EXTRACTION OF MANGANESE FROM SOLUTIONS CONTAINING ZINC AND COBALT BY D2EHPA AND D2EHPA-CYANEX® 272 OR CYANEX® 302 MIXTURES

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This paper presents the results of the studies carried out on the effect of pH on extraction of manganese from aqueous solutions containing zinc and cobalt at ambient temperature. Empirical data indicates that an increase in the ratio of Cyanex® 272 (or Cyanex® 302) to D2EHPA shifts the extraction curve of zinc to the lower pH values and that of manganese to the higher pH values; but it does not affect on the cobalt extraction curve. Selectivity separation parameter (β) obtained experimentally shows that the most suitable extractant for separation of zinc from manganese is a 0.3/0.3 mixture of D2EHPA with Cyanex® 302; while that for separation of manganese from cobalt is pure D2EHPA. The stoichiometric coefficients of the manganese and zinc extraction reactions were obtained to be 3 and 4, respectively.

Introduction

Liquid-liquid extraction is known as an efficient method for separation, removal and purification of the metallic ions that exist in aqueous media. Separation of manganese as a troublous ion from solutions containing cobalt and zinc has previously been investigated. Dhadke and Ajgaonkar carried out a quantitative study of the extraction of Mn(II) and Co(II) from sulfate solutions using Cyanex® 302 in toluene [1]. They extracted Co(II) and Mn(II) in the pH range of 7.0 to 7.5 and 8.5 to 9.5 in presence of 0.1M $(NH_4)_2SO_4$, respectively.

Extraction and separation of Mn(II) and Co(II) from sulfate solutions using sodium salts of D2EHPA, PC 88A and Cyanex® 272 in kerosene have also been investigated [2]. The most suitable extractant for separation of these metals have been found to be 0.05M NaD2EHPA present at an equilibrium pH of 4.45. Hoh et al. [3] have separated manganese from cobalt in sulfate solution by diluted D2EHPA in kerosene. The pH for aqueous and organic systems was controlled to be in the neighborhood of 4.2 and 2.0, respectively.

Mihaylov et al. [4] have carried out the simultaneous extraction of 0.6 gr/lit Co and 6 gr/lit Ni from sulfate solutions containing 3gr/lit Mn using 15% Cyanex® 301 at A/O ratio of 2.5. Cobalt and nickel were reported to extract at a pH of less than 2.0. Manganese did not leave the aqueous phase under these conditions. Separation of Mn(II) and Co(II) from ammoniacal solutions using versatic-10 acid was carried out by Woo and Cho [5]. They found that the best condition for high degree of separation could be achieved with 0.5M $(NH_4)_2SO_4$ at a pH of 9.0 to 9.5. Devi et al. [6] showed that during study of divalent zinc and manganese solvent extraction from sodium salts of Cyanex® 272, the extracted species were $ZnA_2.3HA$ and $MnA_2.3HA$.

The purpose of this study is to determine the synergistic effect of increasing the Cyanex® 272 to D2EHPA ratio and Cyanex®302 to D2EHPA ratio in the extractant mixture on Mn(II) separation from Co(II) and Zn(II). The stoichiometric coefficient of the extractant in Mn(II) extraction equation is an important quantity [7] that has been determined in this work, too.

Experimental Procedure

Materials

All extractants and metallic sulphates (zinc, manganese and cobalt) were laboratory grade materials. Bis-2-ethylhexyl phosphoric acid (D2EHPA) was purchased from Sandong Chemical, Ghengdu, China and both di-2,4,4,-trimethylpentyl phosphinic (Cyanex® 272) and di-2,4,4,-trimethylpentyl monothiophosphinic (Cyanex® 302) acids were prepared from Cytec Netherlands. Tehran Refinery Company supplied kerosene as the diluent. Aqueous solutions having constant cobalt, zinc and manganese concentrations of 5gr/lit were prepared by dissolving metal sulphates made of Panreac Company of Spain in distilled water.

Experiments

All experiments were carried out at ambient temperature. The extractant concentrations were 0.6 mol/lit, in all cases. Equivolume (20 ml) aqueous-organic solutions were agitated for 30 minutes in order to reach equilibrium. Complete separation was then allowed. Ionic concentration of the aqueous phase was directly determined by titration with EDTA. Eirochromblack T was used as an indicator for zinc and manganese determination; while Muroxide was used for cobalt determination. Organic phase was stripped with 300gr/lit sulphuric acid and titration method was used to analyze the solution obtained.

Results and Discussion

Effect of pH

Experiments were carried out to investigate the effect of pH on the extraction of zinc, manganese and cobalt at the ambient temperature. Figure 1 shows the extraction curves of zinc, manganese and cobalt obtained with the use of D2EHPA and a mixture of D2EHPA and Cyanex® 302, as extractant. It can be seen that the increasing of Cyanex® 302 to D2EHPA ratio does not affect the position of the experimental data for cobalt; but it shifts the extraction curve of zinc to the left and that of manganese to the right. Similar results are obtained for D2EHPA-Cyanex® 272 mixture. However, the figures are not the same. Table 1 summarizes the $pH_{0.5}$ (pH at 50% metal extraction) and $\Delta pH_{0.5}$ ($pH_{0.5}$ differences of two metals) data for zinc, manganese and cobalt that were experimentally obtained.

Separation of zinc from manganese

Selectivity of the extractant with respect to zinc and manganese can be attributed to the difference between $pH_{0.5}$ values of the two metals, i.e. $\Delta pH_{0.5}$. Figure 1 shows that the addition of Cyanex® 302 to D2EHPA increases this value for zinc and manganese. According to the data summarized in Table 1, a 0.3-0.3 D2EHPA-Cyanex® 302 mixture is the most suitable extractant for separation of zinc from manganese.

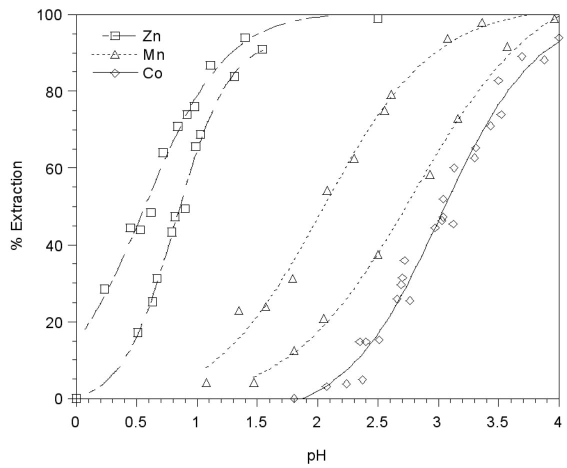


Figure 1. Variation of zinc, manganese and cobalt extraction percentages with pH. Hollow symbols correspond to 0.6 molar D2EHPA. Solid symbols correspond to 0.3 to 0.3 mixture of D2EHPA and Cyanex® 302, having a constant extractant concentration of 0.6 mol/lit.

Table 1. Values of $pH_{0.5}$ for different D2EHPA to Cyanex® ratio at 25 ºC.

[D2EHPA]/[Cyanex®] ratio		$pH_{0.5}$				
		Zn	Mn	Co	Mn-Zn	Co-Mn
272	0.6:0.0	1.30	2.05	3.04	0.75	0.99
	0.5:0.1	1.24	2.07	3.25	0.83	1.18
	0.4:0.2	1.20	2.28	3.39	1.08	1.11
	0.3:0.3	1.17	2.76	3.48	1.59	0.72
302	0.6:0.0	1.30	2.05	3.04	0.75	0.99
	0.5:0.1	0.70	2.18	3.11	1.48	0.93
	0.4:0.2	0.61	2.43	3.11	1.82	0.68
	0.3:0.3	0.57	2.74	3.13	2.17	0.37

Separation of manganese from cobalt

Extractant condition for cobalt-manganese separation is different from that for zinc and manganese. Adding Cyanex® 302 to D2EHPA decreases, for example, the $\Delta pH_{0.5}$ of cobalt and manganese. For separation of cobalt from manganese, best results are obtained with a mixture of 0.5–0.1 D2EHPA-Cyanex® 272. This corresponds with a $\Delta pH_{0.5}$ value of 1.18 (see Table 1).

Effect of addition of Cyanex® 272 and Cyanex® 302 to D2EHPA on selectivity ratio of manganese

The ratio of the two distribution factors D_A and D_B is called separation factor (β):

$$\beta_{A/B} = \frac{D_A}{D_B} \quad (1)$$

where D_A and D_B are the distribution factors of species A and B, respectively. The separation factor $\beta_{A/B}$ indicates how well the extractant can separate the species A from B. Variation of $\beta_{Zn/Mn}$ and $\beta_{Mn/Co}$ versus pH are illustrated in Figure 2. As is seen in the figure, using a mixture of D2EHPA and Cyanex® 302 instead of pure D2EHPA improves the selectivity of zinc in a solution containing manganese. Moreover, for separation of manganese from a cobalt containing solution, utilization of D2EHPA is advised.

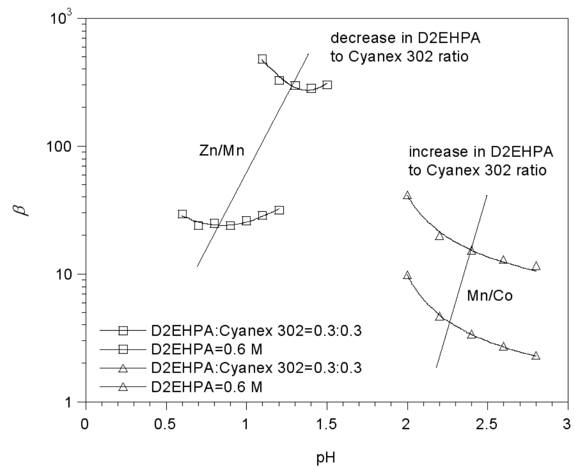


Figure 2. Effect of pH and D2EHPA to Cyanex 302 ratio on the amount of separation factor. Square symbols correspond to separation of zinc from a manganese containing solution. Triangle symbols correspond to separation of manganese from a cobalt containing solution.

Mechanisms of extraction of manganese and zinc

Mechanism of the manganese extraction depends on the stoichiometric coefficient n of the extraction reaction:

$$M^{2+} + nRH \rightleftharpoons MR_2(RH)_{n-2} + 2H^+ \quad (2)$$

Equilibrium constant of the reaction is evaluated from:

$$K = D_M \times \frac{[H^+]^2_{equ}}{[RH]^n_{equ}} \quad (3)$$

where D_M is the distribution coefficient defined by $\frac{\overline{[MR_2(RH)_{n-2}]}}{[M^{2+}]}$

The following expression can thus be derived:

$$\log D_M = \log K + 2pH + n\log\ [RH]_{equ} \quad (4)$$

Considering the amount of the extracted manganese, concentration of the extractant at equilibrium is given by:

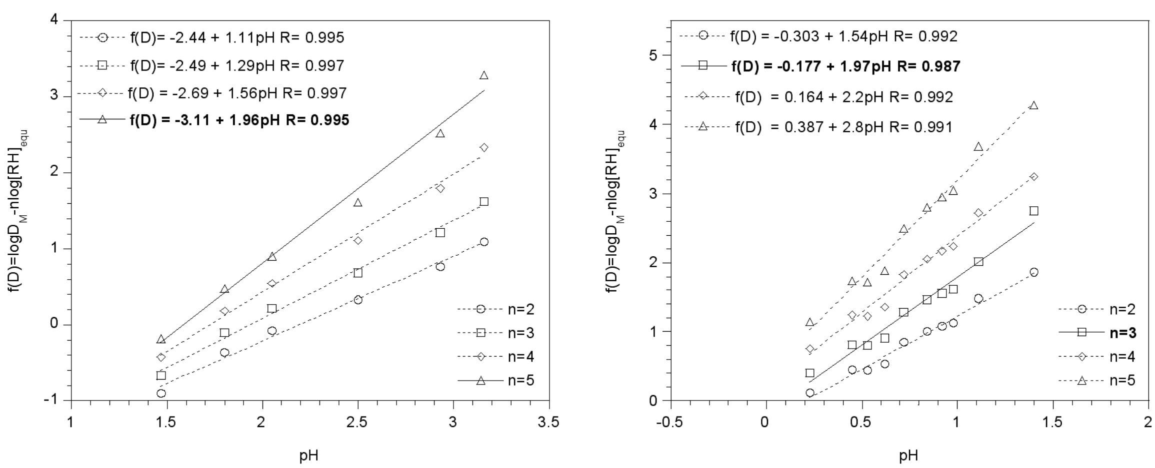
$$[RH]_{equ} = 0.6 - n \times \frac{\%E \times C_{\circ}}{M_W \times 100} = 0.6 - n\overline{[M]}_{org} \qquad (5)$$

where
n = stoichiometric coefficient of the extractant
%E = extraction percentage
$C_{\circ}$ = initial concentration of the element, gr/lit
M_W = molar mass of the element, gr/mol

Combining (4) and (5) gives:

$$\log D_M = n\log\left[0.6 - n[M]_{org}\right] + \log K + 2pH \qquad (6)$$

Stoichiometric coefficient of extractant, n, can be calculated by trial and error method. Plotting ($\log D_M - n\log [RH]_{equ}$) against pH at different values of n, gives straight lines with different slopes and intercepts (see Figure 3). The correct one for manganese or zinc extraction equation is the line with slope 2. The number replaced for n, is the stoichiometric coefficient of the extractant. The values of n in zinc extraction equation, using either D2EHPA or mixture of D2EHPA with Cyanex® 272/Cyanex® 302, were found to be 3. This value in manganese extraction equation, using either D2EHPA or mixture of D2EHPA with Cyanex® 272, was obtained to be 4. Using different D2EHPA to Cyanex® 302 ratios, the value of n was found to be 5. Darvishi et al. [7] found values of n in cobalt extraction equation, using either pure D2EHPA or mixture of D2EHPA with Cyanex® 272/ Cyanex® 302, to be equal to 4.



(a) *(b)*

Figure 3. Variation of $\log D_M$ - $n\log [RH]_{equ}$ versus pH. The data obtained by extractant with ratio of D2EHPA to Cyanex 302 equal 0.3 to 0.3: (a) manganese and (b) zinc

Base on the results obtained from slope analysis, the extraction equation of manganese and cobalt can be represented as follows:

1. With D2EHPA and mixture of D2EHPA with Cyanex® 272 used as extractant:

$$Mn^{2+} + 4RH \rightleftharpoons MnR_2(RH)_2 + 2H^+ \quad (7)$$

$$Zn^{2+} + 3RH \rightleftharpoons ZnR_2(RH) + 2H^+ \quad (8)$$

2. With mixture of D2EHPA and Cyanex® 302 used as extractant:

$$Mn^{2+} + 5RH \rightleftharpoons MnR_2(RH)_3 + 2H^+ \quad (9)$$

Zinc extraction equation at this stage is the same as the above.

Conclusions

The percentages of extraction of all three metals were increased with increasing of the pH of the solution. Zinc and cobalt were extracted at the lowest and highest equilibrium pH for all extractants, respectively. The mixture of D2EHPA with Cyanex® 302 at the ratio of 0.3:0.3 was the most suitable extractant for separation of manganese and zinc. Due to the maximum value of $\Delta pH_{0.5}$, a solution containing 0.6 molar D2EHPA was the best extractant for separation of manganese from cobalt. Stoichiometric coefficient of extractant in the manganese extraction equation was 4 when D2EHPA was merely used as the extractant. Adding Cyanex® 302 to D2EHPA changes the stoichiometric coefficient of the extractant in manganese extraction equation from 4 to 5. However in the case of Cyanex® 272, no change was observed. The stoichiometric coefficient of the extractant in zinc extraction equation was found to be 3 with using either D2EHPA or a mixture of D2EHPA with Cyanex 272/Cyanex 302.

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