

## Solvent Extraction of Zn(II) from Aqueous Sulphate Media by Di(2-Ethylhexyl) Phosphoric Acid in Kerosene

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**Abstract.** The extraction equilibrium studies of Zn(II) from sulphate medium by di(2-ethylhexyl) phosphoric acid (D2EHPA,  $H_2A_2$ ) in kerosene revealed that the distribution ratio (D) decreased with the increase of initial [Zn(II)] in the aqueous phase and increased with the increase of equilibrium pH and extractant concentration. The equilibration is reached within 2 min. The species extracted into the organic phase is thought to be  $ZnA_2.HA$ . The pH and extractant dependencies were about 2 and 1.67, respectively. The distribution ratio decreased with the increase in sulphate ion concentration in the aqueous phase. The extraction equilibrium reaction is suggested as  $Zn^{2+}_{aq} + 1.5 (H_2A_2)_{org} \leftrightarrow [ZnA_2.HA]_{org} + 2H^+_{aq}$ . The extraction equilibrium constant ( $k_{ex}$ ) for the above reaction was calculated to be  $10^{-2.26}$ . The extraction process was endothermic in nature having positive  $DH$  value of 16.27 kJ/mol. The loading of D2EHPA by Zn(II) is about 4.50 g of Zn(II) by 0.10 M D2EHPA. Possible reaction mechanism has been suggested based on distribution data, extractant concentration and equilibrium pH of the aqueous phase.

**Keywords:** solvent extraction, Zn(II) ion, sulphate media, D2EHPA, di(2-ethylhexyl) phosphoric acid, kerosene

### Introduction

Solvent extraction has been one of the most important extraction and separation processes in hydrometallurgy. Especially phosphorus-based extractant, D2EHPA, a commercial extractant, has proved to be of particular importance for its wide range of extraction (from divalent to heptavalent) ability as well as separations of metal ions such as iron, copper, silver, cadmium, cobalt, nickel, manganese, magnesium, calcium, sodium, potassium, arsenic and antimony from different acidic solutions (Park and Fray, 2009; Fouad and Bart, 2008; Keng Xie *et al.*, 2008; Mansur *et al.*, 2008, 2002; Samaniego *et al.*, 2007; Sarangi *et al.*, 2007; Kumar Vinay *et al.*, 2006; Jianbing Ryszard *et al.*, 2006; Takeshita *et al.*, 2003; Singh and Dhadke, 2002; Morters and Bart, 2000).

All the studies made on the extraction of Zn(II) by D2EHPA were done mostly from chloride solutions and with purified D2EHPA (Amer and Luis, 1995; Devi *et al.*, 1995; Alguacil *et al.*, 1992). As the extraction characteristics of a metal ion by an extractant depends on the concentration levels of the metal ions and coexisting anions in the aqueous phase as well as on the diluents used, the objective of the present work was to make an investigation on the possibility of extraction of Zn(II) by commercial grade D2EHPA in kerosene diluent. Presently the kerosene medium is used as the industrial diluent for solvent extraction technology. Zinc extraction from waste leach solution has assumed importance in view of the world-

wide shortage of zinc and consequently its high price. Recovery of zinc from waste zinc containing materials is now a major interest in hydrometallurgy. The present study was undertaken to explore the possibility of extraction of zinc from comparatively concentrated zinc solutions in presence of sulphate ions. Various waste zinc materials are best leached by dilute  $H_2SO_4$ .

### Materials and Methods

A standard solution of Zn(II) (1 g/litre) was prepared by dissolving and diluting calculated amount of their respective sulphate salts ( $ZnSO_4.7H_2O$ ) with distilled water after adding 2.90 cc of 18.337 M  $H_2SO_4$  and standardized by using atomic absorption spectrophotometric method [Atomic Absorption Spectrophotometer (AAS), ANA 180, Tokyo Photoelectric Co. Ltd., Japan] at wavelength 217 nm. The test solution was prepared by taking calculated amount of respective aqueous stock solution of metal ion in a volumetric flask and then adding calculated amount of sulphate ion as either  $H_2SO_4$  or  $Na_2SO_4$  and made up to the mark by distilled water. After mixing, the solution was taken in a beaker for pH adjustment using dilute  $H_2SO_4$  or anhydrous  $Na_2CO_3$ .

The extractant D2EHPA having 98% purity was used without further purification. All other chemicals were of reagent grade and used without further purification. The diluent, kerosene, was purchased from the local market and distilled when the colourless fraction was obtained in the range of 200-260 °C.

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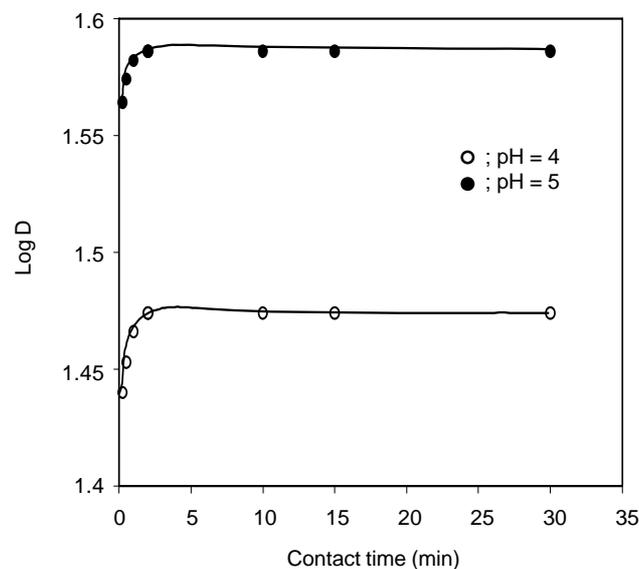
A stock solution of D2EHPA (1 M) was prepared by weighing out exactly 658.02 g of D2EHPA in a 1 litre volumetric flask and diluting with distilled kerosene. Working solutions of different concentrations (0.01-0.50 M) were prepared by proper dilution of this stock solution with distilled kerosene.

A definite aliquot of an aqueous phase (20 ml) was taken in a 125 ml reagent bottle and to it, same aliquot of organic phase (20 ml) was added. The bottle was stoppered and shaken for 5 min in a thermostatic water bath at  $30 \pm 1$  °C (except for temperature dependence). After attainment of equilibrium, the phases were allowed to settle and disengaged by a separating funnel. The aqueous phase was subjected to equilibrium pH measurement and the metal ion content by AAS. Distilled water was used as blank solution. In all the cases, phase separation occurred readily. pH value of aqueous solutions was measured by Mettler Toledo 320 pH meter and checked time to time to set the desired pH.

The equilibrium organic phase metal ion concentrations were estimated by the method of difference. The organic phase Zn(II) concentration was determined by the formula: initial aqueous phase - aqueous phase concentration of Zn(II) after extraction. The distribution ratio (D) of a metal ion was calculated as the ratio of metal ion concentration in the organic phase to that in the aqueous phase at equilibrium. In the case of loading test, the organic phase was repeatedly contacted with fresh equal volume of aqueous solutions until saturation of the organic phase with the metal was attained and tested by measuring aqueous phase concentration.

## Results and Discussion

**Effect of distribution ratio of Zn(II) by D2EHPA on contact time.** Figure 1 represents contact time (in minutes) and the distribution ratio for two different sets of pH 4 and 5. In both the cases, it was found that the extraction ratio of Zn(II) increased continuously with the increase of phase contact time upto 2 min and then remained unchanged with further increase of contact time. The slopes of the lines decreased to zero at around 2 min. Moreover, it was also observed that  $96.70 \pm 0.05\%$  and  $97.45 \pm 0.05\%$  [ $n = 8$ ] of Zn(II) got extracted at pH 4 and 5, respectively, and on further shaking for a long time, extraction ratio did not increase. The extraction of Zn(II) by Cyanex 302 was studied by Alguacil *et al.* (1992) and obtained equilibrium time above 10 min. Therefore, the extraction of Zn(II) by D2EHPA is faster than that of Cyanex 302. It is concluded that the extraction of Zn(II) from sulphate solution by analytical grade D2EHPA in kerosene system takes 2 min. Thus in subsequent experiments, mixing was carried out for 5 min to ensure equilibrium.



**Fig. 1.** Effect of distribution ratio of Zn(II) by D2EHPA on contact time.

[Zn(II)] = 0.200 g/litre;  $[\text{SO}_4^{2-}]_{(\text{ini})} = 0.10$  M; pH = 4.00 and 5.00; phase mixing time = moderate; [D2EHPA] = 0.05 M; O/A=1; temperature =  $(30 \pm 1)$  °C.

**Effect of metal ion concentration on Zn(II) by D2EHPA.** The results obtained from the experiments are plotted as log D vs.  $\log \{[\text{Zn(II)}]_{(\text{ini})} \text{ mol/litre}\}$  which represent variation of distribution ratio on initial metal ion concentration. It is seen that the distribution ratio decreases with increase in initial Zn(II) ion concentration (Fig. 2). The slopes of the plots are steeper at higher concentration region than those at lower concentration. In general, log D should be independent of initial metal ion concentration, provided the equilibrium pH and the equilibrium extractant concentration remain constant, which can occur with very low metal concentration only.

The decrease in extraction ratio with the increase of Zn(II) ion concentration may be explained as follows:

**a) Non-constant aqueous phase acidity, pH.** With the increase in Zn(II) ion concentration in the aqueous phase, the equilibrium pH may drop down due to the liberation of  $\text{H}^+$  by the extraction process. The decreased equilibrium pH with increase of Zn(II) ion concentration will decrease the extraction ratio according to the simplified extraction reaction as follows:



where,  $\text{H}_2\text{A}_2$  is the dimer of D2EHPA

**b) Non-constant equilibrium extractant concentration.** With the increase in initial Zn(II) ion concentration, more extractant

will be consumed to form the extractable Zn(II) complex. As a result, the equilibrium pH and extractant concentration will decrease with the increase in the initial Zn(II) ion concentration in the aqueous phase and eventually, the extraction ratio will decrease and may be expressed according to the following equation:

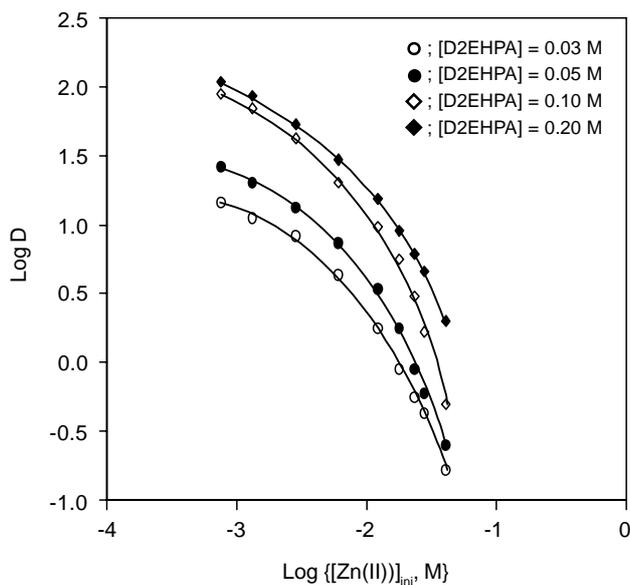
$$\log D = \log K_{ex} + z \log [H_2A_2]_{(ini)} + z \text{pH} - S \quad (2)$$

where:

D = distribution or extraction ratio; z = extractant dependence;

S = concentration of the extractant which is used in forming the metal complex;  $[H_2A_2]_{(ini)}$  = initial extractant concentration in the organic phase; pH = equilibrium pH of the aqueous phase.

Besides these two reasons, the decrease in the extraction ratio with increasing initial Zn(II) ion concentration may be attributed to the non-ideality of the aqueous phase, hydrolysis and polymerization of Zn(II) species in the aqueous phase.



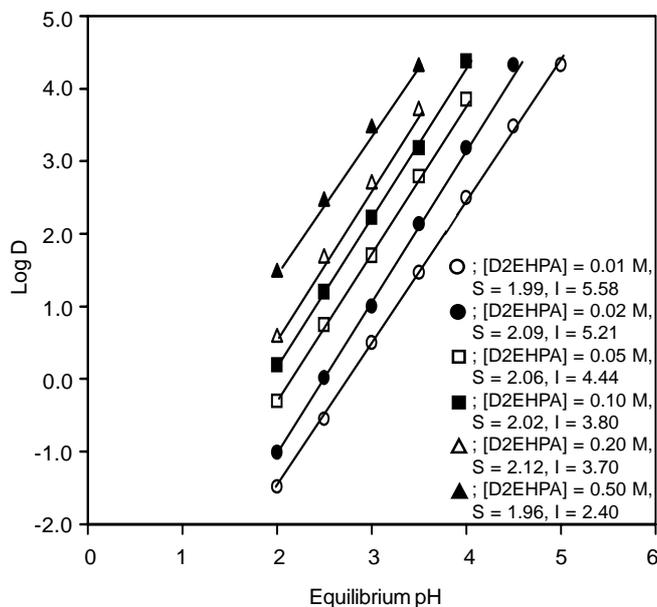
**Fig. 2.** Effect of distribution ratio (D) on Zn(II) ion concentration.

$[SO_4^{2-}]_{(ini)} = 0.10$  M; pH=3.00; phase mixing time = 5 min;  $[D2EHPA] = 0.03, 0.05, 0.10, 0.20$  M; O/A=1; temperature =  $(30 \pm 1)$  °C.

#### Effect of equilibrium pH on the extraction of Zn(II) by D2EHPA.

The results obtained from the experiments at different constant equilibrium pH and at constant  $[Zn(II)]$  concentration are plotted as log D (distribution ratio) vs. equilibrium pH (Fig. 3). It can be seen that the extraction of Zn(II) ions

increases with increase of aqueous phase equilibrium pH. The slopes of the lines were calculated and the values are 1.99, 2.09, 2.06, 2.03, 2.12 and 1.96 for 0.01, 0.02, 0.05, 0.10, 0.20 and 0.50 M D2EHPA systems, respectively. The average slope obtained from this investigation is equal to 2 (two). Similar results were obtained from the extraction of Zn(II) by D2EHPA by other workers (Bart *et al.*, 1992; Svendsen *et al.*, 1990). The intercepts of the lines are -5.58, -5.21, -4.44, -3.80, -3.70 and -2.40 for 0.01, 0.02, 0.05, 0.10, 0.20 and 0.50 M D2EHPA systems, respectively. The slope of the line of Zn(II) is  $\sim 2$ , which indicates that two moles of  $H^+$  are liberated per mole of Zn(II) during extraction. From intercept of the line, the value of extraction equilibrium constant ( $k_{ex}$ ) was calculated after knowing the extractant dependence. The calculated value was found to be  $10^{-2.26}$ .



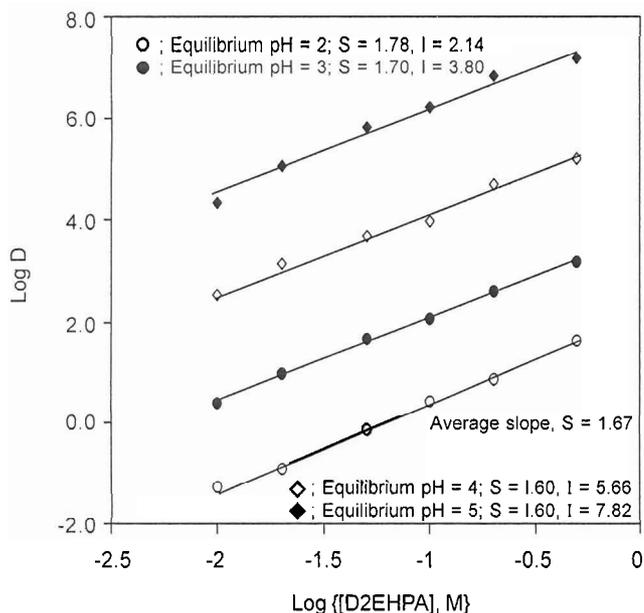
**Fig. 3.** Effect of distribution ratio (D) on equilibrium pH.  $[Zn(II)]_{(ini)} = 0.215$  g/litre;  $[SO_4^{2-}]_{(ini)} = 0.10$  M;  $[D2EHPA] = 0.01, 0.02, 0.05, 0.10, 0.20, 0.50$  M; D2EHPA, phase mixing time = 5 min; O/A=1; temperature =  $(30 \pm 1)$  °C.

#### Effect of extractant concentration on the extraction of Zn(II) by D2EHPA.

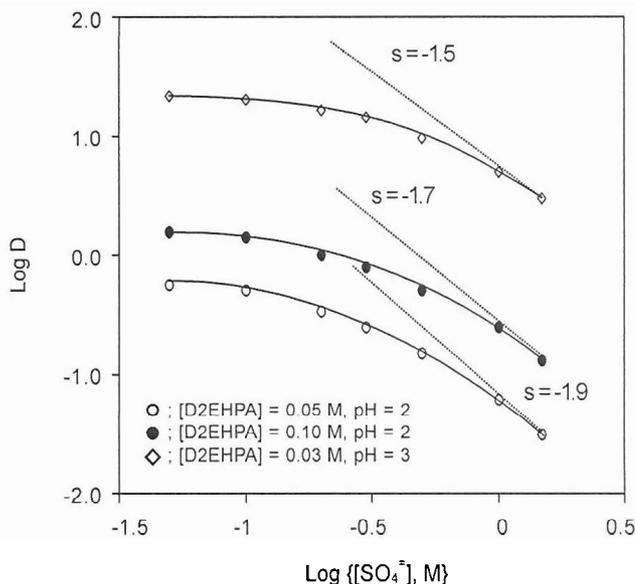
The results obtained from the experiments carried out at different equilibrium pH and for the effect of extractant concentration were plotted as log D vs. log  $[H_2A_2]$  at fixed Zn(II) ion concentration (Fig. 4). The figure represents the effect of variation of distribution ratio (D) on the extractant concentrations. It was observed that the extraction ratio increased with increasing extractant concentration in the organic phase, and a straight-line relationship was obtained.

The slopes (S) and intercepts (I) of the lines were: S=1.78, I=2.14; S=1.70, I=3.80; S=1.60, I=5.66 and S=1.60, I=7.82 for equilibrium pH values of 2, 3, 4, and 5, respectively. Average slope of the lines was 1.67. Similar observations were found by other workers (Bart *et al.*, 1992; Svendsen *et al.*, 1990). Here the linear relationship of the extraction ratio with the D2EHPA concentration indicates that the more is extractant concentration, the more is the extraction of Zn(II). This is the normal behavior of extraction process. The slope of the line

indicates that normal ion exchange mechanism for Zn(II) is followed. Since for a particular initial pH system, the equilibrium pH varies with the variation of extractant concentration, to get actual extractant dependence, it is necessary to get log D vs. log [H<sub>2</sub>A<sub>2</sub>] plots at constant equilibrium pH values. Such type of correction has been made with the help of acidity dependence data. First of all the difference between the initial and equilibrium pH values are determined (termed as ΔpH). As the acidity dependence is always 2, the correction term for



**Fig. 4.** Effect of distribution ratio (D) on extractant concentration. [Zn(II)]<sub>(ini)</sub> = 0.215 g/litre; [SO<sub>4</sub><sup>2-</sup>]<sub>(ini)</sub> = 0.10 M; phase mixing time = 5 min; O/A=1; temperature = (30±1) °C.



**Fig. 5.** Effect of distribution ratio (D) on sulphate ion concentration. [Zn(II)]<sub>(ini)</sub> = 0.215 g/litre; [D2EHPA] = 0.03; 0.05, 0.10 M; phase mixing time = 5 min; O/A=1; temperature = (30±1) °C.

**Table 1.** Evaluation of the extraction equilibrium constant log k<sub>ex</sub> for Zn(II) ion (based on Figs. 3 and 4)

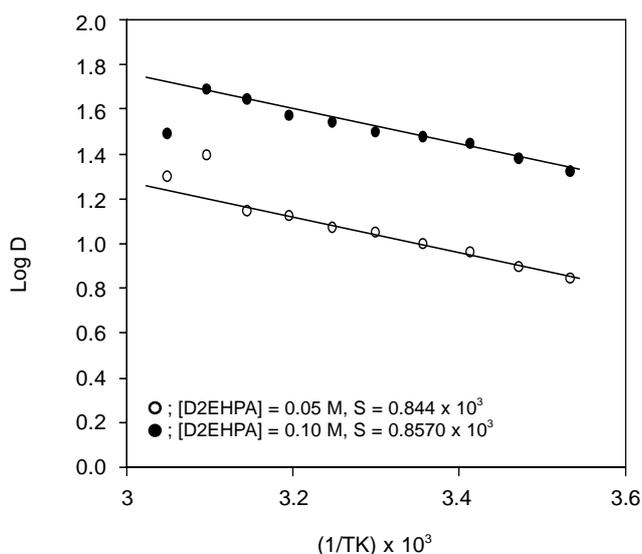
Figure No	Equilibrium pH	[D2EHPA], M	Intercept, I	Log k <sub>ex</sub>	Average log k <sub>ex</sub>	Standard deviation
3		0.01	-5.58	-2.240	-2.258	0.204
		0.02	-5.21	-2.373		
		0.05	-4.44	-2.267		
		0.10	-3.80	-2.130		
		0.20	-3.70	-2.533		
		0.50	-2.40	-1.897		
4	2.0		2.14	-1.94		
	3.0		3.80	-2.32		
	4.0		5.66	-2.50		
	5.0		7.82	-2.38		

$\log D$  is calculated as  $\Delta pH \times 2$ . Then the corrected  $\log D$  value is calculated as  $\log D$  (experimental) +  $\Delta pH \times 2$ , which corresponds to the data at equilibrium, equal to initial pH.

Extractant dependence of about 1.67 indicates the association of 1.67 moles of extractant with 1 mole of ion Zn(II). From the intercept of the line in Fig. 3 and Fig. 4, the value of  $\log k_{ex}$  has been calculated to be -2.258 with the standard deviation of  $\log k_{ex}$  being 0.204 (Table 1).

**Effect of sulphate ion concentration on the extraction of Zn(II) by D2EHPA.** Figure 5 represents the results obtained from the experiments involving the variations of sulphate ion concentration at three constant initial pH (2, 2 and 3) and at three extractant concentrations (0.03, 0.05 and 0.10 M), respectively. Herein,  $\log D$  has been plotted vs.  $\log [SO_4^{=}]$ , M. The variation of extraction ratio with the variation of sulphate ion concentration depends on the extractant concentration as well as on the pH of the aqueous solution. When the pH of the aqueous solution is kept constant, the extraction ratio decreases with the increase in sulphate ion concentration in the aqueous phase. In all the cases, the tangential negative slopes of these curves increased gradually with the increase in sulphate ion concentration. At lower sulphate region, the slope approaches to zero, whereas in the higher region, it approaches to -2.00 depending upon the pH-D2EHPA values.

**Effect of temperature on the extraction of Zn(II) by D2EHPA.** Figure 6 (plot of  $\log D$  vs. inverse of absolute temperature) shows the effect of variation of distribution ratio on



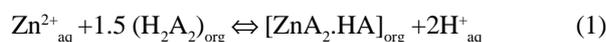
**Fig. 6.** Effect of distribution ratio ( $D$ ) on temperature.  $[Zn(II)]_{(ini)} = 0.205$  g/litre;  $[SO_4^{=}]_{(ini)} = 0.10$  M; pH = 3.00, phase mixing time = 5 min., O/A=1.

temperature i.e. the effect of temperature on extraction. The extraction ratio increases with increase in temperature. The slopes of this line are  $-0.844 \times 10^3$  and  $-0.857 \times 10^3$  for 0.05 and 0.10 M D2EHPA, respectively, in kerosene system. The extraction reaction enthalpy values ( $\Delta H$ ) has been calculated using Vant-Hoff equation. The calculated values are found to be 16.15 and 16.40 kJ/mol respectively for 0.05 and 0.10 M D2EHPA. The average value of apparent enthalpy change is 16.27 kJ/mol. The positive enthalpy change suggests that the extraction process of Zn(II) by D2EHPA is endothermic in nature. The extraction ratio-temperature relationship indicates that the equilibrium reaction of Zn(II) is moderately influenced by temperature. Thus, extraction of Zn(II) by D2EHPA in kerosene system moderately increases by using extraction at a higher temperature.

**Effect of loading on the extraction of Zn(II) by D2EHPA.** Loading is an important factor for the study of mechanism of extraction and also for the industrial evaluation of the extractant. High values of loading capacity are desirable for any particular extractant metal system for industrial applications.

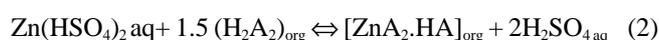
The organic phases (20 ml) were repeatedly contacted for 5 min at  $30 \pm 1$  °C with fresh equal volume of aqueous solution containing fixed concentration of metal ions  $[Zn(II)]$  1.08 g/litre at pH 2 and 3. After equilibration, the phases were disengaged and the aqueous phases were analyzed for Zn(II) contents. The amount of metal ions  $[Zn(II)]$  transferred into the organic phase for each contact was then determined by difference and the cumulative concentration of Zn(II) in the organic phase, after each stage of contact, was estimated. The result obtained from the experiments, plotted as cumulative  $[Zn(II)]$ , g/litre vs. contact number is given in Fig. 7. It can be seen the organic phase is saturated with Zn(II) after the 7<sup>th</sup> and the 11<sup>th</sup> contact, respectively, for pH 2 and 3. The loading of 0.10 M D2EHPA by Zn(II) was as much as 0.92 g and 4.455 g of Zn(II) at pH 2 and 3, respectively, which indicates that the loading capacity of D2EHPA is 1.40 g and 6.77 g of Zn(II)/100 g extractant for pH 2 and 3, respectively. The loading data suggests the ratio Zn : D2EHPA is 1, at pH 3, but at pH 2, the ratio is very low. At pH 2, most of D2EHPA remains uncombined having low distribution ratio.

**Extraction mechanism.** The extractant-dependence of ~1.6 suggests that 1.5 moles of extractant is required for each ion of Zn(II) ion for the extracted species. The hydrogen ion and extractant dependence suggests the following equation for the extraction reaction:



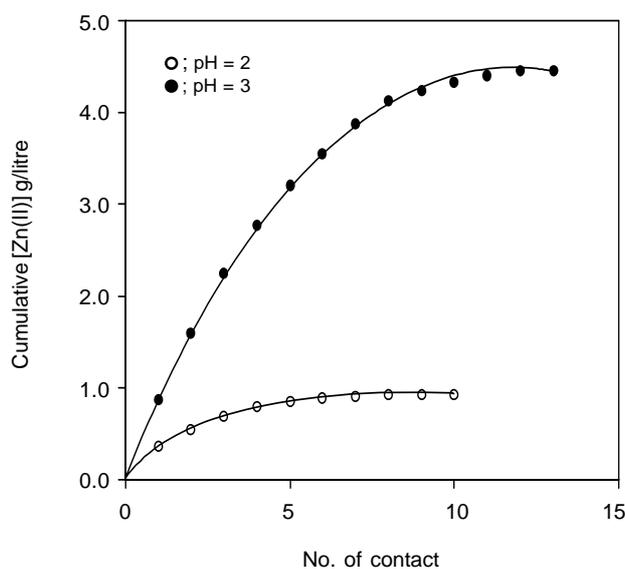
Here the extracted species contains coordinated monomer di-2-ethylhexyl phosphoric acid molecules. The extraction of coordinated extracted species (adducts) is a general observation in the solvent extraction process. The extraction reaction is supported by Mellah and Benachour (2006) and Breno *et al.* (2004).

Sulphate dependence, almost zero below 0.1 M  $[\text{SO}_4^{=}]$ , suggests that Zn(II) ion is the predominant species in the extraction process. However, at higher  $[\text{SO}_4^{=}]$  ion, the species  $\text{Zn}(\text{HSO}_4)_2$  may form to some extent, indicating the reaction involving non-ionized zinc species:



This supports the slopes approaching -2.00 with increasing  $[\text{SO}_4^{=}]$  ion concentration in the aqueous phase.

The loading test suggested that the neutral unreacted HA in the extracted species  $[\text{ZnA}_2\cdot\text{HA}]$  gradually increased to give Zn : D2EHPA( $\text{H}_2\text{A}_2$ ) ratio of 1:1 corresponding to the species  $\text{ZnA}_2$  for high (pH 3) loading. At the low pH the organic phase is not saturated with zinc even after the 11<sup>th</sup> contact.



**Fig. 7.** Loading of Zn(II) in D2EHPA.  $[\text{Zn}(\text{II})]_{(\text{ini})} = 1.08$  g/litre;  $[\text{SO}_4^{=}]_{(\text{ini})} = 0.10$  M; phase mixing time = 5 min;  $[\text{D2EHPA}] = 0.10$  M; O/A=1; temperature =  $(30 \pm 1)$  °C.

## Conclusion

Zn(II) solution can be obtained as leach solution in different industries especially in the pickling industry with acids. Dilute solution can be a good source for Zn(II) if it can be separated. Solvent extraction can be a good technique for

simultaneous separation and concentration of weak Zn(II) solution. Di-2-ethylhexyl phosphoric acid is a moderately effective extractant for Zn(II) from low acidic and low sulphate media. The extractant and hydrogen ion dependence suggests a simple extraction reaction for the process. Temperature has moderate influence on the extraction process. The extracted species is suggested to be  $[\text{ZnA}_2\cdot\text{HA}]_{\text{org}}$  in the kerosene phase. However, complete saturation of the organic phase occurs at high loading, corresponding to  $\text{ZnA}_2$  as extracted species. Low extraction equilibrium constant ( $k_{\text{ex}}$ ) suggests that stripping from the organic phase is much favoured.

## References

- Alguacil, F.J., Cobo, A., Caravaca, C. 1992. Study of the extraction of Zn(II) in the aqueous chloride media by Cyanex 302. *Hydrometallurgy* **31**: 163-174.
- Amer, S., Luis, A. 1995. The extraction of zinc and other minor metals from concentrated ammonium chloride solutions with D2EHPA and CYANEX 272. *Revista de Metalurgia* **31**: 351-360.
- Bart, H.J., Marr, R., Scheks, J., Konkar, M. 1992. Modelling of solvent extraction equilibria of Zn(II) from sulphate solutions with bis(2-ethylhexyl) phosphoric acid. *Hydrometallurgy* **31**: 13-28.
- Breno, S., Morais, Marcelo, B., Mansur. 2004. Characterisation of the reactive test system  $\text{ZnSO}_4/\text{D2EHPA}$  in *n*-heptane. *Hydrometallurgy* **74**: 11-18.
- Devi, N.B., Nathsarma, K.C., Chakravorthy, V. 1995. Solvent extraction of zinc(II) using sodium salts of D2EHPA, PC-88A and CYANEX 272 in kerosene. In: *Mineral Processing: Recent Advances and Future Trends*. S. P. Mehrotra and R. Shekhar (eds.), pp. 537-547, Allied Publishers, New Delhi, India.
- Fouad, E.A., Bart, H.J. 2008. Emulsion liquid membrane extraction of zinc by a hollow-fiber contactor. *Journal of Membrane Science* **307**: 156-168.
- Jianbing, J., Kathryn, H.M., Jilska, M.P., Geoff, W.S. 2006. The role of kinetics in the extraction of zinc with D2EHPA in a packed column. *Hydrometallurgy* **84**: 139-148.
- Keng Xie, Jian-Kang Wen, Yi-Xin Hua, Ren-Man Ruan. 2008. Selective separation of Cu(II), Zn(II), and Cd(II) by solvent extraction. *Rare Metals* **27**: 228-232.
- Kumar, V., Bagchi, D., Pandey, B.D. 2006. Extraction of zinc-cobalt from sulphate solution of cobalt cake by D2EHPA in the processing of Indian Ocean nodules. *Steel Research* **77**: 299-304.
- Mansur, M.B., Slater, M.J., Biscaia, E.C. 2002. Kinetic analysis of the reactive liquid-liquid test system  $\text{ZnSO}_4/\text{D2EHPA}/n$ -heptane. *Hydrometallurgy* **63**: 107-116.
- Mansur, M.B., Rocha, S.D.F., Magalhaes, F.S., Benedetto, J.D.S.

2008. Selective extraction of zinc(II) over iron(II) from spent hydrochloric acid pickling effluents by liquid-liquid extraction. *Journal of Hazardous Materials* **150**: 669-678.
- Mellah, A., Benachour, D. 2006. The solvent extraction of zinc and cadmium from phosphoric acid solution by di-2-ethyl hexyl phosphoric acid in kerosene diluent; *Chemical Engineering and Processing* **45**: 684-690.
- Morters, M., Bart, H.J. 2000. Extraction equilibria of zinc with bis(2-ethylhexyl)phosphoric acid. *Journal of Chemical and Engineering Data* **45**: 82-85.
- Park, Y.J., Fray, D.J. 2009. Separation of zinc and nickel ions in a strong acid through liquid-liquid extraction. *Journal of Hazardous Materials* **163**: 259-265.
- Samaniego, H., Roman, M.F.S., Ortiz, I. 2007. Kinetics of zinc recovery from spent pickling effluents. *Industrial and Engineering Chemistry Research* **46**: 907-912.
- Sarangi, K., Parhi, P.K., Padhan, E., Palai, A.K., Nathsarma, K.C., Park, K.H. 2007. Separation of iron(III), copper(II) and zinc(II) from a mixed sulphate/chloride solution using TBP, LIX 84I and Cyanex 923, *Separation and Purification Technology* **55**: 44-49.
- Singh, R.K., Dhadke, P.M. 2002. Extraction and separation studies of zinc(II) and copper(II) with D2EHPA and *pc-88a* from perchlorate media. *Journal of the Serbian Chemical Society* **67**: 41-51.
- Svendsen, H.F., Schei, G., Osman, M. 1990. Kinetics of extraction of zinc by di(2-ethylhexyl) phosphoric acid in cumene. *Hydrometallurgy* **25**: 197-212.
- Takeshita, K., Watanabe, K., Nakano, Y., Watanabe, M. 2003. Solvent extraction separation of Cd(II) and Zn(II) with the organophosphorus extractant D2EHPA and the aqueous nitrogen-donor ligand TPEN. *Hydrometallurgy* **70**: 63-71.