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Solvent Extraction Studies of Zinc(II) and Cadmium(II) from a Chloride Medium with Mixtures of Neutral Organophosphorus Extractants and Amine Extractants

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ABSTRACT: In the present study, the extraction of zinc(II) and cadmium(II) with mixtures of neutral organophosphorus extractants (aliphatic trialkyl phosphine oxide, Cyanex 923, or branched cyclic trialkyl phosphine oxide, Cyanex 925) and amine extractants (*N*,*N*-di(1-methylheptyl) acetamide, N503, or trialkyl amine, N235) has been investigated. Synergistic effects were observed for zinc(II) with Cyanex 923 + N503 and for cadmium(II) with Cyanex 923 + N235 and Cyanex 925 + N235. However, the other mixing systems do not have synergistic effects on zinc(II) and cadmium(II). According to the different extraction effects, the separation possibilities of zinc(II) and cadmium(II) are discussed. The extraction mechanisms have been studied with the methods of slope analysis and constant moles in the three synergistic systems. The extracted compounds, the equilibrium constants, and thermodynamic functions have also been determined.

INTRODUCTION

In the past, different kinds of reagents have been used as extractants during the solvent extraction process. They have played an important role in the separation and removal of heavy metals.[1] Among the various extractants, neutral organophosphorus extractants have been widely studied. Earlier works were mainly concentrated on tributyl-phosphate,[2−4] di(1-methylheptyl)methyl phosphonate,[5] and 2-ethylhexyl phosphonic acid di-2-ethylhexyl ester (DEHEHP).[6] Recently, several new phosphinic extractants introduced by the Cyanamid Co. have attracted much attention. The extraction of zinc(II) and cadmium(II) with Cyanex 923, Cyanex 925 (hereafter abbreviated as C923 and C925, respectively), and Cyanex 471X has been reported by many authors.[7−18] For instance, Alguacil et al.[7] have studied the extraction of zinc(II) from acidic sulfate solutions with C923 and C925 in toluene in the pH range of 8.0 to 10.0. Rathore et al.[15] have developed a process to remove and recover cadmium(II) from wastewater including solvent extraction and supported liquid membrane transport using C923 as an extractant/carrier.

Amine extractants have also attracted much attention for the extraction of zinc(II) and cadmium(II), e.g., trialkyl amine (Alamine 336, N235),[2,3,19−21] primary amine (N1923),[5,6,8,17] quaternary ammonium salt (N263),[19] and *N*,*N*-di(1-methylheptyl) acetamide (N503).[22] Recently, the synergistic extraction of these divalent transition metal ions with mixtures of the above neutral organophosphorus extractants and amine extractants has been reported since synergistic solvent extraction can not only improve the extraction efficiency and the extraction selectivity but also enhance the stability of the extracted complexes, improve the solubility of the extracted complexes in the organic phase, eliminate emulsification and the formation of a third phase, and increase the extraction reaction rate.[5] In our previous work, the synergistic extraction of zinc(II) with mixtures of TBP and N235 has been carried out.[2] The mixtures have evident synergistic effects on zinc(II) with a synergistic enhancement factor of 12.34. The extracted complex was determined, and the equilibrium constant was calculated. The extraction of zinc(II) and cadmium(II) with mixtures of N1923 and DEHEHP from chloride medium has also been studied.[6] The possibility of separating zinc(II) and cadmium(II) with the mixtures has been investigated according to either synergistic or antagonistic effects.

Growing attention is being paid to the development of new synergistic effects to improve the extractability and selectivity of metal ions. The addition of neutral organophosphorus extractants to amine extractants has great potential for this goal. Therefore, it will be of interest to develop new mixing systems based on these two kinds of extractants. In the present work, the extraction of zinc(II) and cadmium(II) with mixtures of C923 or C925 and N235 or N503 has been studied. The distribution data are analyzed graphically and numerically to investigate the extraction stoichiometries. The separation abilities of zinc(II) and cadmium(II) have also been discussed according to the different extraction effects.

EXPERIMENTAL SECTION

Reagents. All the extractants were used without any purification and diluted in *n*-heptane. C923 and C925 were supplied by Cytec Canada, Inc. and used as extractants. N503 and N235 were obtained from Shanghai Rare-Earth Chemical Co., Ltd.

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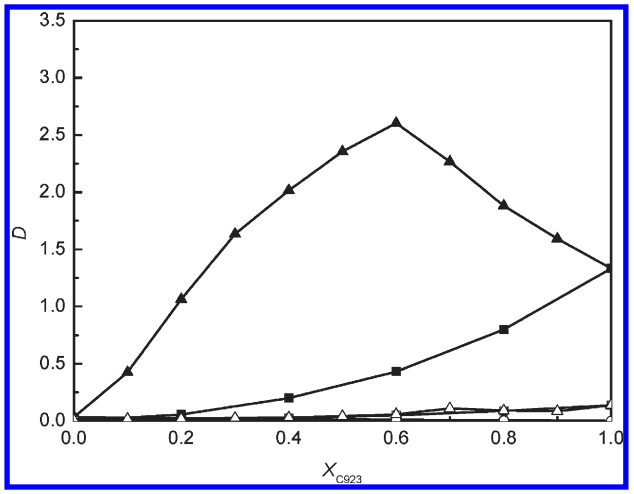
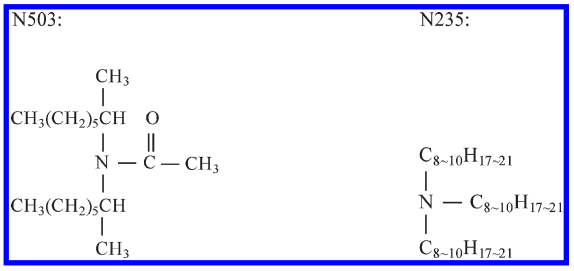


Figure 1. Extraction of Zn^{2+} and Cd^{2+} with C923, N503, and C923 + N503 systems. $[Zn^{2+}] = [Cd^{2+}] = 5 \cdot 10^{-3}$ mol·L^{-1}, μ = 1.5 mol·L^{-1}, $C_{C923} + C_{N503}$ = 0.1 mol·L^{-1}. Symbols: ■, C923−Zn; ●, N503−Zn; ▲, C923 + N503−Zn; □, C923−Cd; ○, N503−Cd; Δ, C923 + N503−Cd.

The structures of N503 and N235 are as follows



The stock solutions of $ZnCl_2$ and $CdCl_2$ were prepared with AR chemicals. All the initial metal concentrations were maintained at $5 \cdot 10^{-3}$ mol·L^{-1}. NaCl (1.5 mol·L^{-1}) was used in all extraction experiments to keep constant ionic strength (μ = 1.5 mol·L^{-1}). All other reagents were of analytical reagent grade.

Extraction Procedures. Aqueous (5 mL) and organic (5 mL) phases were mixed and shaken for 30 min at (293 ± 1) K except temperature experiments. The solutions were settled for 30 min and separated by gravity. After phase separation, the concentrations of Zn^{2+} or Cd^{2+} in the aqueous phase were determined by titration with EDTA, with xylenol orange as an indicator in hexamethylenetetraamine buffer solutions. The concentrations of the metal ions in the organic phase were then determined by difference. These data were used to calculate the distribution ratio.

■ RESULTS AND DISCUSSION

Extraction Effects of Zn^{2+} and Cd^{2+} with Mixtures of C923, C925 and N235, N503. The extraction of Zn^{2+} and Cd^{2+} from a chloride medium with mixtures of the neutral organophosphorus extractants, C923, C925, and the amine extractants, N235, N503, has been studied. As an example, the extraction of Zn^{2+} with C923, N503 and C923 + N503 is shown in Figure 1. X_{C923} represents the mole fraction of C923 in the organic phase, whereas D is the distribution ratio, i.e., the ratio between the concentration of the metal ion in the organic phase

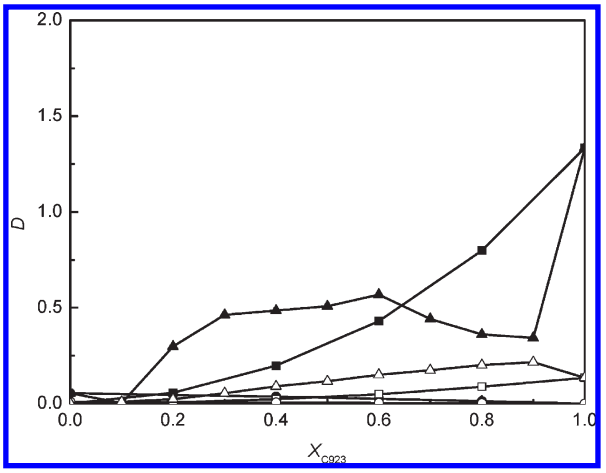


Figure 2. Extraction of Zn^{2+} and Cd^{2+} with C923, N235, and C923 + N235 systems. $[Zn^{2+}] = [Cd^{2+}] = 5 \cdot 10^{-3}$ mol·L^{-1}, μ = 1.5 mol·L^{-1}, $C_{C923} + C_{N235}$ = 0.1 mol·L^{-1}. Symbols: ■, C923−Zn; ●, N235−Zn; ▲, C923 + N235−Zn; □, C923−Cd; ○, N235−Cd; Δ, C923 + N235−Cd.

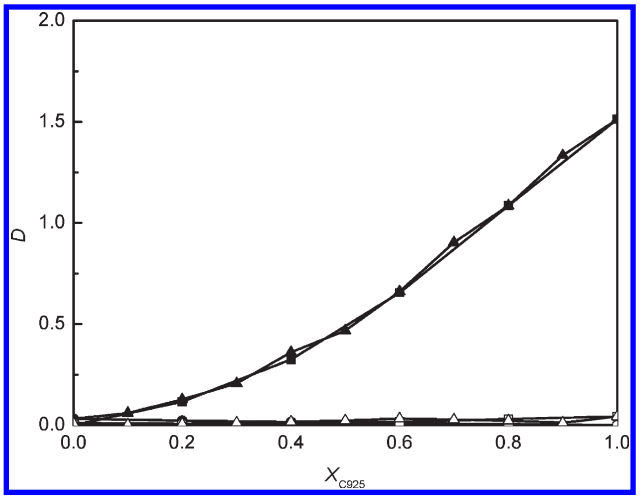


Figure 3. Extraction of Zn^{2+} and Cd^{2+} with C925, N503, and C925 + N503 systems. $[Zn^{2+}] = [Cd^{2+}] = 5 \cdot 10^{-3}$ mol·L^{-1}, μ = 1.5 mol·L^{-1}, $C_{C925} + C_{N503}$ = 0.1 mol·L^{-1}. Symbols: ■, C925−Zn; ●, N503−Zn; ▲, C925 + N503−Zn; □, C925−Cd; ○, N503−Cd; Δ, C925 + N503−Cd.

and that in the aqueous phase. The synergistic enhancement factor, R, can be calculated as follows according to synergistic extraction theory[23]

$$R = \frac{D_{mix}}{D_{C923} + D_{N503}} \quad (1)$$

R_{max} can be calculated as 3.2 when X_{C923} is 0.6.

Figures 1 to 4 show the extraction of Zn^{2+} and Cd^{2+} with C923 + N503, C923 + N235, C925 + N503, and C925 + N235. Synergistic effects can be found when Zn^{2+} is extracted with C923 + N503 and Cd^{2+} is extracted with C923 + N235 and C925 + N235. However, there are no evident synergistic effects for the two metal ions with other mixtures. The reason why a mixing system has synergistic or antagonistic extraction effects on metal ions is not very clear. The extraction processes

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with the two single extractants and the mixtures exist simultaneously in the mixing system. These three reactions affect the extraction effects.[24]

The different extraction effects of Zn^{2+} and Cd^{2+} with the four mixing systems can be considered for the separation of the two metal ions. Table 1 shows the separation factors between Zn^{2+} and Cd^{2+}, $SF_{Zn/Cd}$, which are calculated from the distribution ratios of Zn^{2+} and Cd^{2+}. It can be concluded that compared with the single C923 extractant the mixtures of C923 and N503 have higher separation factors of Zn^{2+} and Cd^{2+}, implying that C923 + N503 can be considered for the separation of the two metal ions. However, the mixtures of C923 and N235 do not have higher separation factors of Zn^{2+} and Cd^{2+} than the single C923 system, and the mixtures of C925 with N503 or N235 do not have higher separation abilities than the single C925 system, either.

Extraction Stoichiometry of Zn^{2+} with Mixtures of C923 and N503. The reaction of Zn^{2+} and neutral organophosphorus extractants can be described as the following[8]

$$ZnCl_{2(a)} + 2A_{(o)} \overset{K_A}{\rightleftharpoons} ZnCl_2 \cdot 2A_{(o)} \quad (2)$$

where "A" represents neutral organophosphorus extractants including C923 and C925. In the present work, the extraction of Zn^{2+} with C923 has been studied to compare the extractability of single C923 with that of C923 + N503.

It can be seen from Figure 1 that the extraction of Zn^{2+} with amine extractants (N235, N503) can be omitted. Therefore, the extraction stoichiometry of Zn^{2+} with N235 or N503 has not been discussed in this work.

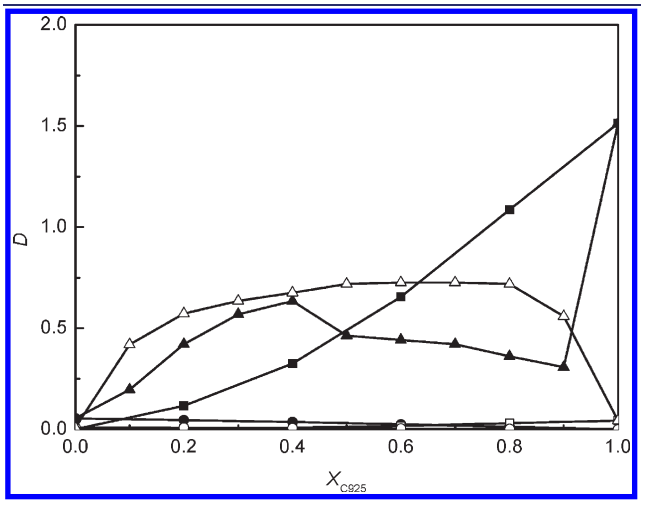

Figure 4. Extraction of Zn^{2+} and Cd^{2+} with C925, N235, and C925 + N235 systems. $[Zn^{2+}] = [Cd^{2+}] = 5 \cdot 10^{-3}$ mol·L^{-1}, μ = 1.5 mol·L^{-1}, $C_{C925} + C_{N235}$ = 0.1 mol·L^{-1}. Symbols: ■, C925−Zn; ●, N235−Zn; ▲, C925 + N235−Zn; □, C925−Cd; ○, N235−Cd; Δ, C925 + N235−Cd.

As mentioned above, C923 + N503 has synergistic effects on Zn^{2+} extraction, while C923 + N235 and C925 + N235 systems have synergistic effects on Cd^{2+} extraction. As an example, the extraction stoichiometry of Zn^{2+} with C923 + N503 is studied with the methods of slope analysis and constant moles.

If the synergistic extraction equation is written as eq 3

$$ZnCl_{2(a)} + xA_{(o)} + yB_{(o)} \overset{K_{AB}}{\rightleftharpoons} ZnCl_2 \cdot A_x \cdot B_{y(o)} \quad (3)$$

where the subscripts "a" and "o" denote the aqueous and organic phases, respectively. "A" and "B" are the abbreviated forms of C923 and N503, respectively. The equilibrium constant, K_{AB}, can be obtained by

$$K_{AB} = \frac{D_{AB}(1 + \sum_{i=1}^{4} \beta_i [Cl^-]^i_{(a)})}{\beta_2 [Cl^-]^i_{(a)} [A]^x_{(o)} [B]^y_{(o)}} \quad (4)$$

where β_i (i = 1−4) are the first to fourth cumulative stability constants of $ZnCl_2$.[25]

If Y is expressed as

$$Y = \frac{1 + \sum_{i=1}^{4} \beta_i [Cl^-]^i_{(a)}}{\beta_2 [Cl^-]^i_{(a)}} \quad (5)$$

The distribution ratio, D_{AB}, can be described as

$$\log D_{AB} = \log K_{AB} - \log Y + x \log[A]_{(o)} + y \log[B]_{(o)} \quad (6)$$

As shown in Figure 1, compared with the C923 and C923 + N503 systems, the extraction ability of Zn^{2+} with N503 alone is negligibly small. Therefore, $[A]_{(o)}$ and $[B]_{(o)}$ in eq 6 can be calculated as follows

$$[A]_{(o)} = C_A - C_{Zn^{2+}} \cdot \frac{2D_A + xD_{AB}}{1 + D_A + D_{AB}} \quad (7)$$

$$[B]_{(o)} = C_B - C_{Zn^{2+}} \cdot \frac{yD_{AB}}{1 + D_A + D_{AB}} \quad (8)$$

To investigate the extraction stoichiometry, a series of experiments have been carried out. First, the relationship between log D_{AB} and log $[C923]_{(o)}$ was determined when the concentration of Zn^{2+}, ionic strength, and the concentration of N503 are fixed. Results are shown in Figure 5, giving straight lines with a slope of about 1. Second, plots of log D_{AB} versus log $[N503]_{(o)}$ can also be obtained. The slope of the straight lines is also about 1.

Table 1. Separation Factors between Zn(II) and Cd(II), $SF_{Zn/Cd}$, in C923, C925, C923 + N503, C923 + N235, C925 + N503, and C925 + N235 Systems

extractant	X_{C923} 0	0.2	0.4	0.6	0.8	1.0	extractant	X_{C925} 0	0.2	0.4	0.6	0.8	1.0
C923	--	9.6	8.7	8.8	9.1	9.9	C925	--	59.3	41.1	38.8	35.9	35.3
C923 + N503	3.2	20.9	46.1	67.2	53.7	9.9	C925 + N503	3.2	49.3	20.5	21.4	18.3	35.3
C923 + N235	6.1	1.7	3.3	4.2	5.5	9.9	C925 + N235	6.1	0.5	0.6	0.9	0.7	35.3

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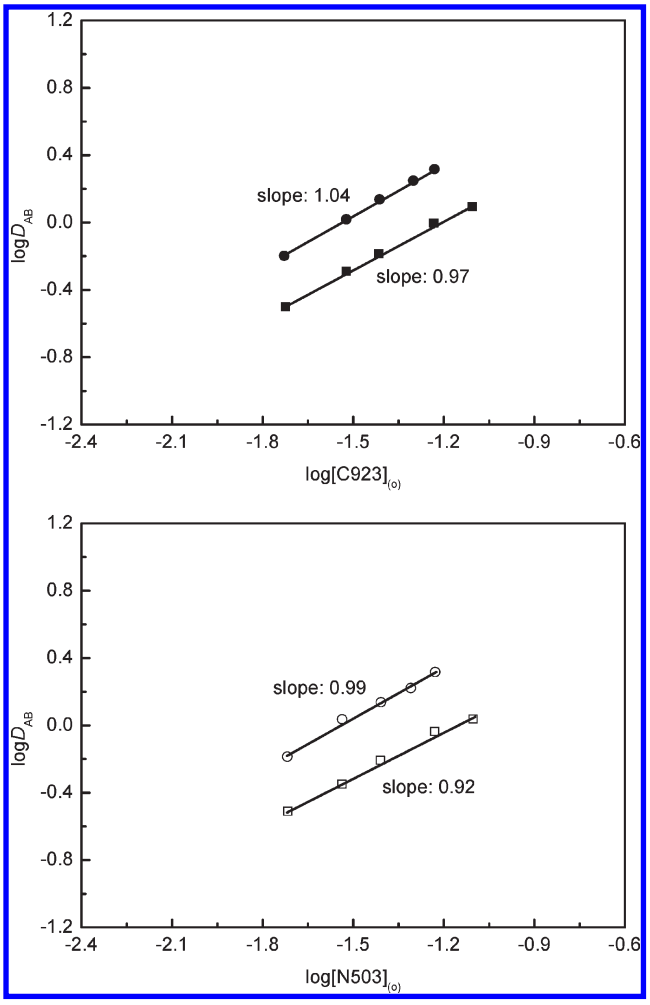

Figure 5. Relationship between distribution ratio of Zn^{2+} and equilibrium concentration of C923 and N503 in the C923 + N503 system. $[Zn^{2+}] = [Cd^{2+}] = 5\cdot0^{-3}$ mol·L^{-1}, μ = 1.5 mol·L^{-1}. Symbols (experimental): ■, [N503] = 0.02 mol·L^{-1}; ●, [N503] = 0.04 mol·L^{-1}; □, [C923] = 0.02 mol·L^{-1}; ○, [C923] = 0.04 mol·L^{-1}.

Therefore, eq 3 can be described by

$$ZnCl_{2(a)} + A_{(o)} + B_{(o)} \overset{K_{AB}}{\rightleftharpoons} ZnCl_2\cdot A\cdot B_{(o)} \quad (9)$$

and log K_{AB} can be calculated as 3.5.

In the same way, the synergistic extraction of Cd^{2+} with C923 + N235 and C925 + N235 systems can be obtained as

$$CdCl_{2(a)} + 1.5C923_{(o)} + 0.5N235_{(o)} \rightleftharpoons CdCl_2\cdot C923_{1.5}\cdot N235_{0.5(o)} \quad (10)$$

$$CdCl_{2(a)} + 0.5C925_{(o)} + 0.5N235_{(o)} \rightleftharpoons CdCl_2\cdot C925_{0.5}\cdot N235_{0.5(o)} \quad (11)$$

The logarithm values of the equilibrium constants were obtained as 2.5 and 2.1 when Cd^{2+} was extracted with C923 + N235 and C925 + N235, respectively.

Thermodynamic Study. Experimental temperature plays an important role in a liquid−liquid extraction process. At fixed concentrations of metal ions and extractants, the influence of temperature has been studied in the present work. If the relationship between the distribution ratio and the temperature is obtained, the change of enthalpy of the reaction, ΔH, can be calculated according to the following

$$\frac{\Delta \log D}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303R} \quad (12)$$

The change of Gibbs energy, ΔG, and the change of entropy, ΔS, of the system at 293 K can be obtained from

$$\Delta G = -RT \ln K \quad (13)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (14)$$

Table 2. Thermodynamic Parameters of Zn^{2+} and Cd^{2+} Extraction Processes[a]

	ΔH	ΔG	ΔS
	(kJ·mol^{-1})	(kJ·mol^{-1})	(J·moL^{-1}·K^{-1})
C923 + N503 + Zn	16.4	−19.6	122.9
C923 + N235 + Cd	6.6	−13.8	69.3
C925 + N235 + Cd	2.6	−11.8	49.4

[a] ΔG and ΔS were calculated at 293 K.

Table 2 shows the ΔH, ΔG, and ΔS values of the synergistic extraction of Zn^{2+} and Cd^{2+} with C923 + N503, C923 + N235, and C925 + N235 systems. It can be seen that the signs of ΔH are all "+", indicating that all three synergistic extraction processes are endothermically driven. The ΔS values in all three extraction systems are positive, implying that the synergistic extraction may occur easily, which is in accordance with the theory of increasing entropy from the view of statistics.

CONCLUSIONS

Four mixing systems, C923 + N503, C923 + N235, C925 + N503, and C925 + N235, have been used for the extraction of Zn^{2+} and Cd^{2+}. C923 + N503 mixtures have synergistic effects on Zn^{2+}, and C923 + N235 and C925 + N235 mixtures have synergistic effects on Cd^{2+}. Mixtures of C923 and N503 have higher separation abilities for Zn^{2+} and Cd^{2+} than the single C923 extractant. The three synergistic extraction processes have been investigated in detail. The extracted complexes are determined as $ZnCl_2\cdot C923\cdot N503$, $CdCl_2\cdot C923_{1.5}\cdot N235_{0.5}$, and $CdCl_2\cdot C925_{0.5}\cdot N235_{0.5}$, with the logarithms of the equilibrium constants of 3.5, 2.5, and 2.1, respectively. In addition, the thermodynamic parameters, ΔH, ΔG, and ΔS, have been calculated, indicating that all three synergistic extraction reactions are endothermically driven.

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