

EFFECT OF SULPHATE AND NITRATE ION ON THE EXTRACTION OF COPPER (II) METAL IONS FROM AQUEOUS MEDIA USING 2,2,2-TRICHLORO-1-(5-HYDROXY-3-METHYL-1-PHENYL-1H-PYRAZOL-4-YL)ETHANONE IN CHLOROFORM

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Abstract

The effect of sulphate and nitrate ions in aqueous media on the extraction of Cu (II) ions into 2,2,2-trichloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethanone (HTcP) solution in chloroform has been studied. The synergistic effect of butanol on the extraction of the metal ion was also examined. The results showed that extraction of Cu(II) ions was found to be more efficient from solutions of 0.05M HTcP between pH 4.00 – 8.00 over the pH range of 1.00 -8.00 studied with optimum percentage extraction above 90%. Increase in sulphate ion concentrations from 0.01M to 1.00M in the aqueous media resulted to a decrease in Cu (II) ion extracted and a shift of the extraction processes to higher pH values. This is due to the masking of the metal by anionic sulphate-copper complexes formed in solution. Similarly, increase in nitrate ion concentrations from 0.01M to 1.00M followed the same trend with optimum percentage extraction (%E) above 70%. Slight synergism occurred in the distribution of the metal ion into the chloroform-butanol phase and the extraction data showed that $pH_{1/2}$ shifted to lower values. Addition of butanol into the organic phase resulted in slight increase of optimum percentage extraction up to 99.57% from 99.15% in the absence of butanol as synergist over the pH range of 3.52-8.00 from aqueous buffer media containing 0.1M concentration of SO_4^{2-} ion. The slope analysis indicated that the $Cu(HTcP)_2$ adduct complex species were extracted during all the extraction processes. The $pH_{1/2}$ and %E of the extraction systems were determined and used for explaining the various extraction processes observed.

Keywords: Sulphate ion, Nitrate ion, aqueous media, copper (II), 2,2,2-trichloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethanone.

Introduction

The importance of liquid-liquid extraction and separation techniques cannot be exhausted. Its application can be seen in different fields of life ranging from the pharmaceutical industry [1, 2], hydrometallurgy [3], separation [4-7] and purification of transition metals [8, 9]. Several studies [10-12] have been carried out on the use of synthesized ligands and Schiff bases as extractants in chelate formation over the use of commercial extractants like LIX 54 [13].

Liquid-liquid extraction and separation techniques using 1-phenyl-3-methyl-4-acylpyrazolone-5 by several authors [14-18] in the extraction and separation of metal ions have generated quite some interest in recent years. Several derivatives of this ligand (acyl pyrazolone-5) have been synthesized, characterized and used in metal extraction studies [12, 19]. The introduction of various compounds as synergists [20,21] has further improved the efficiency of these ligands in solvent extraction studies [22-25]. Uzoukwu and Mbonu 2005 [26] studied the effect of chloride ion concentration in aqueous buffer media on the extraction of nickel (II) and copper (II) ions using the 2,2,2-trichloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethanone or (1-phenyl-3-methyl-4-trichloroacetylpyrazolone-5) derivative (HTcP) and proposed an efficient method for the separation of these metals in a mixture. The extraction of copper

(II), nickel (II) and cobalt (II) ions from concentrations of aqueous bromide ion solutions using the same ligand, HTcP has been reported by Chukwu and Uzoukwu 2012 [27].

Despite very encouraging published reports, extraction studies of metal ions using 4-acylpyrazolones (pKa values > 3) are few [28, 29]. The effect of sulphate and nitrate ions on the extraction of copper (II) using the ligand (2,2,2-trichloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethanone) will be investigated in this study. In addition, the introduction of butanol as a synergist will also be considered in the extraction system.

Experimental

Materials

Reagents of analytical grade (Aldrich or BDH) were used. They include: copper acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$), Sodium sulphate (Na_2SO_4), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl), potassium chloride (KCl), acetic acid (CH_3COOH), sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$), sodium hydroxide (NaOH), potassium dihydrogen phosphate (KH_2PO_4), Chloroform and 98% butanol. Deionized water was used throughout the experiment. Euro EA elemental analyzer, Labtech digital pH meter and buck scientific digital atomic absorption spectrophotometer (250A model) were also used.

Preparation of aqueous and organic phases

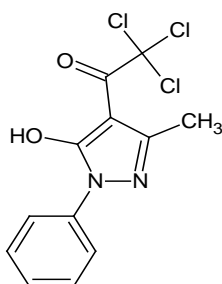


Figure 1. Structure of the ligand 2,2,2-trichloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethanone (HTcP)

The ligand (HTcP) in (figure 1) was synthesized by methods described previously [26] and recrystallized twice from aqueous ethanol after synthesis. Thereafter, the purity was established by UV, IR, ¹HNMR spectral methods as previously reported [26, 27]. The elemental analysis of the ligand was carried out using Euro EA Elemental Analyzer at Fortungszentrum Rossenderf Dresden, Germany.

The organic phase comprised of stock solution of 0.05M HTcP. This was prepared by dissolving an appropriate mass (1.5975g) of the ligand in chloroform. For the aqueous phase, stock solution (500mgL⁻¹) of the metal ion, Cu²⁺ was prepared by dissolving the appropriate mass of the salt of the metal; Cu(CH₃COO)₂·H₂O in 2mL of 0.1M HCl. The mixture was made up to mark in a 100mL volumetric flask using deionized water. Buffer solutions containing 0.01M, 0.1M and 1M SO₄²⁻ and NO₃⁻ ions, were also prepared with appropriate mixtures of 0.1M HCl/KCl (pH 1.00-2.90), 0.1M acetic acid/KCl (pH 3.00-3.49), 0.1M acetic acid/sodium acetate (pH 3.50-5.59) and 0.1M NaOH/KH₂PO₄ (pH 5.60-8.00) solutions. pH of the buffer solutions were determined using a Labtech digital pH meter.

Extraction procedure

Two mL aliquot containing 25mgL⁻¹ of the metal ion concentration and buffer solution of the anion (sulphate or nitrate) concentration made up the aqueous phase. While volume (2mL) of chloroform solution containing 0.05M HTcP made up the organic phase. However, for extraction in the presence of butanol as synergist, a 9:1 HTcP/chloroform: butanol ratio made up the organic phase.

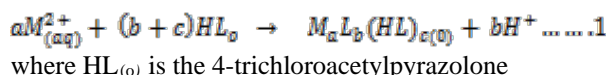
The mixture was thereafter agitated mechanically for 30 mins at room temperature. A shaking time of 30mins was found to be enough for equilibration as previously reported [26, 27]. The phases were allowed to settle and then separated for analysis of the metal ion in the aqueous raffinate. Metal ion concentration in the aqueous raffinate was determined using a buck scientific digital atomic absorption spectrophotometer (250A model). The concentration of the metal ion extracted into the organic phase was determined by difference. Distribution ratio, D, was calculated as the

ratio of metal ion concentration in the organic phase (C_o) to that in the aqueous phase (C) thus, $D = C_o/C$ [30]

Results and discussion

Theoretical considerations

Earlier works reported [26-28] have shown that the ligand is a weak organic acid and therefore behaved as 4-trichloroacetylpyrazolone chelating acids in solution. Thus, the extraction of the metal species (M²⁺) can be represented as follows:



$$K_{ex1} = \frac{[M_aL_b(HL)_c][H^+]^b}{[M^{2+}]^a[HL]_o^{(b+c)}} \dots\dots 2$$

where K_{ex1} is the extraction constant. Hence, the distribution ratio, D, is given by:

$$\log D_1 = \log K_{ex1} + (a-1)\log[M^{2+}] + (b+c)\log[HL]_o - (b)\log[H^+] \dots\dots(3)$$

In the presence of solvating agent such as butanol (BuOH), the distribution ratio becomes:

$$\log D_2 = \log K_{ex2} + (a-1)\log[M^{2+}] + (b+c)\log[HL]_o + d \log[BuOH]_o - b\log[H^+] \dots\dots(4)$$

Where $M_aL_b[HL]_c(o)$ and $M_aL_b[HL]_c[BuOH]_d(o)$ represent the extractible metal complexes in the absence and presence of butanol respectively.

Determination of the values of a, b, c and d for interactions between the ligand and one mole of metal in the equations can be done through evaluation of the partial derivatives of the equations by the method of slope analysis as follows:

$$\frac{d \log D}{d \log [H^+]} = b \dots\dots(5)$$

$$\frac{d \log [HL]_o}{d \log D} = b + c \dots\dots(6)$$

$$\frac{d \log [BuOH]_o}{d \log D} = d \dots\dots(7)$$

$$\frac{d \log [M^{2+}]}{d \log D} = a - 1 \dots\dots(8)$$

The above equations (5 -8) show that the values; a, b, c and d are related to the stoichiometry of the extraction process in each of the systems [30].

Extraction of Cu²⁺ from aqueous solutions of SO₄²⁻ ion into 0.05M HTcP/CHCl₃ at different pH values

Extraction of Cu²⁺ ions from aqueous buffer solutions containing various sulphate ion concentrations (0.01M, 0.1M and 1M) into 0.05M HTcP in chloroform showed that quantitative extraction above 90% yield occurred between the pH of 3.00 – 8.00

over the pH range of 1.00 -8.00 studied. The extraction plots of Cu^{2+} from aqueous SO_4^{2-} medium into 0.05M HTcP/chloroform are presented in Figure 2 for the varying concentrations of SO_4^{2-} .

From the plots in Figure 2, optimal percentage extraction yield (%E) of 99.74%, 99.15% and 95.63% were obtained for 0.01M, 0.1M, 1M sulphate ion concentrations respectively. This shows a slight decrease from 0.01M to 0.1M SO_4^{2-} ion concentrations and a significant decrease from 0.1M to 1M SO_4^{2-} ion concentrations which can be attributed to the masking of the metal ion by the anionic sulphato-copper complex formed in solution at increasing SO_4^{2-} ion concentration. The $\text{pH}_{1/2}$ which is the pH at which 50% extraction has been achieved was found to be approximately 2.70 ± 0.30 for 0.01M SO_4^{2-} ion concentration and 3.00 ± 0.30 for 0.1M and 1.0M SO_4^{2-} ion concentrations. A slope of 2 was obtained irrespective of the sulphate ion concentration which is an indication that two (2) protons were displaced during the extraction process according to equation (1).

Thus, the results show that the extraction of Cu^{2+} is more efficient at relatively high pH values irrespective of SO_4^{2-} concentration in the aqueous buffered phase. Similar results were obtained by Uzoukwu and Mbonu [26] from their studies on the effect of chloride ions in buffer medium in the liquid-liquid extraction of Cu(II) and Ni(II) ions using HTcP. Values of $\log K_d$ and $\log K_{ex}$ were equally calculated and tabulated. Table 1 summarizes the extraction data of Cu^{2+} ions for 0.01M, 0.1M and 1.0M SO_4^{2-} into 0.05M HTcP/chloroform.

Table 1. Extraction data of copper (II) ions from aqueous solutions of 0.01M, 0.1M and 1M SO_4^{2-} using 0.05M HTcP in chloroform organic medium.

	0.01M SO_4^{2-}	0.1M SO_4^{2-}	1M SO_4^{2-}
Slope	2.00 ± 0.01	2.00 ± 0.01	2.00 ± 0.01
$\text{pH}_{1/2}$	2.70 ± 0.30	3.00 ± 0.30	3.00 ± 0.30
%E	99.74 ± 0.01	99.15 ± 0.01	95.63 ± 0.01
$\log K_d$	2.00 ± 0.20	1.70 ± 0.20	1.40 ± 0.20
$\log K_{ex}$	-1.10 ± 0.50	-1.20 ± 0.50	-1.65 ± 0.50

Extraction of Cu^{2+} from aqueous solutions of NO_3^- ion into 0.05M HTcP/ CHCl_3 at different pH values

At different concentrations (0.01M, 0.1M and 1.0M) of aqueous solution of nitrate ion, extraction of Cu^{2+} ions into 0.05M HTcP in chloroform gave over 70% extraction between the pH ranges of 3.00 – 7.50 over the pH range of 1.00 – 8.00 studied. Figure 3 presents the extraction plots of Cu^{2+} ions from aqueous buffered solutions containing varying concentrations of NO_3^- ion into 0.05M HTcP/chloroform medium. The results show that optimal percentage extraction (%E) of 98.75% was obtained from solutions containing 0.01M NO_3^- ion concentrations.

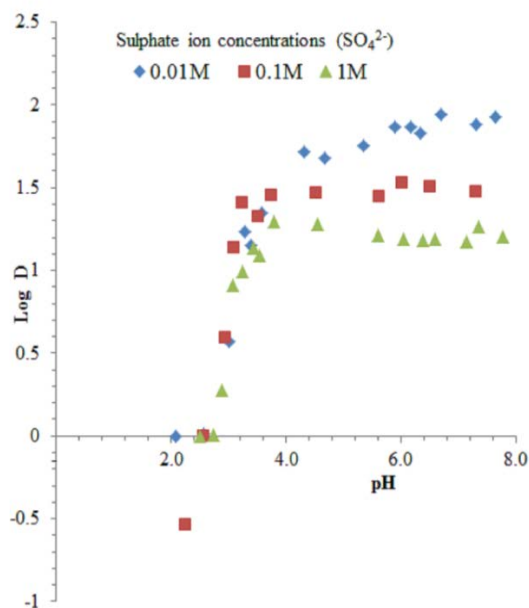


Figure 2. Variation of pH with log D for the extraction of Copper (II) ions from buffer solutions of 0.01M, 0.1M and 1M concentrations of SO_4^{2-} in HTcP/chloroform mixed organic medium at 25°C.

This value decreased in solutions of 0.1M NO_3^- ion concentrations to 96.46% and further to 78.18% in solutions of 1.0M NO_3^- ion concentrations. Hence, increase in nitrate ion concentrations results in masking of Cu^{2+} ions in the extraction system as a result of stable nitro-copper complexes.

From Figure 3, a slope of 2 was equally obtained irrespective of nitrate ion concentration. This is an indication that two (2) protons were displaced during the extraction process according to equation 1. Similar result was obtained earlier for the extraction of Cu^{2+} from sulphate ion concentrations and has also been reported elsewhere [26-28] for extraction of copper (II) using HTcP.

The pH at which 50% extraction was achieved i.e., $\text{pH}_{1/2}$ was found at approximately 3.2 ± 0.30 for all the nitrate ion concentration studied. $\log K_{ex}$ values of -1.25, -2.55 and -3.19 were obtained for the extraction of Cu^{2+} ions from aqueous solutions of 0.01M, 0.1M and 1.0M concentrations of NO_3^- ions. The value of $\log K_{ex}$ gives a means of assessing the ability of a ligand to extract a particular metal ion and the higher the value of $\log K_{ex}$, the better the extraction medium [30]. Therefore, 0.01 M NO_3^- ion aqueous solutions will be the best medium for the extraction of Cu^{2+} ions using 0.05M HTcP in chloroform. Extraction data of Cu^{2+} ions from aqueous solutions of NO_3^- ion concentrations into 0.05M HTcP/chloroform is summarized and presented in table 2.

Table 2. Extraction Data of Copper (II) ions from aqueous solutions of 0.01M, 0.1M and 1M concentrations of NO₃⁻ ions in 0.05M HTcP/ Chloroform mixed organic medium.

	0.01M NO ₃ ⁻	0.1M NO ₃ ⁻	1M NO ₃ ⁻
Slope	2.00 ± 0.01	2.00 ± 0.01	2.00 ± 0.01
pH _{1/2}	3.20 ± 0.20	3.20 ± 0.20	3.40 ± 0.20
%E	98.75 ± 0.50	96.64 ± 0.50	78.18 ± 0.50
Log K _d	1.90 ± 0.20	1.75 ± 0.20	0.75 ± 0.20
Log K _{ex}	-1.25 ± 0.50	-2.55 ± 0.50	-3.19 ± 0.50

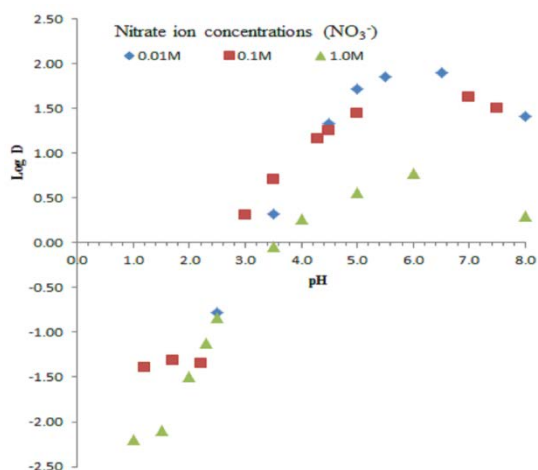


Figure 3. Variation of pH with log D for the extraction of Copper (II) ions from buffer solutions of 0.01M, 0.1M and 1M concentrations of NO₃⁻ in HTcP/chloroform mixed organic medium at 25°C.

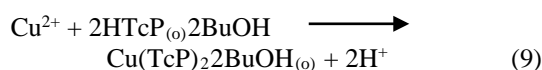
Synergistic extraction of Cu²⁺ into chloroform solutions of HTcP from aqueous solutions containing 0.1M SO₄²⁻ ions

Extraction of Cu²⁺ ions from aqueous media containing 0.1M SO₄²⁻ ions into 0.05M HTcP/chloroform organic phase containing butanol was carried out and presented as a plot in figure 4. The introduction of butanol into the organic phase resulted in quantitative extraction of 99.57% with lower pH_{1/2} value of 2.05 (with synergist) in comparison to pH_{1/2} of 3.30 in the absence of butanol (without synergist). This is an indication that extraction of Cu²⁺ at lower pH values is more effective in chloroform solutions containing butanol as solvating agent. Figure 4 shows a quantitative extraction over wider range of pH values 2.0 – 8.0 when compared to (figure 2); indicating that the synergist (butanol) enhances the extraction. Variation plot of Log D with pH for the extraction of Cu²⁺ from buffer solutions containing 0.1M SO₄²⁻ ion concentration is given in (figure 4).

A slope of 2 was obtained similar to extractions in the absence of butanol. Again, this shows that two (2) protons were displaced during the extraction

processes. The pH_{1/2} was found to be 2.05 and %E obtained was 99.57% as shown in (figure 4). Table 3 summarizes the extraction data of copper (II) ions from aqueous buffer solutions of 0.1M SO₄²⁻ using 0.05M HTcP in chloroform/BuOH organic medium and compares same with extraction in the absence of butanol.

Hence, in the presence of butanol (BuOH) as a solvating agent, the extraction process for copper (II) ion can be represented as:



$$K_{ex2} = \frac{[Cu(TcP)_2]_{(o)} [H^+]^2}{[Cu^{2+}] [HTcP]^2 [BuOH]^2} \quad (10)$$

$$\log D = \log K_{ex2} + \log [Cu^{2+}] + 2 \log [HTcP]_o + 2 \log [BuOH] + 2pH \dots \dots \dots (11)$$

Table 3: Extraction data of copper (II) ions from buffer solutions of 0.1M SO₄²⁻ using 0.05M HTcP in chloroform/BuOH organic medium.

0.1M SO ₄ ²⁻	Slope	pH _{1/2}	%E
Without Synergist	2.00 ± 0.01	3.30	± 99.15 ± 0.01
With Synergist	2.00 ± 0.01	2.05	± 99.57 ± 0.01

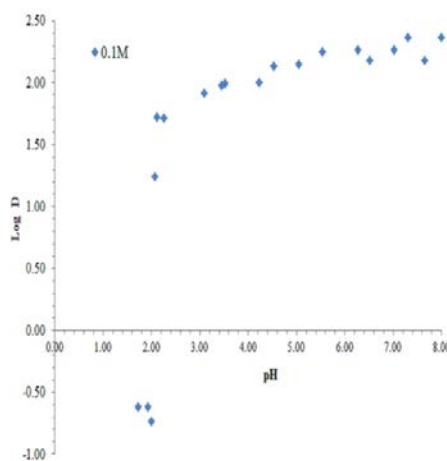


Figure 4. Synergistic extraction of Copper (II) ions from buffer solutions of 0.1M SO₄²⁻ using HTcP in chloroform/BuOH organic medium at 25°C.

Slope analysis of the extraction of Cu²⁺

Plots of the variation of log D with log [HTcP] for the extraction of Cu²⁺ into chloroform solutions of 0.05M HTcP from buffer solutions containing 0.1M SO₄²⁻ at constant pH values of 3.02 and 3.51 are presented in (figure 5). In each curve, a slope of 2 was obtained suggesting that the interaction between Cu²⁺ and the ligand involved two moles of the ligand and as derived statistically according to equation (6) which shows that (b+c) equals 2 (hence “c” is 0).

Earlier works have shown that 2 moles of protons were released during similar interaction [12, 26-29].

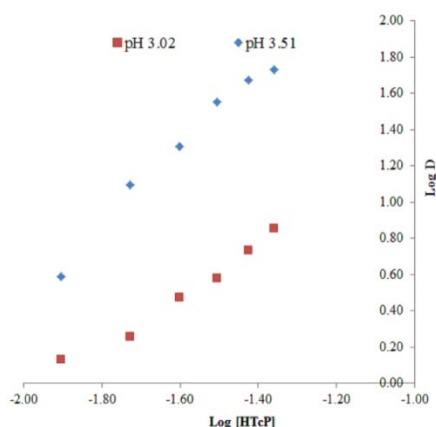


Figure 5. Ligand variation plot at constant pH of 3.02 and 3.51 for the extraction of 25ppm Copper (II) ions from buffer solutions of 0.1M SO₄²⁻ using HTcP in chloroform organic medium at 25°C

The degree of extraction as a function of Cu²⁺ ion concentration is presented in Figure(6) at pH values of 3.02 and 3.51 each containing 0.1M SO₄²⁻ ions in 0.05M HTcP/chloroform. A slope of zero (0) was obtained in each case. This is an indication that the interaction involved 1 mole of metal at each of the pH values studied. After solving equation (7) in which (a-1) equals zero (0). Consequently, 'a' equals 1 showing that 1 mole of metal (Cu²⁺) ion was involved in the interaction statistically. Hence, the metal:ligand ratio was found to be 1:2 and the complex formed under this condition is Cu(TcP)₂. This result is in agreement with that obtained by previous workers [12, 26-29]. The result also showed that the slope of zero (0) indicates that the extraction of Cu²⁺ into the organic phase is independent of the metal ion concentration. The proposed structure of the ligand Cu(TcP)₂ formed in the extraction process is presented in figure 6 below.

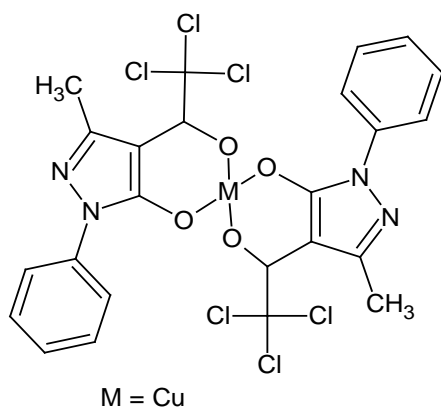


Figure 6: Proposed Structure of the complex Cu(TcP)₂

Conclusion

Extraction of Cu²⁺ ions from aqueous media containing various concentrations (0.01M, 0.1M and 1M) of sulphate ions and nitrate ions into 0.05M HTcP in chloroform has been observed within the pH range of 1.0 to 8.0. Results obtained showed that extraction occurred between pH 2.5 and 7.5 with optimum percentage extraction above 90.00% in the presence of sulphate ion concentrations and above 70.00% in the presence of nitrate ion concentrations. Generally, increase in sulphate and nitrate ion concentrations had a masking effect on the extraction of the Cu²⁺ ion thus leading to corresponding decrease in optimum percentage extraction. Introduction of butanol as a solvating agent into the organic medium resulted in enhanced percentage extraction of the metal ion up to 99.57%. Other extraction data such as log K_d, log K_{ex} and pH_{1/2} were equally calculated for extraction at all anion concentrations and interpreted. From the results, extraction in the presence of 0.01M sulphate ion gave the best conditions for optimum percentage extraction of Cu²⁺ ions. Extraction plots of extraction at varying pH gave a slope of 2, which on interpretation suggests that two protons were displaced from the ligands during extraction. Further analysis using statistical treatment and slope analysis revealed that one mole of the metal ion (Cu²⁺) and two moles of the ligand were involved in the extraction process in the ratio of 1:2. Hence the suggested extracted complex specie is of formula Cu(TcP)₂.

Acknowledgments

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