EFFECT OF TBP AS A MODIFIER FOR EXTRACTION OF ZINC AND CADMIUM WITH A MIXTURE OF DEHPA AND MEHPA

E. Keshavarz Alamdari, D. Darvishi, S. K. Sadrnezhaad*, Z. Mos'hefi Shabestari, A. O'hadizadeh and M. Akbari

Dept. Mining and Metallurgical Engineering, Amirkabir University of Technology,Tehran, Iran
* Dept. Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

The simultaneous extraction of zinc and cadmium by a mixture of di(2-ethylhexyl)phosphoric acid (DEHPA) and mono-2-ethylhexylphosphoric acid (MEHPA) in the presence of tri-*n*-butylphosphate (TBP) as a modifier was investigated. The effects of temperature, pH and TBP concentration on extraction of zinc and cadmium were determined. It was shown that the extraction reaction for zinc is endothermic, while that for cadmium is exothermic. An increase in the TBP concentration caused greater synergistic shifts than when TBP was not dissolved in the organic phase. Separate formulae were deduced from the experimental data for the distribution factors of both zinc and cadmium.

INTRODUCTION

Zinc and cadmium usually occur together in the nature. During leaching of low-grade ores, zinc and cadmium dissolve simultaneously into the leach liquor. The level of impurities in the electrolyte is generally high. The purification process is, therefore, very necessary, especially if production of ultra-high purity (UHP) zinc or cadmium is required.

Cadmium is one of the most toxic constituents of industrial wastes and effluents. It should, therefore, be totally removed from wastes and effluents before disposal to the outdoor environment [1]. Approximately half of the world's total consumption of cadmium is utilized in alkaline storage batteries. Cadmium recycling is, therefore, an important subject both economically and environmentally [2].

The method of solvent extraction may be used for selective extraction of impurities from leach liquors. The extractants can be considered as molecules that are chained together with hydrogen bonds [3]. The number of bonds depends on the acidic nature of the extractant. So ℓ extractant molecules, each having m hydrogen ions, bond together to make a structure that can extract metal ions. The stoichiometric equation describing the solvent extraction process can, therefore, be written as:

$$\ell[RH_m] + mM^{n+} \Leftrightarrow [RH_m]_{(\ell - n)}R_nM_m + mnH^+ \qquad (1)$$

Proceedings of the International Solvent Extraction Conference, ISEC 2002
Edited by K. C. Sole, P. M. Cole, J. S. Preston and D. J. Robinson
© South African Institute of Mining and Metallurgy, Johannesburg, 2002
Produced by Document Transformation Technologies, Published by Chris van Rensburg Publications (Pty) Ltd

where $[RH_m]$ is an organic extractant molecule, $[RH_m]_{(l-n)}\ R_nM_m$ is the extracted metallic complex and H^+ is the proton released by the organic extractant in exchange for the cationic metal species, M^{n+}. The equilibrium constant of the reaction, expressed in terms of the concentration of the reactants, can be defined as:

$$K_c = \frac{[\,[RH_m]_{(l-n)}\,R_nM_m\,].[H^+]^{m.n}}{[RH_m]^{\ell}\,[M^{n+}]^n} \qquad (2)$$

where the concentration equilibrium constant K_C depends on temperature and concentration. Assuming the effect of concentration to be negligible, and taking logarithms of both sides of Equation (2) yields:

$$\log D = \frac{\Delta H_{app.}}{2.3\,RT} + \frac{\Delta S_{app.}}{2.3\,R} + m.n\ pH + \ell \log [RH_m] + (m-1)\log [M^{n+}] + \log m \qquad (3)$$

in which the distribution coefficient, D, is defined as $D = \sum[M_{org}]/\sum[M_{aq}]$.

The thermodynamics of solvent extraction of some metals has recently been investigated by the same authors [4]. We report in this paper the effect of TBP as a modifier for the separation of zinc and cadmium from mixtures of DEHPA and MEHPA serving as suitable organic extractants. Coefficient factors mathematically obtained for quantifying the distribution ratio that prevails in the extraction system are also reported.

EXPERIMENTAL METHODS AND MATERIALS

Organic phases containing 12% DEHPA and 8% MEHPA as extractant plus 0%, 2.5%, 5% and 10% TBP as modifier were prepared by dissolving the materials into pure kerosene. Initial metals concentrations in the aqueous solution were both 5 g/l. NaOH and sulfuric acid were used for adjusting pH of the system. Around 20 ml of aqueous solution was mechanically stirred with equal volume of organic phase in a jacketed vessel for one hour. The mixture was then allowed to disengage into two separate phases. The metal content of the aqueous phase was determined by titration against a standard solution of EDTA (0.09 M) using Eriochrom Black T as the indicator. These experiments were carried out at three temperatures (25, 40 and 60°C) using a thermostatic reaction bath.

RESULTS AND DISCUSSION

Effect of TBP as a Modifier

Experiments were carried out to study the effect of pH on the extent of extraction and determination of the maximum recovery. Extraction curves are presented in Figure 1. It is seen that zinc extraction occurs at $0.6 < pH < 1.7$, while cadmium extraction occurs at $-0.05 < pH < 1.1$. The extraction of cadmium occurs, therefore, under more acidic conditions than that of zinc. Figure 1 also shows that addition of TBP has a small effect on the $pH_{0.5}$ (the equilibrium pH value at which 50% extraction of metal occurs) of zinc and cadmium extraction. Other experiments have, however, shown that at higher TBP concentrations, the rate of extraction of cadmium increases more rapidly with pH.

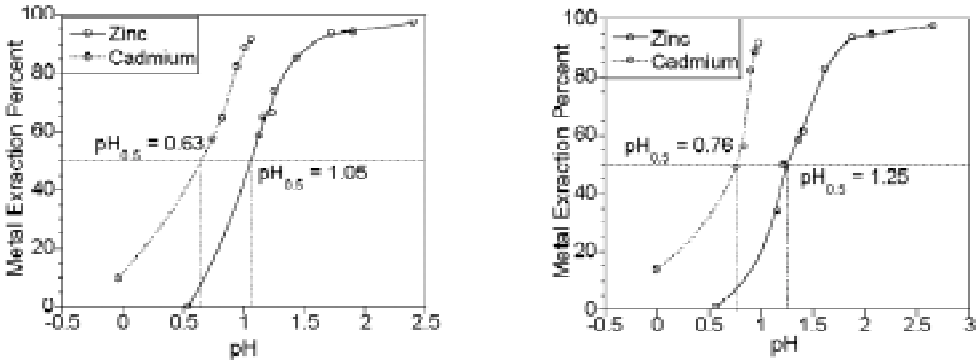


Figure 1. Extraction of zinc and cadmium at 25°C. a) 0% TBP; b) 10%TBP.

The effect of TBP on extraction of zinc and cadmium was investigated at different extractant concentrations. The extraction curves obtained show a synergistic shift to the right by increasing the relative amount of TBP with respect to the extractants (DEHPA and MEHPA). As is seen in Figure 1, the extraction percentage of cadmium and zinc varied from 0% to 90% depending on the pH and the relative amount of the organic modifier. The selectivity of the mixture can be expressed by the difference between the $pH_{0.5}$ values of the two metals. The data obtained for $pH_{0.5}$ and $\Delta pH_{0.5}$ of the metals are illustrated in Table 1.

Table 1. $pH_{0.5}$ for zinc and cadmium and $\Delta pH_{0.5}$.

TBP (%)	$pH_{0.5}$		$\Delta pH_{0.5}$
	Zn	Cd	Zn-Cd
0	1.05	0.63	0.42
2.5	1.13	0.65	0.48
5	1.02	0.56	0.46
7.5	1.19	0.74	0.47
10	1.25	0.76	0.49

The values given in Table 1 show that the presence of TBP facilitates the separation of zinc from cadmium due to its $\Delta pH_{0.5}$ enhancing effect. Figure 2 shows that at constant pH, log D varies linearly with log [TBP] with a slope of –1.00 for zinc and –0.35 for cadmium. A possible reason for this effect is that TBP, DEHPA and MEHPA molecules form hydrogen bonding with each other; hence they reduce the possibility of polymerization of DEHPA and MEHPA molecules to extract metallic ions. This causes diminution of the equivalent extraction potential and decreasing of the distribution ratio for zinc and cadmium extraction reactions. However it increases the gap between the required pH for extraction of Zn and Cd and it can, therefore, improve the selectivity of the extraction process.

As was mentioned before, the reason for synergistic shifts returns to the formation of new bonds in organic media. An equivalent organic value can, thus, be defined and the concentration of extractants can be considered as a function of TBP so that the equivalent concentration of exrtactant reagents can be estimated from the expressions defined for this purpose at TBP concentrations around [TBP]=0:

$$\begin{cases} [RH_n] = \sum [RH] + \sum [RH_2] = 0.66 \\ [RH_n]_{eq} = 0.66 - a[TBP] \end{cases} \qquad (4)$$

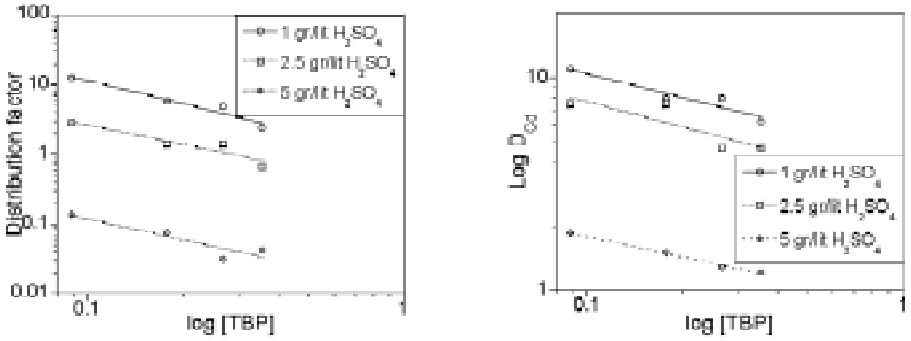


Figure 2. Variation of log D vs. log [TBP] at constant initial pH for a) zinc; b) cadmium.

So that:

$$\ln[RH_n] = \ln 0.66 - \frac{a[TBP]}{0.66} - \frac{a^2[TBP]^2}{2\times 0.66^2} - \frac{a^3[TBP]^3}{3\times 0.66^3} \cdots\cdots - \frac{a^n[TBP]^n}{n\times 0.66^n} \quad (5)$$

Substituting (6) in (3) and eliminating the terms with the order of 3 and more, one can obtain:

$$\log D = \frac{-\Delta H_{app}}{2.3RT} + \frac{\Delta S_{app}}{2.3R} + m.n\,pH + \frac{I\times \ln 0.66}{2.3} - \frac{I\times a[TBP]}{2.3\times 0.66} - \frac{I\times a^2[TBP]^2}{2\times 2.3\times 0.66^2} - \frac{I\times a^3[TBP]^3}{3\times 2.3\times 0.66^3} \cdots\cdots - \frac{I\times a^n[TBP]^n}{n\times 2.3\times 0.66^n} + (M-1)\log[M^{m+}] + \log m \quad (6)$$

Variation of log D versus [TBP] is shown in Figure 3. As was assumed before, the relationship between log D and [TBP] is of polynomial form. The coefficients used in Equation (6) can thus be evaluated by a curve-fitting method. The coefficient of the (log $[RH_m]$) term in Equation (3) can also be obtained by substituting the coefficients of the TBP terms into Equation (6).

Effect of Temperature

The effect of temperature on the distribution coefficients of Zn and Cd was determined at three different temperatures (25, 40 and 60 °C). The results obtained are shown in Figure 4. As shown, by increasing the temperature (decreasing the inverse of temperature) the distribution factor of zinc increases, while that of cadmium decreases. So the extraction of zinc and cadmium are endothermic and exothermic, respectively. The apparent enthalpies of the reactions can be calculated from the slopes of the plots of log D against 1/T.

Devising a Correlation for Estimation of the Distribution Factor

The data obtained at different conditions for both zinc and cadmium were analyzed by SPSS for Windows Ver. 8. The following equations were obtained for prediction of the distribution factors of both zinc and cadmium:

$$\log D_{Zn} = -0.66 - \frac{501.86}{T} + 0.63\,pH + 0.36\,[TBP] - 5.00\,[TBP]^2 + 8.94\,[TBP]^3 - 1.03\log[Zn^{2+}] \quad (7)$$

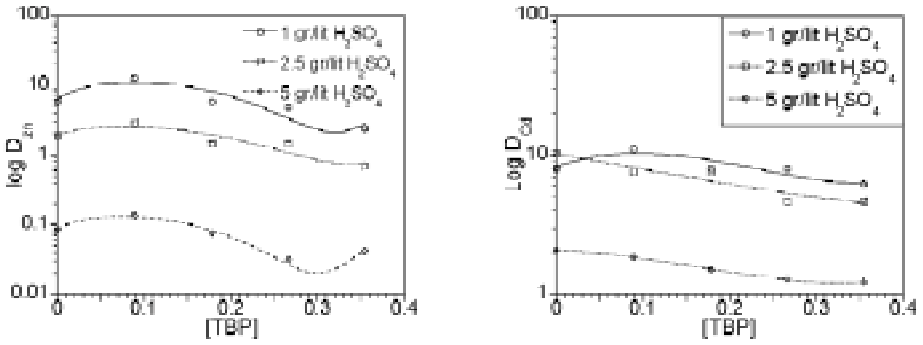


Figure 3. Variation of log D vs. [TBP] at constant initial pH for a) zinc; b) cadmium.

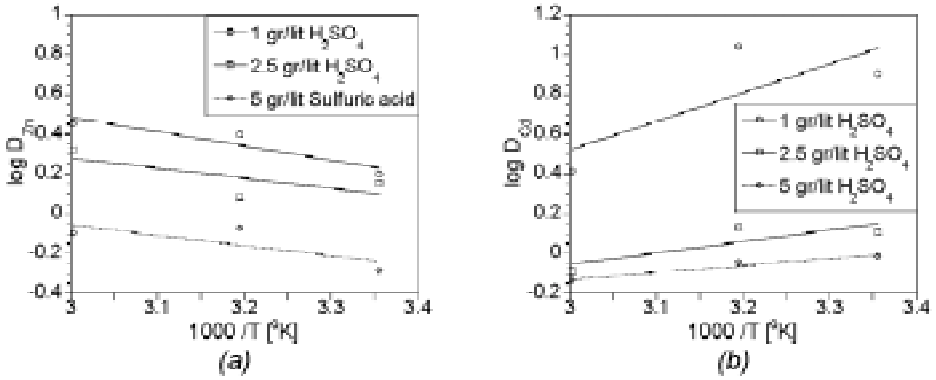


Figure 4. Effect of temperature on log D. a) zinc; b) cadmium.

and

$$\text{Log } D_{Cd} = -2.34 + \frac{195.98}{T} + 0.55\,pH - 0.27\,[TBP] + 2.23\,[TBP]^2 - 5.50\,[TBP]^3 - 0.90 \log [Cd^{2+}] \qquad (8)$$

The experimental values for the distribution factors are compared with those predicted from formulae in Table 2. The values show that the estimated distribution factors for zinc and cadmium are very close to those obtained from the experiments. The values predicted from Equations (7) and (8) are plotted against the experimental values of Figure 5. The slope of the data equals one with a confidence factor of 95% and 96% for zinc and cadmium extraction, respectively.

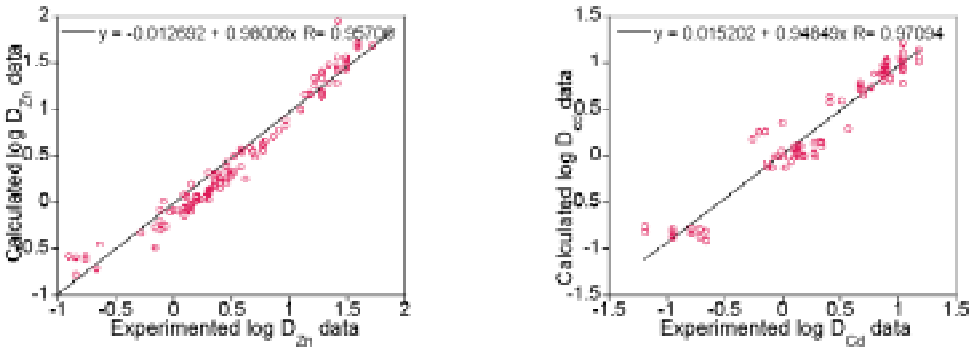
CONCLUSIONS

The extraction of metal ions by DEHPA and MEHPA in presence of TBP was modelled based on theoretical concepts of polymerization reactions of the extractant reagents and utilization of the experimental data. Equations obtained for zinc and cadmium distribution coefficients were assessed through comparison of their results with the experimental data. These equations can be utilized to estimate the extent of the zinc and cadmium extraction reactions and evaluation of log D against log [TBP] as two applicable correlations. The experimental results show that TBP can influence the extraction mechanism and rate of reaction. Proposing the new idea of polymerization of DEHPA and/or MEHPA by TBP helped the modification of Equation (2) and turned out to be useful. TBP caused the

extraction curves to shift to the right of the diagram. However, in the case of cadmium, its shifting effect was not very significant. From the equations given, the apparent enthalpy of extraction of zinc was obtained to be 9.6 kJ and that of cadmium was found to be –3.75 kJ.

Table 2. Comparison of estimated and experimental values of zinc and cadmium distribution factors.

TBP (%)	Experiment		Estimated	
	D_{Zn}	D_{Cd}	D_{Zn}	D_{Cd}
2.5	3.83	10.99	3.77	8.69
	4.55	7.99	4.03	8.16
	2.23	4.82	1.95	5.18
	1.21	1.36	1.21	1.11
5	2.87	8.6	2.7	7.05
	2.89	4.59	2.42	5.34
	1.28	1.50	1.14	1.00
	0.76	1.03	0.83	.98



(a) *(b)*

Figure 5. Comparison of the measured and the calculated data for distribution factors for a) zinc and b) cadmium, treated with a mixture of DEHPA and MEHPA in kerosene with TBP as a modifier from aqueous sulfuric acid media.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Iranian Zinc Mines Development Company, and to the Ministry of Industry and Mining of The Islamic Republic of Iran for their financial support of this project.

REFERENCES

1. S. Zielinski, M. Buca, and M. Famulski (1998), *Hydrometallurgy*, **48** (3), 253-263.
2. J.S. Preston, J. H. Patrick, and G. Steinbach (1994), *Hydrometallurgy*, **36** (2), 141-158.
3. M. Salimi, S. K. Sadrnezhaad, and E. Keshavarz Alamdari (2000), *Proc. 4th Conf. Metal. Eng. Iran*, 17-19 Oct. 2000, Tehran, Iran, pp. 559-566 [in Farsi].
4. S. K.Sadrnezhaad, E. Keshavarz Alamdari, Z. Mos'hefi shabestari, M. Abbaspoor, M. salimi, and M. Akbari (2002), unpublished data.