



## Separation of copper from aqueous sulfate solutions by mixtures of Cyanex 301 and LIX® 984N

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### ABSTRACT

The extraction equilibria of copper(II) with Cyanex 301, LIX® 984N, and their mixtures have been investigated. Extraction was studied as a function of organic phase composition, sulfuric acid concentration, pH, temperature, initial copper concentration, mixing speed, and aqueous/organic volume ratio. Considerable synergistic enhancement has been observed in the extraction of  $\text{Cu}^{2+}$  with mixtures of Cyanex 301 and LIX® 984N. The results demonstrate that copper ion is extracted as  $\text{CuRL}_2\text{H}$  with synergistic mixture. The thermodynamic parameter, enthalpy change ( $\Delta H$ ) of Cyanex 301, LIX® 984N, and their mixtures have been determined and the endothermic process has been found. The synergistic enhancement factor of copper(II) with mixtures is higher at more acidic solutions, which suggests that it is a promising synergistic extraction system for the separation of copper(II) from more acidic medium. HCl was found to be more efficient for copper stripping from loaded synergistic mixtures.

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### 1. Introduction

Major sources for the production of copper, nickel and zinc appears to be from the raw material such as oxidic, silicate and sulphide ore concentrates. In view of the industrial and economic importance of these metals, there is a great need to separate and recover those using cost effective commercial extractants. Copper is one of the hazardous materials contained in waste waters from metallurgy, mines, chemicals, electroplating, and electronic industries and could be prevented from being discharged into the environment by an extractive removal with hydroxyoximes [1,2].

Recently, oxime mixtures based on the combination of ketoximes with salicylaldoximes in about a 1:1 mole ratio have shown surprising advantages over the hydroxyoxime and salicylaldoxime groups [3]. LIX® 860 can be blended with LIX® 84 over a broad range to give copper extraction reagents of variable extractive strength. LIX® 984 is a 1:1 volume blend of LIX® 860 and LIX® 84. Comparative experimental studies were carried out on extraction of copper(II) cations from aqueous acid nitrate media using four LIX-reagents, representatives of different extractant classes: LIX 984N-I, LIX 860N, LIX 84-I and LIX 65N. The mixed extractant of the third generation, LIX 984N, gives better results than expected from summing up the properties of the individual components. The extraction process is endothermic. The negative values of the free enthalpy  $\Delta G^\circ$  received with LIX 984N and LIX 860N-

I indicate that the copper extraction with these extractants can be successfully done at relatively low pH values [4]. The solvent extraction of the cations Cu(II), Fe(III), Ga(III), Ni(II), In(III), Co(II), Zn(II) and Pb(II) with LIX® 984 dissolved in *n*-heptane was explained by Miguel et al. [5]. Using the calculated dimerization constant of LIX® 984, it was shown that association is a very important factor in the organic phase when employing high extractant concentrations. Monomers and dimers of LIX® 984 play an important role in the extraction equilibria [5]. A liquid–liquid extraction procedure was used to study the amounts of Zn and Cu that could be simultaneously extracted from aqueous solution with di(2-ethylhexyl) phosphoric acid (DEHPA) and LIX 984 diluted with *n*-heptane at equilibrium using a polysulfone hollow-fiber membrane module. With a 0.6 mol/L DEHPA-10% (v/v) LIX 984 solution, a 90.5% extraction of zinc and a 93.70% extraction of copper were obtained after 180 min [6]. From the above studies, oximes still have lower copper extraction and slow kinetics.

In recent years, various sulphur containing reagents such as bis(2,4,4-trimethylpentyl)monothio phosphinic acid (CYANEX302) and bis(2,4,4-trimethylpentyl)dithio phosphinic acid (Cyanex 301) have received considerable attention both for their ability to extract soft transition metal ions [7,8] and for their unparalleled ability to differentiate between chemically similar trivalent lanthanides and actinides [9,10]. Their acidic ionization constants in water increased and the values of equilibrium pH in metal ion extraction process became lower [11].

The degree of association of sulfur containing extractants is strongly dependent upon the nature of the donor atoms [12]. This dependence on the size of the donor atom suggests that the asso-

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ciation is mainly due to steric factors, where less-strained ligand bridges replace four-membered chelate rings; strain in the ring increases with decreasing the radii of the donor atoms. Zucal et al. [13] reported that di-*n*-butyldithiophosphoric acid exists as a monomer. Baldwin and Higgins showed that dibutylphosphoric acid exists as a dimer, di-*n*-butyldithiophosphoric acid is a monomer and the corresponding thio acid exhibits an intermediate degree of association [14]. Cote and Bauer [15] and Levin et al. [16] observed that dithiophosphoric acids are monomeric, while monothiophosphoric acids are usually dimeric. In the same manner, Tait [17] and Sole and Hiskey [7] determined that CYANEX 272 and CYANEX 302 form dimers but Cyanex 301 is monomeric.

Recently, these extractants have been successfully employed for the extraction and separation of various metal ions [17–31]. To date, few studies of copper extraction by Cyanex 301 have been published. Sole and Hiskey [7] explained the extraction of copper from sulfate media. They found that copper extraction is strongly dependent upon sulfur substitution in the phosphinic acid and complete extraction of copper by CYANEX 302 and Cyanex 301 occurred below pH 0. Also, they reported that copper is strongly complexed by CYANEX 302 and Cyanex 301 at low pH. So, extreme conditions are required to shift the pH dependent extraction equilibrium in the reverse directions. Even the use of concentrated (18 M) H<sub>2</sub>SO<sub>4</sub> does not strip any copper from Cyanex 301; 13.5 M acid is required to achieve a reasonable level of stripping from CYANEX 302. A significant disadvantage of the use of such concentrated acids is their effect on viscosity of the organic phases, discoloration, and phase separation deterioration.

Synergistic effects are an important phenomenon in the solvent extraction and have been studied extensively. Synergistic enhancements of cobalt and nickel extraction from chloride and sulfate media with mixtures of Cyanex 301 and amine extractants have been observed [32,33]. A large synergistic effect on the stripping kinetics and efficiencies of cobalt and nickel from was also observed. The binary extractant systems also exhibited quantitative cobalt and nickel extraction. Iberhan and Wiśniewski [34] studied the synergistic effect of Cyanex 301 and Cyanex 925 on the extraction of arsenic(III) and arsenic(V) from sulfate medium. The effect of Cyanex 301 on the extraction of lead by CYANEX 302 was observed by Menoyo et al. [35].

The data on synergistic extraction of copper by Cyanex 301 are limited. So, the present research deals with the synergistic extraction of copper from sulfate medium with mixtures of Cyanex 301 and LIX 984 in iso-dodecane, in attempts to improve the stripping efficiency of copper from Cyanex 301 systems. The effects of aqueous acidity, extractant concentration, the ratio of two extractants, mixing time and speed, and experimental temperature on the extraction behavior were examined. Furthermore, the number of the extraction stages was determined by Mc-Cabe Thiele diagram.

## 2. Experimental

### 2.1. Apparatus and reagents

Solvent extraction experiments were carried out in 125 mL glass bottles, which were placed in a thermostated reciprocating shaker for a certain time at 218 rpm. Hitachi Z8100 atomic absorption spectrophotometer (AAS) was used for the measurement of copper ion concentrations in the aqueous phases. Metrohm 632 pH meter was used for pH measurements. Stock solution of copper ions was prepared using the appropriate amount of CuSO<sub>4</sub>·5H<sub>2</sub>O salt. Cyanex 301 was supplied by Cytec Canada Inc. and used without further purification. Cyanex 301 was considered to be 77.2% bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HR), according to the information in the Cytec brochure. LIX<sup>®</sup>

984N, supplied by Henkel, is a 50% mixture of LIX<sup>®</sup> 84 and LIX<sup>®</sup> 860 (mixtures of 5-dodecylsallylaldoxime and 2-hydroxy-5-nonyl-acetophenone oxime) with the average molecular weight of 270. It was used as received. The solvent isododecane with a purity product 98% was used as a diluent was supplied by Gefachem-ProchemierLeverkusen with the main component 2,2,4,6,6-entamethylheptane. The extractants were diluted to a desired concentration with the hydrocarbon solvent isododecane.

### 2.2. Procedure

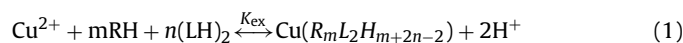
For the equilibrium experiments, 30 mL of aqueous and 5 mL organic phases were mixed and shaken for 30 min although it was proved that the extraction was achieved within 5 min at 303 + 1 K (except for the temperature experiments), which was sufficient for equilibrium attainment. The organic phases contained Cyanex 301 in the concentration range from 0.0184 to 0.285 M in isododecane with constant concentration of LIX<sup>®</sup> 984N (0.1708 M) was applied to study the effect of Cyanex 301 concentration. On the other hand, to study the effect LIX<sup>®</sup> 984N concentration, experiments were done by changing LIX<sup>®</sup> 984N concentration in the range from 0.0337 to 0.1685 M with constant Cyanex 301 concentration (0.149 M). Sulfuric acid concentration in the aqueous phase was varied from 0.5 to 8 M, whereas copper concentration was varied from 200 to 1000 ppm. Synergistic mixture of Cyanex 301–LIX<sup>®</sup> 984N ratios was varied from 0.0119–0.2384 M for Cyanex 301, and LIX<sup>®</sup> 984N (0.0673–0.269 M). After phase separation, the concentration of copper ions in the aqueous phase was determined by AAS. The concentration of metal ions in the organic phase was determined by mass balance. The concentrations were used to obtain the distribution ratio, *D*, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase. The aqueous/organic phase ratio was studied at a range from 1/10 to 20/1. Maximum loading capacity of 0.149 M Cyanex 301–0.1722 M LIX<sup>®</sup> 984N mixture was determined by repeatedly contacted of organic solution with fresh aqueous solution for several times. This data is used to determine the number of stages for copper extraction using Cyanex 301/LIX<sup>®</sup> 984N synergistic mixtures by Mc-Cabe Thiele diagram.

## 3. Results and discussions

### 3.1. Extraction mechanism of copper with Cyanex 301 and LIX<sup>®</sup> 984N and their mixture

The influence of variation in the Cyanex 301 concentration on the extraction behavior of copper ions was examined by changing Cyanex 301 concentration (0.0184–0.285 M) and keeping the metal and acid concentrations constant at 0.0065 and 0.5 M, respectively. From the obtained data, it is observed that the equilibrium time is 2 min for all Cyanex 301 concentrations. With increasing extractant concentration an increase in the extraction of copper was observed.

The extraction of Cu<sup>2+</sup> by the binary mixture of Cyanex 301 (RH) and LIX<sup>®</sup> 984N (LH) can be expressed by the following equations:



$$K_{\text{ex}} = \frac{[\text{Cu}(\text{R}_m\text{L}_2\text{H}_{m+2n-2})][\text{H}^+]^2}{[\text{Cu}^{2+}][\text{RH}]^m[(\text{LH})_2]^n} \quad (2)$$

The distribution ratio *D* defined as:  $D = \frac{[\text{Cu}^{2+}]_{\text{org.}}}{[\text{Cu}^{2+}]_{\text{aq.}}} = \frac{[\text{Cu}(\text{R}_m\text{L}_2\text{H}_{m+2n-2})]}{[\text{Cu}^{2+}]}$

Where the subscript org. denotes the species in the organic phase, aq. denotes the species in the aqueous phase, and, *K<sub>ex</sub>* is

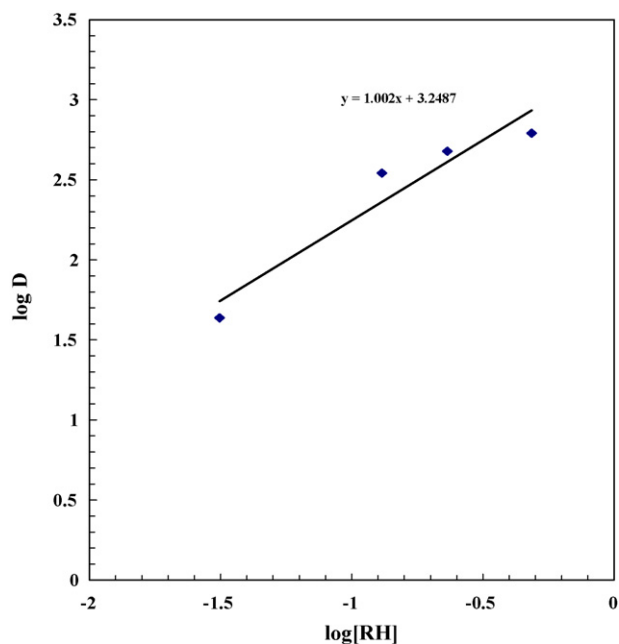


Fig. 1. log [RH] vs. log  $D$  for copper extraction by Cyanex 301 at 0.5 M  $H_2SO_4$ ,  $[Cu^{2+}] = 200$  ppm.

the extraction equilibrium constant.

$$K_{ex} = \frac{D[H^+]^2}{[RH]^m[(LH)_2]^n} \quad (3)$$

Where for constant organic volumes the balance of the free active oxime and Cyanex 301 concentration are calculated according to Eqs. (4) and (5), respectively:

$$[(LH)_2]_{org.} = [(LH)_2]_{org.}^0 - [Cu(R_mL_{2n}H_{m+2n-2})]_{org.} \quad (4)$$

$$[RH]_{org.} = [RH]_{org.}^0 - [Cu(R_mL_{2n}H_{m+2n-2})]_{org.} \quad (5)$$

By taking the logarithm of Eq. (3) and rearrangement:

$$\log D = \log K_{ex} + 2 \log [H^+] + m \log [RH] + n \log [(LH)_2] \quad (6)$$

A set of experiments has been done with different concentrations of Cyanex 301 (RH) and constant LIX<sup>®</sup> 984N, (LH)<sub>2</sub>, concentration. The coefficient  $m$ , is determined by slope analysis of the data obtained by varying Cyanex 301 concentration while the concentration of LIX<sup>®</sup> 984N constant. It is clear from the plot of log ( $D$ ) vs. log [RH] (Fig. 1) that at a constant aqueous acidity and LIX<sup>®</sup> 984N concentration, only one RH molecule is attached to the synergistic species extracted into the organic phase.

In the same way, Slope analysis method was applied for LIX<sup>®</sup> 984N extractant by plotting the logarithmic relationship of  $D$  vs. the concentration of the free active substance ( $[(LH)_2]$ ), LIX<sup>®</sup> 984N, as shown in Fig. 2. Linear relation was attained with slope of 1.038, confirming that one dimeric LIX<sup>®</sup> 984N molecule is involved in the extracted complex of  $Cu^{2+}$ . LIX<sup>®</sup> 984N dissolved in heptane [4,5] observed a similar trend in the extraction of Cu (II).

As shown in Fig. 3, the plots of log  $D$  vs.  $pH_{eq.}$  at constant synergistic mixture concentration (0.149 M Cyanex 301/0.1685 M LIX<sup>®</sup> 984N) gives a straight line with a slope of about 2.0, indicating the release of two hydrogen ions to the aqueous phase. Based on the preceding results (Figs. 1–3), the extraction equilibrium of copper from sulfuric acid solutions with Cyanex 301 and LIX<sup>®</sup> 984N may be represented as:

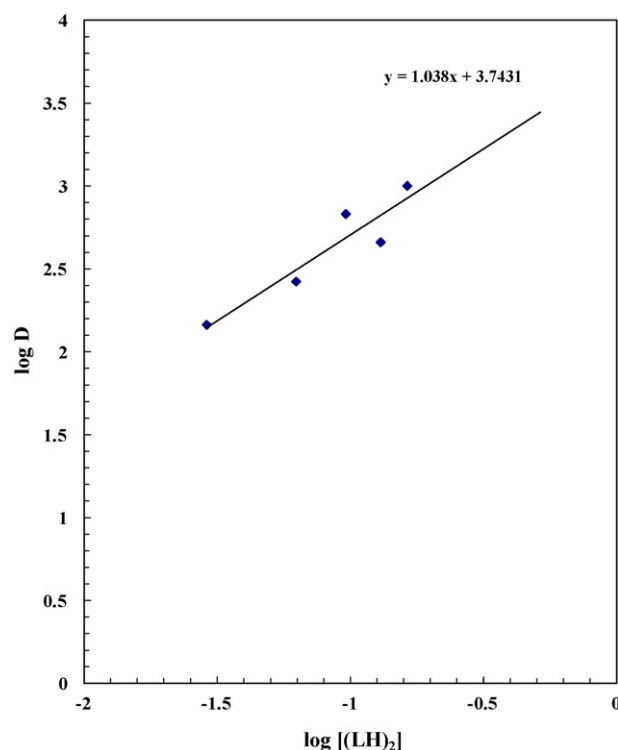


Fig. 2. log  $[(LH)_2]$  vs. log  $D$  for copper extraction by LIX<sup>®</sup> 984N at 0.149 M Cyanex 301, 0.5 M  $H_2SO_4$ ,  $[Cu^{2+}] = 200$  ppm.

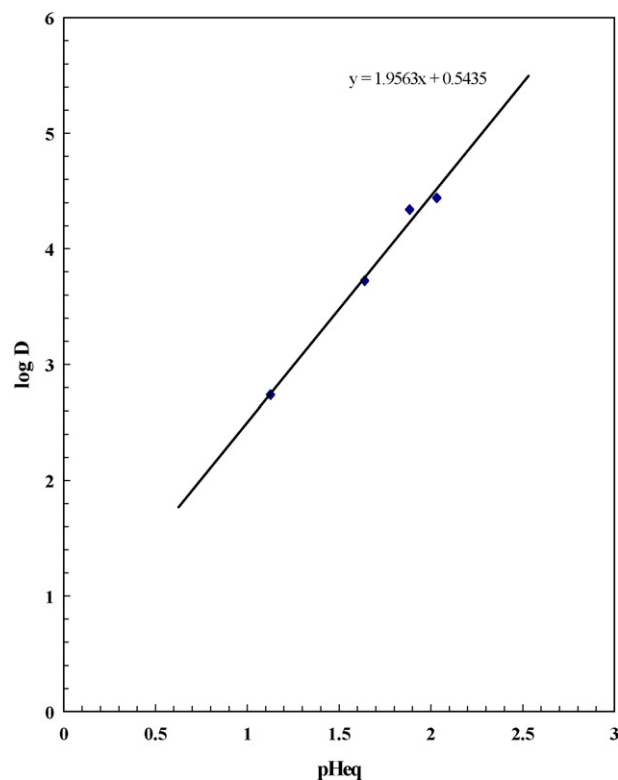
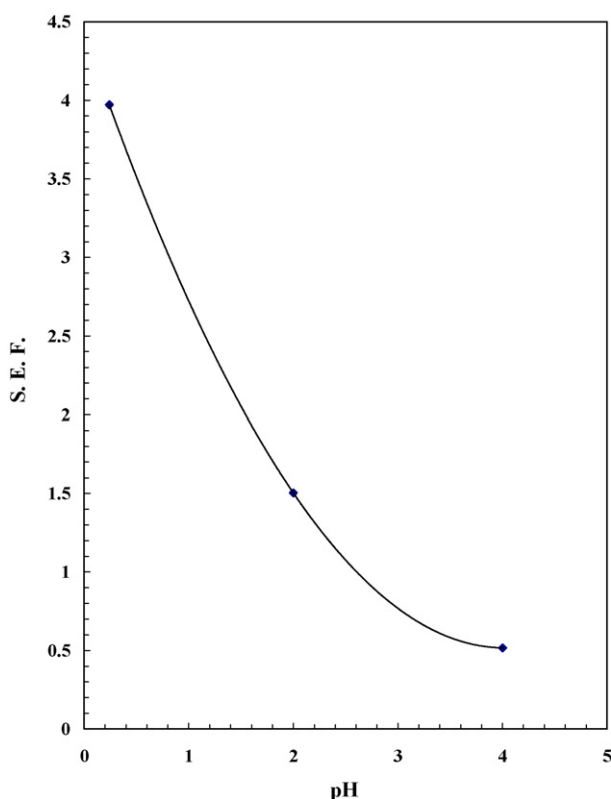
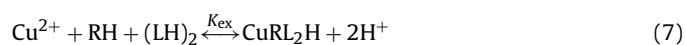


Fig. 3. Log  $D$  vs.  $pH_{eq.}$  plots for extraction of copper by a mixture of 0.149 M Cyanex 301/0.1722 M LIX<sup>®</sup> 984N at 0.5 M  $H_2SO_4$ ,  $[Cu^{2+}] = 200$  ppm.



**Fig. 4.** Synergistic enhancement factor (S.E.F.) as a function of pH for copper extraction by 0.149 M Cyanex 301–0.1708 M LIX® 984N mixture at 0.5 M H<sub>2</sub>SO<sub>4</sub>, [Cu<sup>2+</sup>] = 200 ppm.

Taking the slopes of the relation between  $\log [RH]$  and  $\log [(LH)_2]$  versus  $\log D$ ,  $m = 1$  and  $n = 1$ . Then Eqs. (1)–(3) become:



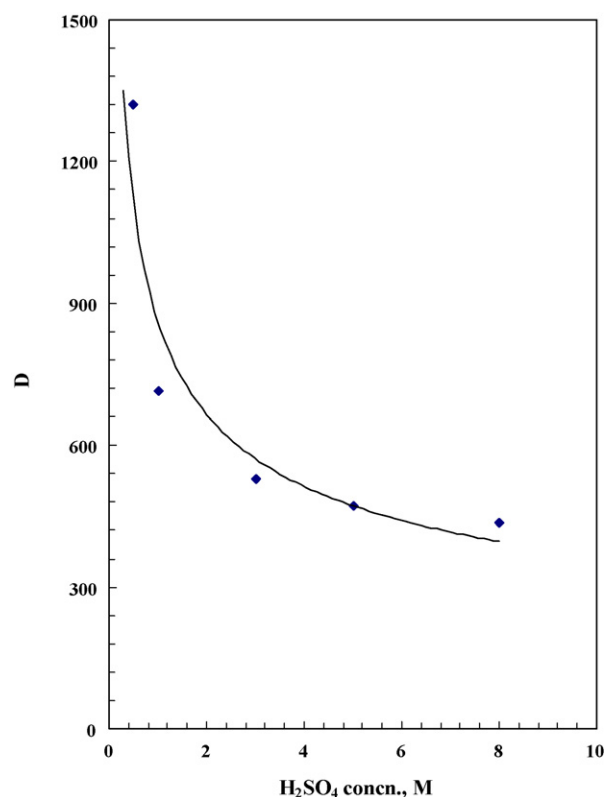
$$K_{ex} = \frac{[CuRL_2H][H^+]^2}{[Cu^{2+}][RH][(LH)_2]} \quad (8)$$

$$K_{ex} = \frac{D[H^+]^2}{[RH][(LH)_2]} \quad (9)$$

At a variety of aqueous phase acidity the synergistic enhancement factor, S.E.F., which is defined as  $S.E.F. = D_{12}/(D_1 + D_2)$  [36–38], is calculated and plotted in Fig. 4. With Cyanex 301/LIX® 984N binary system, considerable synergistic enhancement in the extraction of copper was observed. Moreover, S.E.F. was greatest at lower aqueous acidity, which suggests that the maximal synergistic enhancement could be obtained at more acidic solutions. But at higher pH values, little synergistic effects obtained.

### 3.2. Effect of synergistic mixture composition on copper extraction

Binary extractants operate at lower pH values than cation-exchange extractants and at higher temperatures and concentra-



**Fig. 5.** Effect of sulfuric acid concentration on copper distribution coefficient by 0.149 M Cyanex 301/0.1708 M LIX® 984N mixture.

tions than oxygenated reagents. Subsequently, less time is required to reach equilibrium than with hydroxyoximes [39]. So, synergistic extraction of copper from 0.5 M sulfuric acid solutions with mixtures of Cyanex 301 (0.0596–0.2384 M), and LIX® 984N (0.0673–0.2696 M) into iso-dodecane has been investigated. At a variety of extractant concentrations the distribution ratio and synergistic enhancement factor, S.E.F., are listed in Table 1. With mixtures of Cyanex 301 and LIX® 984N, considerable synergistic enhancement in the extraction of Cu<sup>2+</sup> was observed. Moreover, S.E.F. was greatest with the mixtures of 0.0596 M Cyanex 301 and 0.2696 M LIX® 984N, which suggests that at a ratio of Cyanex 301 to LIX® 984N of 1–5, the maximal synergistic enhancement could be obtained.

### 3.3. Effect of sulfuric acid concentration

The effect of sulfuric acid concentration on the extraction of 0.0065 M Cu(II) was studied using 0.149 M Cyanex 301/0.1708 M LIX® 984N mixture. Sulfuric acid concentration (0.5–8.0 M) has been studied. The data are presented in Fig. 5 as a function of Cu distribution ratio. Data obtained showed inverse dependence. Cu distribution ratio decreased sharply from 1321 at 0.5 M H<sub>2</sub>SO<sub>4</sub> to 670 at 1 M H<sub>2</sub>SO<sub>4</sub>. Increasing acid concentration to 8 M has a slight negative effect on copper distribution ratio.

**Table 1**

Distribution ratios and synergistic enhancement factors (S.E.F.) of copper with mixtures of Cyanex 301 and LIX® 984N (pH, 0.24; [Cu<sup>2+</sup>] = 500 ppm).

Cyanex 301, M	LIX® 984N, M	Cyanex 301 - LIX® 984N	D1	D2	D12	S.E.F.
0.0596	0.2696	0.0596–0.2696	258	8.1	1321.7	4.97
0.149	0.1685	0.149–0.2696	551	9.21	1650	2.94
0.2384	0.0673	0.2384–0.0673	570	3.5	2170	3.78

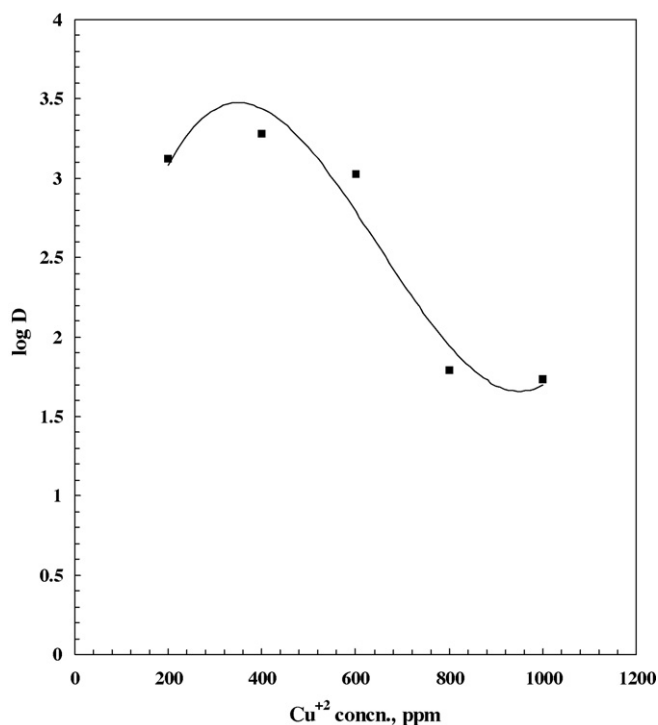


Fig. 6. log  $D$  vs. copper ion concentration using 0.149 M Cyanex 301/0.1708 M LIX® 984N mixture at 0.5 M  $H_2SO_4$ .

#### 3.4. Effect of initial copper ion concentration

To study the effect of copper ion concentration on the distribution ratio of Cu(II) ( $D$ ), its concentration was varied from 200 to 1000 ppm keeping the  $H_2SO_4$  and synergism concentration constant at 0.5 and 0.149 M Cyanex 301–0.1708 M LIX® 984N, respectively. Log  $D$  versus initial  $Cu^{2+}$  concentration is plotted in Fig. 6. It is observed that  $D$  increased as  $Cu^{2+}$  increased from 200 to 600 ppm and then sharply decreased when the initial content of zinc increases up to 1000 ppm.  $D$  reached to 55 for 1000 ppm solution.

#### 3.5. Effect of temperature on copper extraction by Cyanex 301, LIX 984, and their mixture

The effect of temperature on the extraction of copper ions by 0.149 M Cyanex 301, 0.1708 M LIX® 984N, and 0.149 M Cyanex 301/0.1708 M LIX® 984N mixture have been studied at different temperatures (303–323 K) and pH 0.24. The results are illustrated in Fig. 7. Great influence of temperature was observed for Cyanex 301 extraction systems. In the case of LIX® 984N, the higher temperature leads to a slight increase in the copper extraction at this aqueous acidity. The systems with Cyanex 301–LIX® 984N mixture, show a very slight temperature influence.

Log  $D$  vs.  $1/T$  was plotted to estimate the enthalpy change ( $\Delta H$ ) of the extraction process (Fig. 8) from the slope of the plot using the Van't hoff equation in the form [39]:

$$\log D = -\frac{\Delta H}{2.303R} \frac{1}{T} + C \quad (10)$$

where  $R$  is the gas constant and  $C$  is a constant for a solution.

The positive values of  $\Delta H$  showed that extraction with Cyanex 301, LIX® 984N, and Cyanex 301–LIX® 984N synergistic mixture is endothermic. Large heat effects are found to the extracted complex formed between the Cyanex 301 and the copper ions where  $\Delta H$  is calculated and found to be 30.5665 KJ/mol. On the other hand,

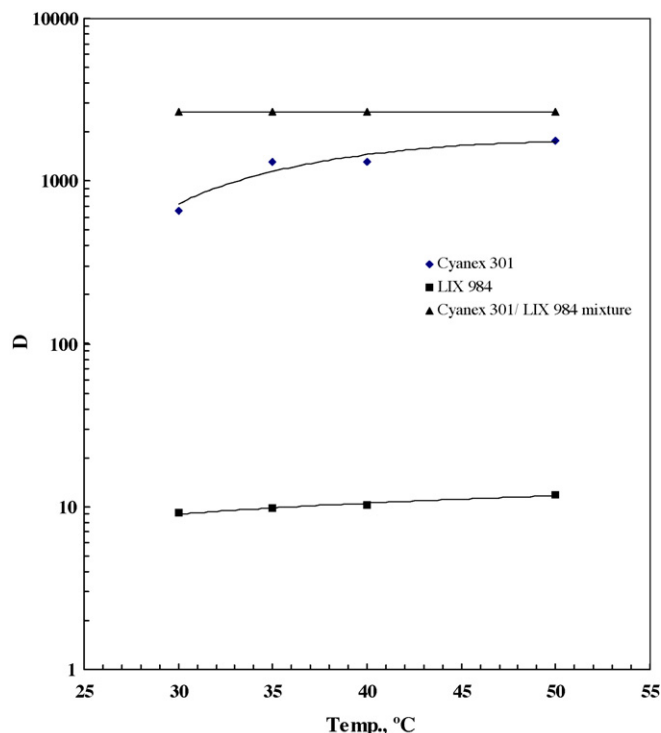


Fig. 7. Effect of temperature on copper distribution coefficient by 0.149 M Cyanex 301, 0.1708 M LIX® 984N, and 0.149 M Cyanex 301/0.1708 M LIX 984 mixture, at pH 0.24.

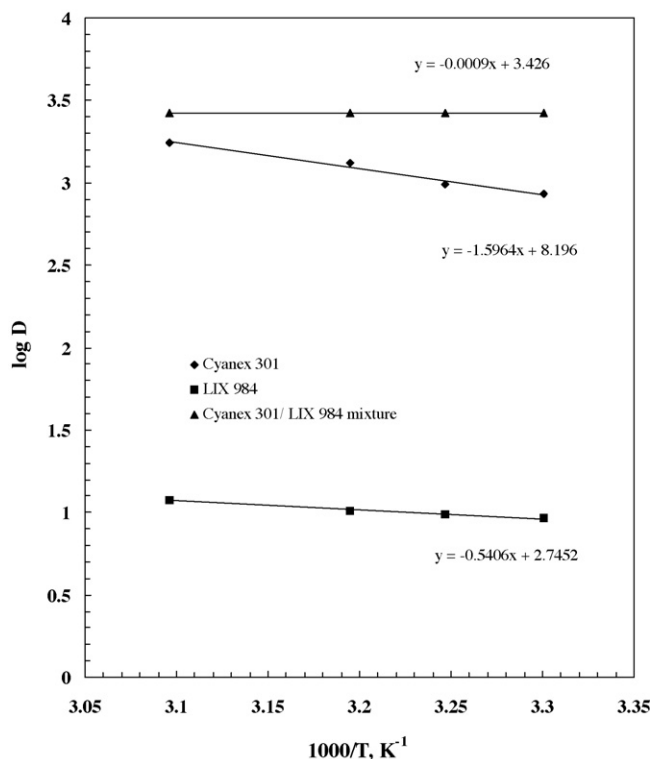


Fig. 8. Log  $D$  vs.  $1000/T$  for copper extraction using 0.149 M Cyanex 301, 0.1708 M LIX® 984N, and 0.149 M Cyanex 301/0.1708 M LIX® 984N mixture, at pH 0.24.

**Table 2**

Effect of diluent on the extraction of  $\text{Cu}^{2+}$  at 0.5 M  $\text{H}_2\text{SO}_4$  using 0.149 M Cyanex 301/0.1713 M LIX® 984N.

Diluent	Dielectric constant	Extraction (%)
Iso-dodecane	2	99.54
<i>n</i> -Pentane	1.8	96.4
<i>p</i> -Xylene	2.3	98.5
Toluene	2.4	97.9
<i>n</i> -Heptane	1.9	98.8

the low values of  $\Delta H$  for extraction of copper(II) with LIX® 984N ( $\Delta H = 10.35$  kJ/mol.) is indicative of relatively smaller heat effects involved in the formation of the extracted complex. It is interesting to find that the enthalpy change of the synergistic extraction process is very small in the experimental temperature range. The value of  $\Delta H$  is calculated to be 0.017 kJ/mol in the temperature range of 303–323 K. It indicates that the dissociation of the metal ion and the formation of the synergistic complex are almost equally responsible for the small value of the enthalpy change in this temperature range. Similar behavior was reported by many authors for yttrium extraction by Cyanex 272 [40] and Cyanex302 [41], germanium extraction with Cyanex 301/Cyanex 923 [42], extraction of Hafnium by Cyanex 301 [31], and copper extraction by LIX reagents [4].

### 3.6. Effect of the nature of diluent

A number of solvents namely toluene, *n*-pentane, *p*-xylene, and *n*-heptane were employed to discern the effect of varying nature of the organic diluents on the extraction of  $\text{Cu}^{2+}$ . From the results depicted in Table 2, no correlation between dielectric constant and percent extraction was observed. The extraction of copper ions varies with the nature of diluents and follows the order ( $E\%$ ): iso-dodecane (99.54) > *n*-heptane (98.8) > *p*-xylene (98.5) > toluene (97.9) > *n*-pentane (96.4).

### 3.7. Loading capacity of Cyanex 301–LIX 984 synergistic mixture

An aliquot 15 mL of 0.149 M Cyanex 301/0.1708 M LIX® 984N synergistic mixture were repeatedly contacted with 60 ml of 0.5 M  $\text{H}_2\text{SO}_4$ , 200 ppm  $\text{Cu}^{2+}$ , pH 0.24, and 10 min mixing time. After equilibrium, phases were separated and  $\text{Cu}^{2+}$  was analyzed in aqueous phase. The concentration of  $\text{Cu}^{2+}$  in the organic phase was calculated by mass balance. The synergistic mixture reached maximum loading after 13 contacts. From the data, it was found that the maximum capacity reached 18.6 g/lit. In order to predict the number of the theoretical stages required for copper extraction, a McCabe–Thiele diagram was constructed (Fig. 9). From this figure, it is clear that complete extraction of 400 ppm copper with a synergistic mixture is reached after two extraction stages.

### 3.8. Effect of aqueous–organic ratio

The effect of a volume ratio of aqueous phase to organic phase on the extraction of copper was studied from 0.156 to 20 (Fig. 10). The increase in the treatment ratio results simultaneously in an increase of the distribution ratio. When the aq./org. ratio increases from 0.156 to 20 the distribution ratio increase from 13.6 to 1946 and still has a very high extraction %. From these results, Cyanex 301–LIX® 984N synergistic mixtures showed a very strong synergism to treat large volumes of aqueous copper solutions and high concentrated loaded organic phase can be attained.

### 3.9. Stripping of copper from synergistic solution

The effect of the concentration of the stripping agent, HCl, on the percentage of Cu(II) stripped, extracted in an organic phase con-

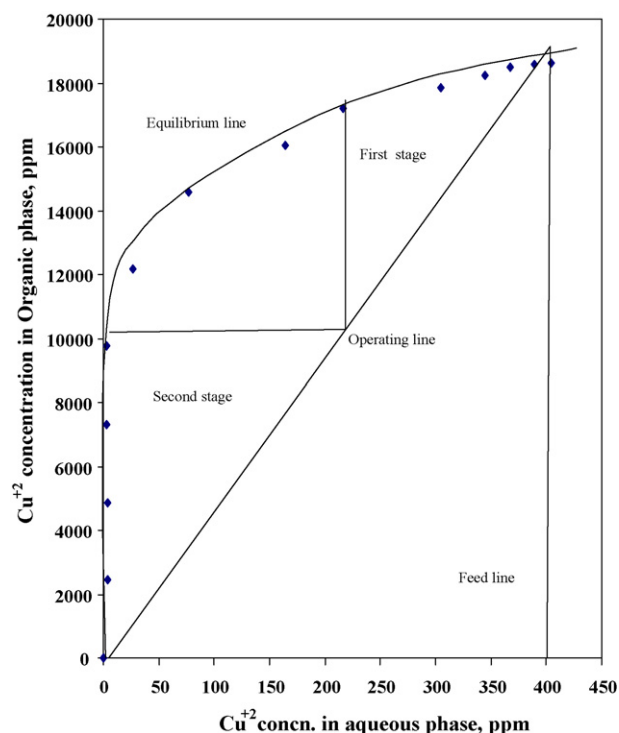


Fig. 9. McCabe–Thiele diagram for the extraction of copper using 0.149 M Cyanex 301/0.1708 M LIX® 984N mixture at pH 0.24 and 400 ppm copper ion concentration.

sisting of 0.149 M Cyanex 301/0.1708 M LIX® 984N, was examined. Fig. 11 illustrates the dependency of the stripping of Cu(II) on the concentration of HCl. The percentage of Cu(II) stripped from the organic phase increased with increasing HCl concentration, showing a maximum value of 90.65% at 6 M HCl. Further increases in HCl

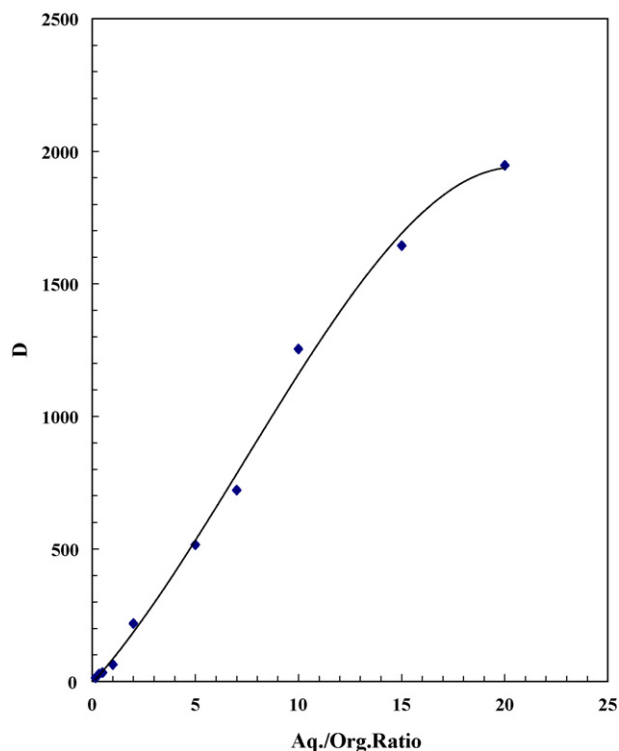


Fig. 10. Effect of aqueous/organic ratio on copper distribution coefficient using Cyanex 301–LIX® 984N mixture at pH 0.24 and 400 ppm  $\text{Cu}^{2+}$ .

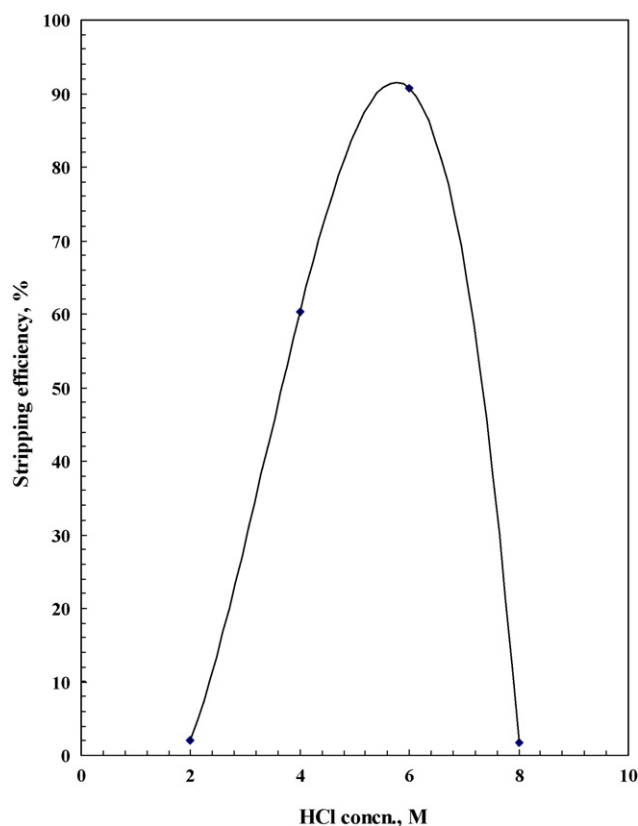


Fig. 11. Effect of HCl concentration on stripping % of copper from 0.149 M Cyanex 301/0.1708 M LIX® 984N loaded organic phase.

concentration decreased the percent stripping of Fe(III). This finding suggests that stripping of Cu(II) with less concentrated HCl solution is to be expected when using a solvent mixture of Cyanex 301–LIX® 984N. The sharp decrease in the percentage of Cu(II) stripped with HCl concentrations above 6 M agrees with the results obtained by Hirato et al. [43] for the stripping of Fe(III), which was extracted with a mixture of D2EHPA–TBP. This fact may suggest that the formation of chloro-complexes of Cu(II) become significant with increasing HCl concentration. The chloro-complexes, thus formed, are easily re-extracted with Cyanex 301–LIX® 984N.

#### 4. Conclusions

The extraction behavior of copper from sulfuric acid solutions has been investigated using Cyanex 301, LIX® 984N, and Cyanex 301–LIX® 984N mixtures. Mixtures of Cyanex 301 and LIX® 984N show evident synergistic effects when used to extract Cu<sup>2+</sup> at comparatively lower concentration of Cyanex 301, and the maximal synergistic enhancement could be obtained at a ratio of Cyanex 301 to LIX® 984N of 1 to 1. That is, the mixture has higher extraction efficiency than those of both Cyanex 301 and LIX® 984N for more acidic solutions. The distribution coefficients are influenced by the initial copper ion concentration in the feed solution as well as by the temperature. With increasing concentration of copper ions in the feed phase, the distribution coefficient decreases. From the data obtained, temperature has a great influence with individual systems of Cyanex 301 and LIX® 984N. From Mc-Cabe Thiele diagram, two extraction stages are sufficient for complete removal of copper from more acidic aqueous solutions by 0.149 M Cyanex 301–0.1708 M LIX® 984N synergism. The stoichiometry of the extracted complex with the synergistic mixture revealed that CuRL<sub>2</sub>H complex was formed. Stripping of Cu(II) from the loaded organic phase was successfully performed using 6 M HCl solutions.

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