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Extraction of Zinc(II) and Cadmium(II) by Using Mixtures of Primary Amine N1923 and Organophosphorus Acids

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ABSTRACT

The extraction of zinc(II) and cadmium(II) from a chloride medium by mixtures of primary amine N1923 and organophosphorus acids [di-(2-ethylhexyl)-phosphoric acid, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP), isopropyl phosphonic acid 1-hexyl-4-ethyloctyl ester, *bis*(2,4,4-trimethylpentyl) phosphinic acid, *bis*(2,4,4-trimethylpentyl) monothiophosphinic acid, and *bis*(2,4,4-trimethylpentyl) dithiophosphinic acid] has been studied in the present paper. Results show that only the mixtures of N1923 + HEH/EHP and N1923 +

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Cyanex272 have synergistic effects on zinc(II), but the other mixtures have no evident synergistic effects. All six mixtures have no evident synergistic effects on cadmium(II). A possible explanation of the different extraction abilities is given based on the structure of the extractants. Furthermore, the possibilities of separating zinc(II) and cadmium(II) with these mixtures are investigated according to the extractabilities. It is possible to separate Zn^{2+} from bulk cadmium with N1923 and HEH/EHP mixtures and separate Cd^{2+} from bulk zinc with N1923 and Cyanex301 mixtures.

Key Words: Extraction; Zinc(II); Cadmium(II); Primary amine N1923; Organophosphorus acids.

INTRODUCTION

Solvent extraction is one of the most efficient methods for separation technology. During the past decades, organophosphorus reagents have been used to extract and separate metal ions extensively. Earlier works were mainly concentrated on di-(2-ethylhexyl)-phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP).[1,2] Isopropyl phosphonic acid 1-hexyl-4-ethyloctyl ester (HEOPPA) is a newly developed extractant, with a p*K*a value of 5.49, which has been used to extract transition metals and rare earths.[3] In recent years, several new phosphinic acids introduced by the Cyanamid Co. (Niagara Falls, Ontario, Canada) attracted much attention. The extraction of Zn^{2+} from sulphate and nitrate solutions by *bis*(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), *bis*(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex302) and *bis*(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex301) has been studied in detail.[4–7] Benito et al.[8] investigated the extraction of Zn^{2+} from chloride medium by Cyanex302 in toluene and determined the extracted species. Alguacil et al.[9] compared the extraction of Zn^{2+} in aqueous hydrochloric media by organophosphorus acids and found that the extraction efficiency followed the order: Cyanex302 > D2EHPA > Cyanex272. The extraction equilibria of Cd^{2+} from acidic media by Cyanex302 and Cyanex301 have also been studied in previous papers.[10,11]

Synergistic effects are an important phenomenon in the solvent extraction and have been studied extensively.[12,13] During the last 20 years, synergistic extraction of Zn^{2+} and Cd^{2+} by organophosphorus extractants or amines has been reported.[14–16] Our group investigated the extraction of Zn^{2+} by mixtures of primary amine N1923 and HEH/EHP and studied the extraction mechanism in detail.[17] More recently, we studied the synergistic extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and Cyanex272 and determined the extracted species and the equilibrium constants.[18] However, the extraction of Zn^{2+} and Cd^{2+} by the mixtures of N1923 and different organophosphorus acids has not been studied systematically. As is well known, it is important to separate Zn^{2+} and Cd^{2+} from the same solutions. Since N1923 and organophosphorus acids are common extractants, it is interesting to investigate the separation abilities of the two cations by their mixtures.

In this article, the extraction of Zn^{2+} and Cd^{2+} from chloride medium by mixtures of primary amine N1923 and organophosphorus acids (D2EHPA, HEH/EHP, HEOPPA, Cyanex272, Cyanex302, and Cyanex301) is investigated systemtically. The differences of the extractabilities are discussed according to the structures of the extractants, and a possible explanation is given. Furthermore, some useful mixing systems have been introduced to separate Zn^{2+} and Cd^{2+} according to their synergistic or antagonistic effects on the cations at different extractant proportions.

EXPERIMENTAL

Reagents

The D2EHPA and HEH/EHP were provided by Tianjin Chemical Reagents Company. The Cyanex272, Cyanex302, and Cyanex301 were kindly supplied by the CYTEC Canada, Inc. The HEOPPA and primary amine N1923 (>99%) were supplied by Shanghai Institute of Organic Chemistry. All the extractants were used as received. The extractants were dissolved in *n*-heptane to the required concentration. Organophosphorus acids were determined by titration with standard sodium hydroxide. The concentration of primary amine N1923 was measured by titration with standard hydrochloric acid solution. The amine N1923 was acidified by an equivalent amount of hydrochloric acid to form the ammonium salt.

Stock solutions of $ZnCl_2$ and $CdCl_2$ were prepared with analytical grade reagent (AR) chemicals. The metal ions were analyzed by titration with EDTA. All extraction experiments were performed at constant ionic strength (1.5 mol/L). All the other reagents were of analytical grade.

Methods

For the equilibrium experiments, 5 mL of the aqueous and the organic solutions, respectively, was mixed and shaken for 30 min at 293 $\pm$ 1 K, which was sufficient for equilibrium attainment. After phase separation, Zn^{2+} and Cd^{2+}

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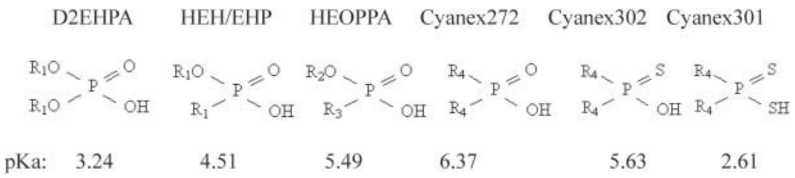
in the aqueous phase were determined by titration with EDTA. The concentration of metal ions in the organic phase was determined by the difference. These concentrations were used to calculate the distribution ratio, *D*.

RESULTS AND DISCUSSION

Extraction of Zn^{2+} and Cd^{2+} by Organophosphorus Acids

The extraction of Zn^{2+} and Cd^{2+} by organophosphorus acids has been studied, as shown in Figs. 1 and 2. The extractabilities follow the order: Cyanex301 > Cyanex302 > D2EHPA > HEH/EHP > Cyanex272 > HEOPPA. The results are in accordance with Alguacil et al.'s[9] where the extraction of Zn^{2+} follows the order: Cyanex302 > D2EHPA > Cyanex272. The authors regarded this order was because the substitution of the oxygen in the P═O bond by a sulphur atom in the phosphinic derivative displaces the zinc pH_{50} extraction value to appreciably more acid levels, thus allowing zinc extraction from more acidic solutions.

The structures of the organophosphorus acids are as follows:



where $R_1 = CH_2CH(C_2H_5)C_4H_9$; $R_2 = CH(C_6H_{13})\ C_2H_4CH(C_2H_5)\ C_4H_9R_3 =$ i-C_3H_7; $R_4 = CH_2CH(CH_3)CH_2C(CH_3)_2CH_3$

It can be seen that the extraction efficiency follows the order: $(RO)_2P(O)OH > R(RO)P(O)OH > (R)_2P(O)OH$, i.e., D2EHPA > HEH/EHP > Cyanex272. A possible explanation may be that the increase of C−P numbers results in decreasing *K*a values and activities of the functional group P(O)OH. The HEH/EHP and HEOPPA have a similar structure but the latter has a lower extraction capacity because of its higher steric hindrance. This steric hindrance is so high that it even results in the extractabilities of HEOPPA and Cyanex272 following the order: Cyanex272 > HEOPPA, which is contrary to that assumed according to their p*K*a values. Cyanex302 and Cyanex301 are the mono- and di-thio substitutes of Cyanex272, whose p*K*a values are less than Cyanex272. Their extracting order of Zn^{2+} and Cd^{2+} can be explained by hard soft acid base (HSAB) theory.[19] The Cyanex272 is a hard base, while Cyanex302 and Cyanex301 are soft bases and are more prone to react with the soft acids, Zn^{2+} and Cd^{2+}. Therefore, the extraction abilities of Zn^{2+} and Cd^{2+} follow the order mentioned above.

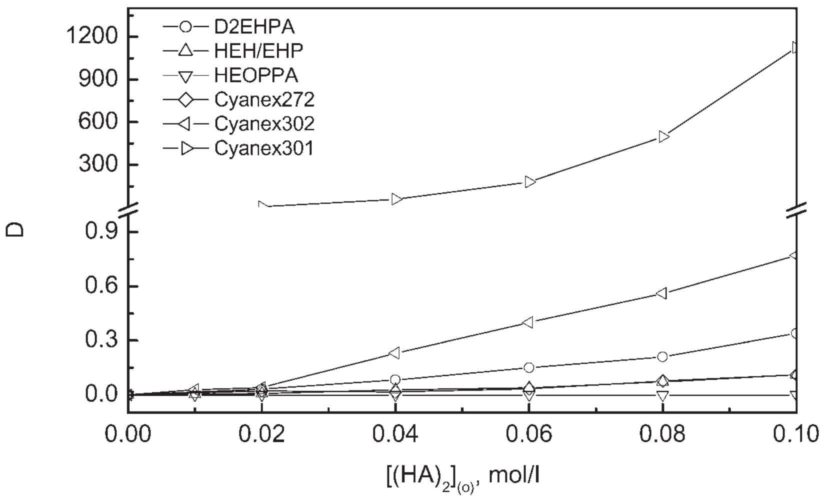


Figure 1. Extraction of Zn^{2+} by organophosphorus extractants; $[Zn^{2+}]_{(a)} = 0.02$ mol/L, pH = 1.56, $\mu = 1.50$ mol/L.

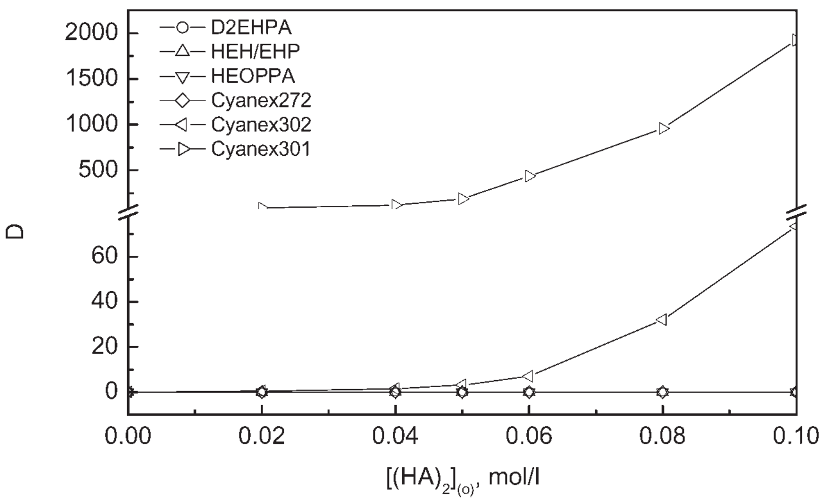
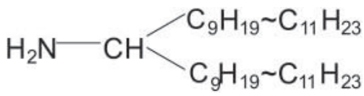


Figure 2. Extraction of Cd^{2+} by organophosphorus extractants; $[Cd^{2+}]_{(a)} = 0.02$ mol/L, pH = 1.51, $\mu = 1.50$ mol/L.

Extraction of Zn^{2+} and Cd^{2+} by Primary Amine N1923

N1923 is a primary amine with the following structure:



Le et al.[20,21] have studied the extraction of Zn^{2+} and Cd^{2+} by N1923 and determined the extracted complexes. N1923 exists predominantly as a trimeric species, and the following reaction occurs when $ZnCl_2$ and $CdCl_2$ are extracted:

$$MCl_{2(a)} + (RNH_3Cl)_{3(O)} \longleftrightarrow (RNH_3Cl)_3 \cdot MCl_{2(o)} \quad (1)$$

where M represents Zn and Cd, a and o denote aqueous and organic phase, respectively.

The distribution ratios D and separation coefficients β of Zn^{2+} and Cd^{2+} from 1.5 mol/L NaCl solutions by N1923 are given in Table 1, showing that it is difficult to separate Zn^{2+} and Cd^{2+} with N1923 alone.

Extraction of Zn^{2+} and Cd^{2+} by Mixtures of N1923 and Organophosphorus Acids

The extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and organophosphorus acids is given in Figs. 3–8, showing that only the mixtures of HEH/EHP or Cyanex272 and N1923 have synergistic effects on the extraction of Zn^{2+}. However, the other four mixtures have no synergistic effects on Zn^{2+}, and all six mixtures have no evident synergistic effects on Cd^{2+}. The synergistic enhancement factors for Zn^{2+}, $D_{max}/(D_1 + D_2)$ for

Table 1. D and $\beta_{Zn/Cd}$ values of Zn^{2+} and Cd^{2+} when extracted by N1923.

	$[(RNH_3Cl)_3]_{(o)}$(mol/L)				
	0.014	0.028	0.042	0.056	0.070
D_{Zn}	0.14	0.26	0.40	0.60	0.82
D_{Cd}	0.16	0.39	0.57	0.85	1.02
$\beta_{Zn/Cd}$	0.88	0.67	0.70	0.71	0.80

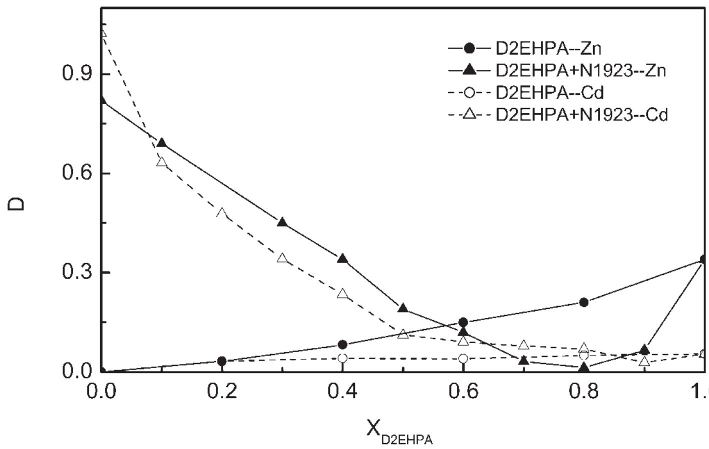


Figure 3. Extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and D2EHPA; $[Zn^{2+}]_{(a)} = 0.02\,mol/L$, pH = 1.56, $\mu = 1.50\,mol/L$; $[Cd^{2+}]_{(a)} = 0.02\,mol/L$, pH = 1.51, $\mu = 1.50\,mol/L$; $N[1923]_{(o)} + [D2EHPA]_{(o)} = 0.20\,mol/L$.

N1923 + HEH/EHP, and N1923 + Cyanex272 systems are calculated following Xu et al.[22] to be 1.34 and 1.79, respectively.

The synergistic extraction of Zn^{2+} by N1923 + HEH/EHP and N1923 + Cyanex272 systems has been investigated in our previous works.[17,18] The extraction reactions can be expressed as follows.

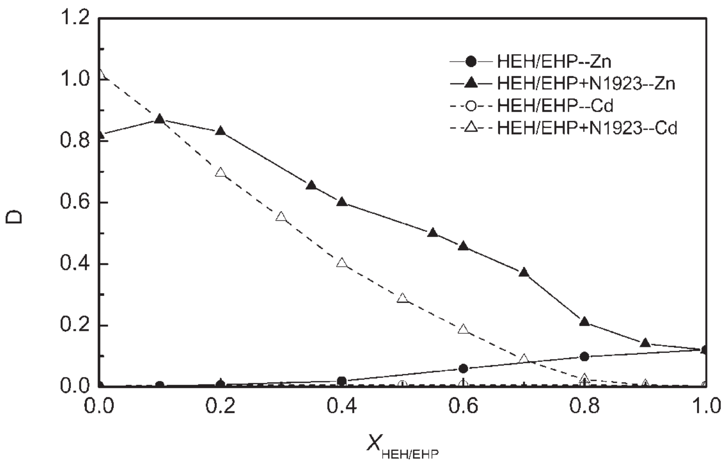


Figure 4. Extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and HEH/EHP.

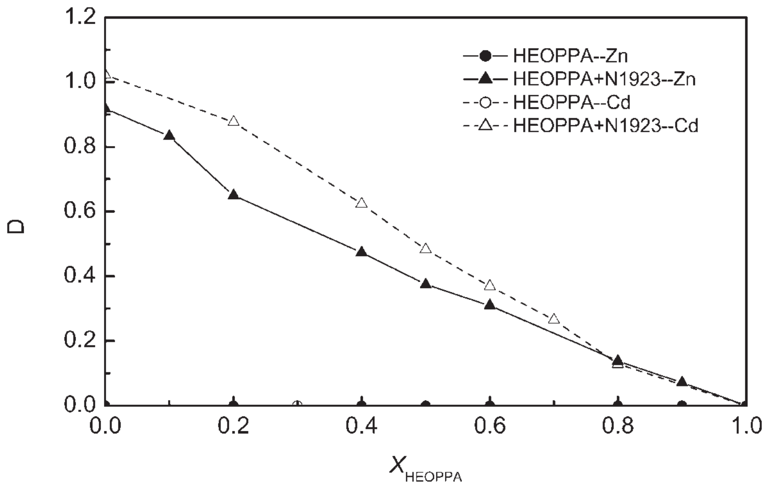


Figure 5. Extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and HEOPPA.

For N1923 + HEH/EHP:

$$ZnCl_{2(a)} + 2(RNH_3Cl)_{3(o)} + \frac{1}{2}(HA)_{2(o)} \overset{K}{\longleftrightarrow} (RNH_3Cl)_6 \cdot ZnClA_{(o)} + HCl_{(a)} \quad (2)$$

For N1923 + Cyanex272:

$$ZnCl_{2(a)} + (RNH_3Cl)_{3(o)} + \frac{1}{2}(HA)_{2(o)} \overset{K}{\longleftrightarrow} (RNH_3Cl)_3 \cdot ZnClA_{(o)} + HCl_{(a)} \quad (3)$$

The equilibrium constants $\log K$ were calculated as 1.73 and 1.94, respectively. The synergistic effect of Zn^{2+} by N1923 + Cyanex272 is higher than that by N1923 + HEH/EHP.

Since the organophosphorus acids considered exist predominantly as dimeric species,[1] a possible explanation can be expressed as the following equation:

$$\frac{1}{2}(HA)_{2(o)} + \frac{1}{3}(RNH_3Cl)_{3(o)} \longleftrightarrow RNH_3 \cdot A_{(o)} + HCl_{(a)} \quad (4)$$

The formation of $RNH_3 \cdot A$ decreases the effective concentrations of organophosphorus acids and N1923, resulting in decreasing extractabilities. The p*K*a values of Cyanex272, Cyanex302, Cyanex301 follow the order: Cyanex272 >

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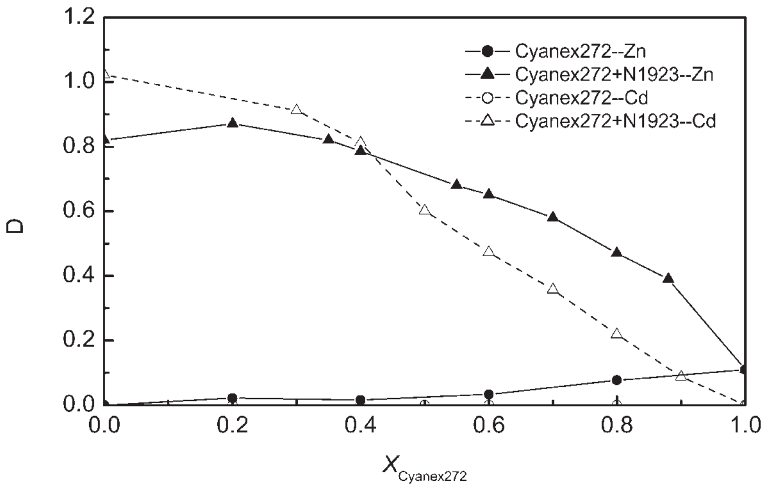

Figure 6. Extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and Cyanex272.

Cyanex302 > Cyanex301, which results in their reaction abilities with $(RNH_3Cl)_3$ following the contrary order. This is the reason why the mixtures of N1923 and Cyanex272 have synergistic effects on Zn^{2+} extraction, while those of N1923 and Cyanex301 have antagonistic effects. Similarly, N1923 + HEH/EHP systems show synergistic effects but N1923 + D2EHPA

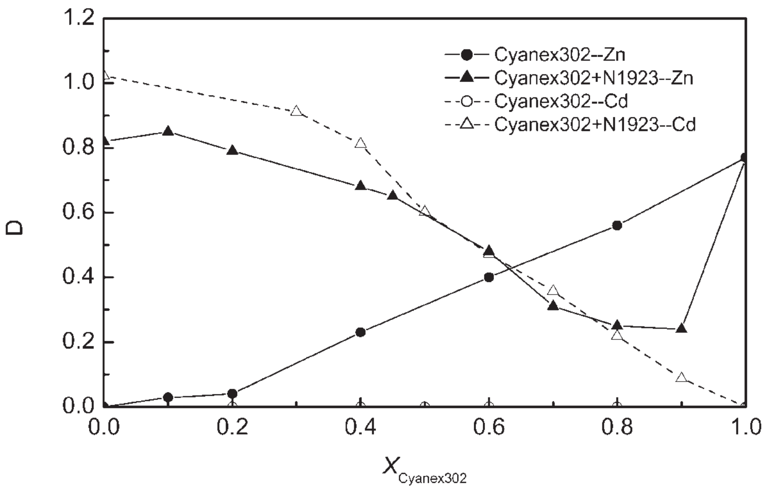

Figure 7. Extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and Cyanex302.

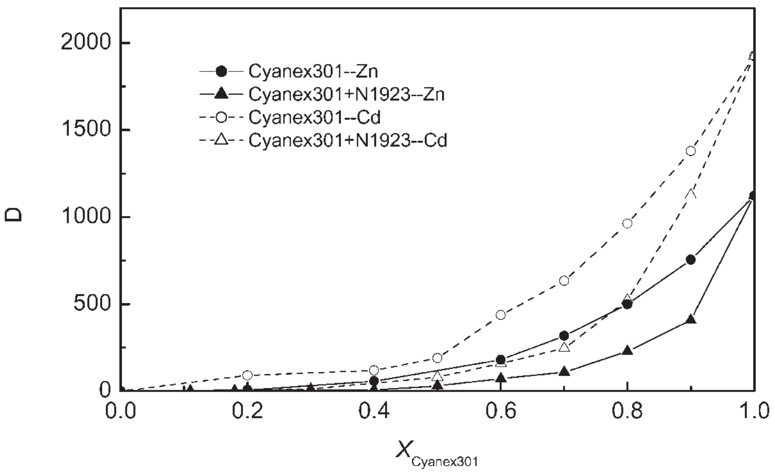

Figure 8. Extraction of Zn^{2+} and Cd^{2+} by mixtures of N1923 and Cyanex301.

systems show antagonistic effects for Zn^{2+} because of the lower p*K*a value of D2EHPA than that of HEH/EHP.

Separation of Zn^{2+} and Cd^{2+} with Mixtures of N1923 and Organophosphorus Acids

The separation of Zn^{2+} and Cd^{2+} has been a problem of interest all along because Zn^{2+} and Cd^{2+} coexist in ores. As mentioned above, it is difficult to separate Zn^{2+} and Cd^{2+} with N1923 alone. The organophosphorus acids have low extractabilities for Zn^{2+} and Cd^{2+} except Cyanex302 and Cyanex301, so it is of low pragmatic value to study the separation of the two cations by organophosphorus acids alone. Since the mixtures of N1923 and the organophosphorus acids have different extraction effects on Zn^{2+} and Cd^{2+}, it is normal to investigate the separation efficiency of the mixtures. In previous work, we have investigated the separation of Zn^{2+} and Cd^{2+} by Cyanex272 and its mixture with N1923.[18] In the present paper, two effective systems, N1923 + HEH/EHP and N1923 + Cyanex301, are carried out to separate the two cations (see Figs. 4 and 8). It is feasible and advantageous to separate Zn^{2+} from bulk cadmium with N1923 and HEH/EHP mixtures because of their evident synergistic effects on the extraction of Zn^{2+}, while these are no similar effects on Cd^{2+}. On the other hand, N1923 and Cyanex301 mixtures can be used to separate Cd^{2+} from bulk zinc because of their different

Table 2. $\beta_{Zn/Cd}$ of N1923 + HEH/EHP and N1923 + Cyanex301 systems.

	X_{N1923}							
	0.1	0.2	0.3	0.4	0.5	0.6	0.8	1.0
N1923 + HEH/EHP	18.93	8.87	4.20	2.47	1.85	1.48	1.19	0.80
N1923 + Cyanex301	0.36	0.44	0.44	0.44	0.37	0.30	0.86	0.80

antagonistic effects on the extraction of the two cations. The separation factors $\beta_{Zn/Cd}$ of N1923 + HEH/EHP and N1923 + Cyanex301 are calculated as shown in Table 2.

CONCLUSION

The extraction of Zn^{2+} and Cd^{2+} by organophosphorus acids, D2EHPA, HEH/EHP, HEOPPA, Cyanex272, Cyanex302, and Cyanex301 and their mixtures with primary amine N1923 has been determined in the present paper. The differences of extraction abilities by organophosphorus acids alone are discussed according to their structures. Their mixtures with N1923 show different extraction effects on Zn^{2+} and Cd^{2+}. Only the mixtures of N1923 + HEH/EHP and N1923 + Cyanex272 have synergistic effects on Zn^{2+}, in which the enhancement factors are calculated as 1.34 and 1.79, respectively. However, the other four mixing systems have no evident synergistic effects on Zn^{2+}, and all six mixing systems have no such effects on Cd^{2+}. The possibility of separating Zn^{2+} and Cd^{2+} is discussed according to the different extraction efficiencies. The mixtures of HEH/EHP and N1923 are possible to separate Zn^{2+} from bulk cadmium, while those of Cyanex301 and N1923 separate Cd^{2+} from bulk zinc.

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