



EFFECT OF COMMON ACIDS AND ANIONS ON THE EXTRACTION OF IRON (II) FROM AQUEOUS SOLUTIONS INTO 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)

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ABSTRACT

The effect of common acids, anions, and auxiliary complexing agents in the solvent extraction of Fe^{2+} from aqueous solutions into chloroform solutions 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) 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 studied. Colorimetric method of analysis using 1,10-phenanthroline was used to determine concentrations of Fe^{2+} in aqueous solutions after extraction and percentage extraction determined by difference. Separation factors β_{xy} were calculated using data from previous studies using same organic phases to determine theoretical conditions for separating Fe^{2+} from Ni^{2+} , Pb^{2+} , and UO_2^{2+} . All acids gave > 90% extraction of Fe^{2+} at most concentrations with HNO_3 and H_2PO_4 giving the highest percentage extraction of 99.93% at 0.01M and 0.1M respectively in the mixed ligands H₂BuEtP/HBuP organic system. H_2PO_4 also gave best extraction of 99.3% at 0.1M in ligand H₂BuEtP alone system. Although all anions used for study also gave > 90% extraction of Fe^{2+} at different concentration in both types of organic phases, $CHCOO^-$, PO_4^{3-} , Br^- and tartrate ions gave the best extraction of Fe^{2+} with H₂BuEtP. Acids and anions behave as salting out agents or masking agents at different concentrations. Calculated separation factors β_{xy} indicated that it was theoretically possible to separate Fe^{2+} from Ni^{2+} with H_2PO_4 only and Fe^{2+} from Pb^{2+} with H_2PO_4 , HCl , and $EDTA$ with H₂BuEtP alone. With mixed ligands H₂BuEtP/HBuP, calculated separation factors β_{xy} showed that it was possible to separate Fe^{2+} from Ni^{2+} with HNO_3 and H_2PO_4 , Fe^{2+} from Pb^{2+} with HCl and oxalate, and Fe^{2+} from $U(VI)$ with $CHCOOH$, PO_4^{3-} , Br^- and oxalate. The number of batches of extraction n needed to achieve 99.9% separations are also calculated and shown.

Keywords: Acids, Anions, Percentage extraction, Ligands, Separation factor and extracting Fe (II).

Contribution/ Originality

This study contributes in the existing literature for the extraction of Fe(II) from aqueous media and offer theoretical prove of acids, anions and auxiliary complexing agents, their concentrations and the batches of extractions n required for the separation of Fe(II) from Ni(II), Pb(II) and U(VI) based on separation factors β_{XY} .

1. INTRODUCTION

Recent studies on extraction of metal ions from aqueous media using the 4-acylbis(pyrazoloneimines) Schiff bases have shown that, they have excellent extraction properties for the so far studied metal ions [1-4]. These 4-acylbis(pyrazoloneimines) derivatives have been reported to be more stable than their less bulky 4-acyl pyrazolones and thus form more stable metal complexes [5]. Mineral acids, ions and auxiliary complexing agents play important role in these extractions that is usually concentration dependent. They have been shown to either act as suppressors/inhibitors or releasing agents/enhancers in these extractions at varying concentrations [1-3, 6, 7]. The effects of common acids, ions and auxiliary complexing agents have also been exploited in the separation of various metal ions from aqueous solutions [8, 9]. In the extraction of Fe(II) from aqueous solutions using chloroform solution of N,N'-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine (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) as organic phase, it was reported that pH of 8.25 was optimal pH at which quantitative extraction of Fe(II) was achieved. The pH at which quantitative extraction of Fe(II) from aqueous solution into the organic phase was reported to slightly drop to 8.00 in the presence of 4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)butan-1-one) (HBuP) as a synergist in the distribution of Fe(II) between the two phases. The extraction parameters; pH_{1/2}, log D from extraction plots, and log K_{ex} calculated using extraction equations derived from slope analysis showed that the values in both type of organic phases were very close even though mixed ligands(H₂BuEtP/HBuP) organic phase values were slightly higher and better. Slope analysis also indicated that the Fe(II) complexes extracted into both organic phases were Fe(BuEtP)_o and Fe(HBuEtP)(BuP)_o respectively [10]. In continuation of our studies on the extraction of Fe(II) from aqueous solution using an organic phase of chloroform solution of N,N'-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine (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) and to completely evaluate the performance of N,N'-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine (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) in the extraction of Fe(II), we have studied the extraction of Fe(II) in the presence of some acids; CH₃COOH, HCl, H₃PO₄, HNO₃ and H₂SO₄, ions; Br⁻, CH₃COO⁻, Cl⁻, F⁻, I⁻, PO₄³⁻, NO₃⁻ and SO₄²⁻, and complexing agents; EDTA, oxalate, tartrate and thiocyanate ions. The effect of

these acids, ions and complexing agents in the mixed ligands ($H_2BuEtP/HBuP$) organic phase was also studied.

2. MATERIAL AND METHOD

All reagents and chemicals used in the study were all analytical grade from BDH and Aldrich. 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)butan-1-one ($HBuP$) (fig. 1) and 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) (fig. 2) were synthesised as described by Uzoukwu, et al. [5]. The ligands were recrystallized from aqueous ethanol and its purity established by elemental analysis for C, H and N. The synthesized ligand 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) melting point was determined with a melting point apparatus to be 234°C. Measurement of IR and NMR spectral data were done at the Institut für Anorganische Chemie, Technische Universität Dresden, Germany. Stock solutions of 0.05M H_2BuEtP and 0.05M ($HBuP$) were prepared by dissolving appropriate mass of the ligands in $CHCl_3$. A 2000mg l^{-1} stock solution of Fe^{2+} was prepared by dissolving 1.404g of Ferrous Ammonium Sulphate [$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$] in 100ml volumetric flask containing 2ml of dilute sulphuric [H_2SO_4] made up to the 100ml mark with deionized water after addition of 1ml of 10% hydroxyl amine solution. Buffer solutions of pH 8.00 and pH 8.25 were prepared with 0.1 M $KH_2PO_4/0.1$ M NaOH. The actual pH of solutions was determined with a Labtech Digital pH meter.

Two sets of 2ml aqueous solutions of 200mg l^{-1} Fe (II) containing various concentrations (0.001 – 1.0M) of acids, or anions with pH 8.00 and 8.25 were prepared in 10 ml extraction bottles. Two millilitres (2 mL) solutions of 0.05 M concentration of H_2BuEtP or 0.05M H_2BuEtP :0.05 M $HBuP$ (9:1 ratio by volume) in chloroform was pipetted into the aqueous phases in the extraction containers. 0.05M H_2BuEtP organic phase was added to aqueous phases containing Fe^{2+} and acids or ions with pH 8.25 and 0.05M H_2BuEtP :0.05 M $HBuP$ (9:1 ratio by volume) organic phases into aqueous solutions containing Fe^{2+} and acids or ions with pH 8.00. The immiscible phases were shaken mechanically for 40 minutes at a room temperature of 30 °C. A shaking time of 40 minutes was found suitable enough for equilibration. The two phases were allowed to settle and separated. The concentration of Fe(II) in the aqueous phase was determined Colorimetrically with a UV spectrophotometer (Spectronic 20 Genesys) at wavelength of 520nm [8, 11]. The colour development for Iron(II) determination was by addition of 10% solutions each of 0.1ml of hydroxylamine hydrochloric acid solution, 0.5ml of 1,10-phenanthroline and 0.5ml of sodium acetate. Fe(II) ion concentration extracted into the organic phase was determined by difference between the concentration of Fe(II) ions in aqueous phase before and after the extractions. 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 $D = C_o/C$.

The results from this study were then compared with results from extraction studies of Pb^{2+} , Ni^{2+} , and UO_2^{2+} [1-3] with same ligand H_2BuEtP and synergist $HBuP$ in the presence of these acids and ions, by calculating separation factors β_{XY} using equation 1.

$$\beta_{XY} = D_x/D_y \quad (1)$$

where $D_x > D_y$

Since equal volume of aqueous phase and organic phase was used during extractions, equation 2 reduced to equation 3.

$$C = C_{aq} \left[\frac{V_{aq}}{DV_{or} + V_{aq}} \right]^n \quad (2)$$

$$C = C_{aq} \left[\frac{1}{(D + 1)} \right]^n \quad (3)$$

Equation 3 was used to calculate n batches of extractions needed to achieve 99.9% separation of metal ions, where C_{aq} is the amount of metal ions originally present in the aqueous phases and C is the amount of one metal ion that remains in an aqueous phase after extractions.

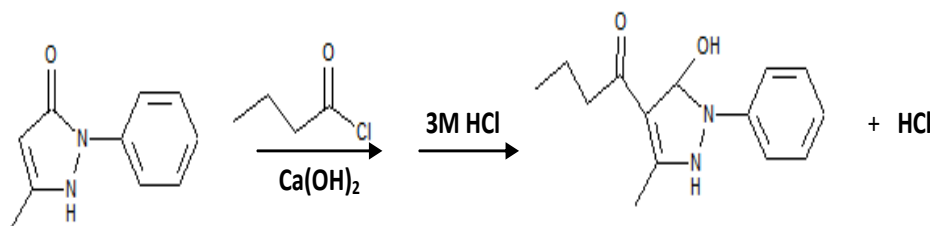


Figure 1: Reaction Synthesis of 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)butan-1-one (HBuP)

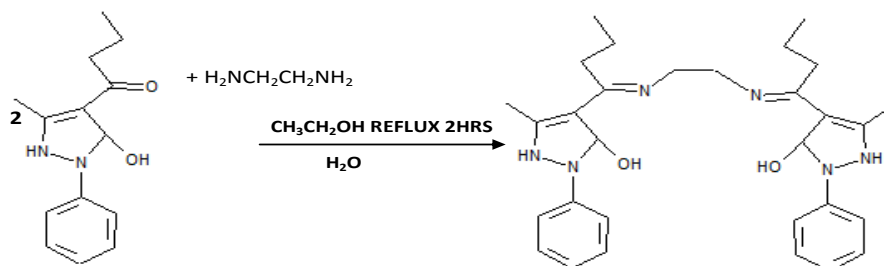


Figure 2: Reaction synthesis of 4,4'-(1E,1E')-1,1'-(ethane-1,2-diylbis(azan-1-yl-ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) Schiff base = H_2BuEtP

3. RESULTS AND DISCUSSION

3.1. Effect of Acids

As shown in fig. 3, percentage extraction of Fe(II) in the presence of mineral acids using the organic phase H_2BuEtP alone decreases as the concentration of the acids increases except for HCl. This has been attributed to unextractible anionic Fe(II) species which are more favourably formed at higher acid concentrations than in dilute acid solutions [3, 8]. Okafor and Uzoukwu [8] observed same behaviour in the extraction of Fe(III) and U(VI) with three derivatives of 1-phenyl-3-methyl-4-acyl-pyrazolone-5. The behaviour in HCl solution could be indicating that chloride ions from HCl is salting out Fe(II) at concentrations of HCl $> 0.05M$ as observed by Godwin and Uzoukwu [2] in the extraction of Pb(II) with same ligand H_2BuEtP . Even though all acids in the study gave $> 90\%$ extraction of Fe(II) at most concentrations studied, H_3PO_4 gave the best result as 99.3% extraction of Fe(II) was obtained at concentration of 0.1M.

In the presence of the mixed ligands H_2BuEtP and $HBuP$ (fig. 4), all the mineral acids showed decreasing percentage extraction of Fe(II) with increasing concentration of acids, confirming that unextractible anionic Fe(II) species are formed at higher acid concentrations. HNO_3 and H_3PO_4 gave the best results in the mixed ligands system as 99.93% extraction of Fe(II) was achieved at 0.01M for HNO_3 and 0.1M for H_3PO_4 . The results generally showed that $HBuP$ did not show significant synergistic improvement in the extraction of Fe(II) with H_2BuEtP .

Comparing results with those obtained for Ni(II), Pb(II), and U(VI) with same mineral acids using the ligand H_2BuEtP , it was observed that calculated separation factors β_{XY} were indicating that with the ligand H_2BuEtP alone, it was theoretically possible to separate Fe(II) from Ni(II) and Pb(II). For the separation of Fe(II) from Ni(II), it was only theoretically favourable in the presence of H_3PO_4 only at concentrations of H_3PO_4 from 0.001M to 0.5M where $> 10^4 \beta_{FeNi}$ was achieved. The calculated separation factors β_{XY} also showed that a single batch of extraction for separation of Fe(II) from Ni(II) was only possible at 0.5M concentration of H_3PO_4 where $> 10^5 \beta_{FeNi}$ was gotten. However, for the separation of Fe(II) from Pb(II), it was observed from results for separation factors β_{FePb} calculations, that it was achievable with HCl at concentrations 0.1M to 1.0M and H_3PO_4 at concentrations 0.05M to 0.1M where β_{FePb} was $> 10^4$. A single batch of extraction for separation of Fe(II) from Pb(II) was also only theoretically possible with H_3PO_4 where $> 10^5 \beta_{FePb}$ was gotten, but at concentration of 0.1M (table 1). Calculated separation factors β_{FeU} results indicated that it was not theoretically possible to separate Fe(II) from U(VI) using the five studied mineral acids with the ligand H_2BuEtP alone.

In the presence of $HBuP$ as a synergist, calculated separation factors β_{XY} indicated that it was only possible to separate Fe(II) from Ni(II) using only HNO_3 at concentration of 0.005M to 0.01M. The calculated separation factor β_{FeNi} at 0.01M of HNO_3 gave 3.5×10^5 , indicating that it was possible to achieve separation of Fe(II) from Ni(II) with a single batch of extraction at this HNO_3 concentration only. Calculated separation factor β_{FePb} in the presence of $HBuP$ showed that, separation of Fe(II) from Pb(II) was possible with HCl at 0.005M and 0.01M and H_3PO_4 at

0.05M and 0.1M as β_{FePb} was $> 10^4$. However, quantitative separation of Fe(II) from Ni(II) in a single batch of extraction was only theoretically possible with 0.1M of H_3PO_4 as β_{FePb} was $1.4 \times 10^6 > 10^5$. In the presence of HBU P, separation factor β_{FeU} results indicated that it was theoretically possible to separate Fe(II) from U(VI) using only CH_3COOH at concentrations of 0.5M to 1.0M as β_{FeU} values were $> 10^4$. The results however, indicated that two batches of extractions were theoretically required to achieve quantitative separation (table 2).

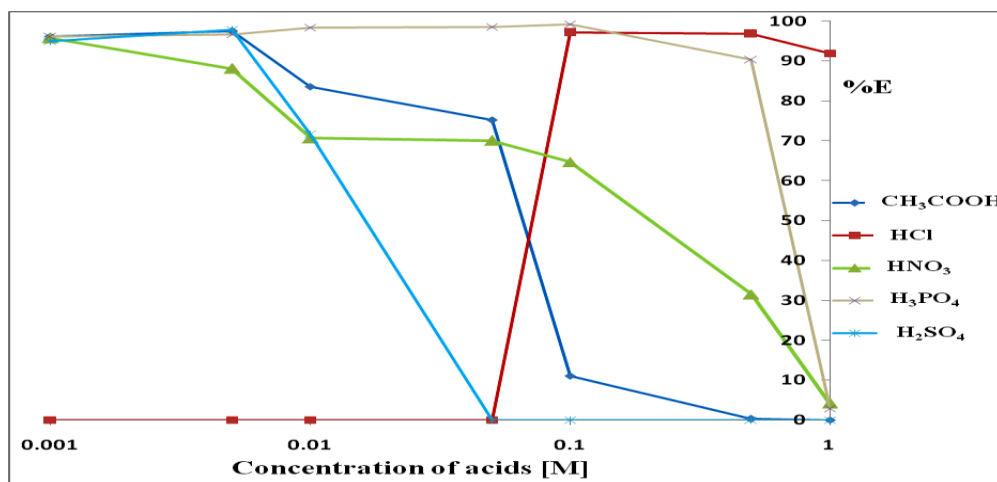


Figure 3: Plots of % extraction of 200 mg l^{-1} of Fe(II) from mineral acid solutions into 0.05M H_2BuEtP solution

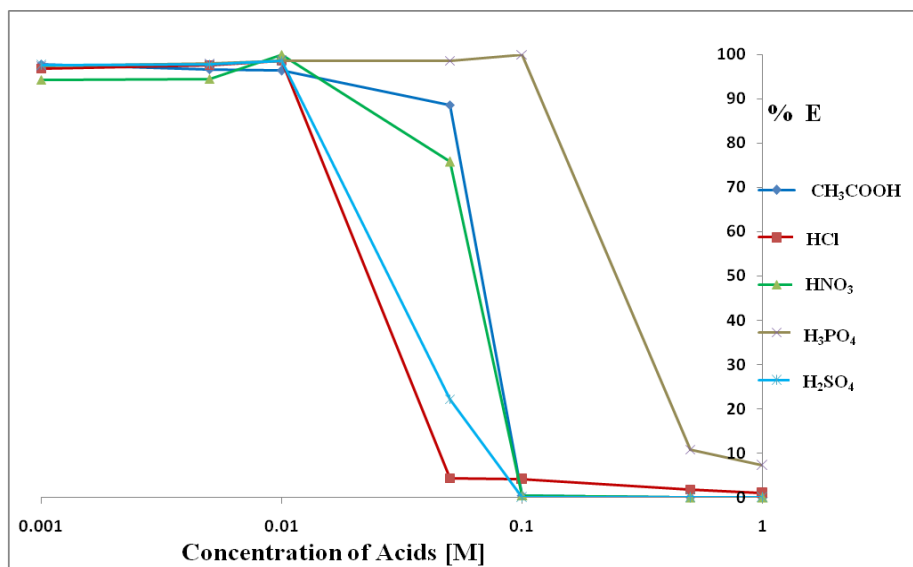


Figure 4: Plots of % extraction of 200 mg l^{-1} of Fe(II) from mineral acid solutions into 0.05 M H_2BuEtP -0.05 M HBU P (9:1) solution

Table-1. Calculated Separation factors $\beta_{XY} > 10^4$ with H₂BuEtP alone

H ₃ PO ₄ [M]	%E _{Fe}	D _{Fe}	%E _{Ni}	D _{Ni}	$\beta_{NiFe}(10^4)$	n _{Fe}	n _{Ni}
0.001	96.24	25.59	0.10	0.001	2.56	2	6911
0.005	96.73	29.55	0.10	0.001	2.96	2	6911
0.01	98.40	61.44	0.10	0.001	6.14	2	6911
0.05	98.54	67.38	0.10	0.001	6.74	2	6911
0.1	99.93	142.60	0.10	0.001	14.3	1	6911
HCl[M]	%E _{Fe}	D _{Fe}	%E _{Pb}	D _{Pb}	$\beta_{PbFe}(10^4)$	n _{Fe}	n _{Pb}
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0.1	97.15	34.02	0.10	0.001	3.40	2	6911
0.5	96.80	30.22	0.10	0.001	3.02	2	6911
1	91.92	11.38	0.10	0.001	1.14	3	6911
H ₃ PO ₄ [M]	%E _{Fe}	D _{Fe}	%E _{Pb}	D _{Pb}	$\beta_{PbFe}(10^4)$	n _{Fe}	n _{Pb}
0.05	98.54	67.38	0.10	0.001	6.74	2	6911
0.1	99.30	142.60	0.10	0.001	14.3	1	6911
EDTA[M]	%E _{Fe}	D _{Fe}	%E _{Pb}	D _{Pb}	$\beta_{PbFe}(10^4)$	n _{Fe}	n _{Pb}
0.001	80.92	4.24	0.10	0.001	8.09	4	6911
0.005	54.67	1.36	0.10	0.001	5.47	8	6911

Table-2. Calculated Separation Factors $\beta_{XY} > 10^4$ with H₂BuEtP and H₂BuP

HNO ₃ [M]	%E _{Fe}	D _{Fe}	%E _{Ni}	D _{Ni}	$\beta_{NiFe}(10^4)$	n _{Fe}	n _{Ni}
0.005	94.50	17.18	0.10	0.001	1.72	2	6911
0.01	99.93	1435.00	0.40	0.004	35.00	1	1688
H ₃ PO ₄ [M]	%E _{Fe}	D _{Fe}	%E _{Ni}	D _{Ni}	$\beta_{NiFe}(10^4)$	n _{Fe}	n _{Ni}
0.1	99.93	1435.00	9.35	0.100	1.44	1	73
HCl[M]	%E _{Fe}	D _{Fe}	%E _{Pb}	D _{Pb}	$\beta_{PbFe}(10^4)$	n _{Fe}	n _{Pb}
0.005	97.63	41.24	0.10	0.001	4.12	2	6911
0.01	98.61	70.80	0.10	0.001	7.08	2	6911
CH ₃ COOH[M]	%E _{Fe}	D _{Fe}	%E _U	D _U	$\beta_{UFe}(10^4)$	n _{Fe}	n _U
0.5	0.10	0.001	97.98	48.50	4.85	6911	2
1	0.10	0.001	95.96	23.75	2.38	6911	2
PO ₄ ³⁻ [M]	%E _{Fe}	D _{Fe}	%E _U	D _U	$\beta_{UFe}(10^4)$	n _{Fe}	n _U
0.05	99.92	1280.00	9.06	0.10	1.28	1	73
Br[M]	%E _{Fe}	D _{Fe}	%E _U	D _U	$\beta_{UFe}(10^4)$	n _{Fe}	n _U
0.5	94.84	18.36	0.10	0.001	1.84	2	6911
Oxalate[M]	%E _{Fe}	D _{Fe}	%E _{Pb}	D _{Pb}	$\beta_{PbFe}(10^4)$	n _{Fe}	n _{Pb}
0.1	0.10	0.001	94.36	16.79	1.68	6911	2
Oxalate[M]	%E _{Fe}	D _{Fe}	%E _U	D _U	$\beta_{UFe}(10^4)$	n _{Fe}	n _U
0.1	0.10	0.001	96.56	28.09	2.81	6911	2

3.2. Effect of Common Anions

The percentage extraction of Fe(II) in aqueous solutions containing the four anions into organic chloroform solution of the ligand H₂BuEtP in fig. 5 showed increasing percentage extraction as the concentration increases. This was attributed to formation of unstable anionic Fe(II) species which permitted the ligand H₂BuEtP to form an extractable complex with Fe(II) at these concentrations. With the ligand alone H₂BuEtP, 0.05M of the anions was observed as the highest concentration at which maximum extraction was attained for all four anions as above this

concentration the percentage extraction begin to decrease. This indicated that above 0.05M concentration of anions different types of anionic species of Fe(II) that are more stable and less hydrophobic were formed and as such the percentage extraction begins to drop. This salting out at lower concentrations and masking at higher concentrations of anions has been reported in many related researches [1, 6, 8]. In the ligand H₂BuEtP only organic phase, > 95% extraction of Fe(II) was achieved for all the anions studied and CH₃COO⁻ was observed as the anion that gave the best percentage extraction of Fe(II) with 99.93% extraction. The extraction of Fe(II) from aqueous solutions containing the anions using an organic chloroform solution of the ligand H₂BuEtP in the presence of HBuP shown in fig. 6 gave similar results as those obtained with the ligand H₂BuEtP alone. This indicated that HBuP did not synergistically enhance the distribution of Fe(II) from the aqueous media containing the various anions into the mixed ligands organic phase. With the mixed ligands, CH₃COO⁻ was also observed as the anion that gave the best percentage extraction of Fe(II) with 94.69% as the lowest percentage extraction at 0.5M, while PO₄³⁻ gave the highest percentage extraction at 0.05M. However, with the mixed ligands system masking of Fe(II) was very pronounced at 0.5M of NO₃⁻(13.27%) and SO₄²⁻(0.63%) as against 64.48% extraction of Fe(II) being the lowest percentage extraction obtained for SO₄²⁻ in the ligand H₂BuEtP alone system.

Calculated separation factors of Fe(II) for Pb(II) and U(VI) indicated that, theoretically it is not possible to separate Fe(II) from Pb(II) using the four anions with the ligand H₂BuEtP both in the absence and presence of HBuP as separation factors β_{FePb} were all $< 10^4$. However, β_{FeU} shown in *Table 1* indicated that while it was theoretically not possible to separate Fe(II) from U(VI) from an aqueous solution containing the two metal ions with the four anions with the ligand H₂BuEtP alone, it was only theoretically possible to separate Fe(II) from U(VI) with the PO₄³⁻ at 0.05M with the mixed ligands H₂BuEtP and HBuP as separation factor β_{FeU} of 1.28×10^4 was gotten as shown in *table 2*.

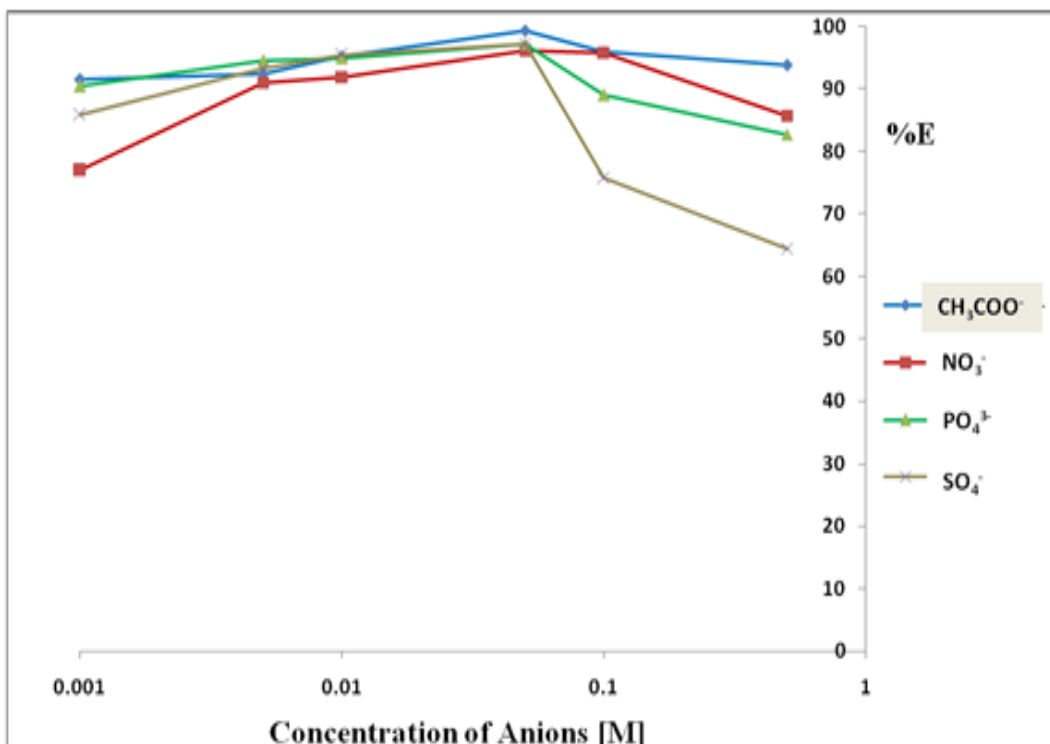


Figure-5. Plots of % extraction of 200 mg^l⁻¹ of Fe (II) in anions solutions into 0.05 M H₂ BuEtP solution

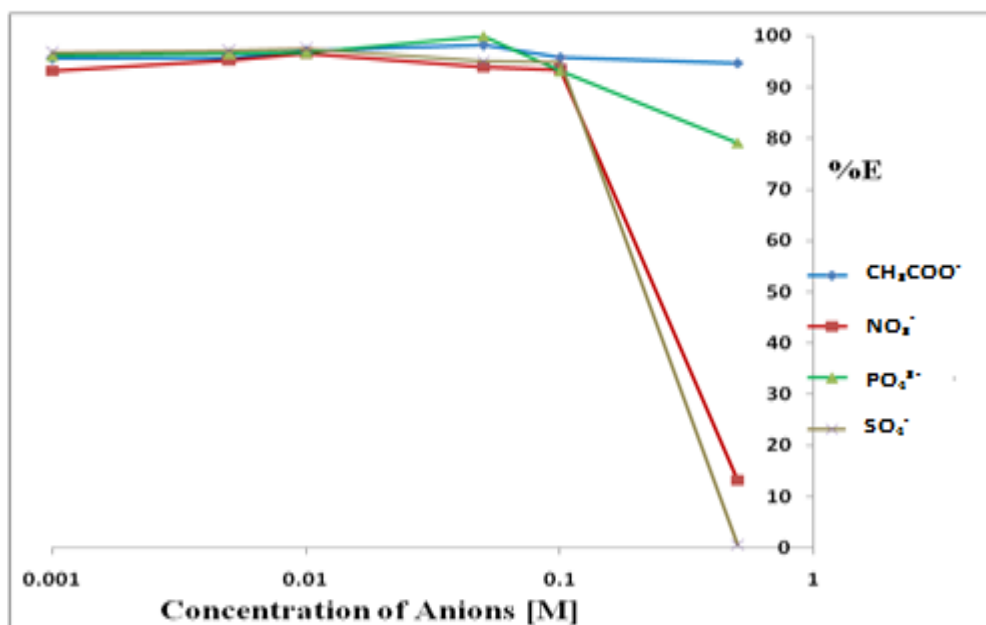


Figure-6. Plots of % extraction of 200 mg^l⁻¹ of Fe (II) in anions solutions into 0.05 M H₂ BuEtP-0.05 M HBuP (9:1) solution

3.3. Effect of Halogen Anions

The percentage extraction of Fe(II) in aqueous media containing the halogen anions in fig. 7 and fig. 8 showed that as the concentration of the anions increases, the percentage extraction of Fe(II) increases and reaches a maximum at a particular concentration of each halogen anion. While this behaviour was reported by Godwin and Uzoukwu, 2012a, for only Br⁻ and I⁻ in the extraction of Pb(II), same behaviour was observed for all the halogen anions in the extraction of Ni(II) [1] and U(VI) [3] with the same ligand H₂BuEtP. This has been attributed to formation of unstable anionic complexes of metals at lower concentrations of halide ions that enable formation of hydrophobic metal ligand complexes that distribute more into organic phases and formation of stable anionic complexes of metals at higher concentrations of anions, which are very hydrophilic and reduces distribution of metals into organic phases [1, 6, 8]. That is, anions of the halogens like other studied anions behave as salting out agents at lower concentrations and masking agents at higher concentrations.

Fig. 7 showed that, even though > 95% of extraction was attained with all the halogen anions, with the ligand H₂BuEtP alone, highest percentage of extraction of Fe(II) from aqueous solutions containing halogen anions was achieved at mostly different concentrations of the halogen anions; I⁻ 0.005M(%E = 96.49), Cl⁻ (%E = 96.69); F⁻ (%E = 95.39) at 0.05M and Br⁻ (%E = 97.73) at 0.1M. Results from fig. 8, however indicated that in the mixed ligand organic phase (H₂BuEtP/HBuP), the highest percentage extraction of Fe(II) was gotten at 0.01M for almost all of the halogen anions (I⁻, Cl⁻ and F⁻) with the exception of Br⁻(%E = 96.21 at 0.1M). Comparing results in the absence and presence of HBuP revealed that HBuP did not enhance the extraction of Fe(II) with the halogen anions as results of extraction of Fe(II) with H₂BuEtP alone, were even slightly better than those obtained with the mixed ligands(H₂BuEtP/HBuP) organic phase. Br⁻ in both H₂BuEtP alone and H₂BuEtP/HBuP gave the best percentage extraction of Fe(II) as > 94% was achieved even at 0.5M of Br⁻ in both type of organic phases. Separation factors β_{FePb} calculated in the presence of halide ions indicated that it would be theoretically difficult to separate Fe(II) from Pb(II) in an aqueous solution containing the halide ions using either the ligand H₂BuEtP alone or in a mixed ligands organic system with HBuP as all the values were < 10⁴. However, calculated separation factors β_{FeU} indicated that while it was not theoretically possible to separate Fe(II) from U(VI) from aqueous solutions containing the various halide ions with the ligand H₂BuEtP alone as $\beta_{FeU} < 10^4$, it was theoretically possible to separate Fe(II) from U(VI) only from an aqueous solution containing 0.5M Br⁻ with the mixed ligands H₂BuEtP/HBuP organic phase as $\beta_{FeU} > 10^4$ (table 2). The n_{Fe} value of 2 indicated that this separation could be only achieved with two batches of extractions.

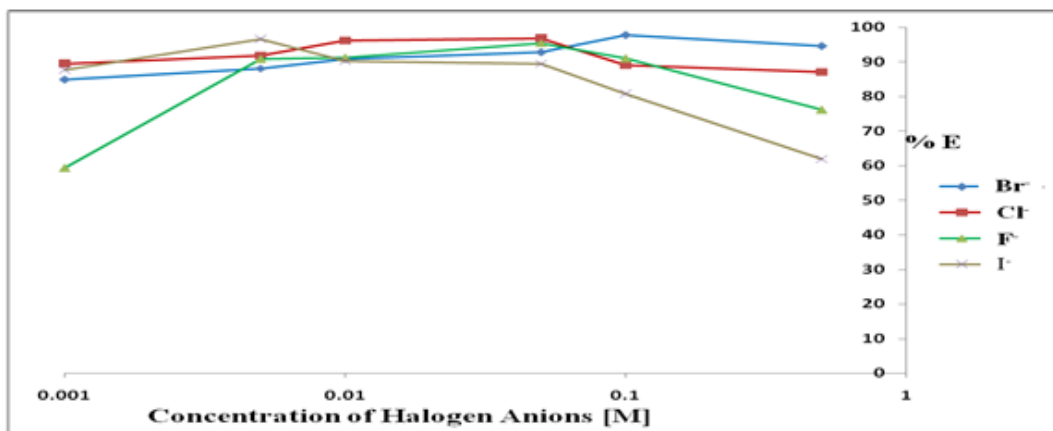


Figure-7. Plots of % extraction of 200 mg^l⁻¹ of Fe (II) from aqueous solutions containing Halogen anions into 0.05M H₂ BuEtP solution

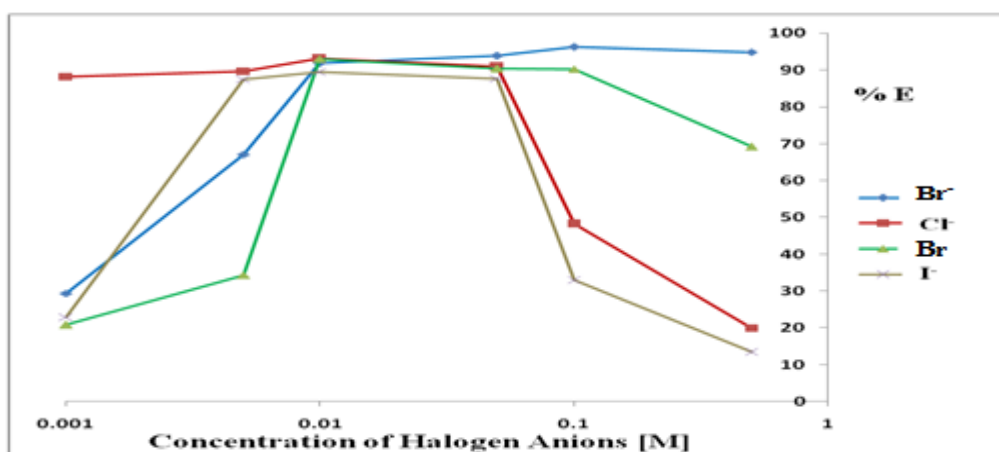


Figure-8. Plots of % extraction of 200 mg^l⁻¹ of Fe (II) from aqueous solutions containing Halogen anions into 0.05 M H₂ BuEtP- 0.05 M H BuP (9:1) solution

3.4. Effect of Auxilliary Complexing Agents

The percentage extraction of Fe(II) in aqueous solutions containing the auxiliary complexing agents into organic chloroform solution of the ligand H₂BuEtP in fig. 9 showed decreasing percentage extraction as the concentration increased above 0.001M for EDTA and Oxalate ion. Thiocyanate ion showed increasing percentage extraction of Fe(II) upto 0.01M(96.19%) before the percentage extraction of Fe(II) begins to decrease. However, tartarte ion gave the highest percentage extraction of Fe(II) with the ligand H₂BuEtP as a constant 99.93% extraction of Fe(II) was achieved from 0.001M – 0.1M before a slight reduction to 98.75% at 0.5M This behaviour has been attributed to formation of unstable anionic Fe(II) species which permitted the ligand H₂BuEtP to form an extractable complex with Fe(II) at these concentrations in which high percentage extraction of Fe(II) was gotten. The extraction of Fe(II) from aqueous solutions containing the auxiliary complexing agents using an organic chloroform solution of the ligand

H₂BuEtP in the presence of HBuP shown in fig. 10 gave results with similar trend as those obtained with the ligand H₂BuEtP alone. Apart from thiocyanate ion, results obtained with the ligand H₂BuEtP alone were slightly better than those obtained with the mixed ligands (H₂BuEtP/HBuP) organic phase. This indicated that HBuP did not synergistically enhance the distribution of Fe(II) from the aqueous media containing the various auxiliary complexing agents into the mixed ligands organic phase. With the mixed ligands, thiocyanate ion was observed as the complexing agent that gave the best percentage extraction of Fe(II) with 99.56% at 0.1M.

Calculated separation factors of Fe(II) for Pb(II) and U(VI) with the auxiliary complexing agents with the ligand H₂BuEtP alone indicated that, while it was theoretically not possible to separate Fe(II) from U(VI), *table 1* indicated that Fe(II) could be separated from Pb(II) using EDTA (0.001M – 0.005M) with the ligand H₂BuEtP alone as separation factors β_{FePb} were in both cases $> 10^4$. However, n_{Fe} values of 4 and 8 indicated that four and eight batches of extractions would be required to achieve quantitative separations. In the mixed ligands H₂BuEtP/HBuP system, calculated separation factors in *table 2* indicated that, it was theoretically possible to separate Fe(II) from Pb(II) and U(VI) from an aqueous solution of the metals ions using only 0.1M of oxalate ion as β_{XY} in this medium was $> 10^4$. Two batches of extraction are theoretically required in both cases to attain 99.9% separation.

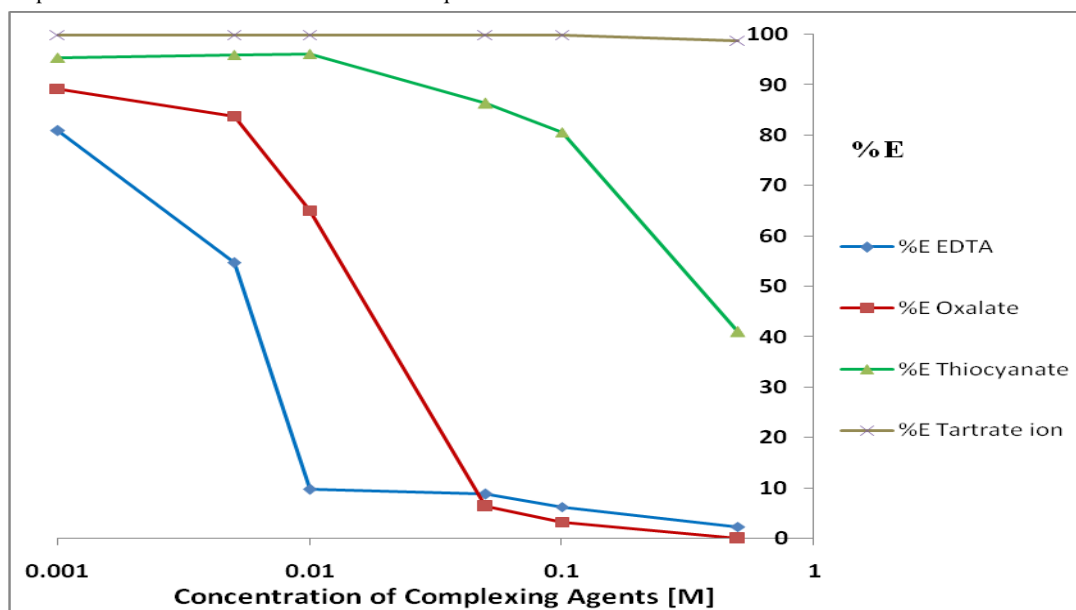


Figure-9. Plots of % extraction of 200 mg l⁻¹ of Fe(II) in complexing agents solutions into 0.05M H₂BuEtP solution

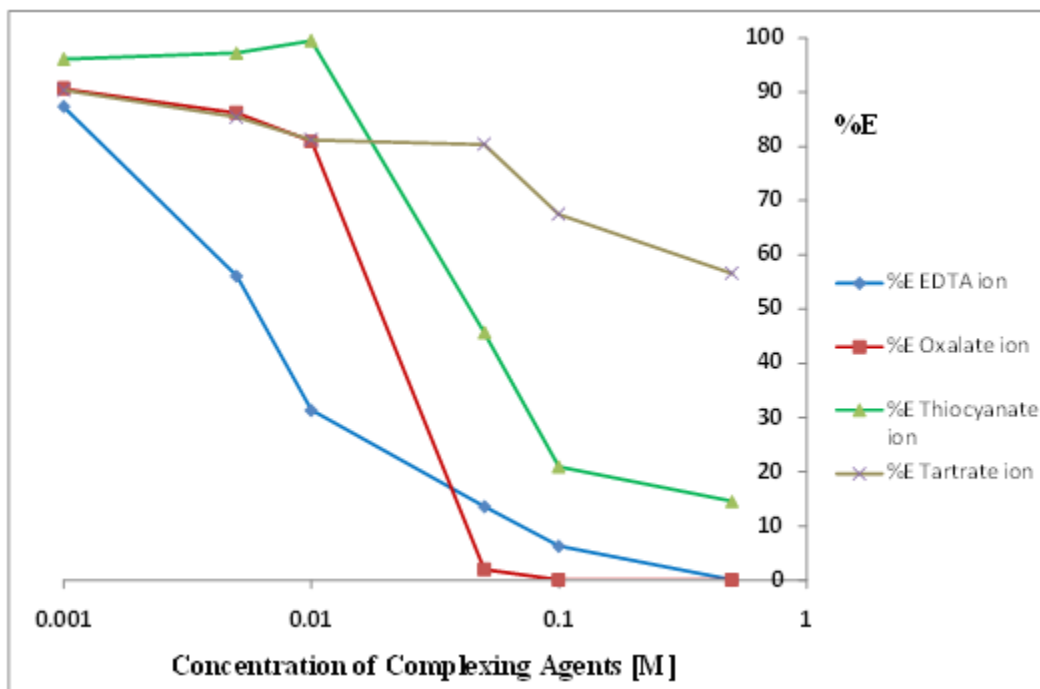


Figure-10. Plots of % extraction of 200 mg l^{-1} of Fe (II) in complexing agents solutions into 0.05 M $_2$ BuEtP 0.05 M H $_2$ BuP (9:1) solution.

4. CONCLUSION

All the acids, anions and auxiliary complexing agents apart from EDTA improved the distribution of Fe(II) from the aqueous phase into the organic chloroform solution of H $_2$ BuEtP as > 90% extraction of Fe(II) was achieved in most cases. High concentrations of acids, anions and auxiliary complexing agents masked extraction of Fe(II) in most cases due to formation of unextractable anionic Fe(II) species. H $_2$ BuP did not synergistically improve extraction of Fe(II) with H $_2$ BuEtP. Theoretically, from separation factors β_{XY} calculated it is not possible to separate Fe(II) from U(VI) using the ligand H $_2$ BuEtP alone.

5. ACKNOWLEDGEMENT

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REFERENCES

- [1] J. Godwin, C. F. Nwadike, and B. A. Uzoukwu, "Extraction of Ni(II) ions into chloroform solution of N, N-Ethylenebis(4-Butanoyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Oneimine) schiff base," *Eur. Chem. Bull.*, vol. 1, pp. 269-273, 2012.
- [2] J. Godwin and B. A. Uzoukwu, "Distribution of Pb (II) ions into chloroform solution of N, N-Ethylenebis(4-Butanoyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Oneimine) as tris-complex species," *Journal of Applied Chemistry (IOSRJAC)*, vol. 1, pp. 14-21, 2012a.
- [3] J. Godwin and B. A. Uzoukwu, "Distribution of U(VI) from aqueous solutions into chloroform solution of N,N-Ethylenebis(4-Butanoyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Oneimine) schiff base," *International Journal of Chemistry*, vol. 4, pp. 105-116, 2012b.
- [4] U. J. Chukwu and J. Godwin, "Solvent extraction studies of uranium (VI) from aqueous media into chloroform solution of N,N'-ethylenebis(4-Propionyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Oneimine)," *American Chemical Science Journal*, vol. 3, pp. 479-488, 2013.
- [5] B. A. Uzoukwu, K. Gloe, and H. Duddeck, "N, N-ethylenebis(1-Phenyl-3-Methyl-4-Acylpyrazoloneimine) derivatives: Synthesis and UV, IR, 1H and 13C NMR spectral studies," *Indian Journal of Chemistry*, vol. 37B, pp. 1180-1183, 1998.
- [6] A. Sangoremi, J. Godwin, and B. A. Uzoukwu, "Effect of SO₄²⁻ concentration on Ni(II) extractions from aqueous solution using 1-phenyl-3-methyl-4-trichloroacetyl pyrazol-5-one in chloroform," *Eur. Chem. Bull.*, vol. 2, pp. 68-71, 2013.
- [7] I. A. Kalagbor and B. A. Uzoukwu, "Effect of anions, complexing and salting - out agents on the extraction of mo (VI) from acid media into chloroform solution of bis (4-Acylpyrazolones)," *American Chemical Science Journal*, vol. 4, pp. 174-186, 2014.
- [8] E. C. Okafor and B. A. Uzoukwu, "Extraction of fe (III) and U (VI) with 1-phenyl-3-methyl-4-acylpyrazolones-5 from aqueous solutions of different acids and complexing agents," *Radiochimica Acta*, vol. 51, pp. 167-172, 1990.
- [9] S. A. M. Fathi, M. Parinejad, and M. R. Yaftian, "Multidentate nitrogen/oxygen donor ionophores; their use as selective extracting and mobile-carrier agents for copper (II) ions," *Separation and Purification Technology*, vol. 64, pp. 1-140, 2008.
- [10] J. Godwin, U. J. Chukwu, and T. D. Gad, "Distribution of iron (II) between buffered aqueous solutions and chloroform solution of N,N'-Ethylenebis(4-Butanoyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Oneimine)," *American Chemical Science Journal*, vol. 8, pp. 1581-1589, 2013.
- [11] A. E. Harvey Jr, J. A. Smart, and E. S. Amis, "Simultaneous spectrophotometric determination of iron(II) and total iron with 1,10-phenanthroline," *Anal. Chem.*, vol. 27, pp. 26-29, 1955.

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