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Equilibrium in the Partitioning of Zn(II) between Aqueous Sulphate Solution and Kerosene Solution of Cyanex 272

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Abstract. The equilibrium in the partitioning of Zn(II) from its sulphate solution to *bis*-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, BTMPPA, H_2A_2) solution in kerosene (paraffin) has been investigated extensively. The equilibration time is < 5 min. Extraction of Zn(II) is found to be increased with increasing equilibrium pH, extractant concentration and temperature; and independent of [Zn(II)] in the aqueous phase provided equilibrium pH and extractant concentration are kept constant. The pH dependence of extraction ratio (D) at a constant $[H_2A_2]_{(o,eq)}$ is found to be 2. The extractant dependence plots at constant equilibrium pH values are not straight lines but are curves with asymptotic slopes of 1 and 2 at lower concentration region (LCR) and higher concentration region (HCR) of extractant, respectively. D is found to be an inverse function of $(1 + 2[SO_4^{2-}])$. The extraction at LCR of extractant is found to occur through the reaction: $Zn^{2+} + H_2A_{2\,(o)} \rightleftharpoons [ZnA_2]_{(o)} + 2\,H^+$; but at HCR of extractant, it occurs via the reaction: $Zn^{2+} + 2\,H_2A_2 \rightleftharpoons [ZnA_2.H_2A_2]_{(o)} + 2\,H^+$. The extraction equilibrium constants, K_{ex} at LCR and HCR of extractant are estimated as $10^{-3.11}$ and $10^{-2.08}$, respectively, at 303 K. The extraction process is found to be endothermic but ΔH value increases with increasing extractant concentration. The maximum loading capacity is estimated to be 11.5 g Zn(II) per 100 g extractant. At a maximum loading, the species exists in organic phase is ZnA_2. The stripping ability of various inorganic acids towards loaded zinc, as well as, the possibilities of separation of Zn(II) from its binary mixtures with 3d - block metal ions have also been investigated.

Keywords: extraction equilibrium, Zn(II) - extraction, Cyanex 272, sulphate medium, kerosene

Introduction

Zinc is a very commercially important metal finding its applications in construction of dry cells, preparation of alloys (particularly, brass and solder) and galvanization. Its commonest ore is sphalerite (ZnS). It can be extracted from sphalerite both by pyrometallurgical and hydrometallurgical (in combination with electrometallurgical) routes. In pyrometallurgical route, high temperature is involved in reductive distillation of zinc; whilst in the hydrometallurgical route, the ore is subjected to either sulphatizing ($ZnS + 2O_2 \rightarrow ZnSO_4$) or complete ($ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2$) roasting, roasted mass being leached with either very weak or ~10% (v/v) sulphuric acid solution to get an aqueous solution of Zinc(II). This solution usually contains Ni(II), Co(II), Cu(II), Cd(II), Bi(III), Fe(III) etc. as impurities. For Fe(III) removal, the advantage of jarrosite formation is utilized followed by either solvent extraction or cementation process being applied to remove other foreign ions. The purified solution may then be electrolyzed for its production. Acid pickle solution, wastes from galvanizing bath, leach solution of waste dry cell powder containing zinc and manganese compounds and deep sea nodules and the parting solution can be processed by the solvent extraction methods to isolate zinc to reduce environmental hazard and fulfill the increasing demand of this metal. Virtually, the recovery of zinc from zinc containing wastes is now a major interest in hydrometallurgy.

Zinc(II) can be extracted by a number of extractants such as TBP, β-diketones, oxine and its derivatives, TOPO, fatty acids, naphthenic and salicylic acid, β-isopropyltropolone, PAN, diethyldithiocarbamate, dithizone, thio-compounds etc. (Sekine and Hasegawa, 1977), D2EHPA (Begum *et al*., 2009; Vahidi *et al*., 2009; Perreira *et al*., 2007; Mansur *et al*., 2002), Alamine 336 (Sayar *et al*., 2007), 5-azidomethyl-8-hydroxyquinoline (Himmi *et al*., 2008), 1-phynyl-3-mryhyl-4-benzoylpyrazol-5-one (Barkat *et al*., 2004), PC 88A (Nathsarma and Devi, 2006), Cyanex 921 (Navarro *et al*., 2007), Cyanex 302 (Mansur *et al*., 2008; Jha *et al*., 2005), Cyanex 301 (Mansur *et al*., 2008; Jha *et al*., 2005), Cyanex 272 (Zhu *et al*., 2011; Awaad *et al*., 2009; Bari *et al*., 2009a; 2009b; Deep and de Carvalho, 2008; Parhi and Sarangi, 2008; Mansur

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et al., 2008; Nathsarma and Devi, 2006; Ali *et al*., 2006; Jha *et al*., 2005; Salgado *et al*., 2003; Sarma and Reddy, 2002; Chah *et al*., 2002; Devi *et al*., 1997; Amer and Luis, 1995; Sole and Hiskey, 1992; Sastre *et al*., 1990) etc. It is evident that D2EHPA and Cyanex 272 have been widely used by workers for extraction and separation of Zn(II). Although the extraction of Zn(II) by D2EHPA has been studied both for equilibrium and kinetic points of view, the extraction of Zn(II) by Cyanex 272 has been reported mostly on separation (from other metal ions) point of view, excepting the works of Sastre *et al*. (1990) and Sole and Hiskey (1992). It appears that the equilibrium in the Zn(II) - Cyanex 272 system has not been reported considering its all equilibrium aspects. This paper reports the mechanistic study on the title system. Stripping abilities of various acids for the extracted zinc has also been reported. Finally the possibilities of mutual separation of Zn(II) from first row transition metal ions in their binary mixtures have been examined.

Materials and Methods

Reagents. Cyanex 272 was donated by Cytec Canada Inc. Kerosene (paraffin) was purchased from the local market and distilled to collect fraction distilling over 200-260 °C. It was colourless and mostly aliphatic in nature. Heptahydrated zinc sulphate (E. Merck, Germany; 99.99%) was used as a source of Zn(II) in the investigated system. A stock solution (5.01 g/L) Zn(II) was prepared by dissolving 22.08 g $ZnSO_4.7H_2O$ in 1 L solution and standardized by EDTA titration. All other chemicals were of analytical grade and products of E. Merck of either Germany or India. All chemicals including Cyanex 272 were used without further purifications.

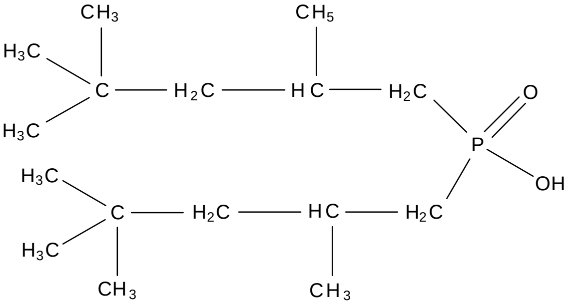
Analytical procedure. The concentration of Zn(II) in the aqueous phase was determined by the EDTA-titration method using Solochrome Black T as indicator (Basette *et al*., 1978). It was also estimated by the AAS method using a Shimadzu AA 6800 spectrophotometer, particularly, when it was low after extraction. The pH values of the aqueous solutions before and after extractions were measured by a Mettler Toledo 320 pH meter. In pH adjustments, either anhy. Na_2CO_3 or conc. H_2SO_4 was added with constant stirring. For temperature control during extraction, a thermostatic water bath was used. A Zencon's Stuart Flask Shaker (220 V, 50 Hz, 8 arms, wrist - twisting) was used for mechanical mixing of phases at 300 strokes/min.

Extraction/partition procedure. The extraction procedures by Biswas and Singha (2007) and Biswas and Begum (1998) were followed. Aqueous solutions containing different amounts of Zn(II) (0.2-3.0 g/L *i.e.* 0.00358-0.0458 M) and SO_4^{2-} (0.0153-1.55 M) were prepared and the pHs of these solutions were adjusted to the desirable values (1-5). Organic phases were prepared by dissolving calculated amounts of Cyanex 272 (as received but considering its purity as 100%) in distilled kerosene. Equal aliquots of the aqueous and organic phases (25 mL each) were taken in 125 mL reagent bottle, stoppered and agitated for predetermined time (5 min, otherwise stated) at (303±0.5) K in a thermostatic water bath. After phase-agitation, the phases were settled, separated and the aqueous phase was analyzed for its pH value and Zn(II) content. The concentration of Zn(II) in the organic phase was calculated by difference. The value of the distribution ratio (D) was estimated as ratio of [Zn(II)] in the organic phase to that in the aqueous phase at equilibrium.

Loading procedure. Loadings of Zn(II) in 0.025 and 0.10 M Cyanex 272 were carried out by vigorous contact of these solutions (100 mL) separately and repeatedly with fresh aqueous solutions (containing 0.95 g/L Zn(II) and 0.015 M SO_4^{2-} at pH = 5.0) of same volume until the organic phases were saturated with Zn(II). After each contact, phases were disengaged and aqueous phases were analyzed for their Zn(II) contents. The amount of Zn(II) transferred to the organic phase for each contact was calculated by the difference and then the cumulative concentration of Zn(II) in the organic phase (cumulative $[Zn(II)]_{(o)}$, g/L) after each stage of contact was estimated.

Stripping procedure. The Zn(II) loaded organic phases obtained above were diluted separately with kerosene so that the resultant solutions contained 1 g/L Zn(II) in the form of complex species at high loading and virtually no free extractant. These solutions were used to study stripping by 1 and 0.1 M H_2SO_4, HCl, HNO_3 and $HClO_4$ solutions. In stripping, 10 mL of Zn(II) - loaded organic phase was equilibrated with an equal aliquot of each of the above acid solutions for 5 min at 303 K. After equilibration, phases were settled, separated and the aqueous phase was analyzed for Zn(II) content. In stage-wise stripping, the organic phase was recycled with equal volume of fresh aqueous solution.

Procedure for Zn(II) - extraction equilibrium data treatment. Cyanex 272 is a commercial extractant containing 84% *bis*-(2,4,4-trimethylpentyl =R) phosphinic acid (BTMPPA, R_2POOH), 5% $RPO(OH)_2$ and 11% R_3PO. BTMPPA has the following structure:

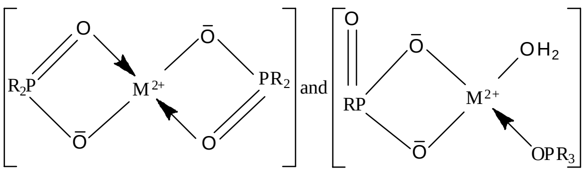


Cyanex 272 can be purified to contain about 99% BTMPPA by the micro-emulsion formation method (Biswas *et al.*, 2005; Zhengshui *et al.*, 1995). But as-received Cyanex 272 has been used in this investigation. BTMPPA and $RPO(OH)_2$ are both acidic chelating extractants but R_2PO is an ion pair solvating agent. Therefore, all components of Cyanex 272 have extracting power. Moreover, equi-molar mixture of $RPO(OH)_2$ and R_3PO may behave as BTMPPA (R_2POOH as illustrated below:

$$M^{2+} + 2\,R_2PO(OH)_{(o)} \rightleftharpoons [M(R_2POO)_2]_{(o)} + 2\,H^+ \;\ldots\; (1)$$

$$M^{2+} + RPO(OH)_{2\,(o)} + R_3PO_{(o)} \rightleftharpoons [MRPOO_2.R_3PO]_{(o)} + 2\,H^+ \;\ldots\ldots\; (2)$$

with the respective structure of the extracted species being:



According to Sousa *et al.* (2010), HSO_4^- predominates at high acidity (~95% at pH 0.5) but with increase in pH, $[HSO_4^-]$ in the medium is decreased with simultaneous increase in $[SO_4^{2-}]$. For example, at pH 1, 2, 3 and 4, free $[HSO_4^-]$ are ~82%, 32%, 5% and < 1%, respectively, with some equilibrium $MHSO_4^+$ complex existing within pH 0.5-4.0 whose maximum concentration would be ~10% at pH 2. On the other hand, at pH 0.5, 1, 2, 3 and 4, free $[SO_4^{2-}]$ are ~9%, 20%, 55%, 70% and 72%, respectively, with some equilibrium $[MSO_4]$ complex started to form at pH 1 and becomes ~25% over pH 3.0. These values are quoted for Mn(II)-SO_4^{2-} system. Stability constant of $MnSO_4$ and $MnHSO_4^+$ are reported as 190 and 182, respectively, at zero ionic strength (Sousa *et al.*, 2010). As the stability constants of $ZnSO_4$ (Bjerrum *et al.*, 1958) and $ZnHSO_4^+$ (Smith and Martell, 1976) are 200 and 240, respectively, at zero ionic strength correspond almost to those of $MnSO_4$ and $MnHSO_4^+$, respectively. Consequently, similar species distribution in Zn(II) - SO_4^{2-} system is expected as in Mn(II) - SO_4^{2-} system. From this discussion, it is apparent that Zn^{2+}, $ZnHSO_4^+$ and $ZnSO_4$ exist at pH 2; whilst the existences of $ZnSO_4$ and $ZnHSO_4^+$ are likely to be disappeared at pH ~1 and ~3.5, respectively. At the extractable pH range, there is no possibility for the existence of $Zn(OH)^+$ as its stability constant is 10^5 (Bjerrum *et al.*, 1958). Considering L^- as the coexisting uni-negative ligand in the aqueous phase and BTMPPA is considered as dimeric (H_2A_2) in non-polar solvents like kerosene (Biswas *et al.*, 2005), the extraction equilibrium reaction can be depicted as follows:

$$ZnL_n^{(2-n)+} + x[H_2A_2]_{(o)} \rightleftharpoons [ZnL_{n-z}A_{(2-n+z)}.\frac{2x-2+n-z}{2}.H_2A_2]_{(o)} + z\,L^- + (2-n+z)H^+ \;\ldots\ldots\; (3)$$

where, subscript (o) represents organic species. The equilibrium constant (K_{ex}) for reaction represented by Eq. (3) at a constant temperature can be expressed as:

$$\log D = \log K_{ex} + (2-n+z)\,pH_{(eq)} + x \log [H_2A_2]_{(o,eq)} - z \log [L^-]_{(eq)} \;\ldots\ldots\; (4)$$

where, D represents extraction ratio *i.e.* the quotient $[ZnL_{n-z}A_{(2-n+z)}.\frac{2x-2+n-z}{2}.H_2A_2]_{(o,eq)} / [ZnL_n^{(2-n)+}]_{(eq)}$. Equation (4) represents the basic equation for a chelate forming solvent extraction system involving a metal ion by an acidic extractant and the value of log D should be independent of initial or equilibrium metal ion concentration provided equilibrium pH and extractant concentration remain constant, whilst the slope of log D vs. $pH_{(eq)}$ (at constant concentrations of H_2A_2 and L^-), log D vs. log $[H_2A_2]_{(o,eq)}$ (at constant pH and $[L^-]$) and log D vs. log $[L^-]$ (at a constant pH and $[H_2A_2]_{(o)}$) would represent (2-n+z), x and -z, respectively.

Moreover, as equilibrium constant of a reaction is related to temperature by Van't Hoff equation, log D will also depend on temperature. The corrected log D *i.e.* log ^{C}D values have been calculated using the following relation:

$$\log {}^{C}D = \log D + y\,(pH_{(ini)} - pH_{(eq)}) + x\,[\log [H_2A_2]_{(o,ini)} - \log ([H_2A_2]_{(o,ini)} - x\,[Zn(II)]_{(o,eq)})] \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where, all concentration terms are in M, y=pH dependence = 2 (as will be seen later) and x = extractant dependence = 1, 2 (as will be seen later).

Results and Discussion

Extraction equilibrium. Some preliminary experiments were carried out to find out the extractable pH range and equilibration time for the investigated system. It is found that 3.5 min is sufficient for distribution of Zn(II) in the (1.0 g/L Zn(II) - 0.0153 M SO_4^{2-} - $pH_{(ini)}$ of 6.0) - (0.025 M H_2A_2 in kerosene) system at 303 K and O/A ratio of 1. However, in subsequent experiments, equilibration time of 5 min has been allowed to ensure equilibration at various experimental parameters. While Zn(II) being distributed between (0.2 - 3.0 g/L Zn(II) - 0.046 M SO_4^{2-} - $pH_{(ini)}$ of 6) and (0.025 M Cyanex 272 solution in kerosene), it is seen that the value of log D decreases (though [Zn(II)] in the organic phase being increased) with increasing initial concentration of Zn(II) in the aqueous phase. This behaviour is contrary to the general principle of solvent extraction chemistry (*cf.* Eq. (4)) but this is certainly due to the non-constancy of equilibrium pH and extractant concentration arising from the various extents of reaction with the variation of initial Zn(II) concentration in the aqueous phase. On the other hand, the log ^{C}D values at constant (chosen) $pH_{(eq)}$ of 2.5 and $[H_2A_2]_{(o,eq)}$ of 0.025 M remain unchanged with initial or equilibrium [Zn(II)] in the aqueous phase. It is therefore concluded that Zn(II) behaves ideally in the system investigated and the aqueous or organic phase Zn(II)-speciation is not changed as well with the variation of [Zn(II)] in the system provided $pH_{(eq)}$ and $[H_2A_2]_{(o,eq)}$ are kept constant.

The variation of D with the variation of extractant concentration have been found out at initial pH values of 8, 6, 4 and 3. Although for a particular set of data, initial pH is kept constant, it is observed that the equilibrium pH values together with the extractant concentrations are varied considerably. So the corrected log D values at a chosen constant equilibrium pH value (log $^{C}D_{const.\ pH}$) have been calculated by the first two terms of the left hand side of Eq. (5). Moreover, log $[H_2A_2]_{(o,eq)}$ values have been calculated by the last logarithmic term of Eq. (5). The log D vs. log $\{[H_2A_2]_{(o,ini)}, M\}$ plots at four different initial pH values are depicted in Fig. 1A; whilst the log ^{C}D vs. log $\{[H_2A_2]_{(o,eq)}, M\}$ plots at $pH_{(eq)}$ values of 2.7, 2.40, 2.05 and 1.85 are shown in Fig. 1B.

Plots in Fig. 1A do not represent the typical plots (not at constant equilibrium pH values) as should be used in solvent extraction equilibrium studies. On the other hand, plots in Fig. 1B are typical (at constant $pH_{(eq)}$ values). But these plots are not straight lines. Curves with asymptotic slopes of 1 and 2 in LCR and HCR of extractant, respectively are obtained. It is concluded from this result that the value of 'x' in Eq. (3) is 1; i.e. 1 mole of Cyanex 272 is added up with 1 g ion of Zn(II) to form the extractable species ZnA_2 whence there is a scarcity of extractant (i.e., in LCR of extractant) in the system; and with the availability of the surplus extractant in the system, solvation of ZnA_2 takes place to form extractable species like $ZnA_2.HA$ and $ZnA_2.H_2A_2$. For the first solvated species to form, the extractant dependence should be 1.5(i.e., x = 1.5) and for the formation of the second solvated species it should be 2 (i.e., x = 2). It is observed that the extractant dependences of 1, 1.5 and 2 are obtained at $[H_2A_2]_{(o,ini)}$ $\leq$ 0.05 M, ~0.1 M and $\geq$ 0.3 M, respectively.

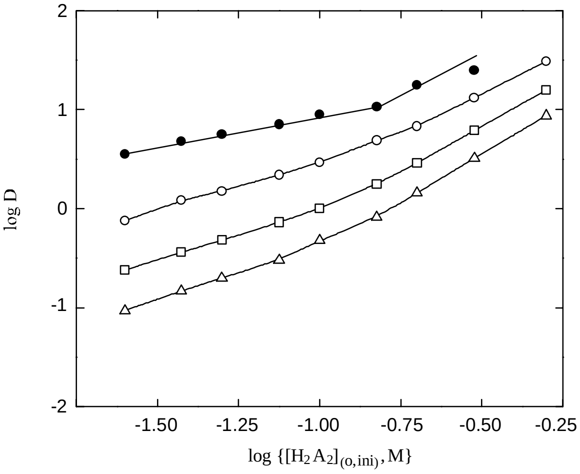


Fig. 1A. Effect of extractant concentration on the extraction of ratio (D): log D vs. log $[H_2A_2]_{(o,ini)}$ plots. [Zn(II)] = 1.00 g/L; temperature = (303 ± 0.5) K; $[SO_4^{2-}]$ = 0.0153 M; equilibration time = 5 min; phase ratio =1:1, (●); $pH_{(ini)}$ = 8 ± 0.1; (○), $pH_{(ini)}$ = 6 ±0.05; (□), $pH_{(ini)}$ = 4 ± 0.02; (△), $pH_{(ini)}$ = 3 ± 0.01.

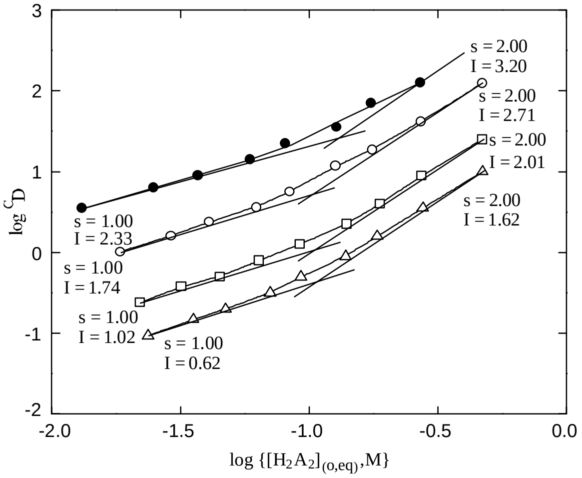


Fig. 1B. Effect of extractant concentration on corrected extraction ratio (^{C}D): log ^{C}D vs. log $[H_2A_2]_{(o,eq)}$ plots. Experimental parameters are in Fig. 1A, (●), constant $pH_{(eq)}$ chosen = 2.70; (○), constant $pH_{(eq)}$ chosen = 2.40; (□), constant $pH_{(eq)}$ chosen = 2.05; (△), constant $pH_{(eq)}$ chosen = 1.85.

The experimental data have been collected for studying the variation of equilibrium pH on D at constant $[H_2A_2]_{(o,ini)}$ of 0.025, 0.05, 0.10 and 0.30 M. As $[H_2A_2]_{(o,eq)}$ will differ from its initial concentration due to various extents of extractions at various pH values, the log ^{C}D values at a chosen constant $[H_2A_2]_{(o,eq)}$ have been calculated by Eq. (5) after excluding its pH containing term. Figure 2 shows the log ^{C}D vs. $pH_{(eq)}$ plots. While the slopes of log D vs. $pH_{(eq)}$ are found to be 1.8-1.9, here the slopes are 2±0.03. It is concluded from this result that the value of (2-n+z) in Eq. (3) is 2 and when n=z, then 2 g ion of H^+ is eliminated from the extractant during its reaction with 1 g ion of Zn(II).

The log ^{C}D vs. log ($[SO_4^{2-}]$, M) plot is shown in Fig. 3 for the (1 g/L Zn(II) at constant $pH_{(eq)}$ of 2.45) - (constant $[H_2A_2]_{(o,eq)}$ of 0.025 M) system at 303 K and O/A = 1. The plot is a curve showing a little and a huge effect at the LCR and HCR of sulphate ion, respectively. In Fig. 3, the curve is theoretical representing: log ^{C}D = 0.075 - log $(1+2[SO_4^{2-}])$; and the horizontal line is the asymptote at LCR of SO_4^{2-} : log ^{C}D = 0.068 and the inclined line is the asymptote at higher $[SO_4^{2-}]$ region: log ^{C}D = 0.068 - log Kso_4^{2-} - log $[SO_4^{2-}]$, so that at the point of inter-section of two asymptotes - log Kso_4^{2-} - log $[SO_4^{2-}]$ = 0 giving Kso_4^{2-} = 2.

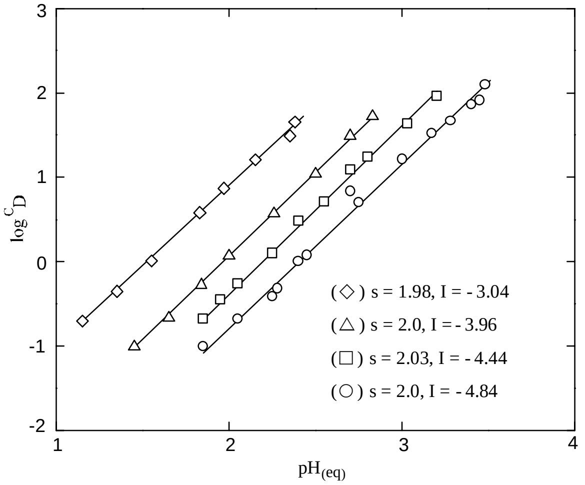


Fig. 2. Effect of aqueous equilibrium pH on corrected extraction ratio (^{C}D): log ^{C}D vs. $pH_{(eq)}$ plots. [Zn(II)] = 1.00 g/L; $[SO_4^{2-}]$ = 4.0153 M; Equilibration time = 5 min; temperature = (303 ± 0.50) K, O/A = 1; (○), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.025 M; (□), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.05 M; (△), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.10 M; (◇), $[H_2A_2]_{(o,ini)}$ = constant $[H_2A_2]_{(o,eq)}$ (chosen) = 0.30 M.

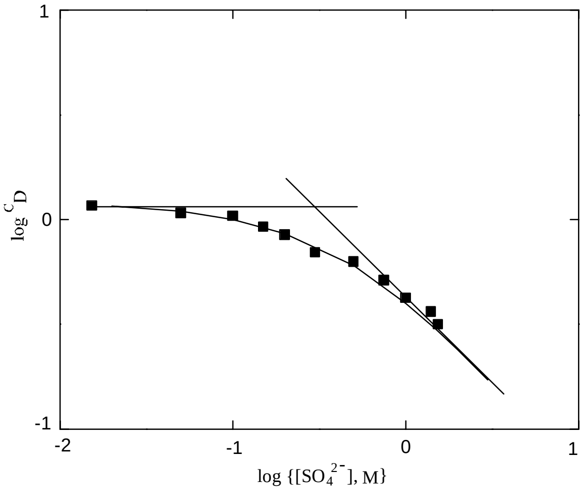


Fig. 3. The log ^{C}D vs. log {$[SO_4^{2-}]$, M} plot at constant equilibrium pH of 2.45 and extractant concentration of 0.025 M. $[Zn(II)]_{(ini)}$ = 1.00 g/L, temperature = (303 ± 0.50) K, equilibration time = 5 min; O/A=1. The points are experimental whereas the curve is theoretical representing: $\log {}^{C}D = \log K_{ex}[H^+]^{-2}_{(eq)}[H_2A_2]_{(eq)} - \log(1 + K_{SO_4^{2-}}[SO_4^{2-}]) = 0.068 - \log(1 + K_{SO_4^{2-}}[SO_4^{2-}])$; where, $K_{SO_4^{2-}}$ is a proportionality constant and its value has been calculated to be 2 M^{-1} by the Curve- Fitting method.

The effects of temperature has been investigated for the extraction of Zn(II) from the aqueous solutions containing 1 gL Zn(II), 0.0153 M SO_4^{2-} and 6 $pH_{(ini)}$ by 0.025, 0.10 and 0.30 M Cyanex 272 solutions. The measured log D values have been converted to log ^{C}D values for $pH_{(eq)}$ = 2.45 and $[H_2A_2]_{(o,eq)} = [H_2A_2]_{(o,ini)}$ by Eq. (5). The log ^{C}D vs. $(1/T)10^3$, K^{-1} plots for 0.025, 0.10 and 0.30 M $[H_2A_2]_{(o,eq)}$ systems have been drawn; straight lines are obtained and from the slopes of the lines, the ΔH values for the reactions have been calculated as 16.45, 25.17 and 45.50 kJ/mol, respectively. It is therefore concluded that the extraction process under investigation is endothermic in nature and the enthalpy change depends on $[H_2A_2]$ range used. With the increase in $[H_2A_2]_{(o,eq)}$, the ΔH value is increased.

From the intercepts and slopes of the lines in various types of plots discussed above (except temperature dependence plots), the values of log K_{ex} at LCR and HCR of extractant have been evaluated (Table 1) to be -3.11 (st. dev. 0.091) and -2.078 (st. dev. 0.065), respectively. The value of log K_{ex} has also been evaluated graphically. The values of log $[H_2A_2]_{(o,eq)}$ + 2 $pH_{(eq)}$ - log (1 + 2 $[SO_4^{2-}]$ = log f(R) at different parameters have been calculated for all data given above in equilibrium studies at 303 K. The log ^{C}D vs. log f(R) plot is given in Fig. 4. It is found that the points are considerably scattered. It is due to the change in extractant dependence on its concentration variation. The Least Squares slope of 0.984 (should be 1.00) with intercept of -2.94 and correlation coefficient of 0.9226 is obtained. The intercept (-2.94) apparently indicates the log K_{ex} value which is between the values obtained at LCR and HCR of extractant.

Mechanism of Zn(II) extraction by Cyanex 272. From the foregoing results, it is seen that the pH, extractant (H_2A_2) and sulphate dependences are 2, 1 and 0, respectively, when SO_4^{2-} and H_2A_2 concentrations are kept low. These results suggest the following extraction equilibrium reaction:

$$Zn^{2+} + H_2A_{2\,(o)} \rightleftharpoons [ZnA_2]_{(o)} + 2H^{+} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (6)$$

In the lower sulphate but higher H_2A_2 concentration region, the extraction equilibrium reaction appears as:

$$Zn^{2+} + 2\,H_2A_{2\,(o)} \rightleftharpoons [ZnA_2.H_2A_2]_{(o)} + 2H^{+} \;\ldots\ldots\ldots\; (7)$$

Table 1. Evaluation of extraction equilibrium constant (K_{ex}) at 303 K

Type of plot: log ^{C}D vs. log..	$[H_2A_2]_{(o,eq)}$ M	$pH_{(eq)}$	$[SO_4^{2-}]$ M	Intercept I	$[H_2A_2]$ dependence (x)	pH dependence (y)	log K_{ex}	Average log K_{ex}	Standard deviation
i) At low concentration region of extractant									
$[Zn(II)]_{(eq)}$	0.025	2.50	0.046	0.20	1.00	2.00	-3.160		
$[H_2A_2]_{(o,eq)}$	Variable	1.85	0.0153	0.62	1.00	2.00	-3.067		
		2.05		1.02	1.00	2.00	-3.036		
		2.40		1.74	1.00	2.00	-3.047		
		2.70		2.33	1.00	2.00	-3.057		
$[H^+]^{-1}_{(eq)}$	0.025	Variable	0.0153	-4.84	1.00	2.00	-3.225		
	0.050			-4.44	1.00	2.00	-3.126	-3.111	0.091
	0.100			-3.96	1.00	2.00	-2.947		
$[SO4^{2-}]$	0.025	2.45	Variable	0.068 (LCR)	1.00	2.00	-3.220		
				-0.230 (HCR)	1.00	2.00	-3.227		
ii) At high concentration region of extractant									
$[H_2A_2]_{(o,eq)}$	Variable	1.85	0.0153	1.62	2.00	2.00	-2.067		
		2.05		2.01	2.00	2.00	-2.077		
		2.40		2.71	2.00	2.00	-2.077	-2.078	0.065
		2.70		3.20	2.00	2.00	-2.187		
$[H^+]^{-1}_{(eq)}$	0.30	Variable	0.0153	-3.04	2.00	2.00	-1.981		

*HCR = higher concentration region; LCR = lower concentration region. Basic equation for calculating K_{ex}: log ^{C}D = log K_{ex} + x log $[H_2A_2]_{(o,eq)}$ + y $pH_{(eq)}$ - log {1 + 2 $[SO_4^{2-}]$}, where, x = 1 at LCR of extractant and 2 at HCR of extractant, whilst x = 2 always.

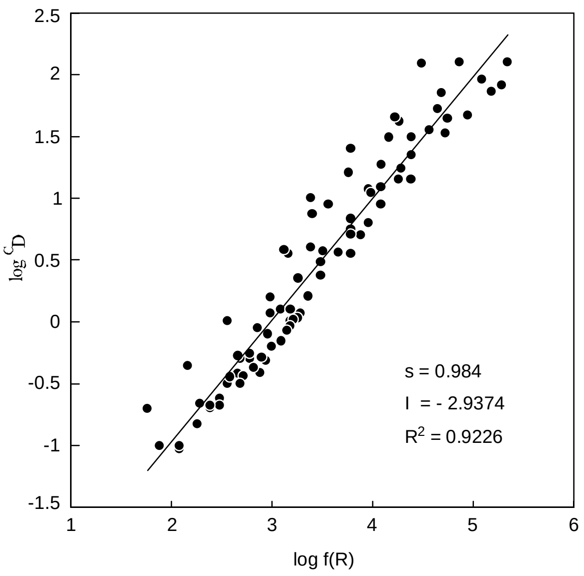


Fig. 4. Plot of log ^{C}D vs. log f(R) for the estimation of extraction equilibrium constant (K_{ex}) at 303 K; where, log f(R) = ([(1-2) log $[H_2A_2]_{(o,eq)}$ + 2 $pH_{(eq)}$ – log (1+2 $[SO_4^{2-}$)]]).

Since H_2A_2 dependence is 2 at its higher concentration region, in higher sulphate and H_2A_2 concentration region, the following reaction takes place during extraction:

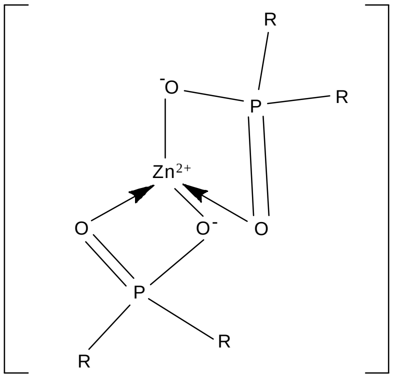
$$[ZnSO_4] + 2\ H_2A_{2\,(o)} \rightleftharpoons [ZnA_2.H_2A_2]_{(o)} + 2\ H^+ + SO_4^{2-} \quad \text{.......} (8)$$

On the other hand, in higher sulphate but lower extractant concentration region, the extraction equilibrium reaction will be represented by:

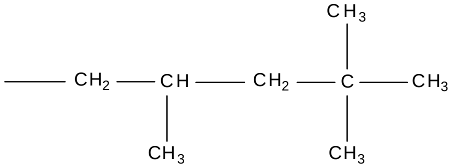
$$[ZnSO_4] + H_2A_{2\,(o)} \rightleftharpoons [ZnA_2]_{(o)} + 2H^+ + SO_4^{2-} \quad \text{.......} (9)$$

In Eqs. (8) and (9), H^+ and SO_4^{2-} ions are liberated which may combine to form considerable amounts of HSO_4^- in the investigated pH regions (particularly in the lower pH region). Moreover, Zn(II)-HSO_4^- complex existing in the lower pH region under investigation may also take part in the extraction reaction.

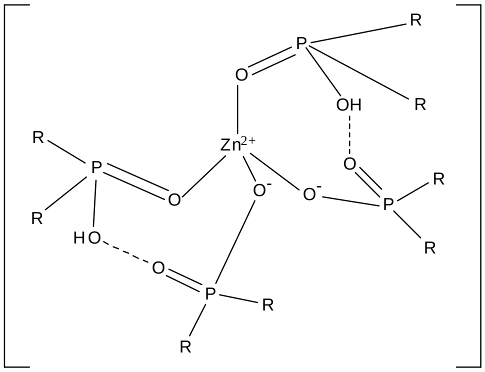
Through sp3-hybridization, Zn(II) usually forms tetrahedral complexes. So the predicted structure of $[ZnA_2]$ is as follows:



where, R =



and that of $[ZnA_2.H_2A_2]$ or better $[Zn(HA_2)_2]$ is:



Loading of Zn(II) in Cyanex 272 solultion. The loadings of Zn(II) in 0.025 and 0.10 M Cyanex 272 solution have been performed accordingly and experimental results together with the experimental conditions are presented in Fig. 5. It is found that the organic phases are saturated with Zn(II) after 11th contact in both cases. At saturation level, the [Zn(II)] in 0.025 and 0.10 M Cyanex 272 solutions are 1.67 and 6.69 g/L which are equivalent to 0.025 and 0.102 M, respectively. So, the existing organic species at saturation is undoubtedly ZnA_2. So the solvated species formed in the surplus of free extractant is supposed to extract more Zn(II) at higher loadings by the following reaction:

$$[ZnA_2.H_2A_2]_{(o)} + Zn(II) \rightleftharpoons 2\ [ZnA_2]_{(o)} + 2\ H^+ \ \text{....} (10)$$

Simple calculation shows that the loading capacity is 11.5 g Zn(II) per 100 g Cyanex 272.

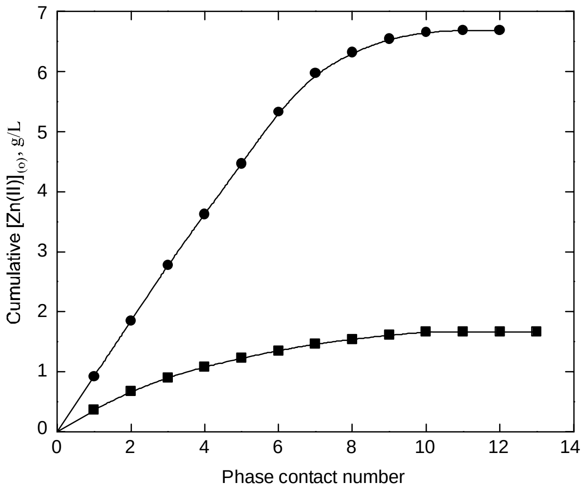


Fig. 5. Loading of Cyanex 272 solution with Zn(II). $[Zn(II)]_{(ini)}$ = 0.9502 g/L; $[SO_4^{2-}]$ = 0.015 M; $pH_{(ini)}$ = 5.00; Equilibration time = 5 min; temperature = (303 ± 0.50) K; O/A = 1; (O = 100 mL) (●); $[H_2A_2]_{(o,ini)}$ = 0.10 M, (■); $[H_2A_2]_{(o,ini)}$ = 0.025 M. The organic phase is recycled in each stage.

Stripping of Zn(II) from organic phase by mineral acids. The stripping of Zn(II) complex extracted at high loading has been investigated with 0.10 and 1 M HCl, HNO_3, $HClO_4$ and H_2SO_4 at 303 K. Table 2 shows the results. All acids of 1 M concentration is capable of stripping by 90% or more. 96% stripping by 1 M H_2SO_4 is reduced to 95%, 92% and 90% by 1 M HNO_3, HCl and $HClO_4$, respectively. In all cases, the decrease in stripping with decreasing concentration of acid is observed; e.g. 96% stripping by 1 M H_2SO_4 solution is decreased to 75% stripping by 0.10 M H_2SO_4 under identical condition. The use of high organic to aqueous phase ratio (O/A) decreases the stripping percentage considerably but the concentration of Zn(II) in the aqueous phase is increased appreciably in single stages. The 96% stripping by 1.0 M H_2SO_4 at O/A = 1 is decreased to 82% and 76% strippings by 1.0 M H_2SO_4 at O/A of 5 and 10, respectively; whilst the aqueous Zn(II) concentration of 0.96 g/L at O/A of 1 is increased to 4.10 g/L and 7.60 g/L at O/A of 5 and 10, respectively. Stage-wise strippings are also possible (by H_2SO_4

Table 2. Stripping of Zn(II)-Cyanex 272 complex by mineral acids, temperature = 303 K; shaking speed = 300 strokes/min; time = 5 min; volume of stripping agent = 10 mL

Acid	[Acid], M	$[Zn(II)]_{(o,ini)}$, g/L	O/A	Stage No.	% Zn(II) stripped	[Zn(II)] in aqueous phase, g/L
HCl	0.10	1.00	1	1	60.0	0.600
	1.00	1.00	1	1	92.0	0.920
HNO_3	0.10	1.00	1	1	66.0	0.660
	1.00	1.00	1	1	95.0	0.950
$HClO_4$	0.10	1.00	1	1	58.0	0.580
	1.00	1.00	1	1	90.0	0.900
	0.10	1.00	1	1	75.0	0.750
				2*	92.0 (c)	0.460 (m)
				3	98.0 (c)	0.370 (m)
	1.00	1.00	1	1	96.0	0.960
				2*	99.8 (c)	0.499 (m)
	1.00	1.00	5	1	82.0	4.100
				2*	96.0 (c)	2.375 (m)
				3	99.0 (c)	1.650 (m)
	1.00	1.00	10	1	76.0	7.600
				2*	90.0 (c)	4.500 (m)
				3	97.2 (c)	3.240 (m)
				4	99.5 (c)	2.488 (m)
H_2SO_4	1.00	6.69	1	1	80.0	5.352
				2*	94.0 (c)	3.144 (m)
				3	98.0 (c)	2.185 (m)
	1.00	6.69	1	1	80.0	5.352
				2#	62.0	9.500 (c)
				3	48.0	12.711 (c)
				4	32.0	14.852 (c)
				5	20.0	16.190 (c)

* = organic phase recycled; # = aqueous phase recycled; (c) = cumulative; (m) = mixed solution.

solution). When O/A = 10 is used and the fresh aqueous solutions are contacted with recycled organic phase, then cumulative 99.5% stripping occurs in the 4th stage. If the stripped aqueous solutions are mixed together then, the Zn(II) concentration is decreased; e.g. 7.6 g/L Zn(II) concentration obtained in the 1st stage is decreased to 4.50, 3.24 and 2.49 g/L Zn(II) in cumulative aqueous solutions of 2, 3 and 4 stages, respectively. The same aqueous (stripping) solution can also be recycled with fresh organic phases to increase [Zn(II)] in the aqueous phase. When the organic phase contains 6.69 g/L Zn(II) and this phase is repeatedly contracted with same aqueous solution (1 M H_2SO_4) at O/A=1, then the [Zn(II)] in the aqueous phase becomes 5.32, 9.50, 12.71, 14.85 and 16.19 g/L in the 1st , 2nd, 3rd, 4th and 5th stages, respectively. These results undoubtedly predict that the counter-current stripping may be carried out with highly loaded organic phase and 1 M H_2SO_4 may be used to get aqueous solution containing high amount of Zn(II) together with the liberation of extractant for further use in extraction.

Separation of Zn(II) from other 3rd - block metal ions in binary mixtures. Table 3 shows the extraction percentages (%E) of Zn(II) and the commonly occurring first row transition metal ions in binary mixtures with Zn(II) at various $pH_{(eq)}$ values of 0-7 with an interval of 0.50, while extracted by 0.10 M Cyanex 272 solution. Almost quantitative separation of Sc(III) and Ti(IV) from Zn(II) is possible by extracting Sc(III) or Ti(IV) at $pH_{(eq)}$ = 1.0 with only 1% Zn(II) and 98.2 % Sc(III) or 95% Ti(IV) extractions. The extraction behaviours of Zn(II) and V(IV) or Fe(III) are almost identical, so their separations are not so easy with Cyanex 272. However, V(V) can be easily separated from Zn(II) by extracting all Zn(II) at $pH_{(eq)}$ of 3.50 leaving all V(V) in the aqueous phase. As Cr(III) is not extracted by Cyanex 272 with in phase contact time of 5 min, Zn(II) can be easily separated from Cr(III) by extracting (100%) at $pH_{(eq)}$ of 3.5 leaving all Cr(III) in the aqueous phase. Manganese(II) can be separated from Zn(II) at $pH_{(eq)}$ of 2.5 (98% Zn(II) extraction with no Mn(II) extraction). At $pH_{(eq)}$ = 2.5, Zn(II) may be separated from Co(II) with only 0.8% co-extraction of Co(II) and 98% extraction of Zn(II). A clear-cut separation of Zn(II) from Ni(II) can be achieved by complete extraction of Zn(II) at $pH_{(eq)}$ of 3.5 with no nickel(II)-extraction. Zinc(II) can also be separated from Cu(II) at $pH_{(eq)}$ = 2.5 with 98% Zn(II) extraction together with only 1% Cu(II) co-extraction. It appears therefore that Cyanex 272 is a very good extractant for separation of Zn(II) from many metallic ions of hydrometallurgical interest.

Table 3. Separation of Zn(II) from its binary mixture with first row transition metal ions, [metal ion] = 1 g/L; $[SO_4^{2-}]$ = 0.10 M above $pH_{(eq)}$ of 1.5 (at $pH_{(eq)}$ < 1.5, $[SO_4^{2-}] = [H_2SO_4]$, [Cyanex 272] = 0.10 M in kerosene; O/A = 1; equilibration time allowed = 5 min, temperature = 303 K

$pH_{(eq)}$ (± 0.05)	Extraction percentage (% E) of									
	Zn(II)	Sc(III)	Ti(IV)	V(IV)	V(V)	Cr(III)	Mn(II)	Fe(III)	Co(II)	^{f}Ni(II)	Cu(II)
0.0	*NE	52.0	5.5	2.6	22.0	NE	NE	NE	NE	NE	NE
0.5	NE	90.0	53.0	5.0	16.0	NE	NE	NE	NE	NE	NE
1.0	1.0±0.1	98.2	95.0	10.0	11.0	NE	NE	0.9	NE	NE	NE
1.5	9.0±0.2	CE	99.3	40.0	7.0	NE	NE	8.8	NE	NE	NE
2.0	68.0±2.0	CE	CE	68.0	4.0	NE	NE	42.0	NE	NE	NE
2.5	98.0±0.5	CE	CE	86.0	2.5	NE	NE	85.0	0.8	NE	1.0
3.0	99.6±0.2	CE	CE	95.0	1.0	NE	4.6	96.0	2.3	NE	7.6
3.5	#CE	CE	CE	99.0	NE	NE	40.0	99.7	8.4	NE	46.0
4.0	CE	CE	CE	CE	NE	NE	86.0	CE	16.2	NE	90.0
4.5	CE	CE	CE	CE	NE	NE	96.0	CE	38.0	NE	97.0
5.0	CE	CE	CE	CE	NE	NE	99.8	CE	80.0	1.6	99.2
5.5	CE	CE	CE	CE	NE	NE	CE	CE	94.0	4.5	CE
6.0	CE	CE	CE	CE	NE	NE	CE	CE	99.0	14.0	CE
6.5	CE	CE	CE	CE	NE	NE	CE	CE	99.8	68.0	CE
7.0	CE	CE	CE	CE	NE	NE	CE	CE	CE	92.0	CE

*NE = not extracted; # = CE = completely extracted; f = 3% (v/v) octanol used in organic phase as de-emulsifier.

Conclusion

Following conclusions have been drawn:

(i) Zinc(II) can be extracted completely from sulphate medium by Cyanex 272 solution in distilled kerosene at $pH_{(eq)} \geq 3.0$.

(ii) The distribution ratio of Zn(II) is independent of initial Zn(II) concentration provided equilibrium pH and extractant concentration are kept constant. The pH, extractant dependence in LCR and extractant dependence in HCR are 2, 1 and 2, respectively. D is found to be inversely proportional to $(1+2[SO_4^{2-}])$.

(iii) Extraction occurs via:

(a) $Zn^{++} + H_2A_{2(o)} \rightleftharpoons ZnA_{2\,(o)} + 2\ H^+$, at LCR of H_2A_2 and SO_4^{2-}

(b) $Zn^{++} + 2\ H_2A_{2\,(o)} \rightleftharpoons ZnA_2.H_2A_{2\,(o)} + 2\ H^+$, at HCR of H_2A_2 and LCR of SO_4^{2-}

(c) $ZnSO_4 + H_2A_{2\,(o)} \rightleftharpoons ZnA_{2\,(o)} + 2\ H^+ + SO_4^{2-}$, at LCR of H_2A_2 and HCR of SO_4^{2-} and

(d) $ZnSO_4 + 2\ H_2A_{2\,(o)} \rightleftharpoons ZnA_2.H_2A_{2(o)} + 2\ H^+ + SO_4^2$, at HCR of H_2A_2 and SO_4^{2-}

with K_{ex} of $10^{-3.11}$ and $10^{-2.08}$ for reactions (a) and (b), respectively. Temperature has a positive effect on extraction and ΔH value increases with increasing Cyanex 272 concentration.

(iv) The extracted complex at high loading is ZnA_2 and consequently, the loading capacity is 11.5 g Zn(II)/100 g Cyanex 272.

(v) The extracted complex is labile for stripping by 0.10 and 1 M mineral acids, particularly by sulphuric acid. Stage-wise stripping by recycling either of the phases and stripping at high O/A are possible. At high O/A with high Zn(II)-content in the organic phase, stripping can be done counter-currently by 1 M H_2SO_4 solution to regenerate Cyanex 272 solution for recycling in extraction and to obtain aqueous solution containing high amount of Zn(II).

(vi) Cyanex 272 is proved as a good extractant for the Zn(II). Zn(II) can be separated from either Sc(III), Ti(IV), V(V), Cr(III), Mn(II), Co(II), Ni(II) or Cu(II) by selecting $pH_{(eq)}$ properly alone. But the Zn(II)/V(IV) and Zn(II)/Fe(III) separations are not possible by Cyanex 272.

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