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Copper (II) Distributions Between Buffered Aqueous Phases and Organic Phases of 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) in Chloroform

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Abstract: The distribution of Cu^{2+} between buffered aqueous phases and chloroform solutions of 4,4´-(1E,1E´)-1,1´-(ethane-1,2-diylbis(azan-1-yl1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) (H_2BuEtP) alone and in the presence of 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one(HBuP) was investigated using solvent-solvent extraction. 200 mgL^{-1} Cu^{2+} was used for the study with an equilibration time of 60 minutes. Concentration of Cu^{2+} in aqueous phases after equilibration was determined with AAS and calculated by difference between Copper concentration in the aqueous phases and the organic phases, and distribution ratios(D) and percentage extractions(%E) were determined. Slope analysis from plots of log D against buffers pHs, ligands concentrations and metal concentrations were used to propose distribution reaction equations and extracted Cu^{2+} complexes as $Cu(HBuEtP.X)_{(o)}$ for ligand alone and $Cu(HBuEtP.BuP)_{(o)}$ in the presence of HBuP. The extraction constant log K_{ex}, obtained for H_2BuEtP (-5.11±0.7) was greater than that for H_2BuEtP/HBuP (-12.94±1.26) which indicated HBuP did not exert any synergic effects in the distribution of Cu^{2+}, even though partition coefficient log D for H_2BuEtP/HBuP of 2.03 ± 0.81 was > 0.97 ± 0.62 for H_2BuEtP. Comparing results with those of other studies, showed carbon chain length of structurally related ligands effects on metal ions distribution is dependent on the particular metal ion. The ligand H_2BuEtP was a better extractant for Cu^{2+} than Ni^{2+} and Fe^{2+} only as the results for Pb^{2+}, UO^{2+} and Cd^{2+} were better based on log K_{ex} values.

Keywords: Distribution, ligands, buffers, extraction constant and partition coefficient

I. Introduction

Heavy metals pollution and efficient remediation methods have been of serious concern to researchers for many decades. One method that has shown to be very efficient in extraction of heavy metals from contaminated soils and industrial effluents is the use of ligands in solvent-solvent extraction (Huang and Keller, 2020: Yu Zhou *et al.*, 2024: Ugwu and Conradie, 2024). The use of ligands in this extraction studies has been reported to lead to the formation of interesting metal complexes with important applications in medicine (Kostova and Saso, 2013: Habala and Valentova, 2020: Paderni *et al*., 2025), agriculture (Dawara *et al.*, 2011: Jimenez-Falcao and Mendez-Arriaga, 2024) and other industrial uses (Kalyanasundaram and Gra Ètzel 1998: Yu *et al.*, 2020). Conditions such as optimum pH and oxidation states of the metals from these extraction studies have been used as the basis for the synthesis of these important metal complexes (Shimazaki, 2013: Rahman, 2024: Rahmati *et al*., 2024). Recent studies show that Schiff bases, a class of ligands containing a C=N bond, are excellent metal extractants. 1-Phenyl-3-methyl-4-acyl-pyrazolone-5 derivatives, such as H_2BuEtP, have been reported to effectively extract Pb(II), U(VI), Ni(II), Fe(II), Cu(II), Cd(II), and Zn(II). Similarly, H_2PrEtP has demonstrated strong extraction properties for U(VI) and Cu(II). In these studies, it is necessary to determine the equilibration time, the range of pH of quantitative distribution of the metal ions between the two phases, the $pH_{1/2}$ which is the pH at which there is 50% extraction of the metals into the organic phases and the optimum pHs of distribution of the metal. Slope analysis from plots of log D against pH, log D and log ligand concentrations and log D against metal concentrations are used to construct reaction equations for the processes from which the structures of the metal complexes and metal adducts can be proposed. The plots are also used to determine extraction parameters such as log D for the distribution of the metal between the buffered aqueous phases and the organic phases containing the ligands. Log K_{ex} values can be used to compare the efficiency of ligand/s systems as extractant for a particular metal or different metals as higher values indicate a better extractant system or conditions. The stabilities of the extracted complexes or adducts can be determined by log K_{ex} values that can be calculated from plots. A higher value of log K_{ex} indicates higher stability and formation constant of that complex compared to one with lower log K_{ex} (Uzoukwu, 2009: Muthaiah et al., 2020). In all these studies with 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 *N*,*N*`-ethylenebis(4-propionyl-2,4-dihydro-5methyl-2-phenyl-3H-pyrazol-3-oneimine)(H_2PrEtP), these extraction parameters $pH_{1/2,}$ log D and log K_{ex} are well reported (Godwin and Uzoukwu, 2012a: Godwin *et al*., 2012: Godwin and Uzoukwu, 2012b: Chukwu and Godwin, 2013: Godwin *et al*., 2013: Nwadiri *et al*., 2016: Godwin and Tella, 2023: Godwin *et al*., 2024).

Copper, specifically, is vital for modern society, being the third most important metal after iron and aluminium (Sverdrup *et al.*, 2014). Despite its essential role in technology and infrastructure, the unchecked release of copper into the environment is problematic. In 2020, global production of copper reached 21 million tonnes, reflecting a 1.9% rise from the previous year, though still falling short of projected growth as a result of the COVID-19 pandemic (Mining, 2020). As industrial activities continue to surge, the release of heavy metals such as copper into the environment often exceeds natural purification capacities, highlighting the urgent need for improved management and remediation strategies. This has necessitated numerous researches in the extraction of copper from industrial effluents and soils (Di Palma and Medici, 2002 : Aslam *et al*, 2004 : Al-Saydeh *et al*., 2017 : Napoli *et al*., 2019).

Nwadire et al. (2016) studied the distribution of Cu(II) ions between buffered aqueous solutions and chloroform solutions of H_2PrEtP, both alone and with HPrP. Their findings indicate that the Schiff base effectively extracted Cu(II), with HPrP exhibiting synergic effects by improving the partition coefficient log D. This study is aimed at evaluating the distribution of Cu(II) between aqueous solutions and chloroform solutions of 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) alone and in the presence 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one(HBuP). The objectives of this study are; to determine the optimum pH/s for quantitative distribution of Cu(II) to the organic extractant phases, the $pH_{1/2}$ for both organic phases, to determine and compare the extraction parameters log D (partition coefficients) and log K_{ex} (formation constants) for the both organic extractant phases, propose the reaction equations, structures of the extracted copper complexes using slope analysis, and also determine the effect of carbon chain length of the 1-Phenyl-3-methyl-4-acyl-pyrazolone-5 derivatives on the distribution of metals.

Experimental

All chemicals used for this study were of analytical grade and supplied by Sigma and Aldrich. The ligand 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) was synthesized using 5.2 ml of butanoyl chloride ($CH_3CH_2CH_2COCl$) introduced into a 25 ml quick-fit dropping funnel. 8.5 g of 1-phenyl-3-methyl-pyrazolone-5 was dissolved in 80 ml of 1,4-dioxane in a 3-necked quick-fit flask carrying a condenser with warming and stirring on a hot plot. When the pyrazolone-5 was completely dissolved the solution was brought down and cooled to room temperature under tap water, before 10 g of calcium hydroxide was added with stirring to get a suspension of the pyrazolone-5. No heat was applied during drop wise addition of the acyl chloride from the dropping funnel within a space of 5 minutes with stirring. The reaction is an exothermic reaction. The reaction between acyl chloride and pyrazolone-5 is in the mole ratio of 1:1 as shown in Figure 1A. Stirring of the hot reaction mixture was continued for another 40 minutes without heating. At the end of which the reaction mixture was poured into a chilled 400 ml of 3 M HCl with stirring to decompose the calcium product. This product was stored in a freezer until the 4-butanoyl-pyrazolone-5 product crystallized. This was filtered and recrystallized from aqueous ethanol to get pure bone white crystals of HBuP. 10 g of the synthesized HBuP was dissolved in 60 ml of ethanol with stirring in a 250 mL beaker on a hot plate. 1.5 ml of ethylenediamine was introduced into a 25 mL dropping funnel.

The temperature of the ethanol solution obtained above was maintained at about 60 ^{o}C while ethylenediamine was added drop-wise to the solution of HBuP within a space of 5 minutes with stirring. The reaction between ethylenediamine and HBuP is in the mole ratio of 1:2 shown in Figure 1B: Stirring was continued for another 30 minutes. At the end the reaction mixture was filtered and recrystallized from aqueous ethanol to get pure white crystals of the Schiff base H_2BuEtP with analytical data determined at the Institut fur Anorganische Chemie, Technische Universitat Dresden, Germany. 70% yield, melting point 235 ^{0}C with molecule formula $C_{30}H_{36}O_2N_6$. Slightly soluble in ethanol, methanol, acetone, CH_2Cl_2, benzene and very soluble in $CHCl_3$ [Uzoukwu, *et al*., *1998*]**.**

The working concentration of Cu (II) in aqueous solutions was 200 mgL^{-1}, obtained by taking 0.2 mL from a 2000 mgL-1 stock solution of copper. This stock solution was prepared by dissolving an appropriate amount of copper(II) sulfate pentahydrate in distilled water, followed by the addition of 0.2 mL of 2 M HNO_3 to prevent copper hydrolysis. The 2 sets of labelled thirty-one 5 mL extraction bottles containing 0.2 mL Cu(II) solution was made up to 2 mL mark by the addition of 1.8 mL buffers ranging from pH 1.5 to 9.0. To one set was added 2 mL of chloroform solution of 0.05 M H_2BuEtP and to the other set of thirty-one bottles were added 2 mL of chloroform solution of 0.05 M H_2BuEtP and 0.05 M HBuP in 9:1 volume ratio. The sixty-two bottles containing the two immiscible phases were agitated with a mechanical shaker for 60 minutes. The 60 minutes in related studies with same organic ligand phase for the extraction of other metals gave the best time for equilibration to occur (Godwin and Uzoukwu, 2012a: Godwin *et al*., 2012: Godwin and Uzoukwu, 2012b: Chukwu and Godwin, 2013: Godwin *et al*., 2013: Nwadiri et al., 2016: Godwin and Tella, 2023: Godwin *et al*., 2024).

The phases were allowed to separate out and 1 mL of aqueous raffinates were then taken with a micropipette 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.

$$D = \frac{Standard\ Absorbance - Raffinate\ Absorbance}{Raffinate\ Absorbance} \qquad \text{---------}1$$

$$\%\ E = \frac{Standard\ Absorbance - Raffinate\ Absorbance}{Standard\ Absorbance} \times 100 \qquad \text{---------}2$$

The log D is plotted against pH for both organic phases and from these plots the optimum pH/s for the distribution of Cu(II) ions between the two phases was determined. The two optimum pHs 6.0 and 8.75 were used in the variation of the ligand concentration (2.50×10^{-3} M to 4.00×10^{-2} M). These pHs were used for the metal distributions at a fixed synergist HBuP concentration of 5.00×10^{-3} M while the concentration of ligand H_2BuEtP varied between 2.50×10^{-3} M and 4.00×10^{-2} M. Similarly, metal distribution was analyzed with a fixed ligand concentration of 2.50×10^{-2} M, while the synergist HBuP concentration was adjusted from 2.50×10^{-3} M to 2.25×10^{-2} M. The Cu(II) concentrations were varied from 100 mgL^{-1} to 140 mgL^{-1} in the ligand H_2BuEtP alone and in the presence of HBuP in a 9:1 volume ratio solution and the process was repeated as earlier described.

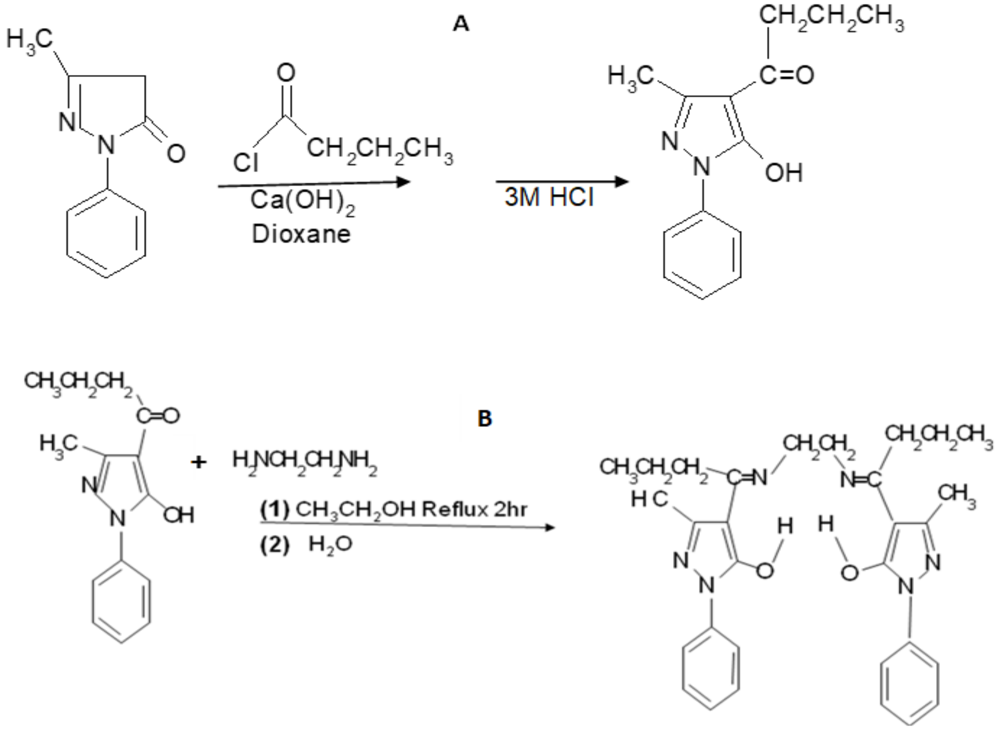


Figure 1: Synthetic route for (A) 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) and (B) 4,4´-(1E,1E´)-1,1´-(ethane-1,2-diylbis(azan-1-yl1ylidene)) bis (5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) (H_2BuEtP)

II. Results and Discussion

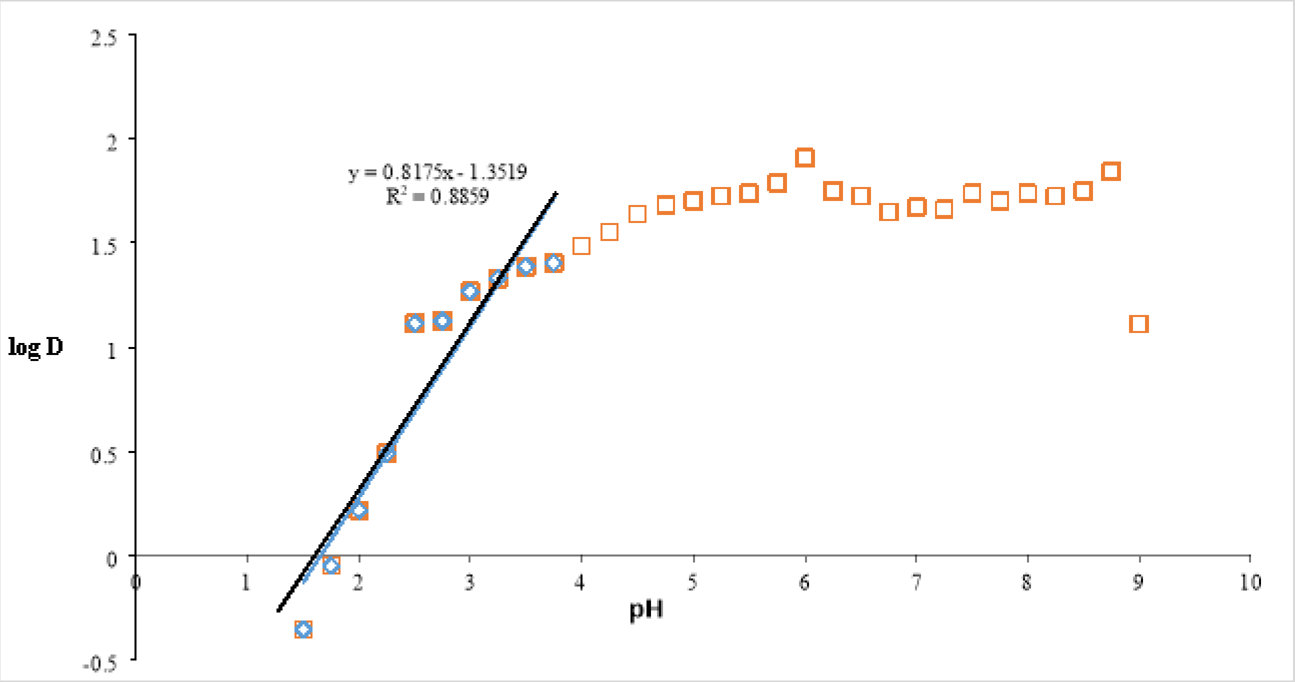


Figure 2: Plot of log D against pH in the Distribution of 200 mgL^{-1} Cu(II) between buffered aqueous phases and chloroform solutions of 0.05 M H_2BuEtP

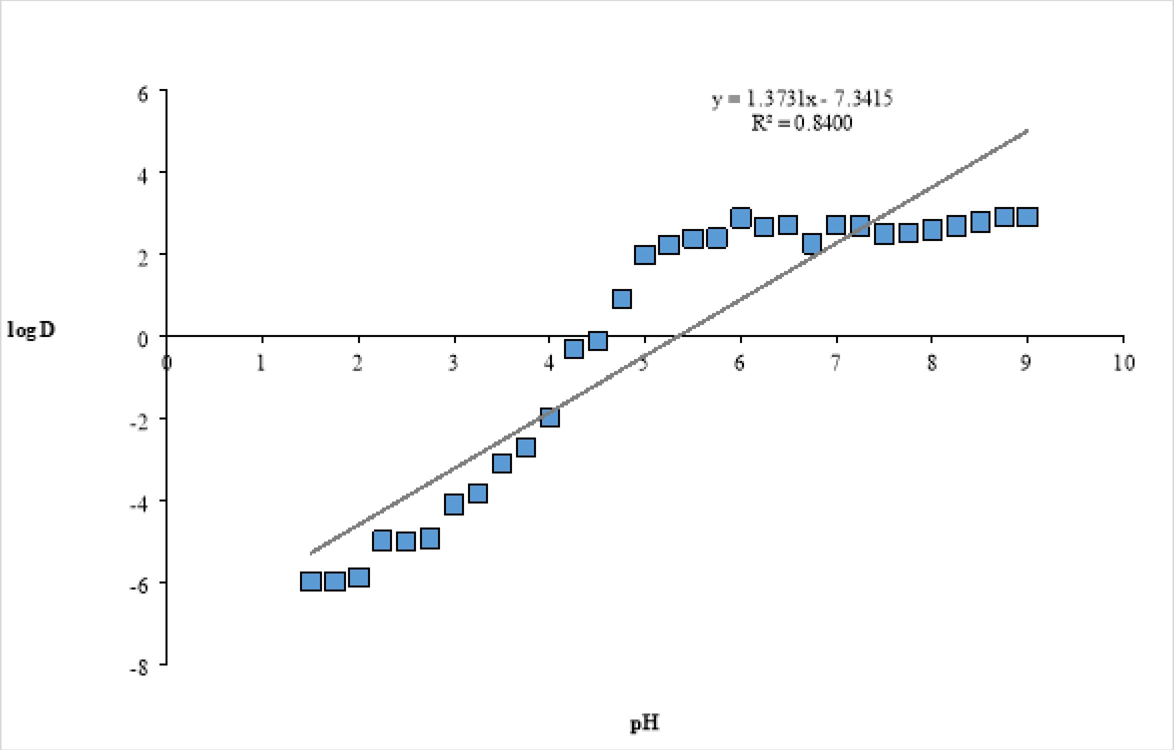


Figure 3: Plot of log D against pH in the Distribution of 200 mgL^{-1} Cu (II) between buffered aqueous phases and chloroform solutions of 0.05 M H_2BuEtP/0.05 M HBuP in a 9:1 volume ratio

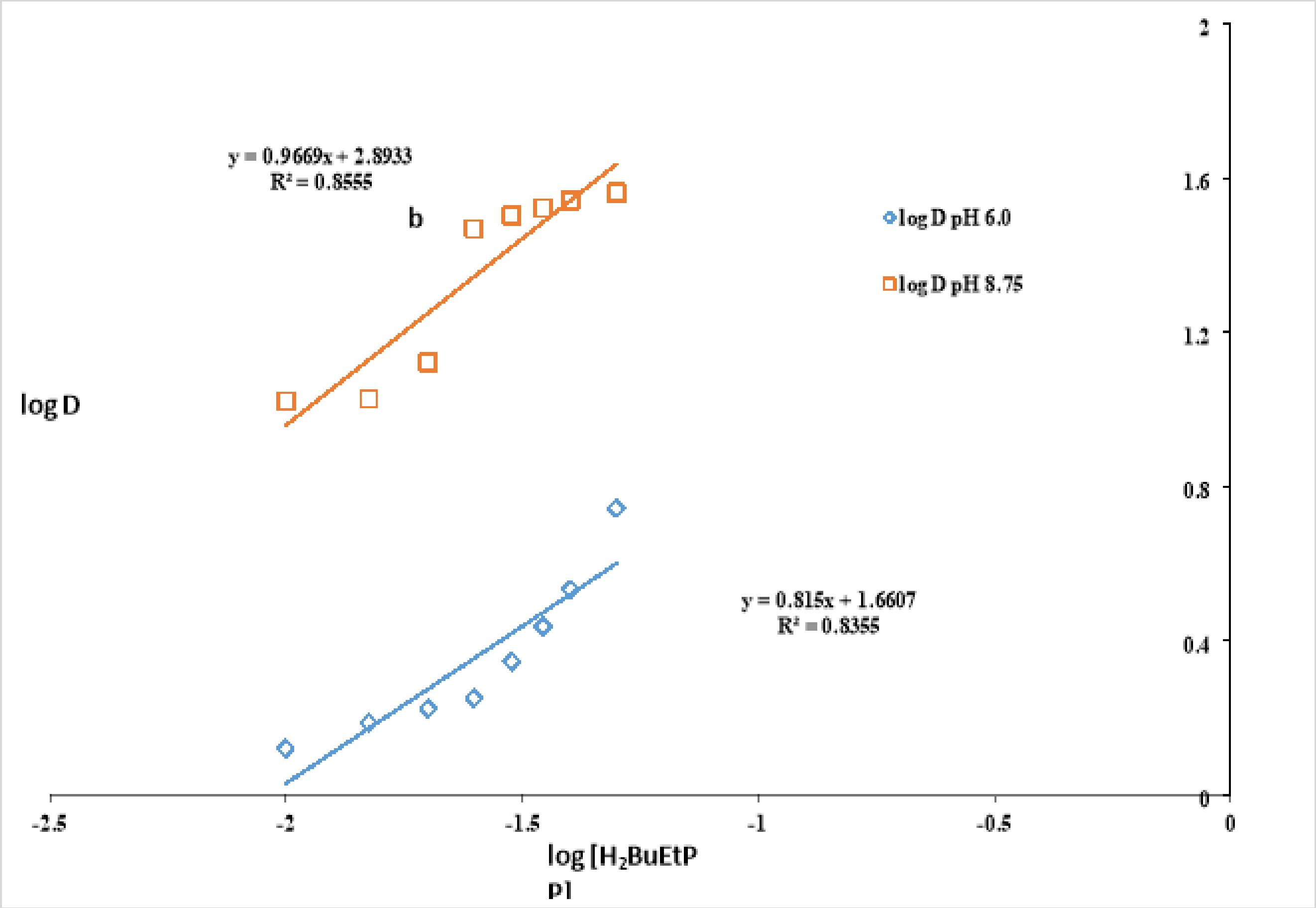


Figure 4: Plots of log D against log [H_2BuEtP] in Cu(II) distributions from aqueous solutions buffered at (a) pH 6.0 and (b) pH 8.75 into chloroform solutions of varied ligand [H_2BuEtP]

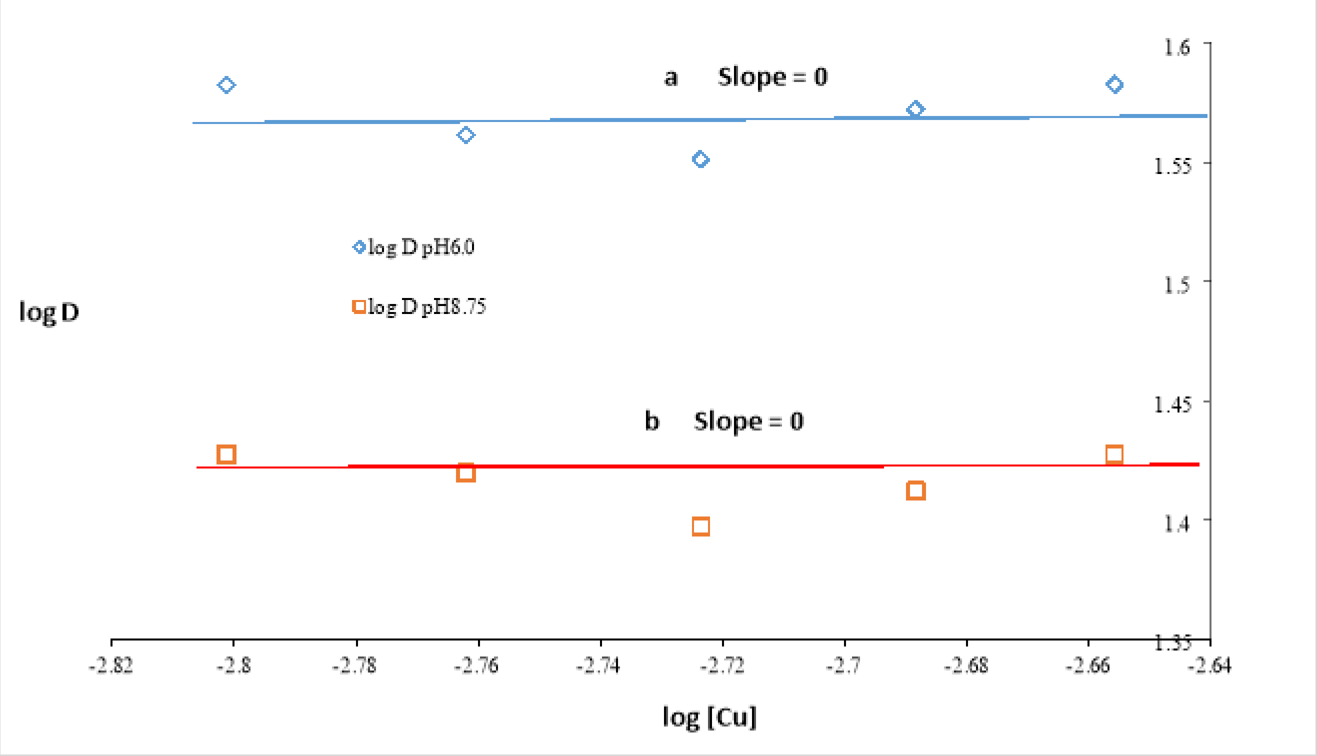


Figure 5: Plots of log D against log [Cu] from aqueous solutions buffered at (a) pH 6.0 and (b) pH 8.75 into chloroform solution of ligand [H_2BuEtP]

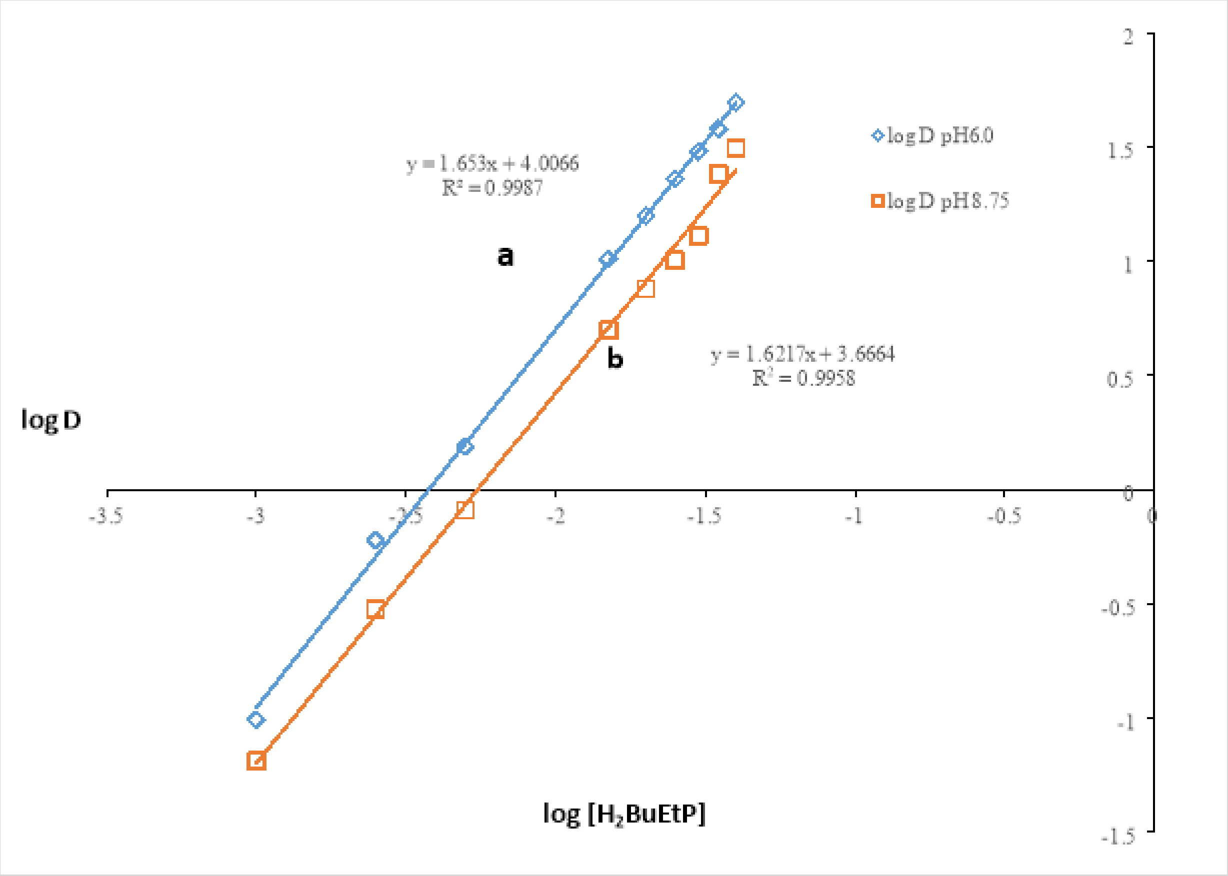


Figure 6: Plots of log D against log[H_2BuEtP] for the extraction of 200 mgL^{-1} Cu (II) from aqueous solutions into H_2BuEtP/HBuP solutions in chloroform with H_2BuEtP varied from 2.50 × 10^{-3} to 4.00 × 10^{-2} M and HBuP kept constant at 5.00 × 10^{-3} M in (a) pH 6.0 and (b) 8.75

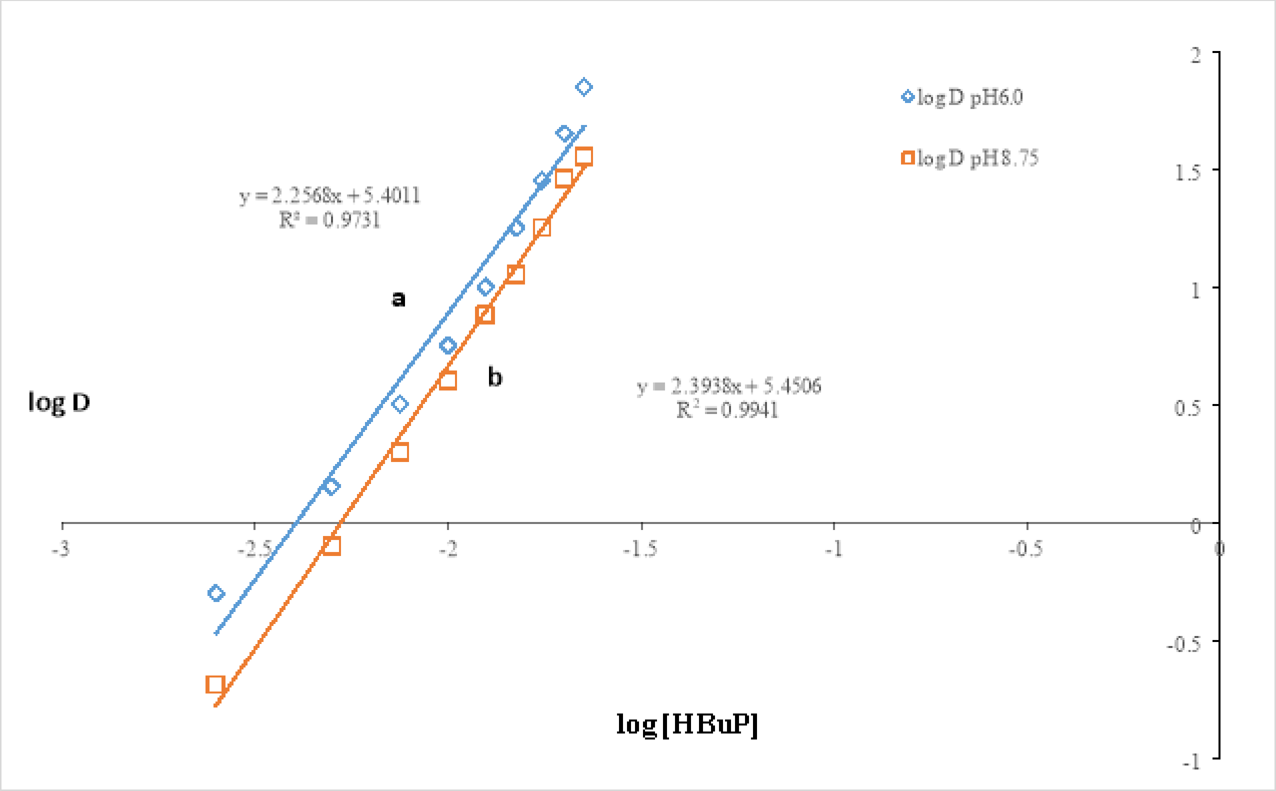


Figure 7: Plots of log D against log [HBuP] for the extraction of 200 mgL^{-1} Cu(II) from aqueous solutions into H_2BuEtP/HBuP solutions in chloroform with HBuP varied from 2.50×10^{-3} to 2.25×10^{-2} M and H_2BuEtP kept constant at 2.50×10^{-3} M in (a) pH 6.0 and (b) 8.75.

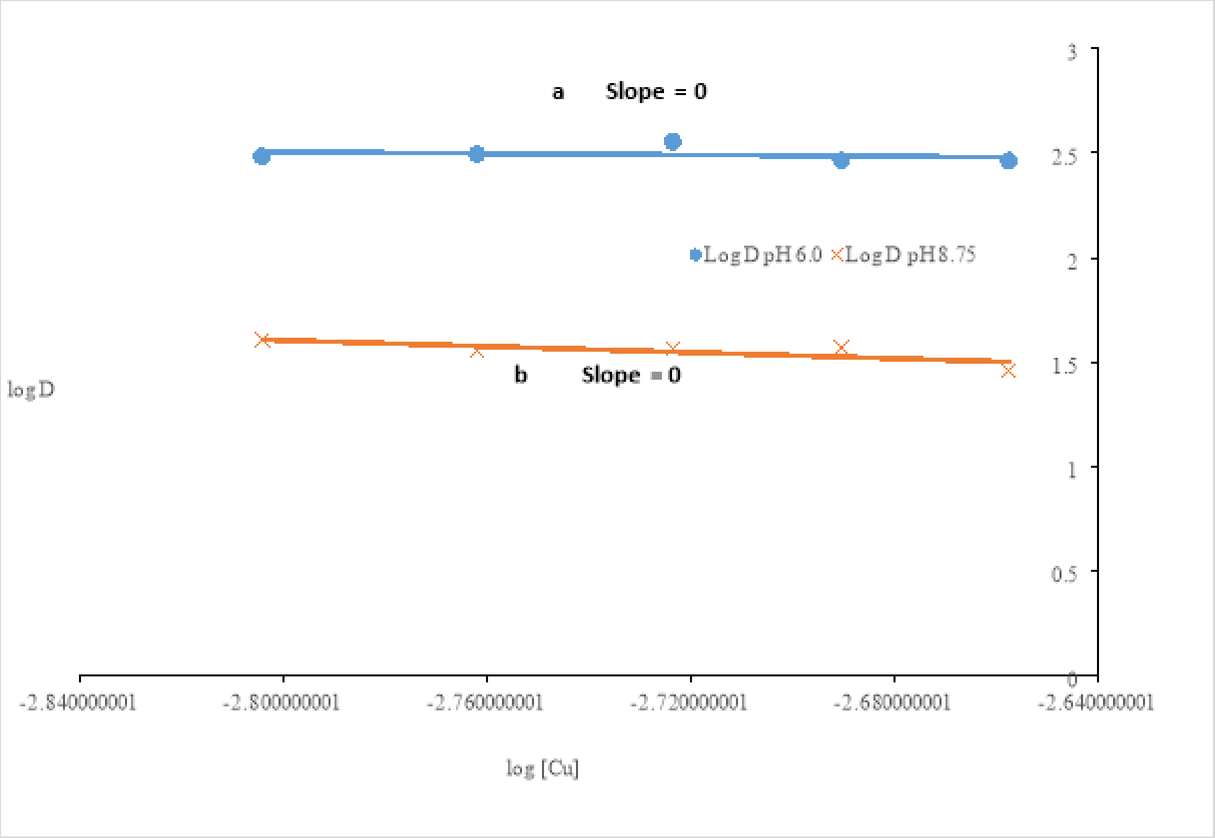


Figure 8: Plots of log D against log [Cu] for the extraction of Cu (II) from aqueous solutions into chloroform solutions of 0.05 M H_2BuEtP /0.05 M HBuP in 9:1 volume ratio at (a) pH 6.0 and (b) pH 8.75.

Distribution with Ligand H_2BuEtP alone

Plots of log D against pH for the extraction of 200 mgL^{-1} Cu(II) from buffered aqueous phases using ligand H_2BuEtP as shown in Table 1 and Figure 2, gave a slope of 0.82 which can be approximated to 1 and indicates that only 1 proton from the ligand H_2BuEtP was displaced in the reaction with Cu(II). The expected reaction of Cu(II) with the ligand H_2BuEtP is shown in equation 3 with displacement of 2 protons.

$$\mathbf{Cu^{2+} + H_2BuEtP_{(o)} \rightleftharpoons CuBuEtP_{(o)} + 2H^+} \qquad \text{---------} \ 3$$

where H_2BuEtP is the tetradentate Schiff base with the assumption that the metal : ligand interaction is in the 1:1 mole ratio.

$$K_{ex} = \frac{[Cu(BuEtP)_{(o)}][H^+]^2}{[[Cu^{2+}][H_2BuEtP_{(o)}]} \qquad \text{---------}4$$

The distribution ratio *D* is given by *D* = $[Cu(BuEtP)_{(o)}]/[Cu^{2+}]$), which on substitution into equation (4*)* gives,

$$\mathbf{Log\ D = log\ K_{ex} + log[H_2BuEtP] + 2pH} \qquad \text{---------}5$$

where K_{ex} is extraction constant.

Figure 2 also showed that pH 6.0 and 8.75 gave the highest Percentage Extraction (%E) of 99.87 and $pH_{1/2}$ at 2.45. The two pHs (Tables 2 and 3) were used in the other studies of ligand variation and metal variation with plots in Figures 4 and 5. Ligand H_2BuEtP concentration variation plots gave approximately slopes of 1 at both pHs, while Cu(II) concentration variation plots gave slopes of zero. These results confirm the reaction between the ligand H_2BuEtP and Cu(II) is in 1:1 mole ratio as the reaction between ligand and metal ion is independent of metal concentrations as shown in Figure 5 with a slope of zero. Thus, the proposed reaction is slightly different from that expected in equation 3 and is given in equation 6 with the resultant distribution ratio *D* given in equation 7.

$$\mathbf{Cu^{2+} + H_2BuEtP(o) + X^- \rightleftharpoons Cu(HBuEtP)X + H^+} \qquad \text{--------}6$$

Where X^- is anions such as Cl^-, CH_3COO^- etc. from the buffers.

$$\mathbf{K_{ex}} = \frac{[Cu(HBuEtP)X_{(o)}][H^+]}{[[Cu^{2+}][H_2BuEtP_{(o)}]} \qquad \text{---------}7$$

Since $[Cu(HBuEtP)X_{(o)/[}Cu^{2+}] = D$

The extraction equation for the distribution is given by equation 8

$$\mathbf{Log\ D = log\ K_{ex} + log\ [H_2BuEtP] + pH} \qquad \text{---------}8$$

The values for log D and log K_{ex} were determined using the slopes and intercepts from plots of log D against log $[H_2BuEtP]$ in Figure 4 and equation 8 to be pH 6.0 (log D = 0.35 and log K_{ex} = -4.35) and pH 8.75 (log D = 1.59 and log K_{ex} = -5.86) and thus, for the ligand H_2BuEtP alone, log D_1 = 0.97 ± 0.62 and log K_{ex} = -5.11 ± 0.75. In a related study with Cu(II) with the ligand H_2PrEtP alone by Nwadiri *et al*., (2016), they reported the $pH_{1/2}$ at 4.57, log D = 1.56 ± 0.01 and log K_{ex} = -3.25 ± 0.10. Comparing the two ligands log D and log K_{ex} indicated that the H_2PrEtP was a slightly better extractant for Cu(II) than H_2BuEtP with a higher extraction constant log K_{ex} and the partition coefficient log D of the formed Cu(II) complex $Cu(HPrEtP.X)_{(o)}$ higher than that of $Cu(HBuEtP.X)_{(o)}$.

Combining all the results from slope analysis we are proposing the structure of $Cu(HBuEtP.X)_{(o)}$ to be that shown in Figure 9.

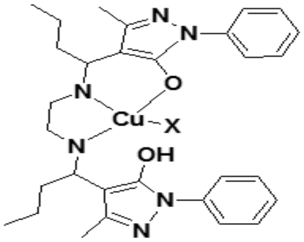


Figure 9: Proposed Structure of Cu(HBuEtP.X)

Distribution with Ligand H_2BuEtP and HBuP

Figure 3 showed that the $pH_{1/2}$ for the mixed ligands H_2BuEtP/HBuP system was established at pH 4.45. The shift in $pH_{1/2}$ to a less acidic media in the presence of the mixed ligands H_2BuEtP/HBuP was also reported in the distribution of Pb(II) and Cd(II) (Godwin and Uzoukwu, 2012a: Godwin and Tella, 2023) as against a more acidic media for the mixed ligands H_2BuEtP/HBuP system reported for UV(VI), Ni(II), Fe(II) (Godwin *et al*., 2012: Godwin and Uzoukwu, 2012b: Godwin et al., 2013) and in Cu(II) study with HPrEtP (Nwadiri *et al*., 2016). Figure 2 also showed again that pH 6.0 and 8.75 gave the highest Percentage Extraction (%E) with > 99.8% and the two buffers were used in the other studies.

In the distribution of Cu(II) from the buffered aqueous phases with the mixed ligands H_2BuEtP/HBuP, plots of log D against pH as in Figure 3 gave a slope of 1.46 which is approximately 2 indicating that 2 protons were displaced from the ligands. This result was different from that reported by Nwadire *et al.*, 2016, for the distribution of Cu(II) with H_2PrEtP/HPrP in which only a proton was displaced. Results for ligand H_2BuEtP concentrations varied with HBuP concentration held constant and HBuP concentrations varied and H_2BuEtP concentration held constant gave slopes of approximately 2. Also, the plots of log Cu(II) concentrations varied against log D with the mixed ligands H_2BuEtP/HBuP at both pH of 6.0 and 8.75 gave slopes of zero and also confirmed the independence of the metal concentrations in the distribution of the metal ions into the organic phases as shown in Figure 8. Combining these results, we are proposing the reaction of Cu(II) in the mixed ligands H_2BuEtP/HBuP organic extractant system as that shown in equation 9

$$\mathbf{Cu^{2+} + H_2BuEtP_{(o)} + HBuP_{(o)} \rightleftharpoons Cu(HBuEtP.BuP)_{(o)} + 2H^+} \qquad \text{---------9}$$

$$K_{ex} = \frac{[Cu(HBuEtP.BuP)_{(o)}][H^+]^2}{[[Cu^{2+}][H_2BuEtP_{(o)}][HBuP_{(o)}]} \qquad \text{---------10}$$

The Distribution ratio (D) which is [Cu(HBuEtP.BuP]/[Cu^{2+}] when substituted in equation 10 will give the extraction equation 11 for the distribution of Cu(II) between the aqueous phases and the mixed ligands H_2BuEtP/HBuP organic extractant system.

$$\mathbf{Log\ D = log\ K_{ex} + log\ [H_2BuEtP] + log\ [HBuP] + 2pH} \qquad \text{--------11}$$

Based on slope analysis from Figures 3, 6, 7, 8 and equation 9, we have proposed Figure 10 as the structure of the formed Cu(II) adduct Cu(HBuEtP.BuP) in the presence of HBuP considering that Figures 3, 6 and 7 are showing that two protons were displaced from the slopes as against 1 from Figure 2. We are considering the second proton to come from the protonated HBuP in the agitation process due to keto-enol conversion (Uzoukwu, 2009).

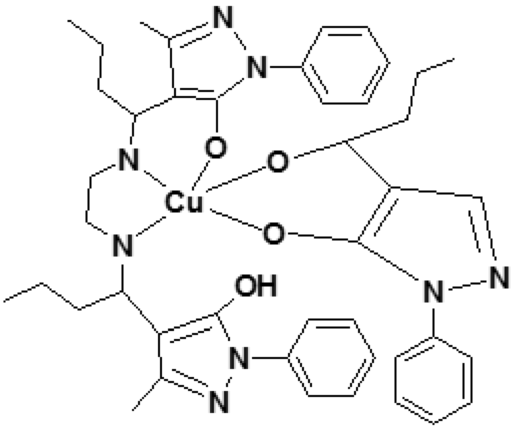


Figure 10: Proposed structure of Cu(HBuEtP.BuP)

The values for log D_2 and log K_{ex2} were calculated using slopes and intercepts from Figures 6, 7 and equation 11 to be pH 6.0 (log D = 2.11 and log K_{ex} = -7.30 and pH 8.75 (log D = 1.96 and log K_{ex} = -12.05). Overall, log D_2 = 2.03 ± 0.81 and log K_{ex2} = -12.94 ± 1.26 were determined for the mixed H_2BuEtP/HBuP organic extractant system. The extraction constant log K_{ex} values are usually used to access the efficiency of an organic extractant for a particular metal ion (Uzoukwu and Adiukwu, 1996): Uzoukwu, 2009 : Ukoha *et al*., 2010). The log K_{ex} values for pH 6.0 were higher than those at pH 8.75 in both ligand H_2BuEtP alone and in the mixed ligands H_2BuEtP/HBuP organic extractants system and thus, considered the optimum buffer pH for the distribution of Cu(II) between aqueous phases and the ligand H_2BuEtP organic phase. Likewise, log K_{ex1} (-5.11 ± 0.75) value for ligand H_2BuEtP is higher than that of log K_{ex2} (log K_{ex2} = -12.94 ± 1.26) for the mixed ligands H_2BuEtP/HBuP organic system and as such the presence of HBuP did not exert any synergic effects even though the partition coefficient log D of the mixed ligands

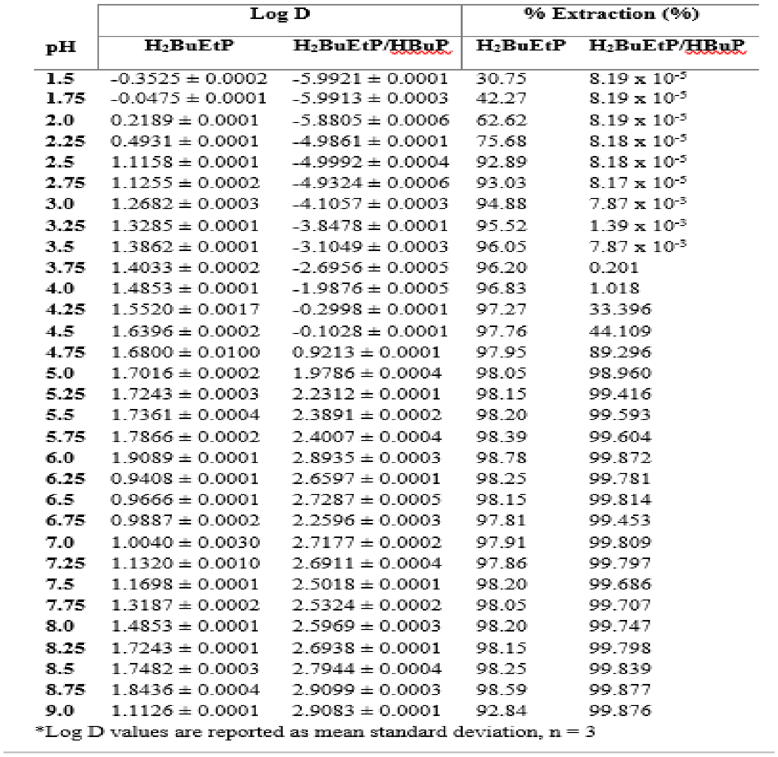
H_2BuEtP/HBuP was higher than that for ligand H_2BuEtP alone system (log D_2 = 2.03 ± 0.81 > log D_1 = 0.97 ± 0.62). An independent t test was performed to compare log D_1 and log K_{ex1} of the ligand alone, and log D_2 and log K_{ex2} for the ligand mixed with the synergist, at the 95% confidence level. There was no significant difference observed for the mean value log D_1 (0.97 ± 0.62) and log D_2 (2.03 ± 0.81; t(4) = 1.7999, p = .15). On the contrary, a significant difference was observed for the log K_{ex1} (-5.11 ± 0.75) and log K_{ex2} (-12.94 ± 1.26) values with p < .05 and t(4) = 9.245.

Nwadire *et al.*, 2016 in related study with Cu(II) reported a slightly higher value for H_2PrEtP/HPrP of -3.12 ± 0.10 than for H_2PrEtP of -3.25 ± 0.10. However in studies of U(VI) with both H_2BuEtP and H_2PrEtP, the H_2BuEtP system was a better extractant system than H_2PrEtP with higher extraction constant log K_{ex}(H_2BuEtP log K_{ex} -1.68 ± 0.12 > H_2PrEtP log K_{ex} -5.84 ± 0.18 and H_2BuEtP/HBuP log K_{ex} -0.72 ± 0.13 > H_2PrEtP/HPrP log K_{ex} -8.74 ± 0.50. While a slight synergic effect was exerted by HBuP, there was no synergic effect in the presence of HPrP (Godwin and Uzoukwu, 2012b: Nwadiri *et a*l., 2016). Thus, the chain length of related ligands effects in the distribution of metal ions from aqueous phases is related to the type of metal ion. In other studies with same H_2BuEtP alone and in the mixed ligands organic extractants system, synergic effect of HBuP was reported for Ni(II) and Fe(II) (Godwin *et al*, 2012: Godwin *et al*, 2013) while no such effects was observed for Pb(II) and Cd(II) (Godwin and Uzoukwu, 2012a: Godwin and Tella, 2023) as shown in Table 4.

Studies on other metals indicate that the extraction efficiency of the ligand H_2BuEtP, based on the extraction constant log K_{ex}, follows this order: Pb(II) > U(VI) > Zn(II) > Cd(II) > Cu(II) > Ni(II) > Fe(II) when using H_2BuEtP alone. In contrast, for the mixed H_2BuEtP/HBuP system, the order is U(VI) > Pb(II) > Cd(II) > Ni(II) > Cu(II) > Fe(II) (Godwin and Uzoukwu, 2012a: Godwin and Uzoukwu, 2012b: Godwin *et al.*, 2012: Chukwu and Godwin, 2013: Godwin *et al.*, 2013: Nwadiri *et al.*, 2016: Godwin and Tella, 2023: Godwin *et al*., 2024) from Table 4.

The changes in partition coefficient log D can be attributed to changes in dielectric constants related directly to the solvent systems with solvents that lead to a more negative enthalpy changes having higher partition coefficients log D and accounts for the closeness in log D values for the ligands in chloroform system with log D > 1.48 with the exceptions being log D values for UO_2^{2+}, Zn^{2+} and Cu^{2+} in H_2BuEtP/chloroform system. Comparatively, the 1-phenyl-3-methyl-4-benzoylpyrazolone (HBP) in Xylene for the extraction of Pb^{2+} and La^{3+} gave lower log D values of < 1.39 as shown in Table 4 (Uzoukwu and Adiukwu, 1996 : Housecroft and Sharpe, 2001). On the other hand, the disparities in the formation constants log K_{ex} shown in Table 4, is attributed to the type and energies of bonds formed between the metal ions and the ligands. Those with higher log K_{ex} values are ones in which the formation of the metal complexes have favourable energy factors and results in the ease in their formation of stronger bonds. A second ligand is expected to result in formation of adducts which are more hydrophobic and thus, expected to be transferred easily to the organic phases and thus can function as synergists but in some cases, due to energy barriers in their formation, their addition leads to lower log K_{ex} values even though their log D values are high as shown in Table 4 (Housecroft and Sharpe, 2001 : Uzoukwu, 2009 : Koh *et al*., 2005 : Imura *et al*., 2006 : Ukoha *et al*., 2010)

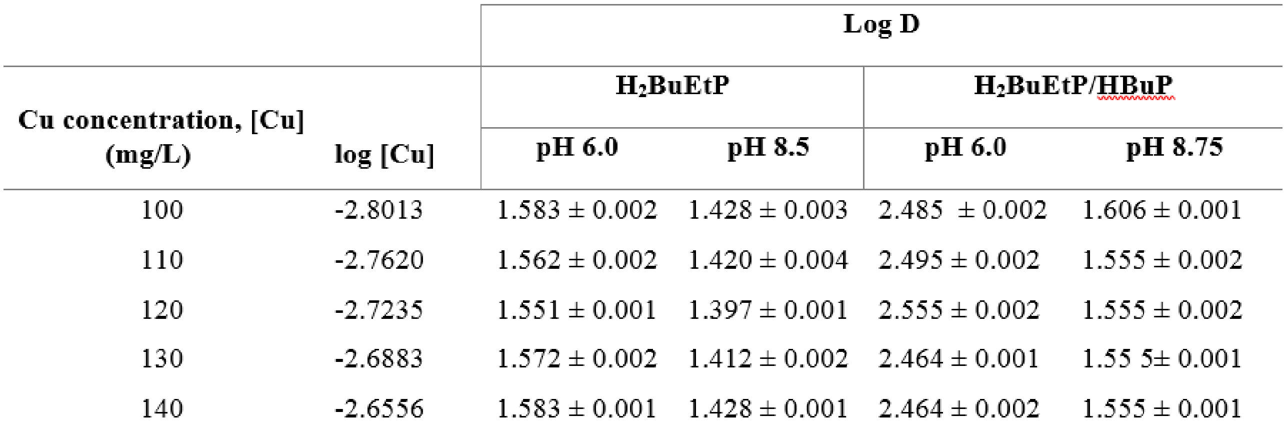
Table 1: Values of log D against pH in the Distribution of 200 mgL^{-1} Cu (II) between buffered aqueous phases and chloroform solutions of 0.05 M H_2BuEtP and chloroform solutions of 0.05 M H_2BuEtP/0.05 M HBuP in a 9:1 volume ratio



pH	Log D		% Extraction (%)	
	H_2BuEtP	H_2BuEtP/HBuP	H_2BuEtP	H_2BuEtP/HBuP
1.5	-0.3525 ± 0.0002	-5.9921 ± 0.0001	30.75	8.19 x 10^{-5}
1.75	-0.0475 ± 0.0001	-5.9913 ± 0.0003	42.27	8.19 x 10^{-5}
2.0	0.2189 ± 0.0001	-5.8805 ± 0.0006	62.62	8.19 x 10^{-5}
2.25	0.4931 ± 0.0001	-4.9861 ± 0.0001	75.68	8.18 x 10^{-5}
2.5	1.1158 ± 0.0001	-4.9992 ± 0.0004	92.89	8.18 x 10^{-5}
2.75	1.1255 ± 0.0002	-4.9324 ± 0.0006	93.03	8.17 x 10^{-5}
3.0	1.2682 ± 0.0003	-4.1057 ± 0.0003	94.88	7.87 x 10^{-3}
3.25	1.3285 ± 0.0001	-3.8478 ± 0.0001	95.52	1.39 x 10^{-3}
3.5	1.3862 ± 0.0001	-3.1049 ± 0.0003	96.05	7.87 x 10^{-3}
3.75	1.4033 ± 0.0002	-2.6956 ± 0.0005	96.20	0.201
4.0	1.4853 ± 0.0001	-1.9876 ± 0.0005	96.83	1.018
4.25	1.5520 ± 0.0017	-0.2998 ± 0.0001	97.27	33.396
4.5	1.6396 ± 0.0002	-0.1028 ± 0.0001	97.76	44.109
4.75	1.6800 ± 0.0100	0.9213 ± 0.0001	97.95	89.296
5.0	1.7016 ± 0.0002	1.9786 ± 0.0004	98.05	98.960
5.25	1.7243 ± 0.0003	2.2312 ± 0.0001	98.15	99.416
5.5	1.7361 ± 0.0004	2.3891 ± 0.0002	98.20	99.593
5.75	1.7866 ± 0.0002	2.4007 ± 0.0004	98.39	99.604
6.0	1.9089 ± 0.0001	2.8935 ± 0.0003	98.78	99.872
6.25	0.9408 ± 0.0001	2.6597 ± 0.0001	98.25	99.781
6.5	0.9666 ± 0.0001	2.7287 ± 0.0005	98.15	99.814
6.75	0.9887 ± 0.0002	2.2596 ± 0.0003	97.81	99.453
7.0	1.0040 ± 0.0030	2.7177 ± 0.0002	97.91	99.809
7.25	1.1320 ± 0.0010	2.6911 ± 0.0004	97.86	99.797
7.5	1.1698 ± 0.0001	2.5018 ± 0.0001	98.20	99.686
7.75	1.3187 ± 0.0002	2.5324 ± 0.0002	98.05	99.707
8.0	1.4853 ± 0.0001	2.5969 ± 0.0003	98.20	99.747
8.25	1.7243 ± 0.0001	2.6938 ± 0.0001	98.15	99.798
8.5	1.7482 ± 0.0003	2.7944 ± 0.0004	98.25	99.839
8.75	1.8436 ± 0.0004	2.9099 ± 0.0003	98.59	99.877
9.0	1.1126 ± 0.0001	2.9083 ± 0.0001	92.84	99.876

*Log D values are reported as mean standard deviation, n = 3

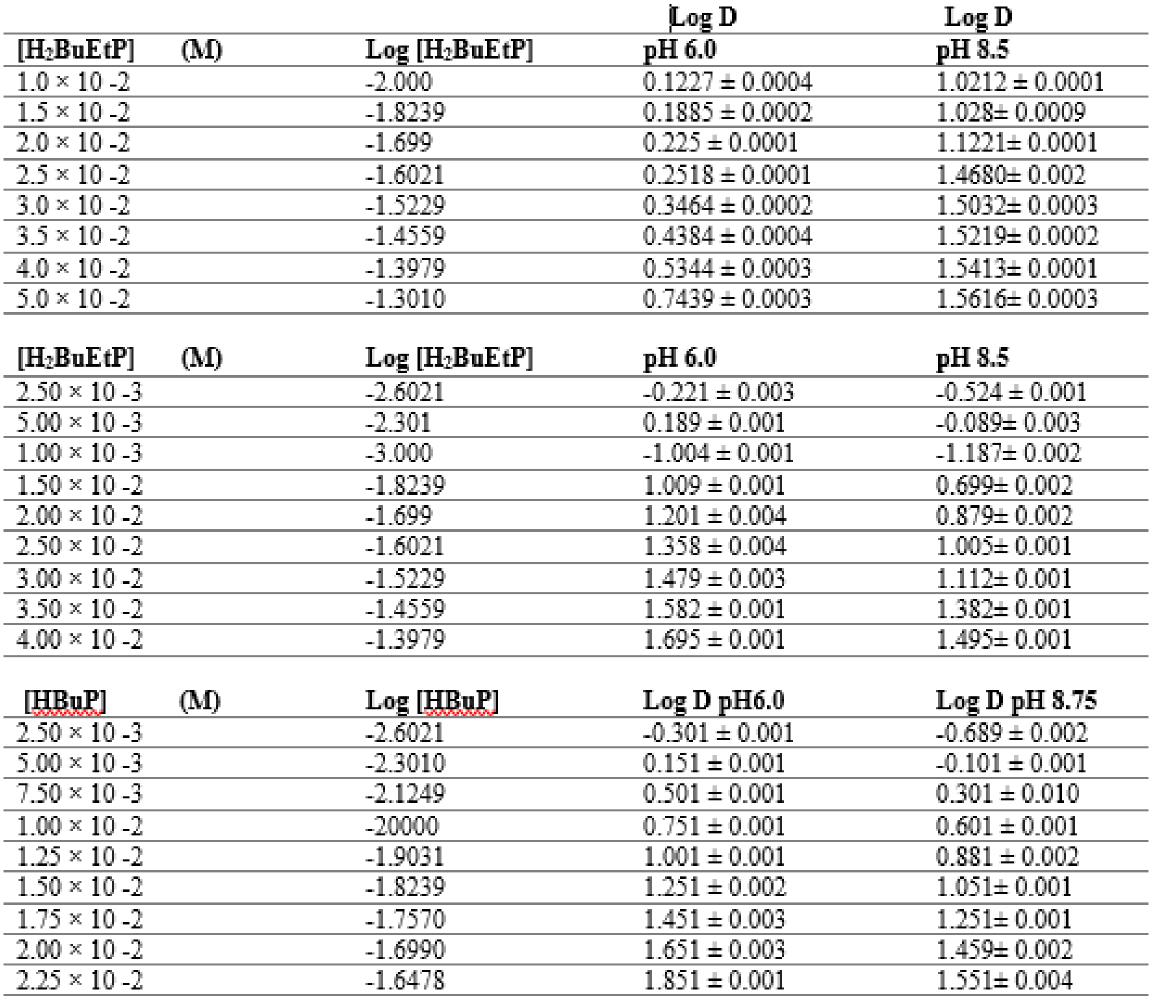
Table 2: Values of log D against log [Cu] from aqueous solutions buffered at (a) pH 6.0 and (b) pH 8.75 into chloroform solution of ligand [H_2BuEtP] and into chloroform solutions of 0.05 M H_2BuEtP /0.05 M HBuP in 9:1 volume ratio at (a) pH 6.0 and (b) pH 8.75.



Cu concentration, [Cu] (mg/L)	**log [Cu]**	**Log D**			
		H_2BuEtP		**H_2BuEtP/HBuP**	
		pH 6.0	**pH 8.5**	**pH 6.0**	**pH 8.75**
100	-2.8013	1.583 ± 0.002	1.428 ± 0.003	2.485 ± 0.002	1.606 ± 0.001
110	-2.7620	1.562 ± 0.002	1.420 ± 0.004	2.495 ± 0.002	1.555 ± 0.002
120	-2.7235	1.551 ± 0.001	1.397 ± 0.001	2.555 ± 0.002	1.555 ± 0.002
130	-2.6883	1.572 ± 0.002	1.412 ± 0.002	2.464 ± 0.001	1.55 5± 0.001
140	-2.6556	1.583 ± 0.001	1.428 ± 0.001	2.464 ± 0.002	1.555 ± 0.001

*Log D values are reported as mean standard deviation, n = 3

Table 3: Values of log D against log[H_2BuEtP] for the extraction of 200 mgL^{-1} Cu(II) from aqueous solutions buffered at pH 6.0 and pH 8.75 into (a) chloroform solutions of varied ligand [H_2BuEtP] (b) into H_2BuEtP/HBuP solutions in chloroform with H_2BuEtP varied from 2.50×10 $^{-3}$ to 4.00 × 10 $^{-2}$ M and HBuP kept constant at 5.00 × 10^{-3} M in (c) log D against log [HBuP] for the extraction of 200 mgL^{-1} Cu(II) from aqueous solutions into H_2BuEtP/HBuP solutions in chloroform with HBuP varied from 2.50 × 10 $^{-3}$ to 2.25 × 10 $^{-2}$ M and H_2BuEtP kept constant at 2.50 × 10 $^{-3}$ M



		Log D	**Log D**
[H_2BuEtP] (M)	**Log [H_2BuEtP]**	**pH 6.0**	**pH 8.5**
1.0 × 10 -2	-2.000	0.1227 ± 0.0004	1.0212 ± 0.0001
1.5 × 10 -2	-1.8239	0.1885 ± 0.0002	1.028± 0.0009
2.0 × 10 -2	-1.699	0.225 ± 0.0001	1.1221± 0.0001
2.5 × 10 -2	-1.6021	0.2518 ± 0.0001	1.4680± 0.002
3.0 × 10 -2	-1.5229	0.3464 ± 0.0002	1.5032± 0.0003
3.5 × 10 -2	-1.4559	0.4384 ± 0.0004	1.5219± 0.0002
4.0 × 10 -2	-1.3979	0.5344 ± 0.0003	1.5413± 0.0001
5.0 × 10 -2	-1.3010	0.7439 ± 0.0003	1.5616± 0.0003

[H_2BuEtP] (M)	**Log [H_2BuEtP]**	**pH 6.0**	**pH 8.5**
2.50 × 10 -3	-2.6021	-0.221 ± 0.003	-0.524 ± 0.001
5.00 × 10 -3	-2.301	0.189 ± 0.001	-0.089± 0.003
1.00 × 10 -3	-3.000	-1.004 ± 0.001	-1.187± 0.002
1.50 × 10 -2	-1.8239	1.009 ± 0.001	0.699± 0.002
2.00 × 10 -2	-1.699	1.201 ± 0.004	0.879± 0.002
2.50 × 10 -2	-1.6021	1.358 ± 0.004	1.005± 0.001
3.00 × 10 -2	-1.5229	1.479 ± 0.003	1.112± 0.001
3.50 × 10 -2	-1.4559	1.582 ± 0.001	1.382± 0.001
4.00 × 10 -2	-1.3979	1.695 ± 0.001	1.495± 0.001

[HBuP] (M)	**Log [HBuP]**	**Log D pH6.0**	**Log D pH 8.75**
2.50 × 10 -3	-2.6021	-0.301 ± 0.001	-0.689 ± 0.002
5.00 × 10 -3	-2.3010	0.151 ± 0.001	-0.101 ± 0.001
7.50 × 10 -3	-2.1249	0.501 ± 0.001	0.301 ± 0.010
1.00 × 10 -2	-20000	0.751 ± 0.001	0.601 ± 0.001
1.25 × 10 -2	-1.9031	1.001 ± 0.001	0.881 ± 0.002
1.50 × 10 -2	-1.8239	1.251 ± 0.002	1.051± 0.001
1.75 × 10 -2	-1.7570	1.451 ± 0.003	1.251± 0.001
2.00 × 10 -2	-1.6990	1.651 ± 0.003	1.459± 0.002
2.25 × 10 -2	-1.6478	1.851 ± 0.001	1.551± 0.004

*Log D values are reported as mean standard deviation, n = 3

Table 4: H_2BuEtP and Two other Ligands and their log D and log K_{ex} Values for Studied Metal ions

Ligand System	Metal ions	Log D	Log K_{ex}
H_2BuEtP in Chloroform	Pb^{2+}	1.92	-32.90
H_2BuEtP/HBuP in Chloroform		1.82	-9.79
H_2BuEtP in Chloroform	UO_2^{2+}	0.56	-1.68
H_2BuEtP/HBuP in Chloroform		1.74	-0.72
H_2BuEtP in Chloroform	Ni^{2+}	1.89	-12.39
H_2BuEtP/HBuP in Chloroform		1.89	-10.57
H_2BuEtP in Chloroform	Fe^{2+}	1.5	-13.45
H_2BuEtP/HBuP in Chloroform		1.68	-13.27
H_2BuEtP in Chloroform	Cd^{2+}	2.19	-3.01
H_2BuEtP/HBuP in Chloroform		3.15	-10.09
H_2BuEtP in Chloroform	Zn^{2+}	-3.05	-2.52
H_2BuEtP in Chloroform	Cu^{2+}	0.97	-5.11
H_2BuEtP/HBuP in Chloroform		2.03	-12.94
H_2PrEtP in Chloroform	UO_2^{2+}	1.49	-5.84
H_2PrEtP/HPrP in Chloroform		2.49	-8.71
H_2PrEtP in Chloroform	Cu^{2+}	1.56	-3.25
H_2PrEtP/HPrP in Chloroform		1.70	-3.12
1-phenyl-3-methyl-4-benzoylpyrazolone (HBP) in Xylene	Pb^{2+}	1.00	-0.43
1-phenyl-3-methyl-4-benzoylpyrazolone (HBP) in Xylene	La^{3+}	1.38	-0.76

III. Conclusion

From the results presented and from other studies of same extractant systems H_2BuEtP and HPrEtP for Cu(II) and other metals, we draw the following conclusions;

The optimal pHs for the extraction of Cu (II) using organic phases of the ligand H_2BuEtP alone or in the presence of HBuP are pH 6.0 and 8.75

The presence of HBuP shifted the $pH_{1/2}$ from more acidic pH of 2.45 in H_2BuEtP alone to a less acidic pH 4.50.

The log K_{ex} value for H_2BuEtP alone (-5.11 ± 0.70) was greater than that for H_2BuEtP/HBuP (-12.94 ± 1.26) and showed there was no synergic effect of HBuP in the distribution of Cu(II) between aqueous phases buffered to pH 6.0 and 8.75 and chloroform solutions of H_2BuEtP alone and in the presence of HBuP.

Slope analysis from plots proposed the reaction equations and structures of Cu(II) complexes distributed into both organic phases as Cu(HBuEtP.X) in ligand H_2BuEtP alone and Cu(HBuEtP.BuP) in H_2BuEtP/HBuP.

Results from this study and those of U(VI) with H_2BuEtP alone and in the presence of HBuP compared with those for H_2PrEtP alone and in the presence of HPrP showed from the extraction constants log K_{ex}, that the carbon chain length effects are dependent on the type of metal ion.

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