn^{2+} + H_2A_{2,(O)} + H_2L_{2,(O)} \overset{K_{12}}{\longleftrightarrow} ZnA_2L_2H_{2,(0)} + 2H^+ \tag{14}$$

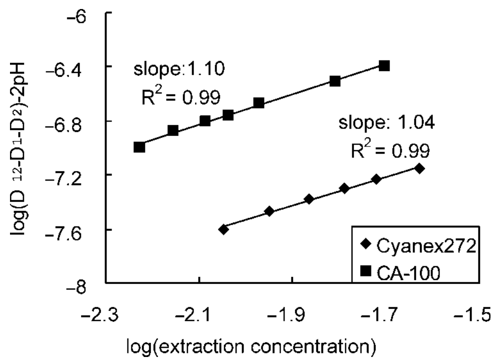


Figure 3. Effect of equilibrium extractant concentration on the extraction of Zn^{2+} with mixtures of CA-100 and Cyanex 272. For CA-100-Zn: pH = 1.3, $C_{NaCl} = 0.6\,mol/L$, $C_{272} = 0.025\,mol/L$, $C_{Zn^{2+}} = 3.2 \times 10^{-3}\,mol/L$. For Cyanex 272-Zn: pH = 1.3, $C_{NaCl} = 0.6\,mol/L$, $C_{CA-100} = 0.025\,mol/L$, $C_{Zn^{2+}} = 3.2 \times 10^{-3}\,mol/L$.

The extracted metal complex $ZnA_2L_2H_2$ is consistent with the results in Table 3 that at a ratio of CA-100 to Cyanex 272 of 1 to 1 the maximal synergistic enhancement could be obtained. The value of K_{12} was calculated and is shown in Table 4.

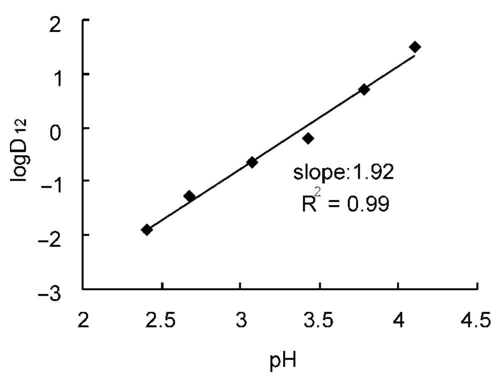


Figure 4. Effect of equilibrium pH on the extraction of Zn^{2+} with mixtures of CA-100 and Cyanex 272. $C_{272} = 0.025\,mol/L$, $C_{CA-100} = 0.025\,mol/L$, $C_{NaCl} = 0.6\,mol/L$, $C_{Zn^{2+}} = 3.2 \times 10^{-3}\,mol/L$.

Table 4. Species concentrations and equilibrium constants of Zn^{2+} extracted with mixtures of CA-100 and Cyanex 272 (ionic strength = 0.6 mol/L).

$C_{CA\text{-}100}$ (mol/L)	C_{272} (mol/L)	Log ($[H_2A_2]_{(o)}$)	Log ($[H_2L_2]_{(o)}$)	Equilibrium pH	D_1	D_2	D_{12}	$\log K_{12}$	Average $\log K_{12}$
0.005	0.025	−2.37	−1.62	3.35	0	0.17	0.52	−2.45	
0.005	0.02	−2.39	−1.72	3.45	0	0	0.62	−2.43	
0.005	0.0175	−2.43	−1.79	3.59	0	0	0.94	−2.39	
0.005	0.015	−2.44	−1.86	3.65	0	0	1.04	−2.37	
0.005	0.0125	−2.43	−1.95	3.68	0	0	0.98	−2.38	
0.005	0.01	−2.40	−2.05	3.68	0	0	0.74	−2.45	
0.025	0.025	−1.70	−1.62	3.55	8.70	0	12.9	−2.36	−2.40 ± 0.05
0.02	0.025	−1.81	−1.63	3.58	3.85	0	7.82	−2.37	
0.015	0.025	−1.97	−1.63	3.57	2.88	0	5.47	−2.36	
0.012	0.025	−2.04	−1.63	3.48	0.50	0	1.94	−2.39	
0.0105	0.025	−2.09	−1.63	3.40	0.28	0	1.15	−2.38	
0.009	0.025	−2.15	−1.62	3.35	0.21	0	0.76	−2.39	
0.0075	0.025	−2.23	−1.62	3.35	0.11	0	0.52	−2.44	

Actually, the following hypothetical reactions may occurs simultaneously in synergistic extraction:

$$ZnA_2 \cdot (HA)_{2,(o)} + H_2L_{2,(O)} \overset{\beta_{121}}{\longleftrightarrow} ZnA_2L_2H_{2,(O)} + H_2A_{2,(O)} \quad (15)$$

$$ZnL_2 \cdot (HL)_{2,(O)} + H_2A_{2,(O)} \overset{\beta_{122}}{\longleftrightarrow} ZnA_2L_2H_{2,(O)} + H_2L_{2,(O)} \quad (16)$$

where β_{121} and β_{122} are formation constants that can be expressed as:

$$\log\beta_{121} = \log K_{12} - \log K_1 \quad (17)$$

$$\log\beta_{122} = \log K_{12} - \log K_2 \quad (18)$$

The values of β_{121} and β_{122} are calculated to be 1.30 and −0.65, respectively, which indicates that equilibrium (15) contributes more to the synergistic extraction. A possible explanation is that the extracted complex of Zn^{2+} with CA-100 is less stable than that with Cyanex 272, consequently, the substitutional reaction of $ZnA \cdot (HA)_2$ with H_2L_2 is easier than that of $ZnL \cdot (HL)_2$ with H_2A_2.

Effect of Temperature on Synergistic Extraction

The enthalpy change (ΔH) of the extraction process was estimated from the temperature coefficient of extractability. This ΔH of extraction was obtained from the slope of the plot of logD vs 1/T (Fig. 5) using the Van't hoff equation in the form[16]:

$$\log D = -\frac{\Delta H}{2.303R}\frac{1}{T} + C \quad (19)$$

where R is the gas constant and C is a constant for a solution of constant ionic strength. The free energy change (ΔG)and the entropy change (ΔS) of the system are defined as follows:

$$\Delta G = -RT\ln K \quad (20)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (21)$$

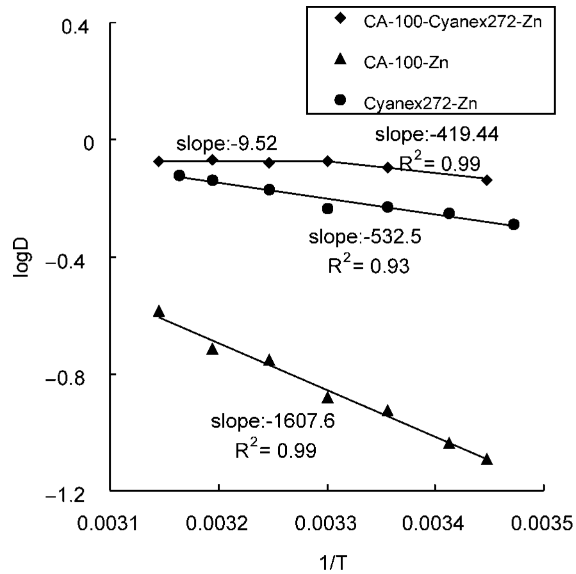


Figure 5. Effect of temperature on the extraction of Zn^{2+} with CA-100, Cyanex 272, and their mixtures. For CA-100-Zn: $C_{CA-100} = 0.025\,mol/L$, $C_{NaCl} = 0.6\,mol/L$, $C_{Zn^{2+}} = 3.2 \times 10^{-3}\,mol/L$, pH = 1.4. For Cyanex 272-Zn: $C_{272} = 0.025\,mol/L$, $C_{NaCl} = 0.6\,mol/L$, $C_{Zn^{2+}} = 3.2 \times 10^{-3}\,mol/L$, pH = 1.4. For CA-100-Cyanex 272-Zn: $C_{272} = 0.025\,mol/L$, $C_{CA-100} = 0.025\,mol/L$, $C_{NaCl} = 0.6\,mol/L$, $C_{Zn^{2+}} = 3.2 \times 10^{-3}\,mol/L$, pH = 1.4.

The thermodynamic values in the 290K to 318K temperature range are shown in Table 5. The positive values of ΔH and ΔS show that extraction with CA-100 is entropy controlled owing to extensive dissociation of the metal ion from its complex containing H_2O or Cl^- ligands as it extracts into the organic phase. Small heat effects are expected from the extracted complex formed between the anionic extractant and the metal ions. On the other hand, the smaller values of ΔH and ΔS for extraction zinc(II) with Cyanex 272 are indicative of larger heat effects involved in the formation of the extracted complex.

It is interesting to find that the enthalpy change of the synergistic extraction process is not constant in the experimental temperature range. The value of ΔH is calculated to be 8.01 kJ/mol in the temperature range of 290 to 303K. The positive value of ΔH suggests that the heat effects involved in the dissociation of the metal cation from its complex containing H_2O or Cl^- ligands are the predominant enthalpy factor. The value of ΔH is calculated to be 0.18 kJ/mol in

Table 5. Thermodynamic parameters for the extraction of Zn^{2+}.

Ligand	ΔH^a (kJ/mol)	ΔH^b (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)
CA-100	30.77 ± 1.55	30.77 ± 1.55	32.42 ± 2.92	21.11 ± 0.68
Cyanex 272	10.19 ± 1.22	10.19 ± 1.22	0.67 ± 2.75	9.99 ± 0.40
CA-100 + Cyanex 272	0.18 ± 0.005	8.01 ± 0.16	− 19.06 ± 0.45	13.69 ± 0.28

ΔH^a: at 303–318K.
ΔH^b: at 290–303K.
ΔS: at 298K.
ΔG: at 298K.

the temperature range of 303 to 318K. It indicates that the dissociation of the metal ion and the formation of the synergistic complex are almost equally responsible for the small value of the enthalpy change in this temperature range. The negative value of ΔS shows that more order is introduced in the system upon metal extraction, that is, the disorder caused by metal ion dissociation is more than compensated for by the reduction of the number of particles brought about by the formation of the synergistic complex.

Separation of Zn^{2+} and Cd^{2+} with Mixtures of CA − 100 and Cyanex 272

The extraction of cadmium(II) with CA-100 alone and the mixtures of CA-100 and Cyanex 272 was studied under the same experimental conditions of Zn^{2+} extraction (Table 6). The extraction of cadmium(II) into heptane with Cyanex 272 alone was negligible under these experimental conditions. Contrary to the case of zinc(II), the combining CA-100 with Cyanex 272 results in the suppression of the extraction of cadmium(II). Thus, we can assume that the separation of zinc(II) from cadmium(II) could be easier with mixtures of CA-100 and Cyanex 272 than CA-100 alone, which was confirmed by analyzing the separation factors (defined as $\beta_{Zn/Cd} = D_{Zn}/D_{Cd}$). It was found in Table 7 that the separation factors of zinc(II) with respect to cadmium(II) with mixtures are higher than that with CA-100 alone. Moreover, the separation factors increase with the increasing of ratio of Cyanex 272 with CA-100. In conclusion, it is efficient to separate Zn^{2+} from Cd^{2+} at a low proportion of CA-100 in the mixtures.

Table 6. Distribution ratios and synergistic enhancement factors of Cd^{2+} with mixtures of CA-100 and Cyanex 272 (pH = 1.8, ionic strength = 0.6 mol/L).

$C_{CA\text{-}100}$ (mol/L)	$C_{CA\text{-}100}$: C_{272}	D_1	D_{12}	R
0	0:0.05	0	0	—
0.005	0.005:0.045	0	0	—
0.01	0.010:0.040	0	0	—
0.015	0.015:0.035	0.011	0	0
0.02	0.020:0.030	0.022	0	0
0.025	0.025:0.025	0.041	0	0
0.03	0.030:0.020	0.096	0.029	0.30
0.035	0.035:0.015	0.19	0.18	0.95
0.04	0.040:0.010	0.44	0.38	0.86
0.045	0.045;0.005	0.75	0.83	1.11
0.05	0.05:0	1.33	1.33	1

CONCLUSION

The extraction equilibria of zinc(II) with CA-100, Cyanex 272, and their mixtures have been investigated, and considerable synergistic enhancement has been observed in the extraction of Zn^{2+} with mixtures of CA-100 and Cyanex 272. The stoichiometries of the extracted complexes have been determined to be $ZnA_2{\cdot}2HA$ with CA-100, $ZnL_2{\cdot}2HL$ with Cyanex 272, and $ZnA_2L_2H_2$ with synergistic mixture. The thermodynamic parameters of the synergistic extraction process have been determined and the endothermic process has been found. The separation factors of zinc(II) with respect to cadmium(II) with mixtures is higher than that with CA-100 alone, which

Table 7. Separation factors of Zn^{2+} with respect to Cd^{2+} with CA-100 and mixtures of CA-100 and Cyanex 272.

$C_{CA\text{-}100}$ (mol/L)	$\beta_{Zn/Cd}$	$C_{CA\text{-}100}$: C_{272}	$\beta_{Zn/Cd}$
0.02	0.68	0.020:0.030	—
0.025	0.46	0.025:0.025	—
0.03	2.19	0.030:0.020	28.97
0.035	1.42	0.035:0.015	7.61
0.04	1.0	0.040:0.010	6.21
0.045	2.55	0.045;0.005	4.31

suggests that it is a promising synergistic extraction system for the separation of zinc(II) from cadmium(II).

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