

Full Length Research Paper

Solvent extraction of copper, nickel and zinc by Cyanex 272

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Studies were conducted on the extraction of copper, nickel and zinc from their sulphate solutions using [bis (2,4,4- trimethylpentyl) phosphinic acid] (Cyanex 272, HA) as an extractant. Effect of various parameters, such as equilibrium pH, extractant concentration, sulphate and acetate ion concentration was investigated. The slope analysis method was used to determine the nature of extracted metal complexes. For the extraction of metal $[M(Ac)(HA_2).2HA]$ species was formed.

Key words: Cyanex 272, solvent extraction, copper, nickel, zinc.

INTRODUCTION

Solvent extraction is one of the most versatile methods used for the removal, separation and concentration of metallic species from aqueous media. It is used for the processing of most of the metals in periodic table. For the extraction of base metals zinc (Zn), manganese (Mn), copper (Cu), cobalt (Co) and nickel (Ni), the extractants, such as D2EHPA and PC 88A are considered suitable extractant (Thakur, 1998). Oxime reagents like LIX 87 QN, LIX 54, LIX 973, LIX 984 and LIX 34 are used for the extraction, separation and recovery of copper, nickel and zinc from sulphate solutions (Reddy and Priya, 2005), and Cyanex 272 with other extractant are extensively used for the separation of cobalt, nickel and cadmium (Sarangi et al., 1999; Sahu et al., 2004; Tsakiridis and Agatzini, 2004; Reddy et al., 2006). Therefore, much research work has been concentrated on the study of zinc extraction with D2EHPA, copper extraction with LIX type extractant and for the separation of cobalt and nickel with alkyl phosphorous reagents, such as D2EHPA, PC 88A, Cyanex 272 or their equivalent (Pereira et al., 2007; Navarro and Alguacil, 1999; Parhi et al., 2008). However, there are few studies that used solid-liquid extraction technique for the extraction of copper, nickel, zinc and cadmium using Cyanex 272 (Cortina et al., 1995, 1996; Bari et al., 2009a, b). Due to having some disadvantages like incomplete removal of interferences, low recovery of

analytes, complicated set-up, lengthy method development and expensiveness, solvent extraction is chosen for this study. Solvent extraction of copper, nickel, and zinc with Cyanex 272 is also studied, but very meager (Sole and Hiskey, 1995; Flett, 2005; Ali et al., 2006; Hubicki and Hubicka, 1996; Biswas and Singha, 2007). Therefore, the novelty of this work is to study the effect of sulphate and acetate ion on the extraction and propose the extracted species.

The aim of this work is to investigate the extraction properties of Cyanex 272 towards copper, nickel and zinc from their aqueous solution and study the different parameters like pH, extractant, sulphate and acetate ion concentration on the extraction process. This study also aims at investigating the extracted species into the organic phase using slope analysis method.

MATERIALS AND METHODS

A Perkin-Elmer Model AAnalyst 700 Atomic Absorption Spectrometer (AAS), wrist-action flask shaker (Model SF1, Stuart Scientific) and a digital pH meter were used for the measurement of metal concentration, to shake the phases and to control pH in the aqueous phase, respectively. Cyanex 272 was supplied by Cytec Inc., and the organic solution was prepared by dissolving it in hexane. Cyanex 272 [bis (2,4,4-trimethylpentyl) phosphinic acid] was used as it is received which is a commercial grade with purity of 92%. Stock solutions of copper, nickel and zinc were prepared by dissolving requisite quantity of laboratory grade $CuSO_4.5H_2O$, $NiSO_4.2H_2O$ and $ZnSO_4.7H_2O$ with purity of 99.8, 99, and 99%, respectively in distilled water. Working standard solutions were

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prepared by suitable dilution of these solutions. All other chemicals were used as analytical grade.

Equal volume of aqueous, containing 20 mg/L nickel, 500 mg/L copper and 20 mg/L zinc with 0.1 M $[\text{SO}_4^{2-}]$ and 0.25 M $[\text{Ac}^-]$, and organic phases of 0.1 M Cyanex 272 were equilibrated in 100 ml Stoppered conical flask by shaking it using wrist-action shaker for 20 min at room temperature. Extraction of nickel reaches equilibrium within a maximum period of 1 min (Bhaskara and Reddy, 2002), and equilibrium is attained rapidly, usually 2 to 3 min for copper (Sole and Hiskey, 1995) and 5 min for zinc (Jha et al., 2007) using Cyanex 272. However, contact time of 20 min, allowed to ensure that equilibrium was reached. Then, the phases were separated and the metal ion concentration in the aqueous phase was estimated by AAS. Metal content in the organic phase was determined by the differences. The distribution ratio, D , was calculated as the concentration of metal present in the organic phase to that of aqueous phase at equilibrium. pH adjustment was performed by the addition of dilute NaOH.

RESULTS AND DISCUSSION

Effect of equilibrium pH

Solvent extraction of copper, nickel and zinc from the sulphate-acetate medium was studied individually using 0.1 M of Cyanex 272 as an organic phase varying the initial pH from 2.5 to 6.0 for copper, 4.48 to 12.0 for nickel and 1.4 to 4.0 for zinc which corresponds with the equilibrium pH of 2.5 to 5.3 for copper, 4.48 to 7.45 for nickel and 1.4 to 3.6 for zinc. The percentage of extraction of copper, nickel and zinc is plotted against the equilibrium pH and is as shown in Figure 1. It was found out that the percentage of extraction was increased for the extraction of all metals with increase in the equilibrium pH, and maximum extraction was obtained at equilibrium pH of 5.3, 7.45 and 3.6 for copper, nickel and zinc extraction, respectively. The effect of equilibrium pH on $\log D$ is as shown in Figure 2, where the D value increased with increase in pH. The plot was linear with slope (S) 1 for copper, nickel and zinc indicating the liberation of one mole of H^+ during extraction.

Effect of Cyanex 272 concentration

The effect of extractant, Cyanex 272 concentration on the extraction of copper, nickel and zinc was studied individually with the extractant range of 0.01 to 0.4 M. Initial pH were 4.0, 8.5 and 1.8 for copper, nickel and zinc, respectively. It was observed that the percentage of extraction increased with increase in the extractant concentration (Figure 3). The effect of Cyanex 272 concentration on the distribution ratio of copper, nickel and zinc is given as shown in Figure 4. The $\log D$ versus $\log[\text{H}_2\text{A}_2]$ plot showed that the distribution ratio increased with increase in extractant concentration in the organic phase. The slope values of 2 for the three metals indicated the involvement of two mole dimeric extractant in

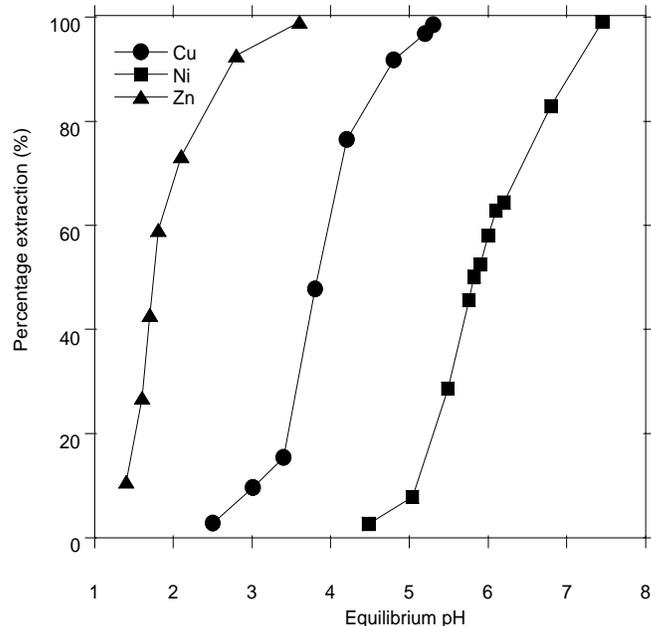


Figure 1. Effect of equilibrium pH on percentage extraction.

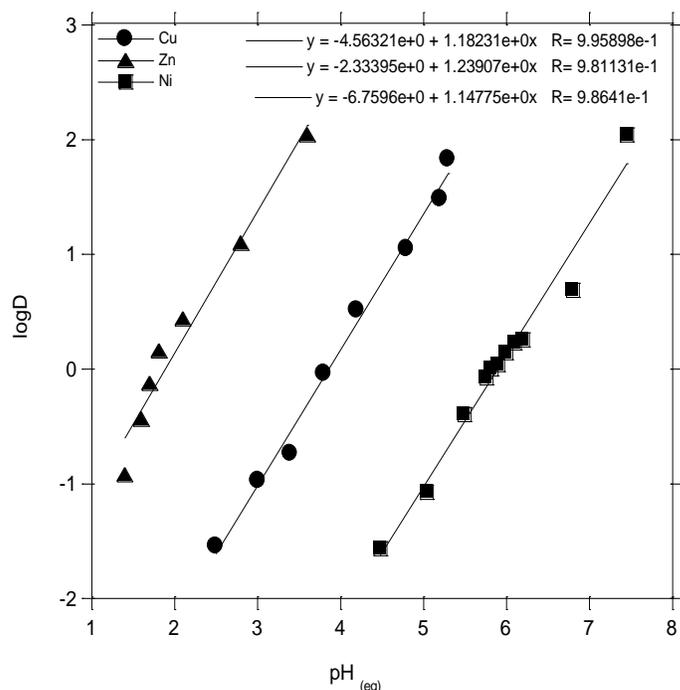


Figure 2. Dependence of distribution ratio on equilibrium pH. Slope = 1 for copper, nickel and zinc.

the extraction reaction. However, Cyanex 272 is a liquid cation exchanger as well as a chelating agent and can extract a diverse range of metal ions. It can be dimerized through hydrogen bonding in the non polar organic diluent (Biswas et al., 2005).

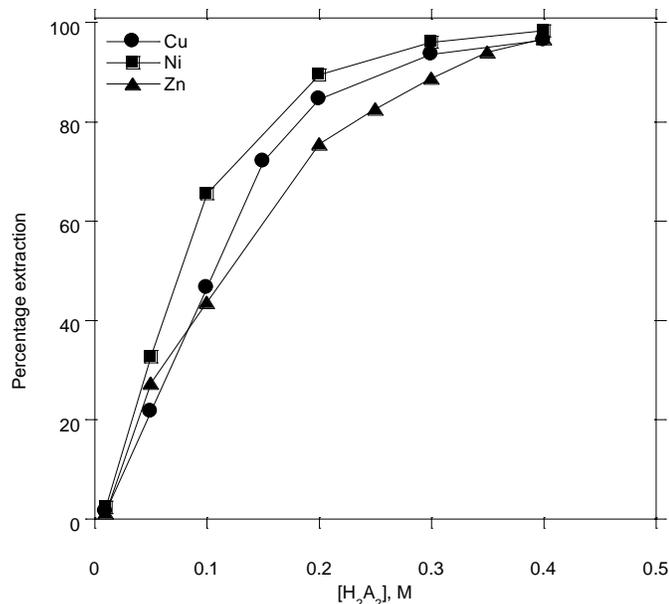


Figure 3. Effect of extractant concentration on percentage of extraction.

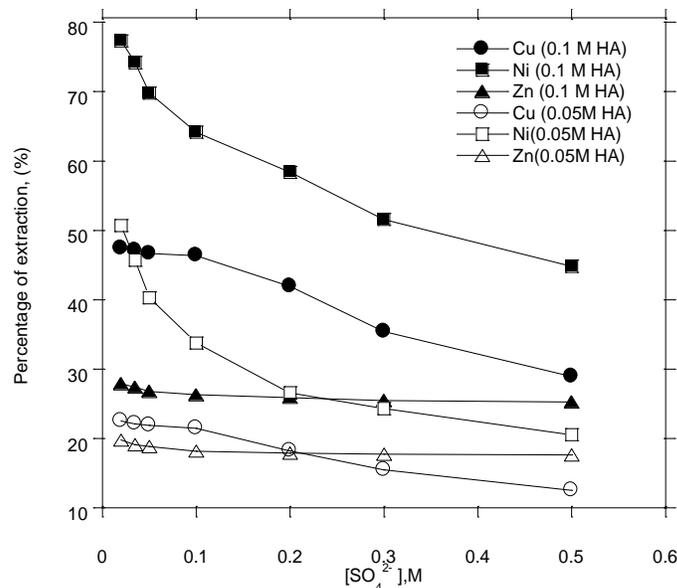


Figure 5. Effect of sulphate ion concentration on extraction percentage.

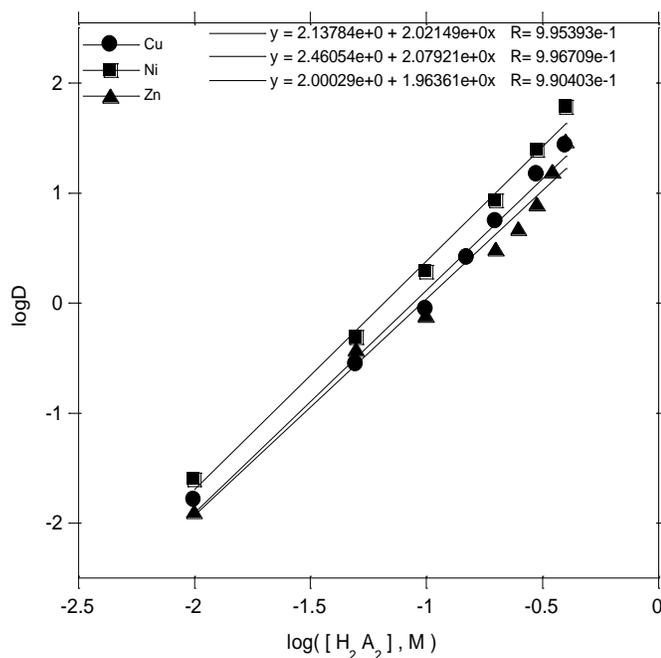


Figure 4. Dependence of distribution ratio on extractant concentration. Slope = 2 for all metals.

Effect of sulphate ion concentration

The influence of sulphate ion concentration in the range of 0.02 to 0.5 M on the extraction of copper, nickel and zinc was studied individually at constant acetate ion

concentration using two concentration level of Cyanex 272 as 0.1 and 0.05 M. Initial pH were 4.0, 8.5 and 1.65 for copper, nickel and zinc extraction, respectively; the result is as shown in Figure 5. The effect of sulphate ion concentration on zinc extraction was not significant; the change of percentage of extraction with increasing sulphate ion concentration was very meager for both extractant concentration of 0.1 and 0.05 M. But in the case of nickel extraction, there was a decrease on extraction. The extraction of nickel fall down from 77.3 to 44.8% and 50.7 to 20.5% by 0.1 and 0.05 M extractant system, respectively. On the other hand, copper extraction was independent at lower sulphate ion concentration upto 0.02 to 0.1 M; thereafter, the percentage extraction decreased with increase in sulphate ion concentration (0.1 to 0.5 M). The percentage of extraction decreased from 46.3 to 28.9% and 21.4 to 12.5% by 0.1 and 0.05 M extractant system, respectively. The logD versus log $[SO_4^{2-}]$ plot is given as shown in Figure 6 at two extractant concentrations of 0.05 and 0.1 M and showed that the sulphate ion did not have effect on zinc extraction both in 0.1 M Cyanex 272 and 0.05 M Cyanex 272 systems, and for the extraction of nickel, the distribution ratio decreased with increase in sulphate ion concentration, this happened due to the fact that as sulphate ion increased in the aqueous phase, the non extractable $Ni^{2+}-SO_4^{2-}$ species might be formed in the aqueous phase. For the extraction of copper, it was discovered that the distribution ratio decreased with increase in sulphate ion at higher sulphate ion concentration region (0.1 to 0.5 M), while at lower sulphate ion concentration region (0.02 to 0.10 M), the

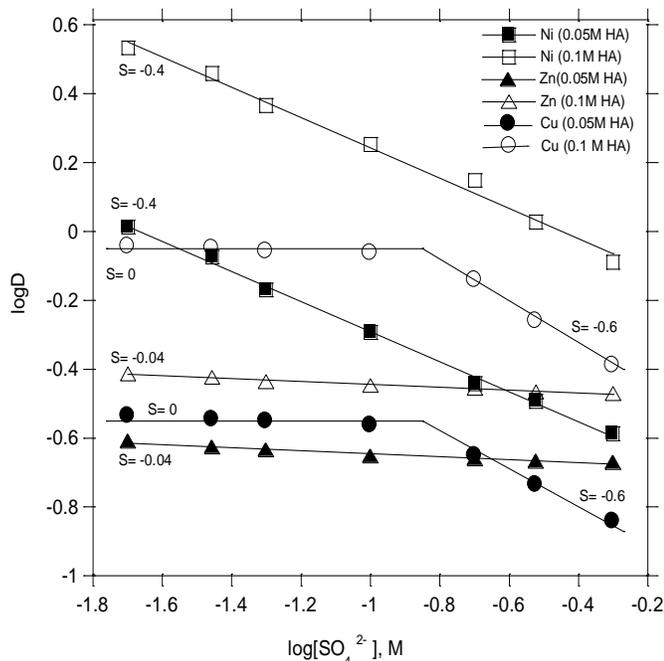


Figure 6. Dependence of distribution ratio on sulphate ion concentration in the aqueous phase.

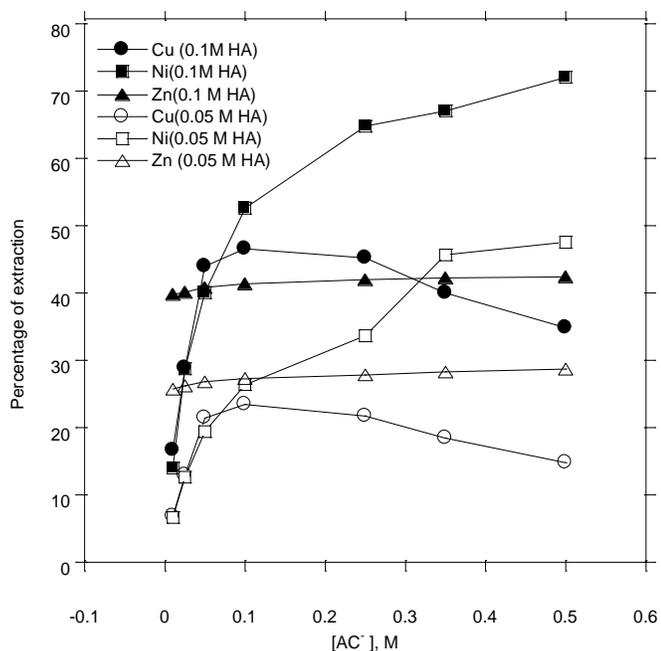


Figure 7. Effect of acetate ion concentration on percentage of extraction.

distribution ratio was independent with sulphate ion concentration (Figure 6). As the sulphate ion concentration increased in the aqueous phase the non extractable

Cu^{2+} , $[\text{Cu SO}_4^{2-}]$ or both were formed gradually, which reduced the extraction. At lower sulphate ion concentration region, sulphate ion had no involvement on the extraction.

Effect of acetate ion concentration

The acetate ions in the aqueous phase can be used as a buffering agent (Nakashio et al., 1982). Cyanex 272 is an acidic extractant, releases hydrogen ion to the aqueous phase during extraction which causes the extraction efficiency to drop. Therefore, the aqueous phase was buffered using acetate ion to prohibit the dropping of the extraction efficiency.

Dependence of percentage of extraction on acetate ion concentration is as shown in Figure 7, which was studied varying the acetate ion concentration from 0.01 to 0.5 M at two extractant system of 0.1 and 0.05 M Cyanex 272. pH of the aqueous solution were 4.0, 8.5 and 1.8 for copper, nickel and zinc, respectively. It was found out that for nickel extraction, the percentage of extraction increased with increase in acetate ion concentration (0.01 to 0.5 M) in the aqueous phase. The extraction was increased from 13.9 to 72.0% and 6.6 to 47.5% for 0.1 and 0.05 M extractant, respectively. For the extraction of zinc, the extraction percentage was increased slowly from 39.7 to 42.4% for 0.1 M extractant and 25.7 to 28.6% for 0.05 M extractant system. For copper extraction, the percentage extraction was increased with increase in acetate ion concentration in the aqueous phase; at lower acetate ion concentration region (0.01 to 0.05), while the percentage of extraction was nearly constant at medium acetate region (0.05 to 0.25 M) after that the extraction was decreased at higher acetate ion concentration region (0.25 to 0.5 M) when the initial metal ion concentration, extractant concentration and pH were kept constant.

The effect of acetate ion concentration on logD values is given in Figure 8. For the extraction of copper, at lower acetate ion concentration region (0.01 to 0.05 M), the distribution ratio increased with increase in acetate ion concentration, after that the distribution ratio was independent in the range of 0.05 to 0.25 M acetate ion concentration region (medium), and thereafter, at higher acetate ion concentration region (0.25 to 0.5 M), the distribution ratio decreased with increase in acetate ion concentration. This happened due to the fact that, as acetate ion concentration increased in the aqueous phase, the species Cu^{2+} , $[\text{Cu}(\text{Ac})]^+$ and $[\text{Cu}(\text{Ac})_2]$ were formed gradually (Bari et al., 2007). From the slope value, it can be concluded that at lower acetate ion concentration region (0.01 to 0.05 M), one mole of acetate ion was participating in forming complex, whereas at medium acetate ion concentration region (0.05 to 0.25 M), acetate ion did not affect the extraction, meaning that acetate ion was not involved in the reaction.

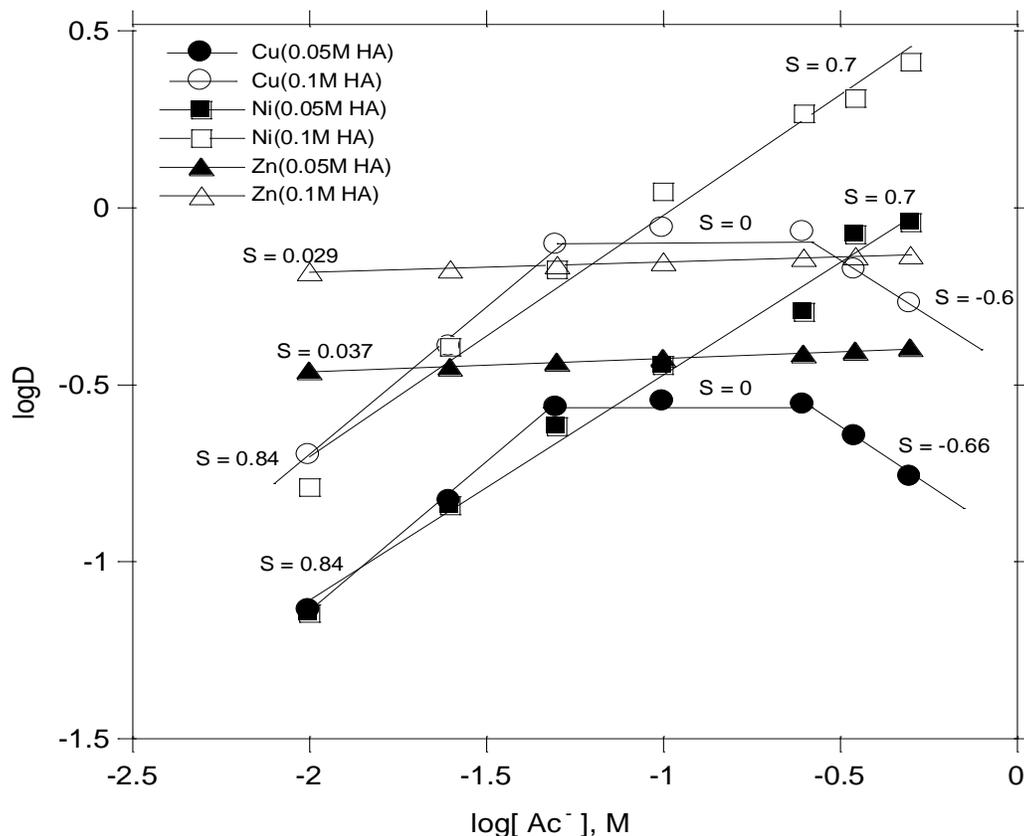


Figure 8. Dependence of distribution ratio on acetate ion concentration in the aqueous phase.

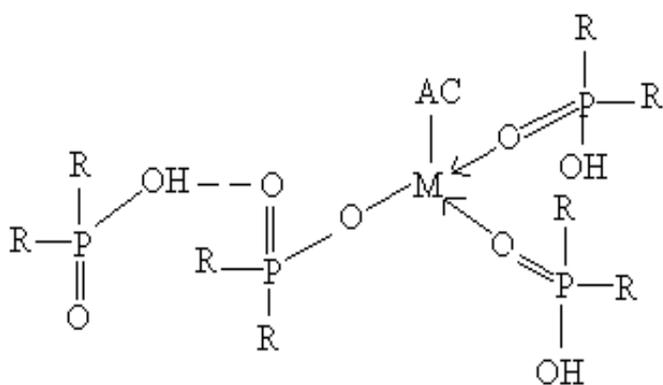


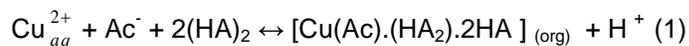
Figure 9. Complex structure of M-Cyanex 272.

At higher acetate ion concentration region (0.25 to 0.5 M), liberation of acetate ion occurred partially during the extraction. For the extraction of zinc, the slope value was almost nil indicating that acetate ion did not affect on the distribution ratio (Figure 8). Finally, for extraction of nickel, the distribution ratio increased with increase in acetate ion concentration and the unit slope value of logD

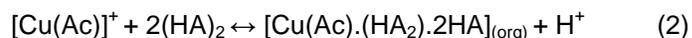
versus log[Ac⁻] plot (Figure 8) concluded that one mole of acetate ion participated during the extraction of both 0.05 and 0.1 M Cyanex 272 systems. The complex structure of metal and Cyanex 272 is as shown in Figure 9 based on the extraction behaviour. Based on the experimental results, the extraction reaction of Cu(II), Ni(II) and Zn(II) ions with Cyanex 272 can be represented as the following.

1) For the extraction of Cu(II):

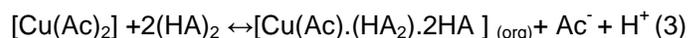
a) At lower acetate and sulphate ion concentration region:



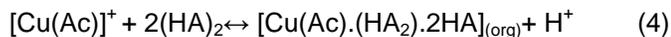
b) At medium acetate and lower sulphate ion region:



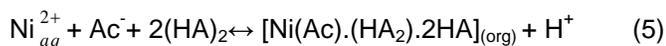
c) At higher acetate and lower sulphate ion region:



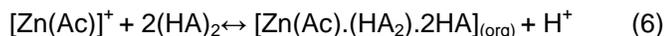
and



2) For the extraction of Ni(II):



3) For the extraction of Zn(II):



Conclusions

Cyanex 272 can effectively extract copper, nickel and zinc. Distribution ratio was dependent on the pH of the aqueous phase and extractant concentration on the organic phase. Sulphate and acetate ion concentration in the aqueous phase affected the distribution ratio of copper and nickel, whereas it did not affect that of zinc. Extraction data showed that during the extraction of metals at all acetate and sulphate ion concentration region, $[\text{M}(\text{Ac})(\text{HA}_2).2\text{HA}]$ species were formed.

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