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Solvent Extraction of Copper from Chloride Solutions with LIX 984N

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Abstract

Copper was recovered from synthetic chloride solutions using solvent extraction. Copper-chloro complexes were observed by plotting speciation diagrams at various pH values. Copper was completely extracted by hydroxyoxime LIX 984N in kerosene at an equilibrium pH of 2.5 using 10 % v/v LIX 984N. The effect of equilibrium pH, copper concentration, chloride concentration on copper extraction were examined. Effect of equilibrium pH on distribution coefficient, Influence of chloride concentration at lower pH values and Influence of chloride concentration at higher pH values were determined to find out formation of copper-chloro complexes and their effect on copper extraction. The loaded organic phase was stripped using 1.5 M H2SO4 in 2 stages to regenerate extractant LIX 984N. 95.96 % and 91.32 % copper was stripped from loaded organic phase from solutions containing 528 ppm copper and 1044 ppm copper respectively.

Keywords*: solvent extraction, copper, LIX 984N, Copper-chloro species*

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I. INTRODUCTION

Solvent extraction of metals has been used for a long time by chemists and engineers. Solvent extraction was used for the first time in hydrometallurgy to satisfy special materials requirements of nuclear energy during World War II. A plant was constructed for uranium extraction using ether and then stripped with water to get concentrated solution of pure uranyl nitrate. The second step took place in the 1960s when solvent extraction was applied to extract copper. In 1942, in order to supply high purity uranium required in the Manhattan Project, the ether extraction process was used first time on an industrial scale [1]. Over the years, many non-nuclear applications of solvent extraction have been developed for plutonium, thorium, niobium, zinc, nickel, tantalum, zirconium, boron, beryllium and others. Solvent extraction is used mainly in large-scale industrial separations, analytical chemistry, pharmaceutical and biochemical industries. Solvent extraction of copper can be done in ferrous and non-ferrous metallurgical industries. In ferrous industries hydrochloric acid is used for pickling steel or non-ferrous metals. The waste pickle solution is treated for copper recovery using various organic extractants. Non-ferrous industries extract copper from nickel, iron or cobalt solutions using solvent extraction [2]. Solvent extraction technique for copper recovery from chloride media using various hydroxyoxime has been developed. The importance of extraction of copper from chloride media using hydroxyoxime was highlighted by Lakhshamanan and Lawson, 1975 [3]. Development of various hydroxyoxime is shown in figure 1.

LIX 984N is a blend of 50 % v/v aldoxime LIX 860N-I (5-dodecyl-salicylaldoxime) and 50 % v/v ketoxime LIX 84-I (2-hydroxy-5-nonyl-acetophenone oxime) and very suitable for copper recovery [5]. It is widely used because of its stable and active components, highly separation factor and high selectivity of copper at very low pH. LIX 984N can selectively extract copper from metal mixture.

The copper recovery from chloride solution has become important because of the development of chloride-based leaching in hydrometallurgy using hydroxyoximes [6]. Electronics industries, ore waters from metal producing plants, copper electroplating plants, copper radiator tubes, cupric chloride etchant are the main sources of generation of copper chloride solutions. Chloride extraction may offer advantages over sulfate system like higher extraction rate, easier leaching of complex chloride concentration, transfer of sulfur to elemental form, operation at mild conditions, lower operating cost [7]. Drawbacks of chloride system are some impurity such as silver is not completely removed from chloride solution and production of dendritic copper cathodes [8].

The present investigation is focused on recovery of copper from chloride solution using solvent extraction. Effect of parameters on copper extraction was examined. A very interesting result on formation of copper-chloro species at lower as well as on higher pH values is presented.

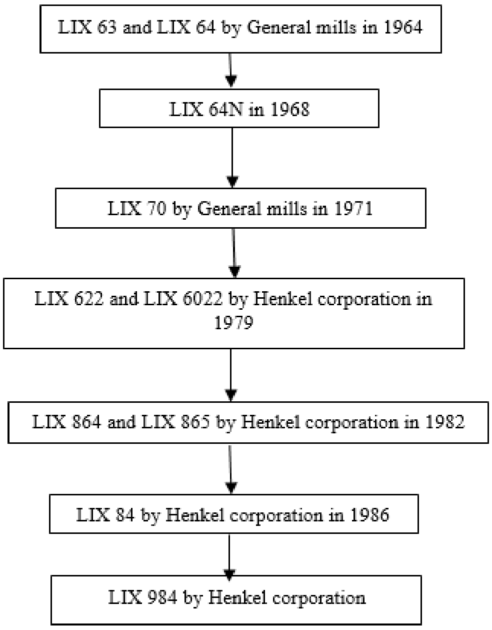

Figure 1: Development of various hydroxyoxime extractants [4]

II. MATERIALS AND METHODS

2.1 Materials

LIX 984N (BASF, Ireland) was used as copper extractant. Copper (II) chloride (AR grade, S.D. FINE CHEM LTD, Vadodara) was used to prepare aqueous phase. Virgin kerosene (Boiling point: 105-214 °C) used as a diluent supplied by Indian Oil Corporation Limited. Sulfuric acid, Sodium hydroxide, Sodium chloride used were of AR grade.

2.2 Methods

Copper solutions were prepared by dissolving the requisite amount of chloride salt in distilled water. pH was adjusted with sulfuric acid or sodium hydroxide and measured with HANNA HI 2215 pH meter. Extraction was carried out in conical flasks at equal organic and aqueous volumes (100 ml each) on a magnetic stirrer (Remi- RS 24BL) at 100 rpm and 30±2 °C. The organic phase for extraction of copper consisted of LIX 984N (10 % v/v) in kerosene as a diluent. pH adjustment before each equilibrium was done using sodium hydroxide. The concentration of metal was determined using Atomic Absorption Spectrometer (Chemito AA-203) for copper at 324.7 nm. The copper concentration in organic phase was calculated from mole balance. Stripping was performed using 1.5 M H_2SO_4 in 2 stages and the stripped phase was analyzed using Atomic Absorption Spectrometer (Chemito AA-203).

III. RESULTS AND DISCUSSION

Experiments were performed with two sets of solutions to check effect of parameters on copper extraction: (1) Solution containing 0.01643 M copper and 4 M chloride concentration (2) Solution containing 0.008309 M copper and 0.008 M chloride concentration. All results were generated at constant aqueous to organic ratio of 1:1.

3.1 Effect of equilibrium pH on copper extraction

Copper extraction was carried out using aqueous solution containing 0.01643 M copper and 4 M chloride concentration. The copper extraction with 10 % v/v LIX 984N as a function of pH was studied in pH range -0.08 to 2.5. Fig. 2 describes that copper extraction starts at -0.08 pH and quantitative extraction takes place at 2.5 pH. Copper was completely extracted at 2.5 pH.

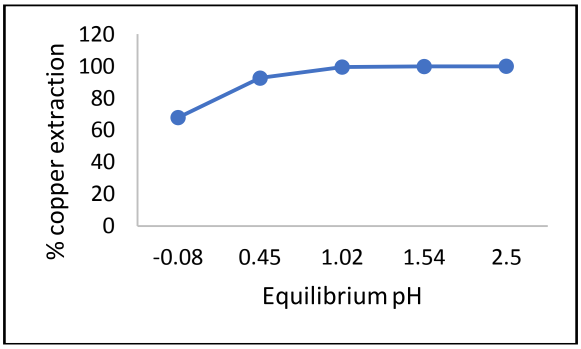

Figure 2: Effect of equilibrium pH on copper extraction

3.2 Effect of equilibrium pH on distribution coefficient

The copper extraction can be expressed by distribution ratio (D) with increase in pH values. Copper extraction from chloride media follows below mechanism:

$$Cu^{+2}{}_{(aqu)} + 2RH_{(org)} \longrightarrow R_2Cu_{(org)} + 2H^+ \qquad (1)$$

Where R = Extractant concentration

Slope of log D vs pH plot gives the value of extractant molecules which bind with extracted copper-chloro species [9]. The experimental data of copper distribution between organic and aqueous phase at different pH and varying copper concentration are reported in Table 1. From equation (1), the slope value of log D vs pH plot should be nearer to 2. Fig. 3 shows that the slope values are less than 2 for both the cases. Copper forms various five species (Cu^{+2}, $CuCl^+$, $CuCl_2$, $CuCl_3^-$, $CuCl_4^{2-}$) in chloride media [10]. Transfer of CuClR type species in organic phase lead to log D vs pH slope value less than 2 [3].

Table 1: Distribution coefficient values at various pH

	Copper concentration			
	0.008309 M Cu		0.01643 M Cu	
Stage	pH	log D	pH	log D
E1	-0.08	0.46	-0.08	0.32
E2	0.42	1.16	0.45	1.09
E3	1.6	3.35	1.02	2.27
E4	1.9	3.47	1.54	2.67
E5	2.43	3.58	2.5	3.50

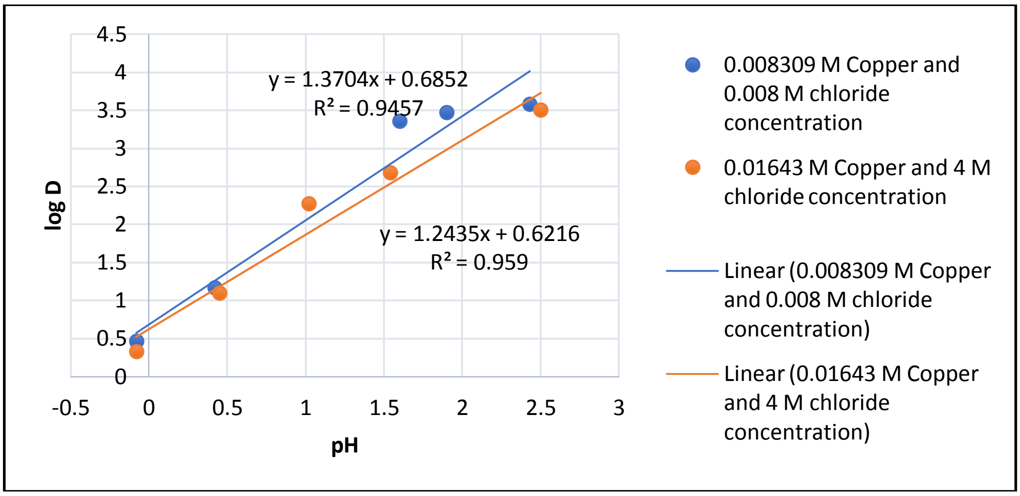

Figure 3: Effect of pH on distribution coefficient

3.3 Effect of copper concentration and equilibrium pH on copper extraction

Effect of various copper concentration as a function of pH on copper extraction was observed. Fig. 4 shows that even at -0.08 pH, LIX 984N extracts almost 67.8 % copper and 74.2 % copper for solution containing 0.01643 M and 0.008309 M copper concentration respectively. It was observed that higher copper concentration recovers less copper from chloride media with increase in pH. Quantitative loading of copper was found in both the cases beyond pH 1.02.

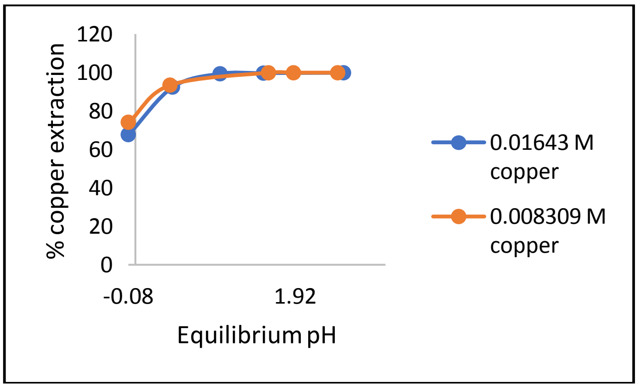

Figure 4: Effect of copper concentration on copper extraction

3.4 Effect of chloride concentration on copper extraction

Two sets were observed to study the effect of chloride concentration on % extraction of copper: (1) solution containing 0.008309 M copper and 0.008 M chloride concentration (2) solution containing 0.01643 M copper and 4 M chloride concentration. Fig. 5 explains that lower concentration of chloride increases the copper extraction with increase in pH value. Reference [6] confirmed the same result.

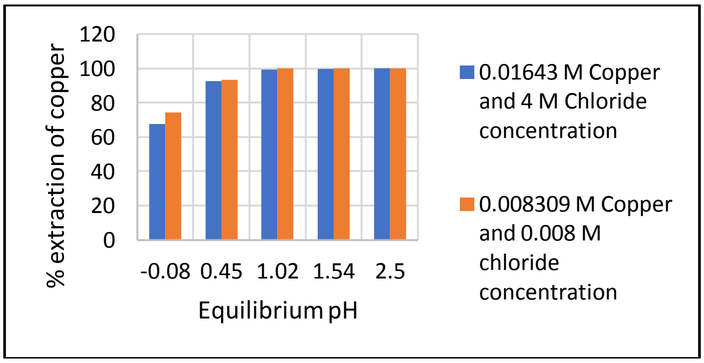

Figure 5: Effect of chloride concentration on copper extraction

3.5 Influence of chloride concentration at lower pH values

The chloride concentration at lower and higher pH values shows different results on copper extraction [11]. The slope value of log D vs pH shows formation of metal species in solution [12]. Table 2 dictates log D values at lower pH for two various copper concentrations.

Fig. 6 shows log D vs pH graph to evaluate copper species formation at lower pH range -0.08 to 1.6. Slopes increase with increase in chloride concentration at lower pH values.

Table 2: Distribution coefficient data at lower pH

	Copper concentration			
	528 ppm Cu		1044 ppm Cu	
Stage	pH	log D	pH	log D
E1	-0.08	0.46	-0.08	0.32
E2	0.42	1.16	0.45	1.09
E3	1.6	3.35	1.02	2.27

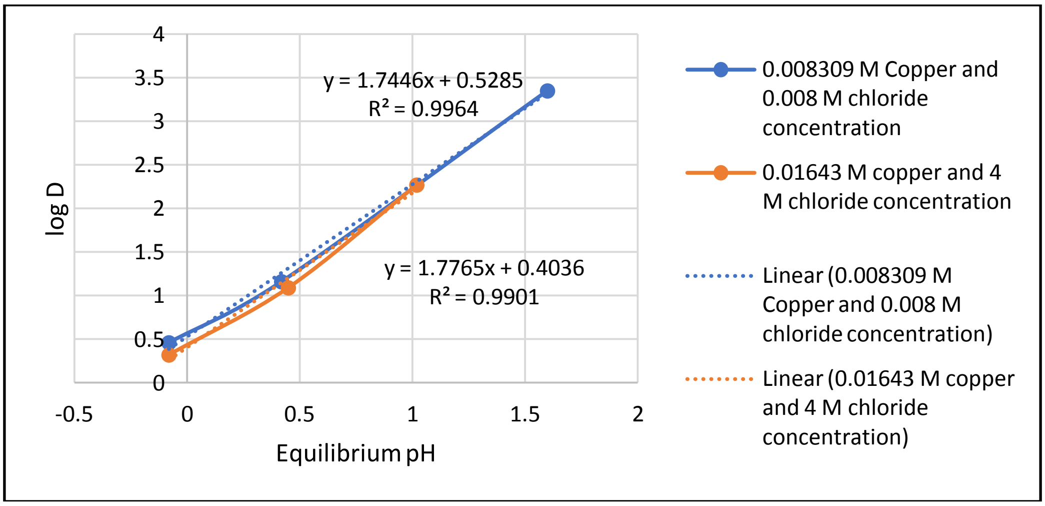

Figure 6: log D vs pH plot at lower pH values

It was found that LIX 984N extracts $CuCl_2$ type species at lower pH values as slope values are nearer to 2. Speciation diagram for $CuCl_2$ type species was drawn using Visual MINTEQ 3.0 software to verify the result. It was observed that $CuCl_2$ complex formation was higher in 4 M chloride solution at lower pH value as fraction of $CuCl_2$ depends on chloride concentration from Fig. 7.

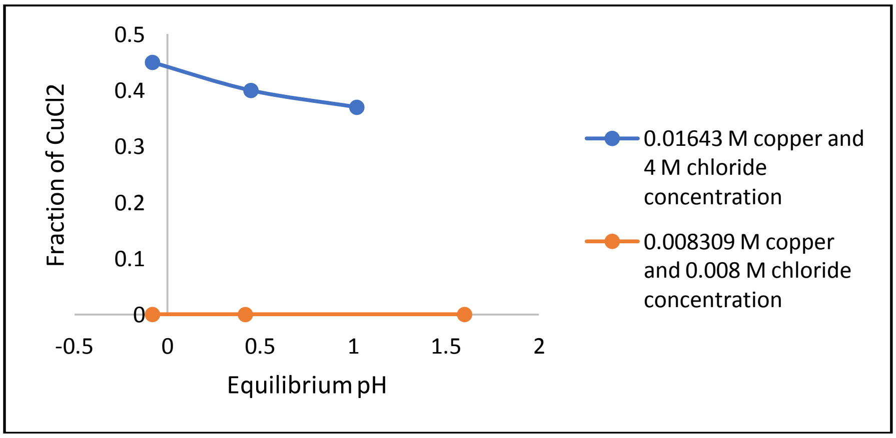

Figure 7: Speciation diagram of $CuCl_2$ species

3.6 Influence of chloride concentration at higher pH values

Effect of log D values on copper extraction at higher pH values are shown in Table 3. The slope values of log D vs equilibrium pH plot are indicated in Fig. 8. The slope for solution containing 4 M chloride concentration was 0.8353 which was nearer to 1. Fig. 9 shows speciation diagram for $CuCl^+$ species which confirms the formation of $CuCl^+$ species in solution containing higher chloride concentration at high pH values.

Table 3: Distribution coefficient data at higher pH

528 ppm Cu		1044 ppm Cu	
pH	log D	pH	log D
1.9	3.47	1.54	2.67
2.43	3.58	2.5	3.5
1.6	3.35	1.02	2.27

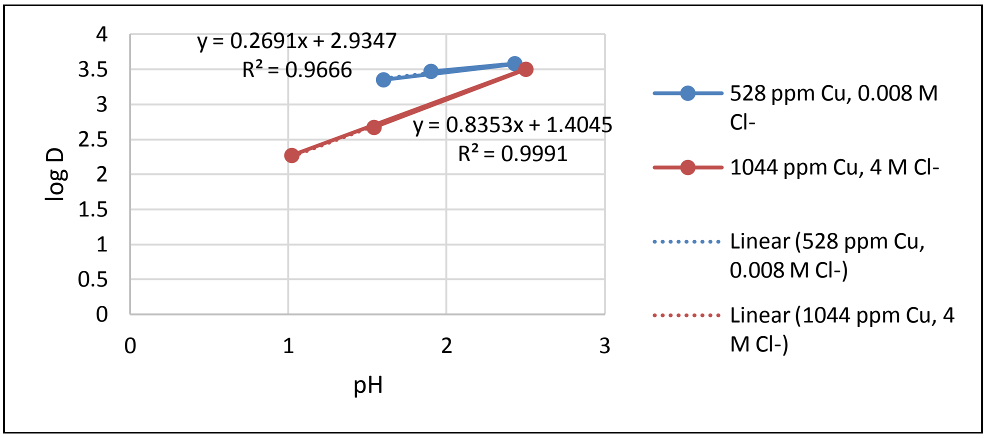

Figure 8: log D vs pH plot at higher pH values

The slope value for solution having 0.008 M chloride concentration was 0.2691. It was found that there was no formation of any copper-chloro complexes and only free cupric ion Cu^{+2} was present in solution. Speciation diagram for Cu^{+2} species was drawn to cross check the result. Fig. 10 shows that Cu^{+2} concentration was very high in solution containing lower copper and lower chloride concentration. The results confirmed that LIX 984N is unable to extract higher copper-chloride complexes such as $CuCl_3^-$ and $CuCl_4^{2-}$.

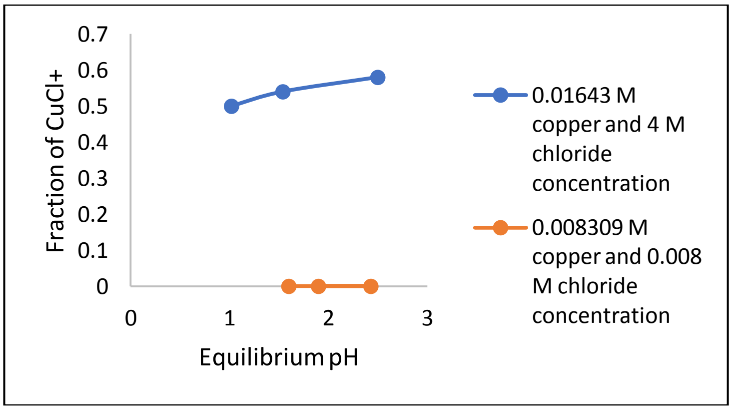

Figure 9: Speciation diagram of $CuCl^+$ species

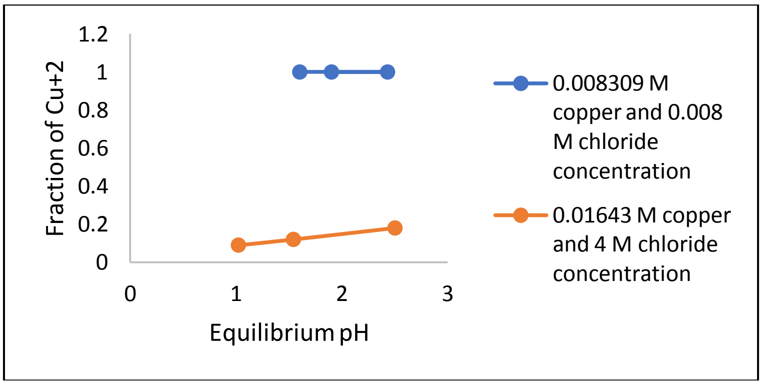

Figure 10: Speciation diagram of Cu^{+2} species

3.7 Stripping of copper from loaded organic phase

Two stage counter-current stripping of copper was carried out using 1.5 M H_2SO_4 at oil to aqueous phase ratio of 1. Results of the stripping experiments are tabulated in Tables 4 and 5. The aqueous phase was checked using AAS. After second stage stripping with 1.5 M H_2SO_4, the organic phase was found to contain up to 0.000346 M copper and 0.001426 M copper for solutions containing initially 0.008309 M copper and 0.01643 M copper respectively.

Table 4: Stripping result of 0.008309 M copper solution

% Stripping (for 0.008309 M Copper solution)	
Stage- I	**Stage-II**
91.23	95.96

Table 5: Stripping result of 0.01643 M copper solution

% Stripping (for 0.01643 M Copper solution)	
Stage- I	**Stage-II**
88.54	91.32

IV. CONCLUSION

Following conclusions can be inferred for copper extraction from chloride media using LIX984N extractant from experimental results and subsequent interpretation:

1. Copper can be extracted using LIX 984N even at very low pH values.
2. Copper concentration and chloride concentration both effect on copper extraction and formation of copper-chloro complexes. Higher chloride concentration depresses the copper extraction.
3. LIX 984N extracts $CuCl^+$ type species at higher pH values and $CuCl_2$ type species at lower pH values.
4. LIX 984N is unable to extract higher copper-chloro complexes such as $CuCl_3^-$ and $CuCl_4^{2-}$.
5. Influence of chloride concentration on higher and lower pH value gives better information about species formation.
6. Copper can be completely extracted from chloride solutions at 2.5 pH using 10 % v/v LIX 984N and 1:1 organic to aqueous ratio.
7. Organic phase can be successfully stripped with 1.5 M H2SO4 to regenerate LIX 984N.

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