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EFFECTS OF ACIDS, ANIONS AND AUXILIARY COMPLEXING SPECIES ON THE DISTRIBUTION OF BIVALENT NICKEL IN LIQUID-LIQUID EXTRACTION

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ABSTRACT

The distribution of Nickel (II) ions between two immiscible solvent medium was investigated using (H_2PrETP and HPrP) in chloroform as the organic extractants. The influence of acid substances (HCl, HNO_3, H_3PO_4, H_2SO_4 and CH_3COOH), anions (Cl^-, SO_4^{2-}, NO_3^-, PO_4^{2-}, CH_3COO^- and I^-), and complexing agents (Br^-, F^-, EDTA, SCN^-, $(COO^-)_2$, $(CHOHCOO^-)_2$) were all studied under a well defined extraction condition. Results obtained showed that Nickel (II) ions were masked in the acid medium both in single and mixed ligand extraction. Percentage extractions (% E) of metal ions were less than 10 % for all the acids at all concentrations studied. Increasing the acid concentration to 2.0M pushes the % E to zero in all cases. Various anions showed varied extraction pattern at different concentration values. The least % E was given by Cl^- at 0.001 M which corresponds to 19.90 % while the anion CH_3COO^- gave the highest percentage extraction at 0.10 M which corresponds to 96.30 %. Increasing the anions concentrations beyond 0.10 M resulted to steady decrease in % E in most cases. No complexing agents gave up to 50 % E in the single ligand extraction. The highest % E was observed at 0.50 M of F^- which corresponds to 47.74 % in the single ligand extraction. The effect of HPrP as a synergist enhanced the extraction tremendously. F^- ion also gave the highest % E at 0.50 M which corresponds to 83.35 %. EDTA and Oxalate ions gave below 50 % at all their studied concentrations while F^- give above 50 % E at all concentration in the presence of HPrP. Generally, anions are better extractants than the auxiliary complexing agents and the acid species.

Keywords; Distribution of bivalent Nickel, effects of acids, anions and complexing agents

INTRODUCTION

The separation and extraction of elements and ions from contaminated aqueous media have been of interest for long. In classical studies of elements, fractional crystallization, fractional precipitation and fractional decomposition processes have been used to achieve this. Metals are playing increased key roles in almost every area of human life. Even though some metals have been found to play vital role in biological systems, metal pollutions resulting from natural and anthropogenic causes and their toxicity to plants and animals are well reported [1, 2]. Cost of exploration, extraction and purification of metals is increasingly getting higher and the search for improved recovery reagents and methods for used metals is on the increase. There are a wide range of analytical methods for analysing metals in biological, environmental and industrial samples. Most of the methods involve a preliminary separation of analytes from sample step, to avoid interferences from sample matrices [3, 4, 5].

Since the discovery of elements and ions, separation of elements and ions similar in size and properties has been very challenging. Fractional crystallization, fractional precipitation and fractional decomposition were the classical separation methods used in earlier studies. However, these conventional classical methods are time consuming, harsh, labour intensive and several operations as many as twenty thousand have been reported in some cases before pure samples were obtained [6].

The dwindling supply of fossil fuels means we must look towards alternative sources of energy such as nuclear power. However, the use of radioactive actinides such as uranium and plutonium has led to a host of waste and environmental contamination issues. Most of the current systems used for extracting actinides work only at acidic pH. However, natural waters are at near neutral to basic pH, and much of the currently stored wastes are at very caustic conditions. Thus, there is high demand for ligands that can extract over a wide range of pH. In order to reduce the risks of environmental pollution, exposure and consumption of poisonous organic solvents, disposal cost, and improve extraction time and efficiency, there is also an urgent need for research to find newer methods and reagents in the area of metal extraction and determination. These separation problems were greatly simplified by the use of solvent extraction and ion exchange techniques [7, 8]. Metal ions can be extracted from an aqueous medium or separated from each other provided that they form complexes that are only insoluble in the aqueous medium or that it forms a hydrophobic complex while the other does not. These extractions and separations can be achieved in many ways; selecting suitable chelating reagents, solvents, pH, masking agents, salting out agents, equilibration time and change of oxidation state. Acetylacetone, 2-ethenoyltrifluoroacetone, 8-hydroxyquinoline, dimethylglyoxime and diphenylthiocarbazone were some of the earlier chelating agents used in solvent – solvent extraction of metals. *Werner's* coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes [9]. Many advances have been made since 1930 for studying complexes.

Schiff bases are polydentate ligands with more than two electron donor groups. In the quest for new chelating agents for the extraction of metal ion, Jenson, [10] and Zolotov [11] were among the first researchers to introduce 4-acyl derivatives of 1-phenyl-3-methylpyrazolo-5-one. These 1,3 diketones have since been found to possess excellent physicochemical properties for extraction purposes. The 4-acylpyrazolones have proved to be very promising reagents in metal extractions because they can effect higher metal separation than corresponding β-diketones, which have the ability to extract metal ions at lower pH values than open chain β-diketones. Their derivatives are stable and easy to synthesize; they are cheap and reagents for their synthesis are easily accessible. [10, 11]

Roy and Nag, [12] and Akama [13] studied and fully developed the synthesis of these 4-acyl substituted pyrazolones. However, a modified method for the synthesis of these 4-acyl substituted pyrazolones was developed by Uzoukwu and Adiukwu [14]. The 4-iso acyl derivatives of pyrazolones and their metal complexes from established method of synthesis by Jenson, [15] and Akama [16] gave oily products. The stability of the chelates that these ligands form and the optimum pH for the extraction process depend on the substituents attached to the diketo group and the solvent used. Electron withdrawing group like $-CCl_3$ group in the diketone molecule decreases the basicity of the ligands and favours extractions from acidic medium [17].

Derivatives of 1-phenyl-3-methyl-4-acyl-pyrazolone-5 are well established as a class of β-diketone that form very stable metal complexes [18. 19]. They are renowned for their wide application in solvent extraction studies [17, 20] and have recently attracted much attention due to their potential application in electronic [21] and spent fuel [22, 23] reprocessing programmes. Beta-diketones as bidentate ligands employ the O=C-C=C-OH moiety as the principal functional group in their complexation reactions with transition metals. Schiff bases are compounds that contain the carbon-nitrogen double bond traditionally connected to an aryl or alkyl group. The synthesis provided an opportunity for a N=C-C-OH bonding moiety and extended the scope of coordination to involve tetradentate ligands from the initial bidentate 4-acylpyrazolone. Earlier studies have shown that Schiff bases of 4-acylpyrazolone are capable of forming interesting metal complexes with appealing coordination properties [24] .

Reports on monovalent and bivalent complexes of Silver (I) and Copper (II) has shown that the complexes are stable and obtainable in acid medium containing Bis(4-hydroxyPent-2-ylidene) diamino ethane [25] and Samarium, Europium and Gadolinium complexes of tridentate salicylidene hydrazone derivatives of 4-acylpyrazolone-5 have shown that their solid complexes have fluorescence properties and the thiosemicarbazone *Schiff base* derivatives exhibited biochemical, photochromic and acidichromic properties due to tautomerism in their molecular structures [26, 27, 28]. Reports of promising anti-tumour, anti-pyretic and anti-inflammatory activity of Schiff bases are also known [29, 30]. The use of new *Schiff* bases in liquid-liquid extraction of metals is one area which has generated lots of interesting and positive results in the past fifty years [31]. New *Schiff* bases and their derivatives have been synthesised, characterised and tested successfully in liquid-liquid extraction of many metals [32]. One of such new Schiff base is N.N'-Ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) and its derivatives N,N'-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine(H_2BuEtP), N.N'-Bis(1-phenyl-3-methyl-4-acetylpyrazoloneimine)-1, 2-propane (H_2ADPP) and N.N'-Ethylenebis (1-phenyl-3-methyl-4-propionylpyrazolohneimine) (H_2PrEtP) which have been successfully synthesised and characterized using ultraviolet, infrared, ^{1}H and ^{13}C NMR [33,34.35].

The 4-acylbis(1-phenyl-3-methyl pyrazoloneimines) are synthesised by the reaction between a 4-acylpyrazolone and a diaminoalkyl derivative. Elemental analyses and spectral data show that the compounds were formed from 4-acylpyrazolone and diaminoalkyl derivative in a mole ratio of 2:1. Like the normal 4-acylpyrazolones, the 4-acylbis (1-phenyl-3-methyl pyrazolones) can exist as ketones and enols, and the presence of the enolic form is necessary to form chelates [24, 35]. The 4-acylbispyrazoloneimines possess heterocyclic pyrazolone moiety and function as quadridendate β-hydroxyimines.

As the search for efficient metal ion extractants goes on, we have studied the application of N,N'-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) which has received little or no attention as a potential metal ion extractant long after its synthesis was reported [36]. The study investigated the effect of pH, acids, anions and auxiliary complexing agents on the extraction of Ni (II), Co (II) and Cu (II) from aqueous solutions using the tetradentate ligand with a view to understanding the role played by these media in the interaction of these metals with Schiff base derivatives of 4-acylpyrazolone. The investigation also looked at the effect of 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one with O=C-C=C-OH moiety as a synergist on the distribution behaviour of Ni (II), Co (II) andCu (II) into a solution of predominantly N=C-C-OH bonding species.

From the reported physicochemical properties of the Schiff base N,N'-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine, it is expected that the potential application of this ligand as complexing agent in extraction studies and coordination chemistry is immense.

Materials and Method

All reagents were of analytical grade and non primary standard reagents (hygroscopic and deliquescent) used in this work were all standardized using the appropriate analytical primary standard reagents before use. . H_2PrEtP (Schiff base) was synthesized by the method reported by Uzoukwu *et al* [35]. The ligand's purity after recrystallization from aqueous ethanol was established by elemental analysis for C, H and N; analysis of IR and NMR spectral data at Institute for Inorganic Chemistry Technology, University of Dresden Germany [35] . All other reagents were used as purchased from Aldrich and BDH. Doubly distilled deionized water was used in all dilutions. Stock solution of 0.05 M H_2PrEtP was prepared by dissolving the required amount of the ligand in chloroform. 0.05 M solution of HPrP was similarly prepared in chloroform. Stock solution of 1.704×10-2 M of Nickel (II) ion was also prepared similarly by dissolving appropriate amount of ammonium nickel (II) tetraoxosulphate (VI) hexahydrate ($NiSO_4.(NH_4)_2SO_4.6H_2O$) in 0.1 ml of 10 M HNO_3 and making up to mark in a 50 ml volumetric flask with deionized water. Stock solutions of the Acids, Anions and Complexing agents were all prepared.

Extraction Procedure

The acids used for this study were HCl, HNO_3, H_2SO_4, H_3PO_4 and CH_3COOH acids with concentration in the range of 0.001M to 2.0M. The study was carried out using both single and mixed ligand system, The single ligand organic phase is 0.05 M H_2PrEtP while the mixed ligand is 10:90 % HPrP / H_2PrEtP all in chloroform

The working concentration of the metal was 50mg/l of Nickel. 0.1 ml of the Ni (II) was taken from 1000ppm stock solution with the aid of a micro pipette into set of 10 ml extraction bottle. 1.9 ml of the appropriate acid solution from the required concentration was added accordingly to make the 2ml aqueous phase. 2 ml from the 0.05M H_2PrEtP chloroform solution was used as organic phase. The mixtures were agitated mechanically for about 30 minutes to allow equilibration between the two immiscible solvents. Thereafter the solution was allowed to settle and 1ml of the aqueous rafinate was taken and analysed using Buck 205 Atomic absorption spectrophotometer (A.A.S). The process was repeated with the various anions and auxiliary complexing agents.

RESULT AND DISCUSSIONS

Effects of Mineral Acids on Extraction of Nickel with H_2PrEtP in Chloroform

In the study of the extraction of Ni (II) ions with ligand H_2PrEtP, the effect of mineral acids on the extraction of Ni (II) ions was investigated and the results are shown in Figure 1. The results showed that no mineral acid gave up to 10% extraction of Nickel (II) in both single and mixed ligand extraction. Increase in the concentration of mineral acids decreased the extraction of Ni (II) ions. This could be attributed to low pH of mineral acids that favoured polarity of solution, the Ni (II) ions are masked in the aqueous phase and as the concentrations of mineral acids in solutions were increased, the % extraction of Ni (II) ions became zero.

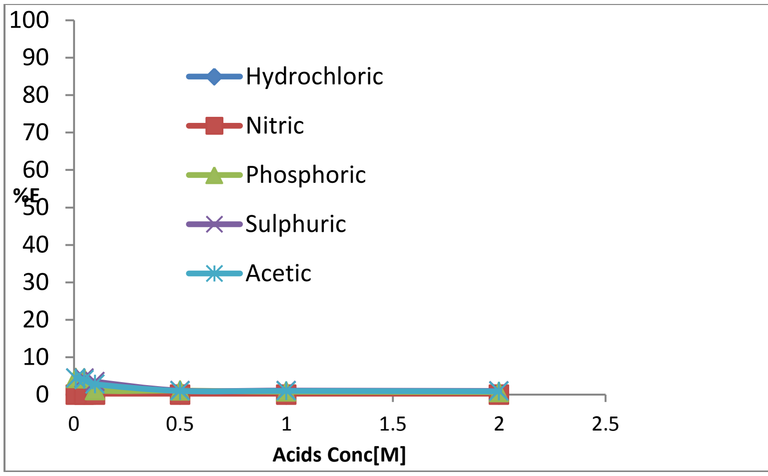

Figure 1 **Plot of % E against Acid Conc. [M] for Effect of Mineral Acids on Extraction of Nickel with H_2PrEtP in chloroform.**

Effect of Mineral Acids on Extraction of Nickel with H_2PrEtP and HPrP as Synergist

Figure 2 showed the result of the effect of mineral acids on extraction of Ni (II) ions with H_2PrEtP and HPrP as synergist in chloroform. From the result it was observed that HPrP increased slightly the extraction of Ni (II) ions by increasing the hydrophobicity of the Ni complex formed. All the mineral acids decreased the extraction of Ni (II) ions when their concentrations were increased.

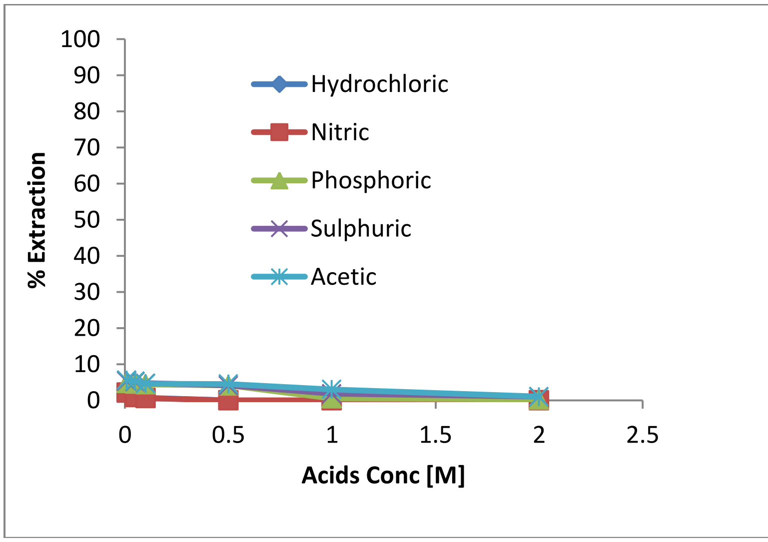

Figure 2 Effect of Mineral Acids on Extraction of Nickel with H_2PrEtP and HPrP as synergist in chloroform

Effect of Anions on Extraction of Nickel with H_2PrEtP

The results of effects of anions on the extraction of Ni (II) ions with H_2PrEtP in the absence of HPrP as synergist are shown in Figure 3. The results showed that the extraction of Ni (II) ions increased with increase in concentration of sulphate ions from 0.001M to 0.10M. Further increase in sulphate ions concentration resulted to tremendous decrease in percentage extraction. This was as a result of formation of stable Ni (II) complex anion which is less hydrophobic (have more affinity for the water medium than the organic phase).

The extraction of Ni (II) ions fluctuates as the chloride ions concentration increased from 0.001M to 0.5M but gave high % E of 60.40% at 0.50M. The effect of nitrate ion on extraction of Ni (II) ion revealed that the extraction of Ni (II) ions increases with increase in nitrate ions concentration from 0.001M to 0.1M concentration where a percentage extraction of 65.90 was obtained. It was also observed that an increase in concentration of iodide resulted to a steady increase in percentage extraction of Ni (II) ions. Increase in percentage extraction of Ni (II) ions was observed as concentration of phosphate ions was increased. The maximum extraction was achieved at concentration of 0.1M, after which further increase in concentration of phosphate ions resulted to decrease in percentage extraction of Ni (II) ions. Phosphate ion gave above 50% extraction in all the concentration studied. It was also observed that percentage extraction of Ni (II) ions increased with increase in concentration of acetate ions. Generally all the anions showed a steady increase in percentage extraction from 0.001M to 0.1M concentration.

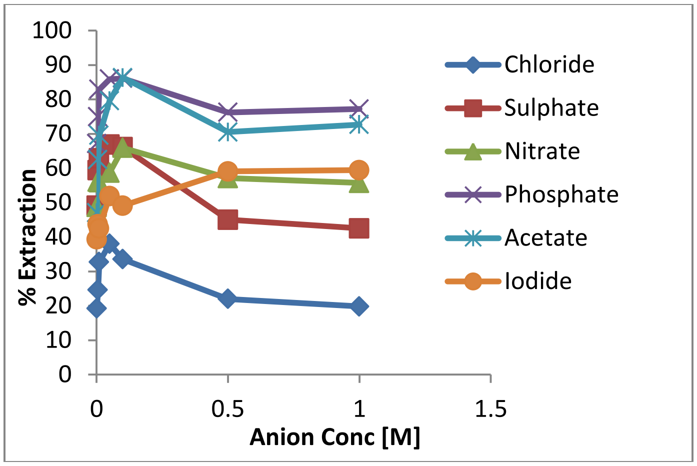

Fig 3 Effect of anion on extraction of nickel with H_2PrEtP in chloroform

Effect of Anions on Extraction of Nickel with H_2PrEtP and HPrP as Synergist

The results shown in Fig 4 indicated that there was a tremendous increase in extraction of Ni (II) ions in the presence of the synergist. The extraction of Ni (II) ions followed the same trend as in the absence of synergy. For sulphate ions, the extractions increased with increase in the concentration of sulphate ions and reached peak at 0.10M sulphate ion where 96.80% E was observed. The extraction of the Ni (II) ions fluctuates as the chloride ions concentration increased, but showed a sharp decrease at 0.01M concentration of chloride ions. The extraction of Ni (II) ions increased with increase in nitrate ions concentration but showed a sharp decrease at 0.5M and 1.0M concentration. It was also observed that an increase in concentration of iodide ions resulted to a increase in percentage extraction of Ni (II) ions but showed an increase at 0.005M and 0.05M concentrations. Increase in percentage extraction of Ni (II) ions was also observed as the concentrations of phosphate ions increased and maximum extraction was attained at 0.10M after which, further increase in concentration of phosphate ions in the solution resulted to decrease in percentage extraction of Ni (II) ions. With acetate as the anion, it was observed that percentage extraction of Ni (II) ions increased with increase in concentration of acetate ions. Acetate ions gave its highest extraction of Ni (II) ions at 0.1M acetate concentration.

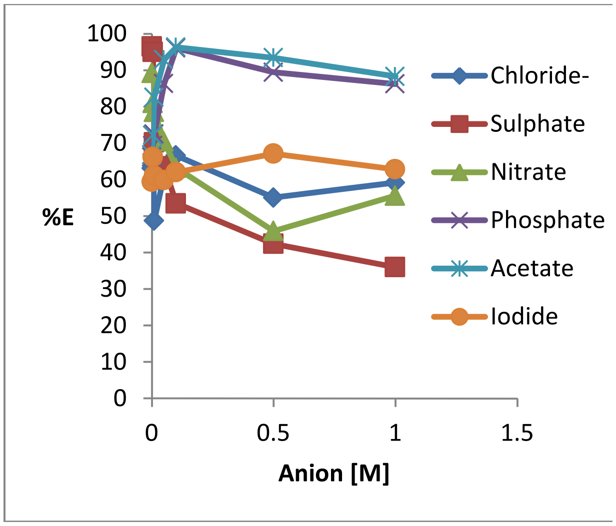

Fig 4 Effect of anions on extraction of Nickel with H_2PrEtP and HPrP as Synergist in chloroform

Effects of Complexing Agents on Extraction of Ni (II) ions with H_2PrETP

The results on the effects of complexing agents on the extraction of Ni (II) ion with H_2PrEtP in the absence of HPrP as synergist are shown in Figure 5. From the results, it was observed that the extraction of Ni (II) ions fluctuates as the thiocyanate, EDTA, and oxalate concentrations of the solutions increased respectively and with all percentage extractions less than 50%. This might be due to formation of the stable charged complexes which masked the Ni (II) ions in the aqueous phase. The extraction of Ni (II) ions decreased with increase in tartrate concentration but showed slight increase in Ni (II) ion extraction at 0.05M and decreased largely with further increase in tartrate concentrations. An increase in concentration of bromide anion from 0.0005M to 0.5M resulted to fluctuation in percentage extraction of Ni (II) ions. It was observed that increasing bromide ions concentration of the solution gave net decrease in percentage extraction of Ni (II) ions.

From the result, it was observed that percentage extraction of Ni (II) ions increased with increase in concentration of fluoride ions in the solution. Quantitative extraction of Ni (II) ions was obtained at pH of 6.05 and 0.01M concentration of fluoride ion. Flouride ions gave highest percentage extraction of Ni (II) ions followed by Tartrate ions while oxalate ions gave the least percentage extraction of Ni (II) ions.

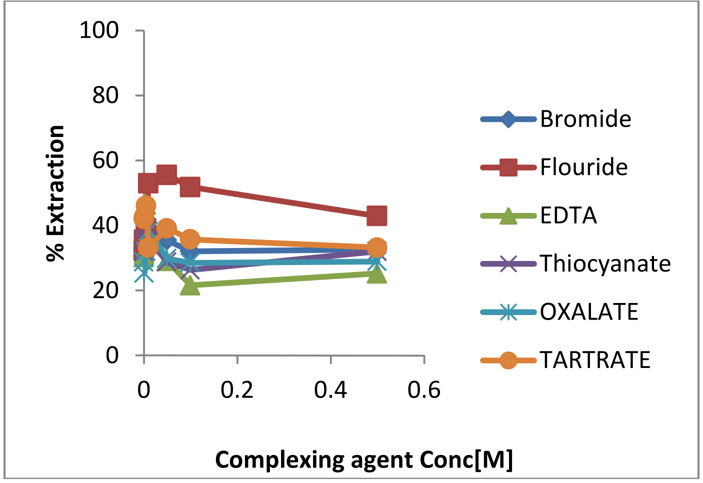

Fig 5 Effects of complexing agents on extraction of Ni (ii) ions with H_2PrEtP in chloroform

Effect of Complexing Agents on Extraction of Ni (ii) ions with Ligand (H_2PrETP) and HPrP as Synergist

Figure 6 showed the effects of complexing agents on the extraction of Ni (II) ions with H_2PrEtP and HPrP as synergist. It was observed that in the presence of the synergist, increase in concentration of complexing agents greatly increased the extraction of Ni (II) ions. Bromide ions gave the highest percentage extraction (71.30%) of Ni (II) ions obtained at pH of 6.07 and 0.10M. It was observed that an increase in concentrations of thiocyanate, oxalate, EDTA and Bromide fluctuates the extraction of Ni (II) ions. The least extraction was observed in EDTA and Oxalate. Extraction of Ni (II) ions increased as the concentration of tartrate was increased from 0.0005M to 0.5 but decreased as the concentrations were increased further. Similar results were obtained by Uzoukwu and Godwin [37] in their work on separation of U(VI) from a mixture with Pb(II) in aqueous solution using N,N'-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine).

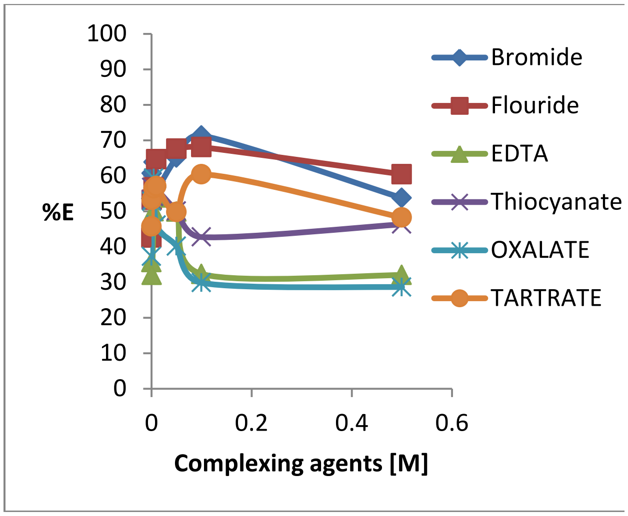

Fig 6 Effect of complexing agents on extraction of Ni(ii) ions with H_2PrEtP and HPrP as synergist in chloroform

Conclusion

The extraction study showed that the metal is quantitatively extracted in a mixed ligand system than in single ligand. Anions are better extractants than the complexing agents while it was observed that acid solutions makes the metal ion highly soluble and stable in aqueous system hence making it difficult for the metal to be transferred into the organic phase of chloroform /H_2PrEtP and chloroform 10:90 HPrP/H2PrEtP. It is therefore recommend that further work should be done to determine the actual mechanism of the reaction between the lagand and metal ion as well as determine the structures of the complex formed as such will enhance the application of this ligand in liquid-liquid extraction of metals.

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