Extraction of Cu(II) Ions Using Chloroform Solution of 4,4´-(1E,1E´)-1,1´-(Ethane-1,2-Diylbis(Azan-1-YL- 1ylidene))BIS(5-Methyl-2-Phenyl-2,3-Dihydro-1H-Pyrazol-3-OL) (H2BuEtP) Under the Influence of Acids, Anions and Complexing Agents

Oguarabau Benson[1]*; Jackson Godwin[2];
Shalom Udochukwu Okanezi[3]; Juliana Consul[4]

[1, 2, 3]Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria
[4]Department of Mathematics, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria
*Corresponding Author Oguarabau Benson[1]

Abstract: The influence of selected acids, anions, and complexing agents on the removal of Cu(II) ions from aqueous solutions was studied using chloroform solutions of H₂BuEtP both alone and in combination with HBuP. Chloroform solutions of the single Schiff base alone or in the presence of the synergist were added to the Cu (II) solutions containing known concentrations of the studied acids, anions, or complexing agents buffered at pH 6.0 and pH 8.75 and allowed to separate after an equilibration time of one hour. The absorbances of the aqueous raffinates were measured using AAS at 324.8 nm and compared with a standard Cu(II) absorbance to determine the percentage extraction (%E), distribution ratios (D), and the number of extraction batches (n), required for 99.9% Cu(II) removal. For the single ligand system for instance at pH 6.0, 0.005 mol/L H₂SO₄ among the acids exhibited the highest releasing effect, with a distribution ratio of 35.59 and an extraction efficiency of 97.28%, requiring two batches only to attain 99.9% Cu(II) extraction. Those exhibiting the highest releasing at the same pH, are 0.01 mol/L Cl⁻ among the anions (D = 83.74, %E = 98.82%) and 0.05 mol/L SCN⁻ among the complexing agents (D = 88.44, %E = 98.88%) also requiring only two batches for 99.9% Cu(II) ions extraction. The binary ligand system (H₂BuEtP/HBuP) showed slightly improved extraction efficiency compared to H₂BuEtP alone, in all studied systems requiring ≤ 2 batches only for 99.9% Cu(II) recovery, except for 0.1 mol/L tartrate at pH 8.75, 0.01 mol/L Cl⁻ at pH 6.0, 0.05 mol/L HNO₃, and 0.001 mol/L CH₃COOH at pH 8.75, which required three batches. Statistical analysis of their distribution ratios showed significant differences (P ≤ 0.05) between single H₂BuEtP and the mixed ligand systems in most cases, except for CH₃COOH at pH 6.0 (P > 0.05). When compared to previous studies on Pb(II), U(VI), Fe(II), Ni(II), Cd(II) and Zn(II), the results indicated strong extraction potential for both single and multi-metal systems, with selective releasing effects supporting potential multi-metal separations. These findings highlight the efficiency of H₂BuEtP and the synergistic effect of HBuP in Cu(II) extraction and provide insights for optimizing metal recovery from aqueous solutions.

Keywords: *Acids, Anions, Complexing, Extraction Efficiency and Copper.*

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I. INTRODUCTION

Environmental contamination by heavy metals arises from both natural routes and human activities (Herawati *et al.,* 2000). As our reliance on metals like copper increases, the issue becomes even more pressing. A major contributor to this problem is industrial discharge, where metal-laden effluents are often released into freshwater systems without adequate treatment, further exacerbating pollution (Salomons *et al.,* 1995). The extraction of metals using solvent-solvent techniques has attracted considerable attention in the field of heavy metal remediation (Černá, 1995; Lee *et al.,* 2005; Li *et al.,* 2017). Many studies have focused on evaluating the impact of common anions, acids, and supporting complexing agents on their roles in either facilitating the release or masking metal ions during extractions involving ligands, chelates, and Schiff bases (Nwadire *et al.,* 2020; Qasem *et al.,* 2021). It has been established that the nature and strength of interactions between anions and metal ions at varying concentrations play a critical role in determining whether they act as releasing or masking agents (Al Zoubi *et al.,* 2016; Narbutt, 2020). Additionally, alterations in the dielectric constant and polarizability of solvents due to changes in acid and anion concentrations have also been linked to their influence on the distribution of metals between the organic and aqueous phases (Al Zoubi *et al.,* 2016; Singh *et al.,* 2014). These interactions can be exploited in multi-metal extraction processes, where a particular acid or anion at a specific concentration may serve as a releasing agent for multiple metals (Smolinski *et al.,* 2017). Moreover, acids and anions can be utilized for the selective separation of metal ions. If an acid or anion demonstrates a masking effect on one metal while significantly enhancing the extraction of another within the same aqueous solution—resulting in a separation factor (B_{xy}) of at least 10^4—then this condition could be leveraged to effectively separate the metal ions (Rodrigues *et al.,* 2022; Godwin *et al.,* 2022). Furthermore, acids and anions have been examined for their role in metal preconcentration and recovery from organic solutions. At certain concentrations, they form strong and stable bonds with metals, enabling their removal from the organic phase following extraction (Kara & Alkan, 2002; Ye *et al.,* 2019).

Since their synthesis by Uzoukwu et al. (1998), the mixed Schiff base N,N-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-onimine) (H_2BuEtP) and 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)butan-1-one (HBuP) have been studied for extracting Cd(II), Fe(II), Pb(II), and Ni(II) from aqueous to organic phases (Godwin & Uzoukwu, 2012a; Godwin *et al.*, 2012, 2014, 2019). For Pb(II) extraction, all acids showed a masking effect except H_2SO_4 (>80% efficiency), though extraction fluctuated between 0.1M and 1M. Anions reduced efficiency from >90% to <20% with increasing concentration, except acetate and nitrate (>90% stable). Complexing agents decreased extraction from 0.05M to 0.5M (Godwin &

Uzoukwu, 2012). For Ni(II) extraction, all acids showed masking effect in all acids for the mixed ligand system (H_2BuEtP/HBuP) with <10% efficiency. Most anions gave enhanced extraction, but sulphate, nitrate, and iodide caused reductions (<70%, <90%, and <100%, respectively). Fluoride exhibited a high releasing effect (~90%) (Godwin *et al.,* 2012). For Fe(II) extraction, all acids caused a strong masking effect (<10% efficiency), though a slight increase occurred between 0.01M and 0.1M, except for H_3PO_4. PO_4^{2-} and CH_3COO^- increased extraction (>80% and >100%), while halogen anions, except Br^- (<70% to <100%), showed strong masking effects. Only tartrate did not show masking effect (Godwin *et al.,* 2014). For Cd(II) extraction, upon addition of the synergist (HBuP) high releasing effects (>50% efficiency) occurred for all acids, anions and complexing agents. Minor decreases occurred between 0.1M and 0.5M, except for H_3PO_4. CH_3COO^- and SO_4^{2-} that remained stable, while other anions showed unstable, high-releasing effects (>50%). Halogen anions stayed > 60%, with Br^- being most unstable. Complexing agents had high-releasing effects (>50%), fluctuating between 0.005M and 0.05M (Godwin *et al.,* 2019). Out of necessity, this study aimed to evaluate the role of selected anions, acids, and supplementary complexing agents in the removal of copper(II) ions from buffered aqueous solutions at pH 6.0 or 8.75 using chloroform solutions of the Schiff base 4,4´-(1*E*,1*E´*)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene)bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) only and in combination with a different Schiff base, 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) as a synergist. This was to be achieved by investigating their releasing effects at different concentrations, calculating the theoretical number of batches required at these concentrations to achieve 99.9% extraction of Cu(II) ions. and statistically comparing the results for the two organic phases.

II. EXPERIMENTAL

All chemicals used for this study were of analytical grade and supplied by Sigma Aldrich and used as obtained without further purification. The compounds 4,4´-(1*E*,1*E´*)-1,1´-(ethane-1,2-diylbis(azan-1-yl1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) and 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)butan-1-one (HBuP) were made and characterized using procedures clearly stated in literature [Uzoukwu et at., 1998]. 100 mL of a 2000 mgL^{-1} stock solution of copper (II) sulphate pentahydrate was prepared by dissolving an appropriate amount of copper (II) sulphate pentahydrate salt in distilled water, followed by the addition of 0.2 mL HNO_3 to inhibit hydrolysis of copper. The working concentration of 200 mg/L Cu(II) ions was obtained by diluting the stock solution.

The amounts of mineral acids, anions and complexing agents were in the range 0.001 mol/L – 0.1 mol/L obtained from dilutions of their respective stock solutions of the selected acids and sodium/ammonium salts of these anions and complexing agents and buffered at 6.0 for one set and buffered at 8.75 for the other set. To each of 2 sets of 170 clearly-labelled 5 mL extraction bottles containing 0.2 mL of the 200 mg/L Cu(II) solution was added 0.8 mL of the buffered solutions and 1.0 mL of the mineral acids, anions and complexing agents in their various concentrations at pH 6.0 or 8.75. Afterwards, 2 mL of chloroform solution of 0.05 mol/L H_2BuEtP was added to each bottle of one set containing the buffered aqueous solutions and to the other set of one hundred and seventy bottles were added 2 mL of chloroform solution of 0.05 mol/L H_2BuEtP and 0.05 mol/L HBuP in 9:1 volume ratio. The three hundred and forty bottles containing the two immiscible phases were agitated with a mechanical shaker for 60 minutes. The two phases were allowed to separate out and 1 mL of aqueous raffinates were then taken with a micropipette, made up to the 4 ml with distilled water and analysed for copper by difference, using Atomic Absorption Spectrophotometry (AAS) at wavelength of 324.8 nm (Porento *et al.,* 2011). Absorbance results were used to calculate extraction parameters, distribution ratios (D) and percentage extraction (%E) using equations 1 and 2.

The R software package was used to statistically analyze for significant differences between distribution ratios of the two sets of data (single ligand and mixed ligand solutions) using p value 0.05. If the value of the test statistics is > the significant level of 0.05, the null hypothesis is accepted indicating no significant difference between the groups of interest and the null hypothesis is rejected if the test statistics value is < 0.05, implying there is significant difference

between them (Sprinthall, 2011). Equation 3 was used to estimate the number of batches needed theoretically to achieve 99.9% extraction of Cu(II) ions where n is the number of batches needed, C_{aq} is the concentration of metal ions originally present in the aqueous phase and C is the concentration of metal ions remaining in the aqueous phase after extractions.

$$D = \frac{Standard\ Absorbance - Raffinate\ Absorbance}{Raffinate\ Absorbance}$$

$$\text{---------} 1$$

$$\%\ E = \frac{Standard\ Absorbance - Raffinate\ Absorbance}{Standard\ Absorbance} \times 100$$

$$\text{---------} 2$$

$$C/C_{aq} = [1/(D + 1)]^n$$

$$\text{---------} 3$$

III. RESULTS & DISCUSSION

The extraction parameters due to the considered mineral acids, anions and complexing agents on the extraction of 200 mg/L of Cu(II) ions from their buffered solutions at pH 6.0 and 8.75 into 0.05 mol/L H_2BuEtP alone chloroform solution and a 9:1 volume ratio choroform solution of 0.05 mol/L H2BuEtP and 0.05 mol/L HBuP mixture as shown in Tables 1 to 6 and Figures 1 to 3 do not indicate any particular trend with increasing concentrations for both systems.

Table 1: Effect of mineral acids on Cu(II) ions extraction using H_2BuEtP alone

Acid Concentration (mol/L)	Distribution Ratio, D					Number of extractions, n				
	HCl	HNO₃	H₂SO₄	H₃PO₄	CH₃COOH	HCl	HNO₃	H₂SO₄	H₃PO₄	CH₃COOH
	pH 6.0					pH 6.0				
0.001	35.59	31.20	37.33	26.75	18.87	2	2	2	2	2
0.005	33.25	26.28	35.59	27.75	21.36	2	2	2	2	2
0.01	34.77	27.24	6.89	18.87	19.37	2	2	3	2	2
0.05	29.96	30.56	9.12	17.29	19.64	2	2	3	2	2
0.1	29.37	23.76	24.96	20.46	19.37	2	2	2	2	2
	pH 8.75					pH 8.75				
0.001	29.37	31.85	32.54	15.77	19.12	2	2	2	3	2
0.005	30.56	31.20	30.56	16.88	19.86	2	2	2	3	2
0.01	27.24	30.56	32.54	18.63	16.69	2	2	2	2	2
0.05	30.56	29.96	6.70	18.87	18.63	2	2	3	2	2

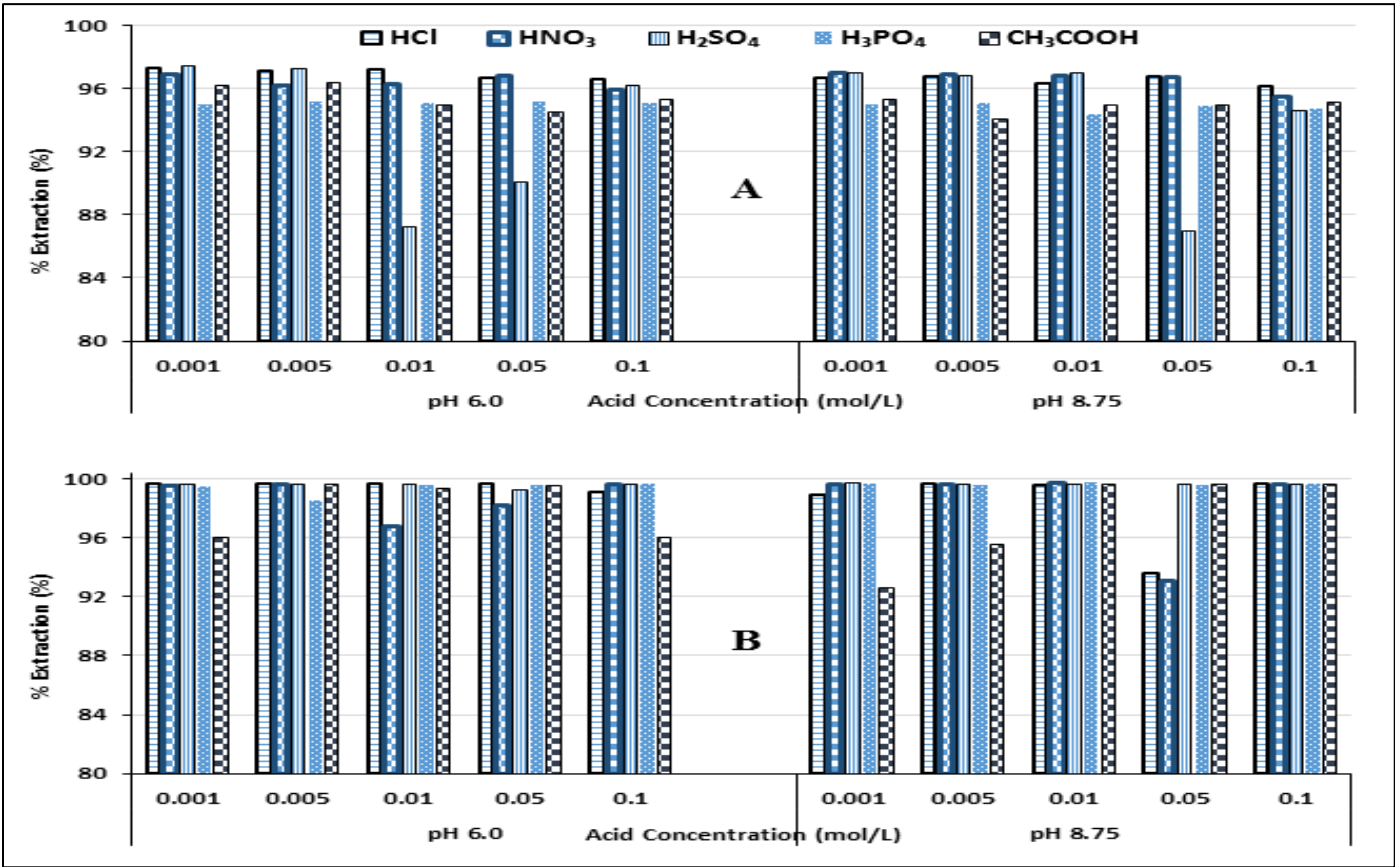| **0.1**	26.28	21.05	17.50	19.37	17.94	2	2	2	2	2
*10 mg/L Cu(II) Standard Absorbance = 0.1610; H₂BuEtP system alone										

Fig 1: Percent extraction of 200 mg/L of Cu(II) from solutions of mineral acids at pH 6.0 and 8.75 into (A) 0.05 M H₂BuEtP solution, and (B) 9:1 volume ratio solution of 0.05 M H₂BuEtP and 0.05 M HBuP

Table 2: Effect of mineral acids on Cu(II) ions extraction using mixed H₂BuEtP/HBuP solution

Acid Concentration (mol/L)	Distribution Ratio, D					Number of extractions, n				
	HCl	HNO₃	H₂SO₄	H₃PO₄	CH₃COOH	HCl	HNO₃	H₂SO₄	H₃PO₄	CH₃COOH
	pH 6.0					pH 6.0				
0.001	140.62	243.18	359.17	191.09	24.01	1	1	1	1	2
0.005	359.17	359.17	359.17	72.50	359.17	1	1	1	2	1
0.01	334.04	29.784	359.17	227.68	159.07	1	2	1	1	1
0.05	359.17	55.277	143.07	224.10	243.18	1	2	1	1	1
0.1	104.93	359.17	359.17	359.17	23.84	1	1	1	1	2
	pH 8.75					pH 8.75				
0.001	98.35	359.17	435.57	359.17	359.17	2	1	1	1	3
0.005	359.17	359.17	359.17	235.18	235.18	1	1	1	1	2

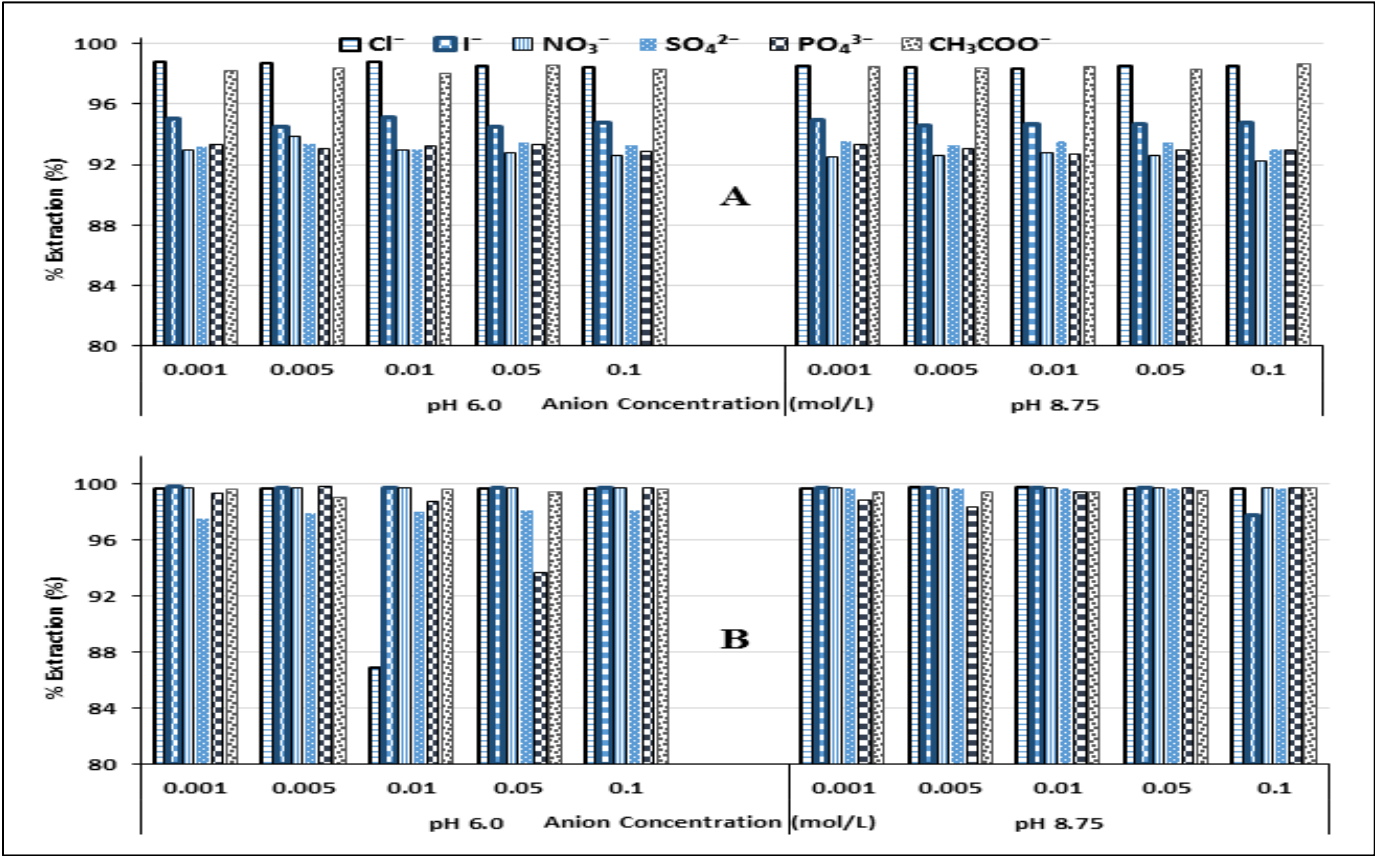| 0.01 | 243.18 | 653.86 | 312.19 | 532.59 | 532.59 | 1 | 1 | 1 | 1 | 1 |
0.05	14.65	13.582	359.17	256.26	256.26	2	3	1	1	1
0.1	359.17	359.17	359.17	359.17	359.17	1	1	1	1	1
*10 mg/L Cu(II) Standard Absorbance = 1.4407; H₂BuEtP/HBuP mixed system										

Figure 2: Percent extraction of 200 mg/L of Cu(II) from solutions of anions at pH 6.0 and 8.75 into (A) 0.05 M H₂BuEtP solution, and (B) 9:1 volume ratio solution of 0.05 M H₂BuEtP and 0.05 M HBuP

Table 3: Effect of anions on Cu(II) ions extraction using H₂BuEtP alone

Anion Concentration (mol/L)	Distribution Ratio, D						Number of extractions, n					
	Cl^-	I^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	CH_3COO^-	Cl^-	I^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	CH_3COO^-
	pH 6.0						pH 6.0					
0.001	83.74	19.12	13.12	13.63	13.63	54.51	2	2	3	3	3	2
0.005	75.67	17.29	12.87	14.04	14.04	60.92	2	2	3	3	3	2
0.01	83.74	19.64	13.24	13.24	13.24	50.93	2	2	3	3	3	2
0.05	66.08	17.29	12.87	14.18	14.18	69.00	2	2	3	3	3	2
0.1	63.40	18.16	12.52	13.90	13.90	58.63	2	2	3	3	3	2
	pH 8.75						pH 8.75					
0.001	66.08	18.63	12.41	14.04	14.63	63.40	2	2	3	3	3	2
0.005	63.40	17.72	12.64	13.37	13.90	60.92	2	2	3	3	3	2
0.01	60.92	17.94	12.87	12.76	14.48	63.40	2	2	3	3	3	2

| 0.05 | 66.08 | 17.94 | 12.64 | 13.12 | 14.18 | 56.50 | 2 | 2 | 3 | 3 | 3 | 2 |
| 0.1 | 69.00 | 18.16 | 12.08 | 13.24 | 13.37 | 75.66 | 2 | 2 | 3 | 3 | 3 | 2 |

*10 mg/L Cu(II) Standard Absorbance = 0.1610; H_2BuEtP system alone
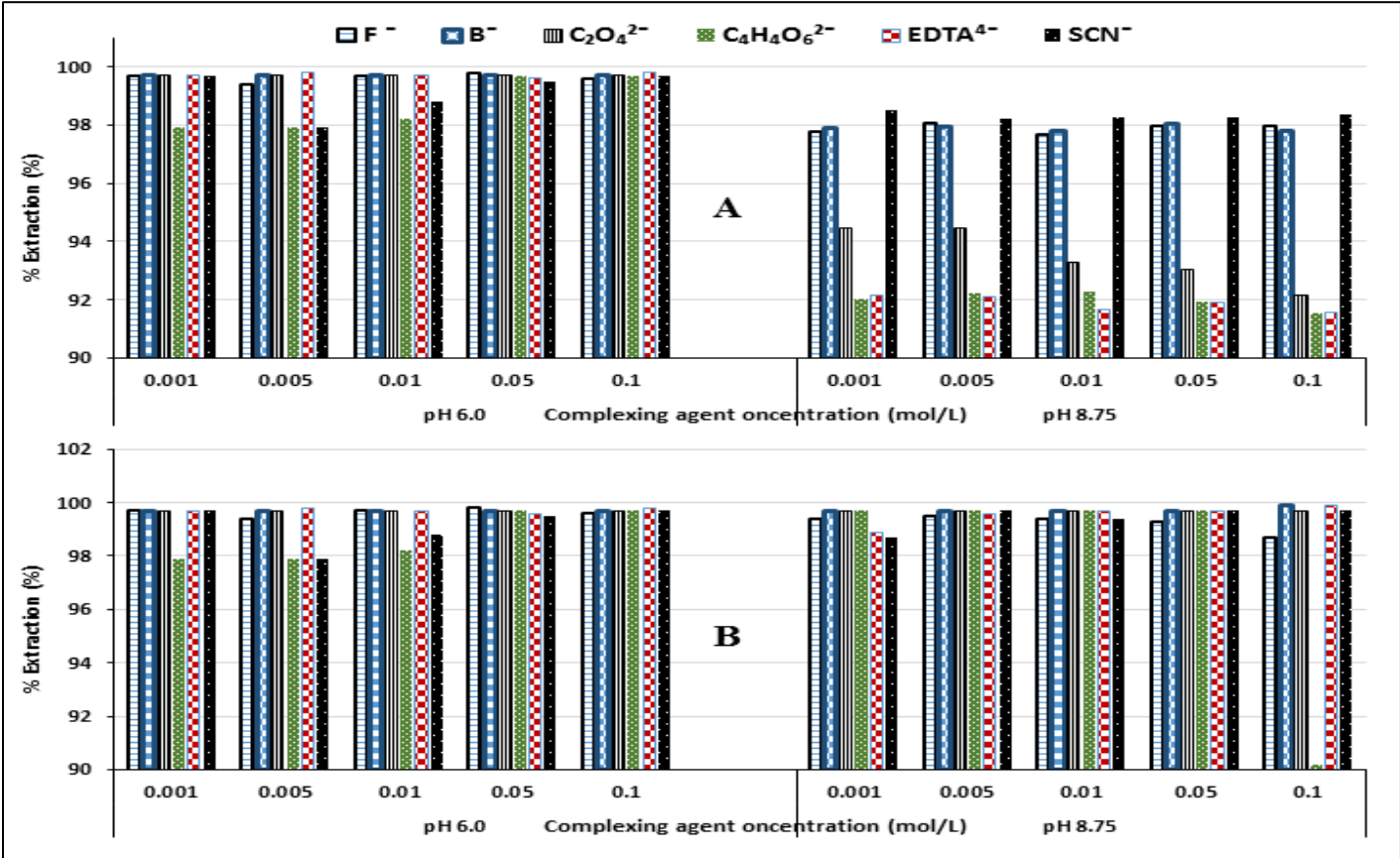

Fig 3: Percent extraction of 200 mg/L of Cu(II) from solutions of auxiliary complexing agents at pH 6.0 and 8.75 into (A) 0.05 M H_2BuEtP solution, and (B) 9:1 volume ratio solution of 0.05 M H_2BuEtP and 0.05 M HBuP

Table 4: Effect of anions on Cu(II) ions extraction using mixed H_2BuEtP/HBuP solution

Anion Concentration (mol/L)	Distribution Ratio, D						Number of extractions, n					
	Cl^-	I^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	CH_3COO^-	Cl^-	I^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	CH_3COO^-
	pH 6.0						pH 6.0					
0.001	359.17	495.79	359.17	140.24	140.24	281.49	1	1	1	1	2	1
0.005	359.17	359.17	359.17	599.29	599.29	112.44	1	1	1	1	2	1
0.01	6.64	359.17	359.17	83.74	83.74	227.68	3	1	1	2	2	1
0.05	359.17	359.17	359.17	14.76	14.76	157.31	1	1	1	2	2	1
0.1	359.17	359.17	359.17	359.17	359.17	239.11	1	1	1	1	2	1
	pH 8.75						pH 8.75					
0.001	359.17	359.17	359.17	89.04	359.17	176.86	1	1	1	2	1	1
0.005	513.53	359.17	359.17	60.56	359.17	157.31	1	1	1	2	1	1
0.01	422.73	359.17	359.17	168.49	359.17	155.59	1	1	1	1	1	1
0.05	350.39	359.17	359.17	359.17	359.17	199.09	1	1	1	1	1	1
0.1	359.17	399.19	359.17	359.17	359.17	359.17	1	1	1	1	1	1

*10 mg/L Cu(II) Standard Absorbance = 1.4407; H_2BuEtP/HBuP mixed system

Table 5: Effect of complexing agents on Cu(II) ions extraction using H_2BuEtP alone

Anion Concentration (mol/L)	Distribution Ratio, D						Number of extractions, n					
	F^-	Br^-	$C_2O_4^{2-}$	$C_4H_4O_6^{2-}$	$EDTA^{4-}$	SCN^-	F^-	Br^-	$C_2O_4^{2-}$	$C_4H_4O_6^{2-}$	$EDTA^{4-}$	SCN^-
	pH 6.0							pH 6.0				
0.001	54.52	46.35	17.29	12.08	11.48	11.38	2	2	2	3	3	3
0.005	46.35	46.50	19.12	11.77	11.38	66.08	2	2	2	3	3	2
0.01	50.94	42.51	19.38	12.76	11.57	58.63	2	2	2	3	3	2
0.05	49.31	56.50	19.12	11.98	11.38	88.44	2	2	2	3	3	2
0.1	47.79	49.31	17.72	11.88	11.57	83.73	2	2	2	3	3	2
	pH 8.75							pH 8.75				
0.001	43.72	46.35	17.09	11.67	11.77	66.08	2	2	2	3	3	2
0.005	50.94	47.79	17.09	11.98	11.67	54.51	2	2	2	3	3	2
0.01	42.51	45.00	13.90	12.08	11.10	56.50	2	2	3	3	3	2
0.05	47.79	49.31	13.37	11.48	11.48	56.50	2	2	3	3	3	2
0.1	47.79	45.00	11.77	11.01	11.01	54.51	2	2	3	3	3	2
*10 mg/L Cu(II) Standard Absorbance = 0.1610; H_2BuEtP system alone												

Table 6: Effect of complexing agents on Cu(II) ions extraction using mixed H_2BuEtP/HBuP solution

Anion Concentration (mol/L)	Distribution Ratio, D						Number of extractions, n					
	F^-	Br^-	$C_2O_4^{2-}$	$C_4H_4O_6^{2-}$	$EDTA^{4-}$	SCN^-	F^-	Br^-	$C_2O_4^{2-}$	$C_4H_4O_6^{2-}$	$EDTA^{4-}$	SCN^-
	pH 6.0							pH 6.0				
0.001	359.17	495.79	359.17	48.67	359.17	359.17	1	1	1	2	1	1
0.005	176.86	359.17	359.17	48.67	479.23	48.67	1	1	1	2	1	2
0.01	305.53	359.17	359.17	54.41	359.18	82.27	1	1	1	2	1	2
0.05	463.74	359.17	359.17	359.17	281.49	220.64	1	1	1	1	1	1
0.1	239.11	359.17	359.17	359.17	553.12	359.17	1	1	1	1	1	1
	pH 8.75							pH 8.75				
0.001	170.51	359.17	359.17	359.18	91.35	74.82	1	1	1	1	2	2
0.005	181.36	359.17	359.17	359.17	281.49	305.53	1	1	1	1	1	1
0.01	176.86	359.17	359.17	359.17	359.17	172.57	1	1	1	1	1	1
0.05	146.01	359.17	359.17	359.17	359.17	359.17	1	1	1	1	1	1
0.1	75.22	719.35	359.17	9.21	719.35	359.17	2	1	1	3	1	1
*10 mg/L Cu(II) Standard Absorbance = = 1.4407; H_2BuEtP/HBuP mixed system												

For the acids, % extraction for Cu(II) ions exceeding 90% (Figure 1A) was observed for all concentrations at both pH levels when using H_2BuEtP alone and in combination with HBuP. However, H_2SO_4 exhibited a slight decline at 0.05 mol/L concentration for both pH values and HNO_3 at 0.01 mol/L at only pH 6.0 while maintaining good extraction efficiency (> 80%). This confirms that all mineral acids demonstrated strong releasing effects (>80%) at both pH levels. The calculated *n* values shown in Table 1 suggest that two extraction batches using all mineral acids can theoretically achieve 99.9% Cu(II) recovery, except for 0.05 mol/L H_2SO_4 at both pH levels and 0.001 mol/L – 0.005 mol/L H_3PO_4 at pH 8.75, which required three batches with H_2BuEtP alone. At pH 6.0, 0.005 mol/L mol/L H_2SO_4 exhibited the highest releasing effect, with a distribution ratio of 35.59 and an extraction efficiency of 97.28%, also requiring two batches only to attain 99.9% Cu(II) extraction. These results differ from previous studies on Pb(II) (Godwin & Uzoukwu, 2012a), U(VI) (Godwin *et al.,* 2013), and Ni(II) (Godwin *et al.,* 2012) using H_2BuEtP, where masking occurred at all tested concentrations, except for Pb(II) with H_2SO_4 and U(VI) with H_3PO_4.

When mixed with the synergist HBuP (Figure 1B, Table 2), extraction significantly improved for all concentrations, exceeding 99% at both pH levels. However, at pH 8.75, a slight decline was observed between 0.01 mol/L and 0.05 mol/L HCl and HNO₃, likely due to the formation of a less hydrophobic Cu(II) complex favouring the aqueous phase over the organic phase. The calculated n values indicate that all extractions required ≤ 2 batches for 99.9% Cu(II) recovery, except for 0.05 mol/L HNO₃ and 0.001 mol/L CH₃COOH at pH 8.75, which required three batches upon synergist addition. Notably, mineral acids at pH (8.75) exhibited high releasing effects, achieving 99.8% extraction efficiency (Figure 1B) with H₂SO₄, H₃PO₄, and HNO₃, requiring just one batch for 99.9% Cu(II) extraction. Statistical analysis revealed significant differences ($P ≤ 0.05$) in the distribution ratios between single and mixed-ligand systems at both pH levels, except for CH₃COOH at pH 6.0 ($P > 0.05$). The results for H₂SO₄ with H₂BuEtP alone align with previous findings for Fe(II) (Godwin *et al.,* 2014) and Cd(II) (Godwin *et al.,* 2019), where extraction efficiency only decreased at higher concentrations.

All concentrations (0.001 mol/L to 0.1 mol/L) of the six anions investigated at both pH values, had high percent (> 90%) extraction for H₂BuEtP alone as shown in Figure 2A, with the values for chloride and acetate far exceeding 98% extraction. The calculated n values (as shown in Table 3) suggest that only two extraction batches are required to recover 99.9% of Cu(II) ions theoretically, using all concentrations of I⁻, CH₃COO⁻ and Cl⁻ at both pH levels. Conversely, PO₄³⁻, SO₄²⁻ and NO₃⁻ at both pH levels required three batches at all concentrations with H₂BuEtP alone. At pH 6.0, 0.01 mol/L Cl⁻ exhibited the highest releasing effect, with a distribution ratio of 83.74 and an extraction efficiency of 98.82%, also requiring only two batches to attain 99.9% Cu(II) extraction.

In the presence of HBuP (Figure 2B, Table 4), all anions showed similar but higher extractions across all concentrations. However, a slight decrease from 99.7% to 86.9% at 0.005 mol/L – 0.01 mol/L Cl⁻ at pH 6.0 was observed possibly due to stable Cu(II) complex formation, and consequent reduction in hydrophobicity. The calculated n values (as shown in Figure 4) indicate that all extractions required ≤ 2 batches for 99.9% Cu(II) recovery, except for 0.01 mol/L Cl⁻ at pH 6.0, which required three batches upon synergist addition. Notably, all anions at higher pH (8.75) exhibited high releasing effects, achieving ≥ 98% extraction efficiency and requiring just one batch for 99.9% Cu(II) extraction. Statistical analysis showed significant differences ($P ≤ 0.05$) for all anions except SO₄²⁻ and PO₄³⁻ which showed no difference ($p = 1$) at both pH values. Comparisons with previous studies revealed different masking behaviours for Pb(II), U(VI), Ni(II), Fe(II), Zn(II), and Cd(II) (Godwin & Uzoukwu, 2012a, 2012b; Godwin *et al.,* 2012, 2014, 2019). These findings suggest the anions' potential for multi-metal extractions as opposed to the study by Nwadire (2017) with lower Cl⁻ extraction (> 40%) for Ni(II) using H₂PrEtP.

All concentrations (0.001 mol/L to 0.1 mol/L) of the complexing agents had high percent (> 90%) extraction at both pH levels for H₂BuEtP alone as shown in Figure 3A, with the values at pH 8.75 much lower at those at pH 6.0, especially for oxalate, tartrate and EDTA ions at lower concentrations. Remarkably, SCN⁻ caused a slight increase in extraction between 0.001 mol/L and 0.005 mol/L at pH 6.0. The calculated n values (Table 5) show that only two extraction batches using all complexing agents can theoretically achieve 99.9% Cu(II) ion recovery, except for 0.01 mol/L – 0.1 mol/L oxalate at pH 8.75 and all concentrations of tartrate and EDTA at both pH levels, which required three batches with H₂BuEtP alone. At pH 6.0, 0.05 mol/L SCN⁻ exhibited the highest releasing effect, with a distribution ratio of 88.44 and extraction efficiency of 98.88%, also requiring only two batches for 99.9% Cu(II) ions extraction.

In combination with HBuP as presented in Figure 3B, extraction remained high (> 90%) across the 0.001 mol/L – 0.1 mol/L range. A slight % extraction decrease from 99.7% to 90.2% was observed at 0.05 mol/L – 0.1 mol/L tartrate at pH 8.75 which can be attributed to stable Cu(II) complex formation. The calculated n values (Table 6), show that, all extractions required ≤ 2 batches for 99.9% Cu(II) recovery, except for 0.1 mol/L tartrate alone at pH 8.75, which required three batches upon synergist addition. The results confirm that the complexing agents enhanced Cu (II) ions extraction effectively at the studied concentration range and pH values, especially in the mixed ligand systems where very large distribution ratios were observed with only one batch of extraction required to theoretically attain 99.9% extraction of the Cu(II) ions in solution. Statistical analysis showed significant differences in distribution ratios (D) of the complexing agents for the H₂BuEtP alone solution and for when mixed with H₂BuP for all ($P ≤ 0.05$) at both pH 6.0 and 8.75 except for SCN⁻ ($P = 0.053$) and tartrate ($P = 0.065$) at pH 6.0. Previous studies on Zn(II), Pb(II), U(VI), Ni(II), Fe(II) & Cd(II) showed varying masking effects (Godwin & Uzoukwu, 2012a, 2012b; Godwin et al., 2012, 2014, 2019, 2023) unlike this study. This study confirms H₂BuEtP provides superior extraction efficiency in the presence of the studied auxiliary complexing agents unlike the lower extraction values (>50%) reported for Ni(II) using H₂PrEtP (Nwadire, 2017).

IV. CONCLUSION

All the acids, anions and auxiliary complexing agents showed potentials in the extraction of Cu(II) from an aqueous solutions buffered to pH 6.0 or 8.75 using chloroform solutions of the Schiff base 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene)bis(5-methyl-2-phenyl-2,3-

dihydro-1H-pyrazol-3-ol) (H$_2$BuEtP) both alone and in combination with HBuP, as > 98% extraction of Cu(II) was achieved in most cases. Statistical analysis confirmed significant differences (P ≤ 0.05) between the distribution ratios of single and mixed ligand systems across most conditions, except for CH$_3$COOH at pH 6.0, which showed no significant variation. The binary H$_2$BuEtP and HBuP chloroform solution was slightly a better extractant for Cu(II) in most cases, in the presence of all the acids, anions and complexing agents. This is indicated in the calculated n values showing that all extractions required ≤ 2 batches for 99.9% Cu(II) recovery, except for 0.1 mol/L tartrate at pH 8.75, 0.01 mol/L Cl$^-$ at pH 6.0, 0.05 mol/L HNO$_3$ and 0.001 mol/L CH$_3$COOH at pH 8.75, which required three batches at both pH levels. Comparing these results to similar reported studies indicated all tested acids, anions, and complexing agents demonstrated strong extraction potential in both single and multi-metal systems. These findings highlight the effectiveness of H$_2$BuEtP, both independently and in synergy with HBuP, for Cu(II) ion extraction.

RECOMMENDATIONS

Future studies should optimize extraction conditions, explore multi-metal applications, investigate alternative ligands and solvents, and assess kinetic and thermodynamic parameters for improved selectivity and sustainability.

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Conflict of Interest
The authors do not have any conflicting interest.

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