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Liquid – Liquid Equilibrium between Aqueous and Organic Copper Solutions

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With the depletion of rich ore resources, hydrometallurgy is becoming more popular since it is suitable for lean ores as well as metal containing wastes. Taking place at normal temperature, it consumes less fuel, emits less gas and poses less risk of fire and explosion. In hydrometallurgy, solvent extraction is a typical technique to concentrate and/or purify the leachate obtained from ore leaching step. Although developments such as membrane contact extraction or electrically enhanced extraction can speed up the process and eliminate some technical obstacles such as phase separation, important performance indicators such as recovery or extract concentration are inherently dictated by liquid – liquid equilibrium (LLE). In this paper, we investigated the LLE between D2EHPA and feed solvent contains copper, a metal commonly found in e-waste. The equilibrium curves at well controlled pH were obtained. Although the importance of pH in equilibrium is well known, this is the first time its effect on the degree of polymerization (DoP) of copper complex is recognized and quantified: ten times reduction of proton concentration resulted in nearly ten times increase of DoP. The relationship between copper concentrations in aqueous and organic phase was strictly linear (in log scale), allowing accurate prediction of extraction efficiency. The pH of aqueous phase between 3.5 and 4 was found to be the appropriate condition for copper recovery.

1. Introduction

The ever-growing generation of electric and electronic waste (e-waste) presents a significant environmental challenge. Global e-waste generation increased 2.3 Mt annually, from 34 Mt in 2010 to 62 Mt in 2022 – equivalent to 7.8 kg per capita. According to Baldé et al. (2024), global e-waste generation is projected to be 82 Mt by 2030, which will cost $15 billion directly for treatment and $93 billion indirectly for coping with impacts on people and environment. Among the various materials found in e-waste, heavy metals such as copper (Cu), particularly in its Cu^{2+} form, pose a significant threat to both the environment and human health. Copper is widely used in electric and electronic devices such as printed circuit boards (PCBs), wires and connectors. Cu^{2+} ions are toxic to aquatic ecosystems and can disrupt microbial processes in soils, making their management crucial for environmental sustainability (Cui et al., 2024). Excessive level of copper in soil can inhibit plant photosynthesis (Xu et al., 2024) and root acquisition of nitrate (Feil et al., 2022). For human, prolonged exposure to high levels of copper, whether through water or supplements, may lead to severe health issues such as copper-induced oxidative stress (Fu et al., 2025) or cognitive impairment (Xu et al., 2025). From another point of view, e-waste is also a significant source of metals with economic value of $91 billion in 2022. Among these metals, copper values the most at $19 billion. However, only 22.3 % of e-waste was documented as properly collected and recycled, underscoring the urgent need for more efficient recycling processes at the regional level (Baldé et al., 2024).

Copper is primarily produced from high-grade copper sulphide ore by pyrometallurgy and from low-grade copper oxide ore by hydrometallurgy (Krishnan et al., 2021). The second method can be adapted for recovering copper from e-waste. In this method, solvent extraction plays a crucial role in the recovery and purity of both copper and discharged waste water. The process involves contacting an acidic aqueous solution containing copper

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ions with an organic solution containing a metal-selective extractant. The performance of the extractant directly influences the extraction efficiency. Some extractants like methyl isobutyl ketone or mesityl oxide are capable of extracting copper in aqueous solution at trace level and suitable for analysis but limitations such as long extraction periods (Singh and Dhadke, 2002) render them unsuitable for copper production. For the later purpose, organophosphorus acids and hydroxy oximes are important extractants for not only copper but also other metals (Noah et al., 2025; Balogun et al., 2025). Of these extractants, Di(2-ethylhexyl)phosphoric acid (D2EHPA) and its caustic salts diluted in organic diluent (paraffin, benzene) were commercialized thanks to the high load, low solvent loss and reasonable price.

For separation process design and calculation, equilibrium data are essential and works on the equilibria of water – copper – D2EHPA system have been published for decades. These data are limited to either very dilute copper solution (Ihm et al., 1988) or dilute D2EHPA solution (Grimm and Kolarik, 1974b) or arbitrary pH at equilibrium (Sato et al., 1977). Different mechanisms of complex formation have been proposed. According to Kojima et al. (1969), the extracted species is $CuA_2.2HA$ (HA is the monomeric molecule of D2EHPA) and extraction equilibrium can be formulated as (subscript "a" denotes aqueous phase, subscript "o" denotes organic phase):

$$Cu^{2+}_{(a)} + 2(HA)_{2(o)} \leftrightarrows CuA_2.2HA_{(o)} + 2H^+_{(a)} \quad (1)$$

The equilibrium constant of Eq(1) is $K = 4.07 \cdot 10^{-4}$. Komasawa et al. (1981) made a more generic assumption: the metal cations are extracted as j-merized complexes of composition $(MA_2.x(HA)_2)_j$ (M were nickel, copper and cobalt in the study) and plotted equilibrium curves of complex concentration against $[Cu^{2+}]/[H^+]^2$ in logarithm scale. From the slope of the curves and the intersection with axis, the proposal by Kojima et al. (1969) was confirmed (j = x = 1) but the equilibrium constant was determined as $6 \cdot 10^{-5}$, about seven times less. Grimm and Kolařík (1974a, 1974b) presented a more complicated picture in their two papers: the complexes were monomers of composition $CuA_2.2HA$ at low level of metal and oligomers of composition $(CuA_2)_n$ (with n = 2.4 – 3.5 depended on the concentration of the complexes) at very high level of metal. Later, Stoyanov and Mikhailov (1988) studied bivalent metal M^{2+} and found that various polymeric complexes of the type $M_nA_{2n}(HA)_2$ might form during extraction. In case of copper(II), n ranged from 1 to 4. Reaction (1) can be generalized as ion-exchange reaction (Sato and Nakamura, 1972):

$$nM^{2+}_{(a)} + (n+1)(HA)_{2(o)} \leftrightarrows M_nA_{2n}(HA)_{2(o)} + 2nH^+_{(a)} \quad (2)$$

At very high metal load, free D2EHPA is depleted and polymeric molecules $M_nA_{2n}(HA)_2$ will be replaced by M_nA_{2n} with n may be up to several hundreds (Kolarik and Grimm, 1976). This means the complex molecules start as monomers at low load of M^{2+} and become polymers with increasing molecular weight at higher load. At certain load, the extract species are polymers of different DoPs. The value n determined from the slope of equilibrium curve as in (Ghebghoub and Barkat, 2009) or from vapor-pressure osmometry as in (Grimm and Kolarik, 1974b) was just the average one, $\bar{n}$. This can explain the difference between the values of equilibrium constant determined by Kojima et al. (1969) and Komasawa et al. (1981): $\bar{n}$ is a little more than 1 due to the presence of some oligomers. Forcing it to be 1 will cause some error in equilibrium constant determination.

In laboratory condition, the organic phase can load as much as 0.5 $\frac{mol\ Cu^{2+}}{\text{mol D2EHPA}}$ (Grimm and Kolarik, 1974b). As polymeric copper complexes grow larger and larger, the organic phase becomes so viscous that mass transfer rate is negligible from industrial point of view. This is more severe in the absence of diluent and the organic phase will be apparently saturated at much lower load. High load in the organic phase can be obtained by increasing copper concentration or pH in aqueous phase. Although the influence of pH on equilibrium is undoubtable, its influence on the DoP was not well studied. Komasawa et al. (1981) obtained monomeric complex at different pH. His results give an impression that the DoP is independent of pH but this may be due to low level of metal. Other studies revealed irregular behaviour of the equilibrium at certain values of pH. T. Sato et al. (1977) plotted isotherms for extraction of $CuCl_2$/HCl aqueous solution using D2EHPA: the distribution coefficient – $\log[Cl^-]$ slope changed notably at initial pH ≈ 3. R. Singh and P. Dhadke (2002) extracted copper perchlorate using D2EHPA and plotted extraction efficiency versus pH, it can be noticed that distribution coefficient (D) changed dramatically at pH ≈ 4 – 4.5. These irregularities may relate to the variation of DoP but no further investigation was taken.

Because of the interest in copper recovering from e-waste, it was felt that equilibrium of highly concentrated copper solution and D2EHPA in the pH range of 3 – 4.5 is worthy of more investigation. This study focused on pH at equilibrium, which was not well controlled in previous studies, and its impact on the DoP as well as looking for appropriate value for extraction process. In this study, sulphuric acid was chosen to generate acidic aqueous solution because it is not only a cheap, abundant commodity chemicals suitable for waste treatment but also the best stripping agent for D2EHPA reported in previous study (Singh and Dhadke, 2002). D2EHPA was undiluted to exclude the effect of diluent, the data can be used as base case for comparison with mixture of

D2EHPA and various diluents in previous and further study. Average DoP will be determined from distribution data to verify whether it is influenced by pH or not.

2. Methods

2.1 Materials and solution preparation

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Sigma-Aldrich) was used without further purification.
Copper (II) sulphate solution of the desired concentration was prepared using $CuSO_4 \cdot 5H2O$ (China) and distilled water. The concentration was verified by titration before every experiment. Similarly, NaOH 1M and H_2SO_4 1M solutions were prepared.
A Murexide indicator solution was prepared by dissolving 0.03 g of Murexide in ethylene glycol to produce a 0.15 % Murexide solution.
An EDTA solution of the desired concentration was prepared using EDTA (≥99 %, China) and distilled water.

2.2 Preliminary test

In preliminary tests, 300 ml of $CuSO_4$ solution at low concentration were mixed with 30 ml of D2EHPA. The pH of aqueous phase was monitored and controlled by adding NaOH. When the pH stopped changing, aqueous phase was sampled and analysed to determine copper concentration. Copper concentration was then raised by adding concentrated copper solution. Aqueous phase was sampled when equilibrium was reached again and so on. The volumes of all solutions taken from or added to aqueous phase (sample, $CuSO_4$, NaOH) were controlled and the copper concentration of organic phase was calculated by mass balance. The preliminary equilibrium data are not presented here because more accurate data were obtained from main experiments.

2.3 Equilibrium experiment

Before each experiment, a target point of the equilibrium curve was chosen based on preliminary data, parameters include approximate pH, organic and aqueous concentrations. Assuming aqueous/organic phase ratio of 10:1 v/v, the simplified Eq(3) was used to calculate the initial aqueous concentration of copper(II) and proton which will react with clean D2EHPA to produce the mixture at targeted equilibrium point.

$$Cu^{2+}_{(a)} + (HA)_{2(o)} \leftrightarrows CuA_{2\,(o)} + 2H^{+}_{(a)} \quad (3)$$

50 ml of aqueous phase were prepared from sulphuric acid, copper(II) sulphate solution and distilled water. The solution was then mixed with 5 ml of D2EHPA under constant stirring (1000 rpm) and room temperature (25 ℃). The pH of aqueous phase was continuously monitored and NaOH solution 1 M was added dropwise if it is lower than the desired value. Stirring was stopped when the pH stabilized and reaction time reached one hour. Experimental duration was similar to previous study (Ren et al., 2007) but equilibrium was further ensured by continuous high-speed stirring while mixture had been shaken for only first 30 minutes in (Ren et al., 2007). The organic and aqueous phases were completely separated first by separation funnel then by centrifuge.

2.4 Analysis

The copper concentration in the aqueous phase was determined by EDTA titration, using Murexide as the indicator and NH_4Cl + NH_4OH mixture as buffer solution. The amount of copper in the organic solution was calculated by mass balance.

3. Results and Discussion

The solubility of D2EHPA is 90 mg/l (Grymonprez et al., 2024) so 2.6 ‰ D2EHPA dissolved in copper solution at organic/aqueous phase ratio of 1/10. D2EHPA shows excellent hydro stability in sulphuric acid (Principe and Demopoulos, 2003) so its hydrolytic decomposition is negligible. On the other hand, Grimm and Kolarik (1974b) tried various nonpolar diluents (benzene, dodecane, n-hexane) and found no significant amount of water coextracted with copper into organic phase. With all the information, we can safely assume that the volumes of both aqueous and organic phases remained constant during extraction. The concentration and amount of copper in both phases can be easily calculated from each other by multiplying or dividing by phase volume.
In Figure 1, equilibrium data are presented in pCu coordinates (here pCu is defined as $-\log_{10}[Cu^{2+}]$). When pH increased from 3 to 4, the curve moved to the right, which means a higher distribution coefficient. This is because lowering concentration of proton shifted the equilibrium of Eq(2) to the right. However, when pH further increased to 4.5, the curve moved back to the left, meaning reaction (2) was somehow hampered. Noting the the solution of D2EHPA and copper complexes at this pH became very viscous and formed gel-like phase, very low mass transfer rate is supposed to be the reason. Because reaction (2) was promoted at phase interface by high pH, a layer of polymeric complexes quickly formed and prevented fresh D2EHPA deep inside the droplets from

diffusing to the boundary and taking part in reaction (2). The equilibrium curve plotted at pH = 4.5 is not true but apparent as mentioned before. Overall, maximum distribution coefficient was obtained around equilibrium pH = 4, which is in agreement with previous study where the maximum distribution coefficient was obtained at equilibrium pH ≈ 4.1 – 4.27 (Ren et al., 2007).

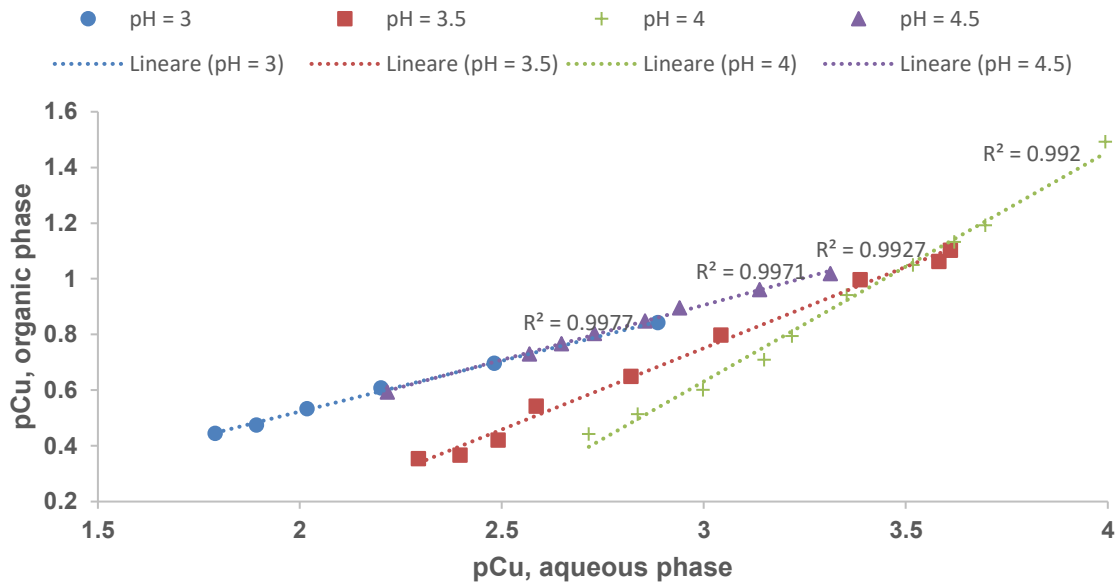

Figure 1: Equilibrium curves at different pH

In all pH values, the relationship between pCu in aqueous phase and organic phase is linear with high coefficients of determination (> 0.992):

$$pCu_o = a.pCu_a + b \quad (4)$$

Since reaction (2) is reversible, its equilibrium constant can be written as:

$$K = \frac{[Cu_nA_{2n}(HA)_2]_{(o)}[H^+]^{2n}_{(a)}}{[Cu^{2+}]^n_{(a)}[(HA)_2]^{n+1}_{(o)}} \quad (5)$$

Taking the logarithm of Eq(5) gives:

$$\log_{10}K = \log_{10}[Cu_nA_{2n}(HA)_2]_{(o)} + 2n\cdot\log_{10}[H^+]_{(a)} - n\cdot\log_{10}[Cu^{2+}]_{(a)} - (n+1)\cdot\log_{10}[(HA)_2]_{(o)} \quad (6)$$

Since $[Cu_nA_{2n}(HA)_2]_{(o)} = n.[Cu^{2+}]_{(o)}$, Eq(6) is equivalent to:

$$pCu_o + (n+1)\cdot\log_{10}[(HA)_2]_{(o)} - \log_{10}n = n\cdot pCu_a - 2n\cdot pH - \log_{10}K \quad (7)$$

The initial concentration of undiluted $(HA)_2$ is 1.51 M so the concentration of $(HA)_2$ at equilibrium is calculated by Eq(8):

$$[(HA)_2] = 1.51 - (n+1)\,[Cu_nA_{2n}(HA)_2] \quad (8)$$

Because $[(HA)_2]$ and $[Cu_nA_{2n}(HA)_2]$ are related by linear function, the left side of Eq(7) can approximately express as linear function of pCu_o with slope of (n+2). This leads to approximate calculation: $a \approx \frac{\bar{n}}{\bar{n}+2}$. The values of parameters a and b in Eq(4), $\bar{n}$, and coefficient of determination are in table 1. The results suggested that at pH = 3, the copper complexes in organic phase were mostly monomer $CuA_2(HA)_2$. At pH = 3.5, the organic phase contained a mixture of mainly di-, tri- and tetrameric complexes as previous study with similar range of copper concentration in organic phase (Stoyanov and Mikhailov, 1988). At pH = 4, the most abundant molecules supposed to be nonamers and decamers. At pH = 4.5, $\bar{n}$ drop to 1.3 because of the unreacted D2EHPA which can be consider as complex with n = 0. In this case the DoP cannot be guessed.

Grimm and Kolarik (1974b) observed that when the concentration of copper in the organic phase increased from 0.01 M to 0.1 M, the average DoP increased from 2 to 3.5. This indicates that a high copper load, which is desirable in the extraction process, is associated with a high DoP, which, in turn, results in a lower mass transfer

rate due to the increased viscosity. In more advanced techniques, such as supported liquid membrane, the mass transfer rate suffers more from molecular size due to the small pore diameter. However, as the authors noted, the equilibrium pH had not been well controlled and the initial pH ranged from 3 to 4.5, their study could not decouple the effects of copper and proton concentration. In this study, Figure 1 illustrates that the DoP depends rather on equilibrium pH than on copper concentration, either in the aqueous or organic phase. Therefore, pH can be effectively used to manipulate the DoP and consequently the mass transfer properties of the extraction process.

Table 1: Parameters in equation (2) and estimated degree of polymerization

pH	a	b	$\bar{n}$	R^2
3	0.364	-0.2055	1.1	0.9977
3.5	0.584	-1.0013	2.8	0.9927
4	0.825	-1.8436	9.4	0.992
4.5	0.394	-0.2752	1.3	0.9971

Because the equilibrium of reaction (1) is affected by D2EHPA and complexes concentration, beside pH it can also be manipulated by dilution. In a recent report on equilibria of copper(II) and D2EHPA, Ren et al. (2007) have noticed that distribution coefficient increased with increasing D2EHPA concentration in kerosene but failed to keep two other important factors – pH and copper concentration in aqueous phase – constant. The effect of D2EHPA concentration cannot be quantified. In table 2, some values of distribution coefficient in (Ren et al., 2007) with similar conditions was selected and compared with this study to highlight the effect of D2EHPA dilution. It is clear that D_{10} – the distribution coefficients in case of D2EHPA 10 % vol. – are much lower than D_1 – the distribution coefficients in case of D2EHPA 100 % vol. – but still higher than 10 % of D_1. This means despite lower distribution coefficient, the number of $(HA)_2$ molecules required to extract one copper(II) ion were reduced by dilution. In an extraction process, diluting requires larger equipment and more extraction solvent per feed mass to achieve the same extraction efficiency. The benefit is lower D2EHPA/feed ratio, which – according to Azam et al. (2010) – reduces D2EHPA solubility/degradation and helps cut down D2EHPA loss.

Table 2: Distribution coefficient

$[Cu^{2+}]_a$, mM	pH	D_{10} in D2EHPA 10 % vol.	D_1 in D2EHPA 100 % vol.	D_1/D_{10}
0.6	3.49	22.48	204	9.09
0.15	3.96	96.07	319	3.32

4. Conclusion

This paper presents a study on distribution of copper(II) between sulphate media and D2EHPA. The relationship of the logarithm of copper(II) concentration in organic and aqueous solution has been experimentally determined as linear with very high coefficient of determination. These linear functions, valid in a wide range of load, allow designer to predict the efficiency of extraction stages with high accuracy. The slope of the function depends on the DoP of the copper complexes, which in turn depends on the pH of aqueous solution at equilibrium. The complexes are mainly monomer at low pH and oligomer at high pH. For the purpose of extracting copper(II) from sulphate media using either undiluted or kerosene diluted D2EHPA, the optimal pH (one with highest distribution coefficient) is around 4 while further increase of pH may lead to premature saturation. Although dilution decreases distribution coefficient, it can cut down D2EHPA loss during extraction process because the Cu^{2+}/D2EHPA ratio in ion-exchange reaction will be improved.

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