Extraction of Cd(II) and Zn(II) with Dialkylthiophosphinic Acid and Hexadentate Nitrogen-donor Ligand

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The extraction equilibrium of Cd(II) and Zn(II) with a commercial extractant, Cyanex 301, and an aqueous complexing agent, TPEN [*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine] was measured. When TPEN in amounts equimolar with heavy metal (Cd or Zn) was added in the aqueous solution, only the extraction of Zn was depressed. Then, the extraction constant of Cd was little changed and that of Zn was decreased to about 10^{-4} times. TPEN acts as a strong masking agent for Zn.

Soft metals can be extracted effectively with extractants containing soft-donors (nitrogen or sulfur atoms), such as calixarenes with pyridine and thioamide, TPTZ [2,4,6-tri(2-pyridyl)-1,3,5-triazine], BTP [2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine], Cyanex301 [bis(2,4,4-trimethylpentyl)dithiophosphinic acid] and Cyanex302 [bis(2,4,4-trimethylpentyl)-monothiophosphinic acid].[1] Noble metals, Pd, Au, and Ag, and highly toxic metals, Hg and Cd, are classified as soft metals. The recovery of soft metals from wastewater is of great value from the viewpoints of metal recycle and environmental protection. In this study, a new extraction system of Cd(II) with a commercial extractant, Cyanex 301, and an aqueous nitrogen-donor ligand, TPEN [(*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine)], was proposed. The extraction equilibrium data of Cd and Zn were measured and both the stoichiometric relations for the extraction of these metals and the extraction constants were evaluated by the slope analysis technique.

TPEN was synthesized according to the previous papers by Chang.[2] 2-Chloromethylpyridine hydrochloride (6.56 g, Wako Chemicals) was dissolved in 5 ml pure water and the solution obtained was neutralized with 5.4 mol/L NaOH solution. Ethylenediamine (0.67 ml) was added in the solution and stirred for 4 days. Then, the pH of solution was kept in the range of 8 to 9 by a pH-stat (718 STAT Titrino, Metrohm Ltd.) using 4 mol/L NaOH solution. White crystal particles formed in the solution were separated by filtration and washed several times by pure water. The crystals were identified as TPEN by elemental analysis, IR and ^{1}H NMR.

Cyanex301 was purchased from CYANAMID Co. and purified because of low content bis(2,4,4-trimethylpentyl)dithiophosphinic acid (purity ≈80%). The commercial Cyanex301 was reacted with ammonium carbonate at 343 K for 1 h after dissolving in benzene. A white crystal, ammonium dithiophosphinate, was formed by cooling the reaction mixture at 273 K. The recrystallization operation was repeated twice by using benzene-ethanol mixture. The white crystal obtained was dissolved in petroleum ether and washed by 4 mol/L HCl. The petroleum ether was removed by an evaporator and Cyanex 301 crystal purified was obtained. Then, the content of bis(2,4,4-trimethylpentyl)dithiophosphinic acid, which was measured by ^{31}P NMR, was evaluated as 98%.

The purified Cyanex 301 was dissolved in toluene. The concentration of Cyanex301 was adjusted in the range of 0.001 to 0.005 mol/L. Two aqueous nitrate solutions containing 0.89 mmol/L Cd^{2+} and 1.53 mmol/L Zn^{2+} were prepared. The ionic strength was adjusted to 0.1 by $NaNO_3$. TPEN in amounts corresponding to 1.0 to 2.5 times the concentration of heavy metal (Cd or Zn) was weighted and dissolved in the aqueous solutions. Both the organic and aqueous solutions were added in a small vial (volume ratio = 1 : 1) and shaken vigorously for 5 min. In the preliminary tests, it was confirmed that the extraction equilibrium was reached within 5 min. After phase separation, the concentration of metal in the aqueous phase was measured by an inductively coupled plasma spectrometer (ICPS, SPS-4000, Seiko Instruments Co.). The distribution ratio of heavy metal, D, defined as the concentration ratio of metal ion in the organic phase to that in the aqueous phase, was calculated. All extraction tests were carried out at 298 K.

Figure 1 shows the results of extraction tests. In this figure, "TPEN m (m = 0 to 2)" denotes the initial content of TPEN and the numeral "m" means that TPEN in amounts corresponding to the m-times the concentration of heavy metal is added in the aqueous phase. The extraction percent of Cd increased with increasing the concentration of Cyanex301, however, it was little changed by increasing the content of TPEN. On the other hand, that of Zn was decreased remarkably by the addition of TPEN. TPEN acts as a masking agent for Zn. From these results, the stoichiometric relations for the extraction of these heavy metals with and without TPEN were evaluated by the slope analysis technique.

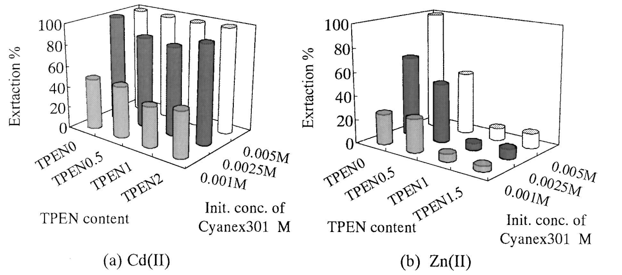

Figure 1. Extraction behavior of Cd and Zn with Cyanex301 and TPEN.

In the case without TPEN, the extraction of metal ion (M^{2+}) with Cyanex301 (HR) was represented as

$$M^{2+} + n(HR) \rightleftarrows MR_2(HR)_{n-2} + 2H^+ \quad K_{ex_1} \qquad (1)$$

where K_{ex_1} and n denote the extraction constant and the number of

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Cyanex301 molecules coordinating with metal ion, respectively. Note that Cyanex301 exists as monomer in toluene.[3] Both the hydrolysis of metal ion and the formation of nitrato complex in the aqueous phase,

$$M^{2+} + H_2O \rightleftarrows M(OH)^+ + H^+ \qquad (2)$$

$$M^{2+} + NO_3^- \rightleftarrows M(NO_3)^+ \qquad (3)$$

were considered for the analysis of extraction equilibrium. The equilibrium constants of these reactions, K_{Hy} and K_{NO_3}, were given from the previous papers.[4,5] From the equilibrium relations of Eq. (1) to (3), the relation between the extraction constants, K_{ex_1}, and the distribution ratio, D, is described as

$$\log D\left(1 + \frac{K_{Hy}}{[H^+]} + K_{NO_3}[NO_3^-]\right) + 2\log[H^+] = \log K_{ex_1} + n\log[HR] \qquad (4)$$

where [HR] denotes the concentration of free Cyanex301. The slope obtained from the relation between log[HR] and $\log D(1 + K_{Hy}/[H^+] + K_{NO_3}[NO_3^-]) + 2\log[H^+]$ represents the n-value of Eq. (1).

On the other hand, for the addition of TPEN, the extraction of metal ion with Cyanex301 was assumed as

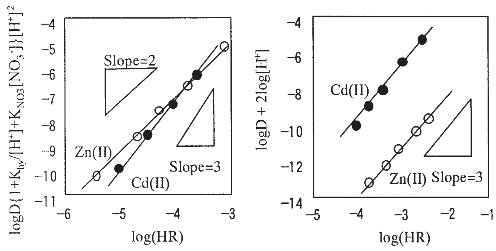
$$M(TPEN)^{2+} + n(HR) \rightleftarrows M(TPEN)R_2(HR)_{n-2} + 2H^+ \quad K_{ex_2} \qquad (5)$$

It is known that the metal-TPEN complex in the aqueous phase is described as $M(TPEN)^{2+}$ and the stability constant for the formation of $M(TPEN)^{2+}$ is very large ($K_{M(TPEN)} > 10^{13}$ for M = Cd or Zn).[6,7] The transport of $M(TPEN)^{2+}$ to the organic phase was confirmed by UV spectrometry of aqueous phase and organic phase before and after the extraction. Both the hydrolysis and the nitrato complex formation are negligible, because of large stability constants of $M(TPEN)^{2+}$. Therefore, the relation between K_{ex_2} and D is described as

$$\log D + 2\log[H^+] = \log K_{ex_2} + n\log[HR] \qquad (6)$$

The n-value of Eq. (5) can be determined from the relation between log[HR] and $\log D + 2\log[H^+]$.

Figure 2 shows the results of slope analysis. The linear relations were found for all analytical results. The coordination of Cyanex301, n, and the extraction constant, K_{ex_1} or K_{ex_2}, which were determined from the slope and the intercept, were summarized in Table 1. For the extraction of Zn, it should be noted that the n-value for Zn was increased from 2 to 3 and the extraction constant was decreased to about 10^{-4} times by the addition of TPEN. On the other hand, both the extraction constant and the n-value for Cd were little affected by the addition of TPEN. The remarkable reduction of extraction percent and extraction constant observed only for Zn, as shown in Figures 1 and 2, suggests that TPEN acts as a strong masking agent for Zn. Thus, the enhancement of separation factor of Cd/Zn is expected by adding a slight amount of TPEN in the aqueous phase.



(a) Without TPEN (b) With TPEN

Figure 2. Results of slope analysis for the extraction of Cd and Zn with Cyanex301: (a) in the case without TPEN and (b) in the case that TPEN in amounts equimolar with the heavy metal (Cd or Zn) was added in the aqueous phase.

Table 1. Summary of slope analysis

Metal	TPEN	n	K_{ex_1} or K_{ex_2}
Cd	absent	3	10^3
	present	3	$10^{2.6}$
Zn	absent	2	31
	present	3	$10^{-2.6}$

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References and Notes

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