



Study of the extraction liquid-liquid of copper (II) in the aqueous media: sulphate and nitrate with Di-2-ethyl hexyl phosphoric acid

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Abstract

The solvent extraction of copper(II) from sulphate and nitrate media by Di-2-ethylhexyl phosphoric acid (D2EHPA) in chloroform was studied. The effect of pH, D2EHPA concentration and ionic strength on the extraction processes has been investigated. The ionic strength effect of the aqueous phase shows that the extraction of copper(II) increases with decreasing concentration of sulphate. However in the nitrate medium, the extraction of copper(II) is independent of the ionic strength. At initially 10^{-4} M in the aqueous phase, copper(II) is extracted as the complex $\text{CuL}_2 \cdot 2\text{HL}$. The Debye-Hückel extended limiting law of ionic activity coefficient has been introduced in order to gain information about the copper-sulphate interaction.

Keywords: Solvent extraction; D2EHPA; Copper(II); Ionic strength effect.

1. Introduction

Liquid-liquid extraction is an important separation process that is used in a wide range of industries such as petroleum refining, food industry, nuclear fuel processing, pharmaceuticals, biochemistry, metal extraction, waste management and other areas [1-2]. Heavy metals are major pollutants in marine, ground and industrial wastewater [3-4].

Among these heavy metals, copper, nickel and zinc ingestion beyond the permissible limits causes various chronic disorders in human beings. Therefore, a systematic study on the preconcentration and separation of copper, nickel and zinc ions from natural water is of considerable significance from an environmental point of view [4-5]. Elimination of heavy metals from industrial wastes at the point of environmental aspects was always important. Furthermore there is an attitude toward the recovery of precious metals from low-grade or complex ores, secondary resources and industrial wastes because of the reduction of world's high grade resources and metals high prices. Generally, hydrometallurgical route (leaching-solvent extraction-electro winning) is found suitable to process lower grade ores, wastes such as slag, tailings and recycled solutions [6-7].

The sulphate solution is most commonly employed for the leaching of metals on commercial scale and the subsequent recovery following solvent extraction using organic extractants such as MOC-45 and Cyanex 272, and due to easy handling and environmental friendly [8-10]. Previously, it has been shown that the extraction of a metal using a sulphate medium is less good than that in nitrate aqueous medium [11]. This arises from the fact that the nitrate is a non-complexing medium and the sulfate is a moderate complexing medium commonly used [12].

Ionic strength is an important factor in chemical reactions in aqueous solutions, because it affects the rates at which ions react with each other and thus, the equilibrium and the extent to which the reaction occurs. Ionic strength is very important in studying the behavior of metals and high radioactive wastes in repository sites for waste disposal, such as Yucca Mountain in the USA since they contain high salt concentrations, such as chlorides or nitrates [13].

Barkat et al investigated the effect of ionic strength on extraction of zinc(II) and cadmium(II) from sulphate medium, by the 1-phenyl-3-methyl-4-benzoylpyrazolo 5-one in chloroform, and they found that the metal extraction increases with decreasing ionic strength [14].

In the present paper, the study of solvent extraction of copper(II) from sulphate and nitrate media with Di-2-ethyl hexyl phosphoric acid in chloroform is carried out. Our interest is to illustrate the effect of the ionic strength of the aqueous sulphate and nitrate media on the extraction of copper(II) and also to see if the complexes of metal could be formed in the aqueous phase.

The copper-sulphate interaction was investigated by using the Debye-Hückel extended limiting law of ionic activity coefficient.

2. Materials and methods

2.1. Reagents

2.1.1. Aqueous solution

The aqueous solution was composed from copper sulphate $[Cu^{2+}] = 1,57 \times 10^{-3} M$ and various concentrations of sodium sulphate from 0.33 M to 0.033 M or copper nitrate $[Cu^{2+}] = 1,57 \times 10^{-3} M$ and various concentrations of sodium nitrate from 1, 0.5, 0.25, 0.125 and 0.1M.

2.1.2. Organic solution

The organic solution was composed from D2EHPA in analytical grade, and was used without further purification. The organic diluents, chloroform was pre-equilibrated with aqueous solutions which did not contain any metals. The D2EHPA was used at three concentrations, 0.04, 0.02 and 0.01M in chloroform.

2.2. Procedures

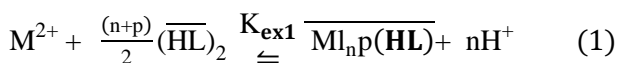
The distribution measurements were performed using a batch technique in thermostated vessels at 25°C. Equal volumes (30 mL) of both phases were contacted under magnetic stirring until the equilibrium was attained (max 30 min). The pH was adjusted by NaOH 0.1M. The ionic strength of the aqueous phase was assumed to be 1, 0.5, 0.25, 0.125 and 0.1 mol Kg⁻¹ from the aqueous sulphate and nitrate. After the two phases were separated completely, the metal ion concentrations were determined in aqueous phase photometrically at 810 nm using a Philips UV-VIS SP6-36. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

3. Results and discussion

3.1. Solvent extraction of copper(II) with D2EHPA in chloroform from the different media at constant ionic strength

3.1.1. Effect of pH

The extraction of copper(II) from sulphate and nitrate media by D2EHPA may be expressed as:



The bar denotes the organic phase species or organic phase concentration, n and p are the stoichiometric coefficients for the ligand.

The extraction constant, K_{ex1} is defined as:

$$K_{ex1} = \frac{[\overline{M}_{n,p}(\overline{HL})_n] [H^+]^n}{[M^{+2}] [(\overline{HL})_2]^{(n+p)/2}} \quad (2)$$

The using of the distribution coefficient D, Eq. (2) is rewritten as Eq. (3)

$$\text{Log } D = \text{Log } K_{ex1} + (n+p)/2 \text{Log} [(\overline{HL})_2] + n \text{pH} \quad (3)$$

The extraction equilibrium for each extraction system was analyzed according to slope analysis method [15] on the basis of Eq. (3). If the metal complex is not formed in the aqueous solution and the concentration of the extractant is not changed during the extraction reaction, the slope for the plot of Log D against pH becomes the charge on the aqueous metal ion, n:

$$\left[\frac{\partial \text{Log } D}{\partial \text{pH}} \right] = n \text{ at constant } [(\overline{HL})_2] \quad (4)$$

Figures 1 and 2 shows the relationship between Log D and pH for various concentration of D2EHPA in chloroform, were linear and the slope of straight line is $n = 2$ in this systems from the aqueous sulphate and nitrate medium respectively. Confirming that the metal extracting in organic phase is $CuL_2 \cdot pH_L$.

3.1.2. Effect of the D2EHPA concentration

When the equilibrium pH is not changed during the extraction reaction, the plot of Log D against $\text{Log} [(HL)_2]$ gives a slope $(n + p)/2$, from which the value of p can be determined. Therefore, substituting n and p into Eq. (1) and (3), gives information from the extraction reactions and the equilibrium constants.

The number of D2EHPA molecules involved in this system can be determined from the slope of the plots of log D against $\text{Log} [(HL)_2]$, as shown in Figure 3 and 4, $(n + p)/2$ is determined to be 2 and the value of p thus becomes 2, and the composition of the extracted species in the organic phase is $CuL_2 \cdot 2HL$.

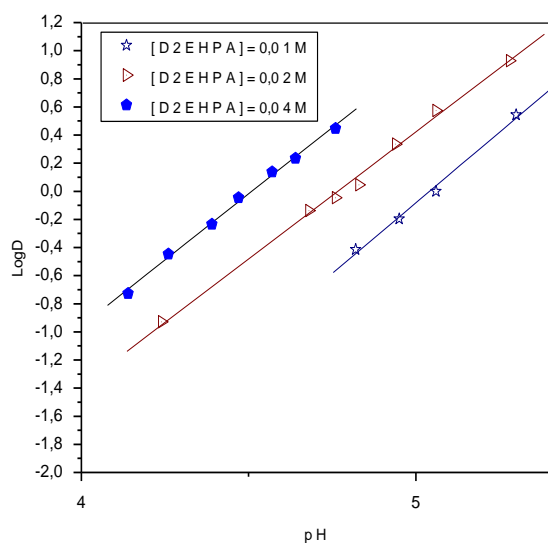


Figure 1: Variation of Log D with pH in sulphate medium (I=1)

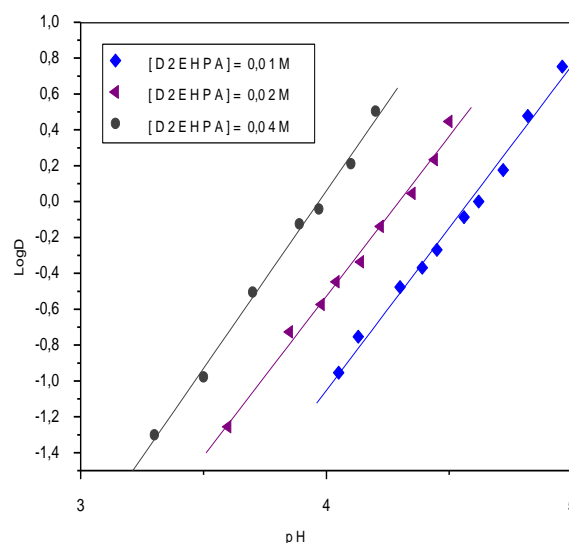


Figure 2: Variation of Log D with pH in nitrate medium (I=1)

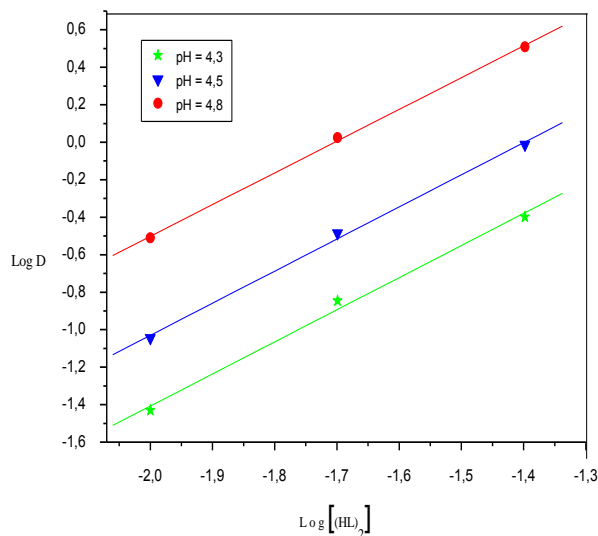


Figure 3: Variation of Log D with $\text{Log} [(HL)_2]$ in sulphate medium (I=1)

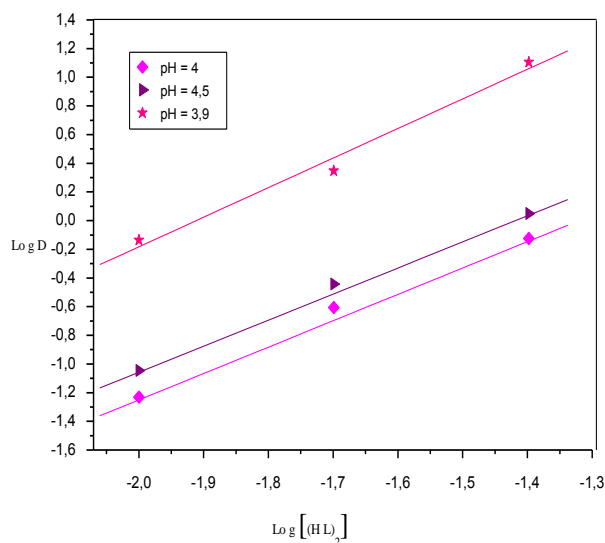


Figure 4: Variation of Log D with $\text{Log} [(HL)_2]$ in nitrate medium (I=1)

3.2. Effect of ionic strength from sulphate and nitrate on the extraction of copper(II)

The effect of ionic strength from sulphate and nitrate media on the extraction was measured by using the modification concentration method of different aqueous media at various ionic strengths 1, 0.5, 0.25, 0.125 and 0.1 molK⁻¹.

Figure 5 illustrates the Log D vs pH relationship from sulphate medium at ionic strengths 1, 0.5, 0.25, 0.125 and 0.1 molK⁻¹. Extraction of copper(II) is remarkably influenced by the presence of sulphate ion, were increases with decreasing ionic strength. Therefore, Figure 6 represent plots of Log D vs pH obtained during the extraction of copper(II) at different ionic strengths from nitrate medium, the extraction from nitrate medium is independent of the ionic strength.

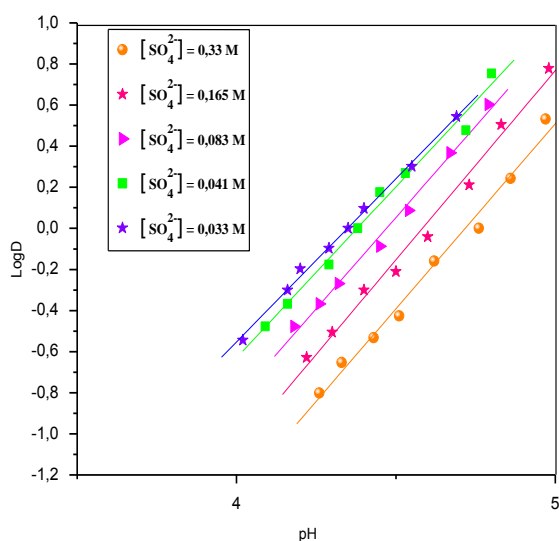


Figure 5: Effect of ionic strength in sulphate medium [D2EHPA] = 0,02M

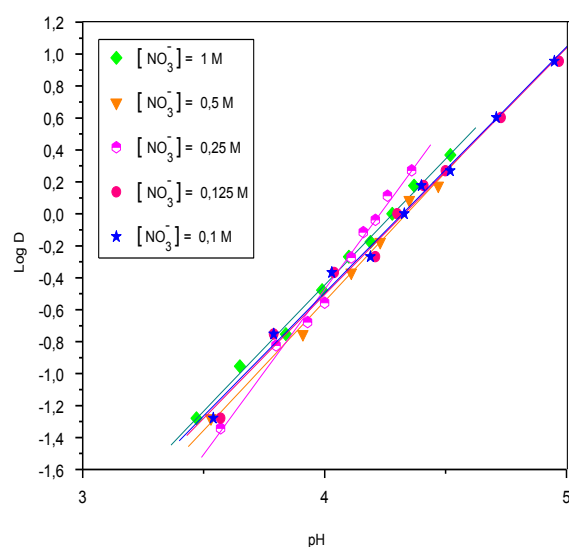
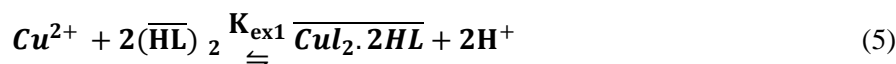


Figure 6: Effect of ionic strength in nitrate medium [D2EHPA] = 0,02M

4. Discussion

The activity coefficient may be introduced as a useful parameter to explain the effect of the ionic strength upon the solvent extraction of copper(II) from sulphate medium into chloroform.

The extraction process can be written as the following equation:



The extraction constant, K_{ex1} describing process may be defined in terms of the activity coefficients:

$$K_{\text{ex1}} = \frac{[\overline{\text{CuL}_2 \cdot 2\text{HL}}]_{\text{org}} [\text{H}^+]^2 \gamma_{\text{CuL}_2, \text{org}} \gamma_{\text{H}^+}^2}{[\text{Cu}^{2+}] [(\overline{\text{HL}})_2]_{\text{org}}^2 \gamma_{\text{Cu}^{2+}} \gamma_{(\overline{\text{HL}})_2, \text{org}}^2} \quad (6)$$

The logarithmic values of D can be written as:

$$\text{Log D} = \text{Log} \frac{\text{Cu}_{\text{org}}}{\text{Cu}} = \text{Log K} + 2\text{Log}[\overline{\text{HL}}]_{\text{org}} + 2\text{pH} + \text{Log} \frac{\gamma_{(\overline{\text{HL}})_2, \text{org}}^2}{\gamma_{\text{CuL}_2, \text{org}}} + \text{Log} \frac{\gamma_{\text{Cu}^{2+}}}{\gamma_{\text{H}^+}^2} \quad (7)$$

$\text{Log} \frac{\gamma_{\text{CuL}_2 \cdot 2\text{HL}_{\text{org}}}^2}{\gamma_{\text{Cu}^{2+}} \gamma_{\text{H}^+}^2}$ of the organic phase does not vary because it is independent of the ionic strength of the aqueous phase. Therefore, at constant pH the values of Log D depend upon $\text{Log} \frac{\gamma_{\text{Cu}^{2+}}}{\gamma_{\text{H}^+}^2}$.

The ionic activity coefficients can be determined using the extended Debye-Hückel limiting law by taking into account the size of the ions (ai), [16].

$$-\log_{10} \gamma_A = \frac{A_m Z_A^2 \sqrt{I_m}}{1 + B_m a_i \sqrt{I_m}} \quad (8)$$

Where, on the molality scale, the constants A_m and B_m are defined by:

$$A_m = \left(\frac{2\pi N d_0}{1000} \right)^{\frac{1}{2}} \frac{e^3}{2.3026 (kTD)^{\frac{3}{2}}} \quad (9)$$

And

$$B_m = \left(\frac{8\pi N d_0}{1000} \right)^{1/2} \frac{e}{(kTD)^{1/2}} \quad (10)$$

In the formulae (9) and (10), e, N, d₀, k, T, D and Z_A represent respectively the electron charge, the Avogadro constant, the density of the solvent, the Boltzmann constant, the absolute temperature, the dielectric constant of the solvent, and the valency of the cation.

Since in Eq. (8), the ionic size (ai) is not clearly defined, it has been introduced by us the radius of hydrated cation [17].

The values of the hydrated radii (ai = ri) used for the tabulation of the ionic activity coefficient value of Cu²⁺ and H₃O⁺ are taken from [17]. The calculated values of these ionic activity coefficients are summarized in Table 1.

Table 1: The calculated values of the ionic activity coefficients of Cu²⁺ and H⁺ at 25°C from the sulphate medium.

Ionic strength (molKg ⁻¹)	Ionic activity coefficient γ_{H^+}	Ionic activity coefficient $\gamma_{\text{Cu}^{2+}}$	$\text{Log} \frac{\gamma_{\text{Cu}^{2+}}}{\gamma_{\text{H}^+}^2}$
1	0.7439	0.2067	-0.4277
1/2	0.7650	0.2506	-0.3683
1/4	0.7896	0.3072	-0.3074
1/8	0.8167	0.3765	-0.2484
1/10	0.8300	0.4010	-0.2350

Where it is shown on Table 1, Log ($\gamma_{\text{Cu}^{2+}} / \gamma_{\text{H}^+}^2$) increases with decreasing values of the ionic strength, therefore, Log D increases according to Eq. (7), this result agrees satisfactorily with the experimental values shown on Figure 5.

The curves of Figure 5 could be in good agreement with the formation of the complex CuSO₄ not extractible, which would reduce the concentration of copper(II) and thus decrease their extraction.

In the experimental conditions, this hypothesis becomes valid when the interaction constant of Cu²⁺- SO₄²⁻ is taken into account Eq. 11.



The interaction constant value of Cu²⁺- SO₄²⁻ is equal to 0.018. it was determined by making the difference between the extraction constants of copper (II) in sulfate (Log K_{ex}(SO₄²⁻) = - 5.10) and nitrate aqueous media (Log K_{ex}(NO₃⁻) = -3.36).

Conclusion

Extraction of copper(II) from sulphate and nitrate media by Di-2-ethylhexyl phosphoric acid was carried out. The extracted species from sulphate medium into chloroform diluents was found to be $\text{CuL}_2 \cdot 2\text{HL}$ at different ionic strength and the extraction of copper(II) from sulphate medium increases with decreasing ionic strength. However the extraction of copper(II) from nitrate medium is independent of the ionic strengths.

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