SYNERGISTIC EFFECT OF TBP ON SEPARATION OF ZINC AND CADMIUM WITH D2EHPA

E. Keshavarz Alamdari, D. Darvishi*, S.K. Sadrnezhaad*, D.F Haghshenas*

Dept. Mining, Metallurgical and Petroleum Eng; Amirkabir University of Technology, Tehran, IRAN
*Center of Excellence for Advanced Materials Forming Processes, Department of Materials Science and Engineering, Sharif University of Technology, Tehran, IRAN

This paper investigates TBP selectivity effects for extraction of zinc and cadmium. Empirical results show that existence of M2EHPA in D2EHPA causes extraction curve of zinc and cadmium to reach the same. Separating zinc from cadmium is encountered, therefore, with difficulty. Addition of TBP, as a modifier, to D2EHPA can improve undesirable separation conditions due to the presence of M2EHPA in D2EHPA. Results shows that up to 2 Vol.% of M2EHPA existing in D2EHPA decreases the value of the selectivity parameter, β, to less than 10; while addition of up to 5 Vol.% of TBP to D2EHPA in presence of M2EHPA increases the value of β to nearly 30.

Introduction

D2EHPA as a general and practical extractant is widely used in solvent extraction of zinc [1-3]. Almost all solvent extraction units of zinc utilize D2EHPA as the organic solvent [4]. This compound is commercially supplied with an assay of near 95%. All impurities present in this compound, including M2EHPA, influence on separation of zinc from cadmium during the extraction process [4-5]. Presence of M2EHPA as an impurity in D2EHPA yields an undesirable synergistic effect on co-extraction of zinc and cadmium [4].
Use of oxidizing agents such as $KMnO_4$ and a highly concentrated acid in stripping units provides the conditions for decomposition of D2EHPA to M2EHPA [4]. It seems, therefore, that the concentration of M2EHPA will increase during the extraction cycle. TBP is utilized, therefore, as a most suitable modifier for solvent extraction of zinc [6-8]. Adding of TBP to the organic phase improves the phase separation and decreases the viscosity of the organic phase. Previous studies showed that TBP yields a synergistic effect that decrease the unwanted synergistic effect of M2EHPA [4].
This paper tries to deal with properties of TBP as a modifier during zinc and cadmium separation when M2EHPA is present as an impurity in D2EHPA. Presence of the latter can be due to poor purification or due to hydrolysis of D2EHPA with M2EHPA.

Experimental Procedure

Materials and reagents

All used chemical reagent except kerosene were analytical grade. D2EHPA (Bis-2-ethylhexyl phosphoric acid) was prepared from Merck chemical company, Germany. TBP (tri-n-butyl phosphat) and M2EHPA (mono-2-ethylhexyl phosphoric acid), used as a mix of D2EHPA and M2EHPA, reagents were provided by Fluka, Swiss. The needed concentration of organic extractant with sum of D2EHPA and M2EHPA amounting to 20 vol% was prepared with diluting of the calculated amount of D2EHPA and Mix D2EHPA – M2EHPA in Kerosene. Kerosene was provided by Tehran Refinery Company, Iran. Organic phases containing D2EHPA and M2EHPA with ([M2EHPA]: [D2EHPA]) ratio 0, 0.11and 0.25 as extractant plus 0%, 2.5%, 5% and 10% TBP as modifier were prepared by dissolving the materials into pure kerosene, respectively. Aliquot samples containing 5 g/L zinc or Cadmium in ionic form were prepared by dissolving analytical grade of zinc or cadmium sulfate made in Fluka AB, Switzerland, in distilled water. Sulfuric acid and ammonium hydrate (Ammonium solution) from Baran Chemical Company of IRAN was employed for adjusting pH of the system.

Experiments

Batch experiments were carried out in a flask containing equal volumes (20 ml) of both aqueous and organic phases. The mixture was agitated at a constant temperature with a mechanical shaker. The experiments were allowed to run for one hour in order to reach equilibrium. The samples were retained for three hours and the two phases were separated by passing through a separation funnel. The initial concentration of zinc or cadmium in the aqueous phase in all experiments was 5 g/L. Zinc or cadmium content of the aqueous phase was analyzed with titration method with EDTA at presence of Eirochromblack T as indicator. Zinc or cadmium concentration of the organic phase was determined through mass balance calculations.

Results and Discussion

Effect of M2EHPA on zinc and cadmium extraction

Extraction curves of zinc and cadmium obtained for 20 Vol.% D2EHPA and M2EHPA are illustrated in Figure 1. As can be seen from the figure, the presence of M2EHPA in D2EHPA causes the zinc and cadmium extraction curves to shift to lower pH values. The figure also shows that the cadmium ΔpH ($pH^{D2EHPA} - pH^{D2EHPA+M2EHPA}$) variation is more sensitive to increasing of M2EHPA Vol.% in D2EHPA than that of zinc. The values of ΔpH for cadmium and zinc are 0.58 and 0.14 unit pH, respectively. So it seems that separation of zinc and cadmium would not be simple. More scrubbing stages are necessary for a highly selective separation.

Effect of addition of TBP on zinc and cadmium extraction

As mentioned before, TBP is usually used as modifier in order to improve solvent extraction conditions. So experiments were carried out to find out the effect of TBP on zinc and cadmium extraction. Extraction curves of zinc and cadmium with respect to increasing of TBP, are shown in figure 2. As can be observed in figure 2-a, increasing of TBP up to 10 vol% has not affected on zinc extraction curve considerably, while the results of figure 2-b show that increasing of this compound to D2EHPA causes cadmium extraction curve shifts to right, vice versa of M2EHPA performance. In other words, presence of TBP in D2EHPA,

including impurity as M2EHPA, could have a synergistic effect in order to modify the separation of zinc and cadmium. The values of $pH_{0.5}$ (the equilibrium pH value at which 50% extraction of metal occurs) for zinc and cadmium due to variation of M2EHPA and TBP are listed in Table 1.

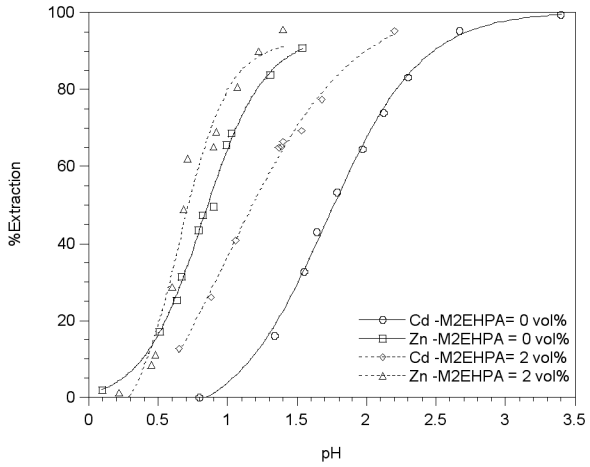

Figure 1. Variation of extraction percentages of zinc and cadmium versus pH,TBP Vol.% = 0.

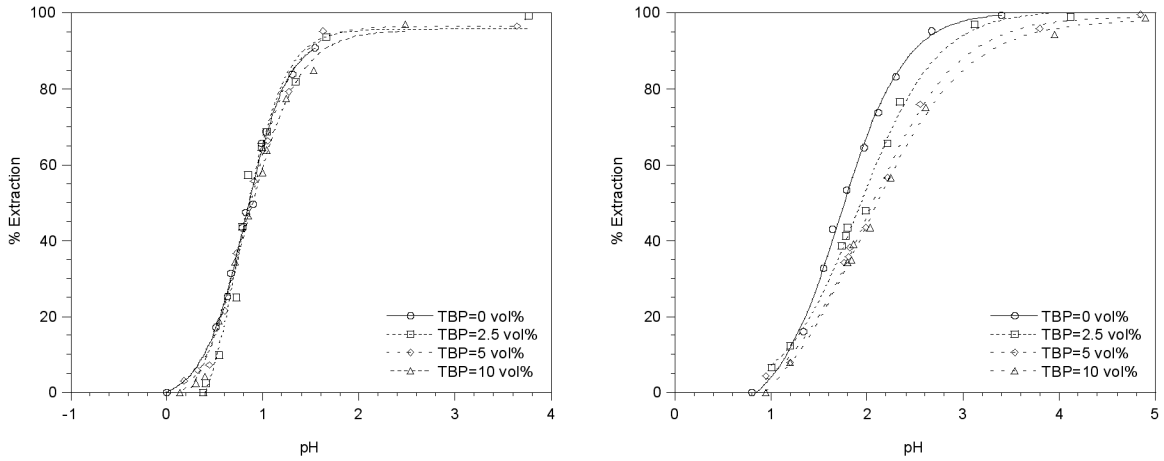

Figure 2. Variation of extraction percentages of zinc and cadmium versus pH, using 20 Vol.% D2EHPA as extractant (a) zinc and (b) cadmium.

Effect of addition of TBP on zinc and cadmium extraction in presence of M2EHPA

According to the results obtained from Figure 1, presence of M2EHPA, weather as an impurity or produced by D2EHPA decomposition under unsuitable stripping conditions causes the unsatisfactory separation of these two metals. Based on the data given in Figure 2 it can also be concluded that the presence of TBP would improve the separation conditions. Therefore, a number of experiments were carried out to determinate the effect of addition of TBP in presence of M2EHPA in separation process of zinc and cadmium.

As shown in Figure 3, addition of up to 5 Vol.% TBP can reduce the undesirable effect of increasing of M2EHPA up to 2 Vol.% (compare with Figure 1). The effect of TBP and M2EHPA on $pH_{0.5}$ and $\Delta pH_{0.5}$ of zinc and cadmium are illustrated in Table 1.

Table 1. Values of $pH_{0.5}$ for zinc and cadmium due to variation of M2EHPA and TBP.

MEHPA Concentration (vol. %)	TBP Concentration (Vol. %)	$pH_{0.5}$		
		Zn	Cd	Cd - Zn
0	0	0.86	1.76	0.90
	2.5	0.86	1.94	1.08
	5	0.86	2.04	1.18
	10	0.86	2.11	1.25
2	0	0.72	1.18	0.46
	2.5	0.72	1.31	0.59
	5	0.73	1.56	0.83
	10	0.80	1.64	0.84
4	0	0.60	0.90	0.30
	2.5	0.65	0.92	0.27
	5	0.73	1.13	0.40
	10	-	1.19	-

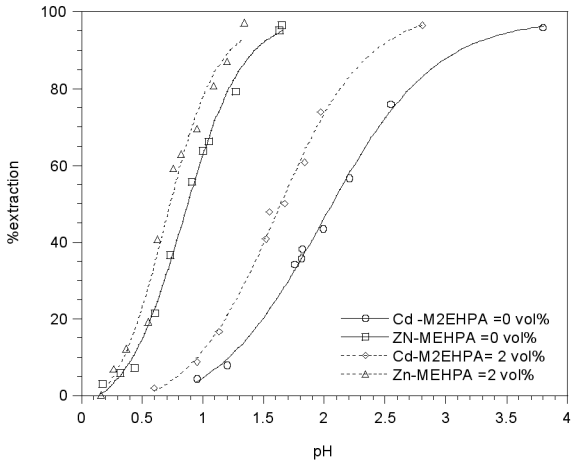

Figure 3. Variation of extraction percentages of zinc and cadmium versus pH, Vol.% of TBP = 5.

Effect of TBP and M2EHPA on zinc and cadmium separation

The separation factor (β) is a measure of selectivity in extraction of metals. In case of zinc and cadmium, this factor is defined as:

$$\beta_{Zn/Cd} = \frac{D_{Zn}}{D_{Cd}} \qquad (1)$$

The existence of a tendency towards lowering of cadmium distribution factor indicates a better separation of zinc over cadmium. In other words, at a higher separation factor it is easier to perform a selective extraction procedure.

The values of $\beta_{Zn/Cd}$ are illustrated in Table 2. As is seen, values of $\beta_{Zn/Cd}$ decrease strongly when up to 2 Vol.% of M2EHPA exists as an impurity in D2EHPA, in which these values decrease to less than 10. Addition of up to 5 Vol.% TBP to D2EHPA in presence of

M2EHPA would improve the separation conditions in which the values of $\beta_{Zn/Cd}$ increase to nearly 30. Based on these results, it can be concluded that TBP improves the selective separation parameter $\beta_{Zn/Cd}$ as well as purified D2EHPA, if the percentage of M2EHPA is less than 2 Vol.%.

Table 2. Experimental results on distribution coefficient and separation factor of zinc and cadmium.

TBP Concentration (%Vol.)	pH	MEHPA Vol. % = 0			MEHPA Vol. % = 2		
		D_{Zn}	D_{Cd}	$B_{Zn/Cd}$	D_{Zn}	D_{Cd}	$B_{Zn/Cd}$
0	0.5	0.20	0.00	∞	0.23	0.05	4.44
	0.7	0.50	0.00	∞	0.94	0.18	5.33
	0.9	1.19	0.01	84.50	2.59	0.42	6.15
	1.0	1.87	0.04	42.87	4.04	0.59	6.89
	1.1	2.68	0.08	33.92	5.67	0.79	7.15
	1.3	5.24	0.19	27.44	7.70	1.35	5.69
	1.5	8.57	0.41	20.71	17.02	2.42	7.04
5	0.5	0.18	0.00	∞	0.28	0.00	∞
	0.7	0.47	0.00	∞	0.86	0.03	26.64
	0.9	1.11	0.02	54.40	2.19	0.09	23.99
	1.0	1.68	0.05	35.70	3.42	0.14	24.58
	1.1	2.59	0.07	36.51	5.11	0.19	26.74
	1.3	5.68	0.14	39.58	12.04	0.35	34.03
	1.5	11.48	0.26	44.37	70.43	0.67	105.38

Conclusions

Presence of M2EHPA in D2EHPA caused shifting of the extraction curves of zinc and cadmium to the lower pH values. The experimental data showed that with increasing Vol.% of M2EHPA in D2EHPA, the ΔpH ($pH^{D2EHPA} - pH^{D2EHPA+M2EHPA}$) of cadmium varies more than that of zinc. Increasing up to 10 Vol.% of TBP does not considerably affect the zinc extraction; while increasing of this compound to D2EHPA causes cadmium extraction curve to shift to the right. Addition of TBP in D2EHPA containing M2EHPA has a synergistic effect, which modifies the separation of zinc from cadmium. Existence of M2EHPA in D2EHPA causes the unsatisfactory separation of zinc from cadmium. Addition of up to 5 Vol.% TBP can reduce the undesirable effect of increasing of M2EHPA up to 2 Vol.%. Presences of up to 2 Vol.% M2EHPA decreases the values of $\beta_{Zn/Cd}$ to less than 10. Addition of up to 5 Vol.% TBP to D2EHPA in presence of M2EHPA improves the separation conditions in which increases the values of $\beta_{Zn/Cd}$ to nearly 30.

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