



Extractive Spectrophotometric Determination of Fe(III) and Co(II) from Steel Sample Using Azo Ligand 1,5-dimethyl-2-phenyl-4-[(E)-(2, 3, 4-trihydroxyl phenyl) diazenyl]-1,2-dihydro-3H-pyrazole-3-one

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Abstract

Spectrophotometric studies and liquid-liquid extraction of Fe(III) and Co(II) using azo ligand 1,5-dimethyl-2-phenyl-4-[(E)-(2, 3, 4-trihydroxyl phenyl) diazenyl]-1,2-dihydro-3H-pyrazole-3-one (H₃L) were carried out using CHCl₃ and CH₂Cl₂ as solvents, respectively. The azo ligand and its metal complexes were synthesized and characterized. Stoichiometric study of the ligand to metal using Job continuous variation method was 2:1 [Fe(H₂L)₂]⁺, [Co(H₂L)₂]. The conductivity test of the ligand and its complexes showed slight conducting properties. The IR spectral of H₃L and its Fe(III) and Co(II) complexes showed that the metals coordinated through hydroxyl, azo, nitrogen and carbonyl group. The potential determination of pK_b (8.37) and pK_a (5.63) indicated that H₃L can be protonated and deprotonated. The spectrophotometric analysis of Fe(III) and Co(II) were carried out with potassium thiocyanate in acetone and ammonium thiocyanate in acetone which gave red colouration and blue colouration, respectively. The liquid-liquid extraction of Fe(III) from steel was quantitative at pH 6 and in 0.001 M HClO₄ up to 96% was extracted at 5 min, while Co(II) extraction was quantitative up to 80.2% was extracted at pH 11 in 0.001 M H₂SO₄ at 5 min. Thus, azo ligand (H₃L) is a promising extractant for Fe(III) and Co(II) ions.

Keywords: Extraction, ligand, aqueous phase, organic phase, metal ion and spectrophotometric analysis

1. Introduction

Liquid-liquid extraction refers to the distribution of a solute between two immiscible liquids in contact with each other, a two-phase distribution of a solute [1]. The solute (or analyte) dissolves more readily and becomes more concentrated in the solvent in which it has a higher solubility. Most organic compounds will partition into organic phase, salts and ionic forms of the solute will remain in the aqueous phase since ionic species will not cross the inter phase boundary [2]. The separation of solute between two immiscible liquid phases in solvent extraction is based on solubility differences while selectivity is controlled by pH and complexation. All of these basic principles can link together to produce pure metals on an industrial scale from dilute aqueous solutions. Liquid-liquid extraction is applied in refining of vegetable oils and animal

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fats, separation of metal cations, separation and purification of pharmaceutical and natural products, recovery of pollution chemicals, biodiesel, metallurgical industries, petroleum industries, coaltar industries and fertilizer industries [3].

Often in solvent extraction, a solute forms extractable complex with a chelating agent or a ligand. The chelating agent converts the metal-aquo complex into a neutral metal chelate that distributes itself between the two liquid phases in definite ratio [4]. Dimethyl-glyoxime is used for the complexation of nickel, palladium and bismuth [5]. Nouioua reported the solvent extraction of Fe(III) from the hydrochloric acid leach liquor of iron ore from mine of Ouenza, Algeria with tributylphosphate (TBP) in chloroform. It was found that, for 2 min 3M TBP in the presence of 5M HCl and 2 M KCl solutions led to a high yield of extraction (98.57 %) of Fe(III) [6]. Liquid-liquid solvent extraction of Fe(III) from metal salt using 1, 5-dimethyl-2-phenyl-4[(E)-(2, 3, 4-trihydroxy phenyl) diazenyl]-1,2-dihydro-3H-pyrazole-3-one (H₃L) as earlier reported by Opara et al. [7] gave a quantitative extraction up to 96.25% of Fe(III). Kuliev et al. [8] reported the extractive spectrophotometric determination of Fe(III) using 2, 6-dithiol-4-methylphenol (DTMP) as a photometric reagent in the presence of aminophenols gave instantaneous and stable red colour with Fe(III) in the pH range 4.2 to 5.3. Extraction-photometric determination of Co(II) with o-Hydroxythiophenol derivatives (HTPD) and hydrophobic amines (Am) reported by Aliyev et al. [9] revealed that complete extraction was achieved at reagent concentrations not lower than $1.3-1.5 \times 10^{-3}$ mol mL⁻¹ HTPD and $1.2-1.5 \times 10^{-3}$ mol mL⁻¹ Am and the colour developed almost immediately after the reagents addition. Nikam and Mohite [10] reported a simple liquid-liquid extraction method for the quantitative extraction of Co(II) from an aqueous solution of 0.5 M sodium acetate using Cyanex 272 [bis (2,4,4 trimethyl phenyl) phosphinic acid] in toluene as extractant. The result showed that the extraction of Co(II) was quantitative with toluene only and incomplete with other solvents employed for the extraction of Co(II).

In this research, the chelating agent used in the organic phase is an azo ligand (H₃L) and spectrophotometric techniques were used to measure the amount of Fe(III) and Co(II) extracted and unextracted.

2. Materials and Methods

2.1. Chemical Reagents

4-aminoantipyrene, 1,2,3-trihydroxybenzene, concentrated hydrochloric acid (37%), trioxonitrate (V) acid, tetraoxosulphate(VI) acid, perchloric acid, potassium/ammonium thiocyanate were obtained from Sigma Aldrich, England. Sodium hydroxide, sodium acetate and sodium nitrite were obtained from Merck, dimethyl formamide was obtained from Kermel Chemical Reagent Co., Ltd. All reagents used were of analytical grade.

2.2. Synthesis of 1, 5-dimethyl-2-phenyl-4[(E)-(2, 3, 4-trihydroxy phenyl) diazenyl]-1, 2-dihydro-3H-pyrazole-3-one

The azo ligand (Fig. 1) was synthesized following the Heinosuke method [11]. It was done by dissolving 4-aminoantipyrene in dilute hydrochloric acid and diazotizing with sodium nitrite solution below 5°C with hand stirring. The resulting 4-aminoantipyrene was poured into a solution of 1,2,3-trihydroxybenzene and sodium acetate using mechanical stirring at room temperature. The product was left overnight, filtered and washed with methanol. The compound was recrystallized and stored in desiccators over CaCl₂.

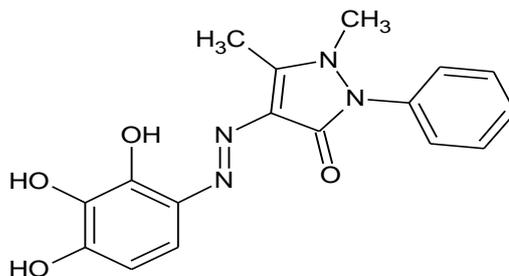


Figure 1. Proposed structure of the ligand 1, 5-dimethyl-2-phenyl-4[(E)-(2, 3, 4-trihydroxy phenyl) diazenyl]-1,2-dihydro-3H-pyrazole-3-one

2.3. Synthesis of Fe(III) and Co(II) Complexes of 1,5-dimethyl-2-phenyl-4[(E)-(2,3,4-trihydroxy phenyl) diazenyl]-1,2-dihydro-3H-pyrazole-3-one

The metal complexes were prepared following the method of El Saied et al. [12]. The metal solution of 2 moles of metal salt with 1 mole of H₃L in 50 mL EtOH was magnetically stirred for a period of 6 h at 60°C. The resulting solids were filtered off, washed with EtOH and stored in desiccator over CaCl₂. The proposed structures of the Co(II) and Fe(III) complexes of H₃L are represented in Figures 2 and 3.

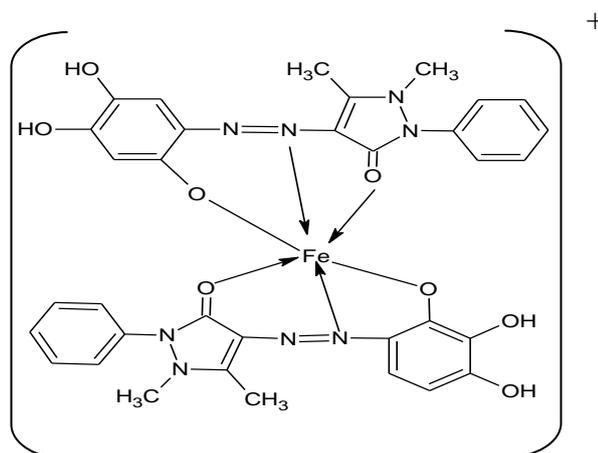


Figure 2. Proposed Structure of $[\text{Fe}(\text{H}_2\text{L})_2]^+$

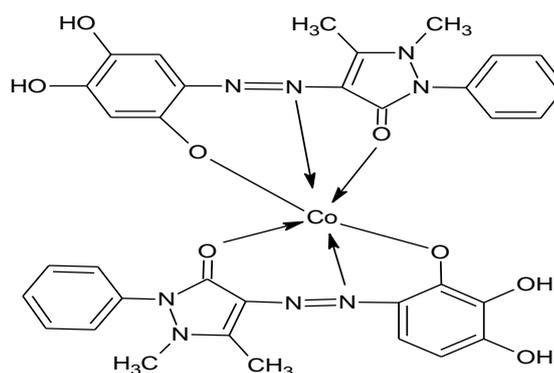


Figure 3. Proposed Structure of $[\text{Co}(\text{H}_2\text{L})_2]$

2.4. Steel Digestion

A 1.0 g of steel sample was weighed and added in a beaker; 20 mL (1:1) hydrochloric acid was added and covered with watch glass. The beaker and its content were heated to remove the white fumes. 10 mL of high purity concentrated nitric acid was added and heated to remove oxides of nitrogen and to decompose the matrix. When the entire steel sample had gone into solution, it was made up to 100 mL with deionized water in a volumetric flask and analyzed using AAnalyst 400 AA Spectrometer Perkin Elmer.

2.5. Extraction Procedure

In a normal extraction, the following extraction procedures are usually considered for effective extraction.

2.5.1. Agitation Speed

The mechanical shaker was set at a high constant speed such that increase in agitation speed did not change the extraction rate.

2.5.2. Equilibration Temperature

Solutions of both organic and aqueous phases were allowed to equilibrate at room temperature $27 \pm 1^\circ\text{C}$ before mixing for extraction. All extractions were carried out at the temperature stated.

2.5.3. Equilibration Time

The time required for the metal complex to transfer from aqueous phase to the organic phase was investigated in buffer solution. 1 mL of $10\mu\text{g/mL}$ of Fe(III) or $30\mu\text{g/mL}$ of Co(II) was pipette into different extraction bottles, and 1.5 mL of buffer (pH 6.0) added and made up to 5 mL with distilled water. Equal volume (5 mL) of $8.0 \times 10^{-3}\%$ solution of H_3L in solvent (dichloromethane for Fe(III) or chloroform for Co(II)) was added into each bottle. The bottles were shaken and one bottle removed after each of desired time interval; 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90 min.

The two phases were centrifuged and separated. The amount extracted in the organic phase and the amount unextracted in the aqueous phase was determined spectrophotometrically with 1 M potassium thiocyanate/acetone for Fe(III) or ammonium thiocyanate/acetone solution for Co(II).

2.5.4. Extraction from Buffer Solution

1 mL of 10 µg/mL or 30 µg/mL of the metal ion solution under study was pipetted into different extraction bottles to cover a pH range 1-13. A 1.5 mL of the buffer solution of known pH was added into each bottle. The solutions were adjusted to the appropriate pH using either dilute hydrochloric acid or ammonium solution and finally made up to 5.0 mL with the corresponding buffer solution. A 5.0 mL of $8.0 \times 10^{-3}\%$ H₃L in suitable solvent was added to each of the extraction bottles. The phases were equilibrated for the appropriate time determined for each metal, centrifuged and separated. The amount of metal ion extracted into the organic phase and that unextracted in the aqueous phase were determined spectrophotometrically.

2.5.5. Extraction from Acid Media

1 mL of 10 µg/mL or 30 µg/mL solution of metal ion under study was pipetted into different extraction bottles and the appropriate volume of the acid (H₂SO₄, HCl, HNO₃ or HClO₄) was added such that on final dilution to 5 mL with distilled water the concentration range 0.001-2.0 M was covered. Equal volume of $8.0 \times 10^{-3}\%$ ligand in solvent was added and the mixture equilibrated for the appropriate time determined for each metal. The amount of metal extracted and unextracted was determined spectrophotometrically.

3. Results and Discussion

3.1. Physical Characterization and Molar Conductivity Data of the Ligand and its Fe(III) and Co(II) complexes

H₃L is a dark brown powdery solid with melting point 190°C and gave a yield of 35.21%. It is soluble in methanol, ethanol, DMF, DMSO, dichloromethane and chloroform but slightly soluble in water. Fe(III) complex is a black powdery substance with melting points 185°C and gave a yield of 21.25%. Co(II) complex is a black powdery substance with melting points 188°C and gave a yield of 35.63%. Table 1 shows the physical data and also the molar conductivity values of aqueous solutions of the ligand, the complexes and some metal salts at room temperature (25-30 °C). [Fe(H₂L)₂]⁺ is a cationic complex and behaved as an electrolyte, while the ligand and [Co(H₂L)₂] are non-electrolyte, with respect to the values for KCl and CuSO₄.5H₂O used as control. This indicates that the ligand and [Co(H₂L)₂] does not appreciably dissociate in solution.

Table 1. Physical Characteristics and Molar Conductivity of the Ligand and its Fe(III) and Co(II) complexes

Compound	Color	Texture	Melting Point (°C)	Yield (gram)	% Yield	Molar Conductivity (µScm ⁻¹)
H ₃ L	Dark Brown	powdery	190	0.36	35.21	26.10
[Co(H ₂ L) ₂]	Black	Powdery	188	0.37	35.63	38.20
[Fe(H ₂ L) ₂] ⁺	Black	powdery	185	0.22	21.25	45.00
KCl Salt	-	-	-	-	-	370.00
CuSO ₄ .5H ₂ O	-	-	-	-	-	570.00

3.2. Dissociation and Protonation Constants of the Ligand

0.01 M H₃L gave a pH of 5.50. Applying potentiometric titration method [13] by titrating the solution with 0.01 M HCl, pK_b value of 4.6 was obtained. This shows that the ligand (H₃L) can be protonated as in Equations 1 and 2 and represented in Figure 4.



The determination of the acid dissociation constant, pK_a, using potentiometric titration method by titrating 0.01 M H₃L with 0.01 M NaOH gave a value of 8.4. This means that in a basic medium, there is simultaneous loss of three protons from the ligand as in Equation 3 and shown in Figure 5.



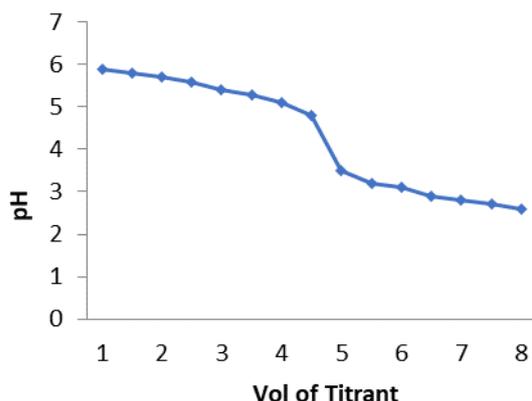


Figure 4. Titration of 0.01 M H₃L with 0.01 M HCl

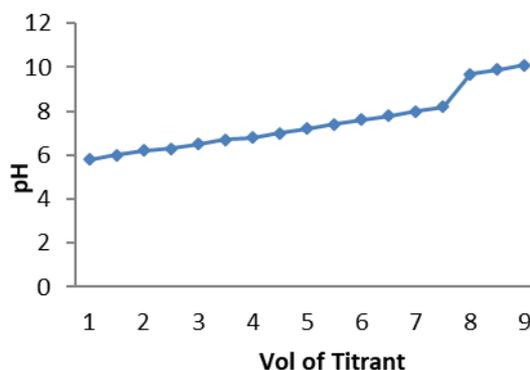


Figure 5. Titration of 0.01 M H₃L with 0.01 M NaOH

3.3. Spectrophotometric Analysis of Fe(III) and Co(II)

The organic phase extracted and evaporated was treated with an appropriate amount of perchloric acid to break down the ligand and thereafter treated with distilled water to ensure that the ligand does not affect the result. The resulting solution which has the metal ion under study was treated with an appropriate amount of hydrochloric acid followed by the addition of potassium thiocyanate in acetone 50% in volume which forms [Fe(SCN)]²⁺ complex and gives a red colouration and the absorbance of the solution was taken immediately at 480 nm against the reagent blank. While for the cobalt ammonium thiocyanate in acetone 50% in volume which forms [Co(CSN)₄]²⁺ and gives a blue colouration and the absorbance of the solution were taken immediately at 625 nm against the reagent blank. The amount of Fe(III) and Co(II) extracted were determined from the standard curve.

3.4. Equilibration Time

The equilibration time of metal ions under study, Fe(III) and Co(II), was carried out with 8.0 x 10⁻³% H₃L in dichloromethane and chloroform, respectively. The percentage Fe(III) extracted at different time intervals are shown in Figure 6. For the extraction of Fe(III), an equilibration time of 5 min was established. This time was employed in subsequent extraction of Fe(III).

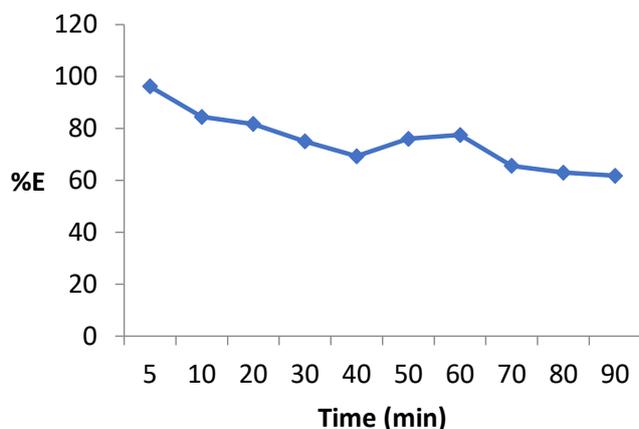


Figure 6. Profile for Fe(III) Equilibration Time

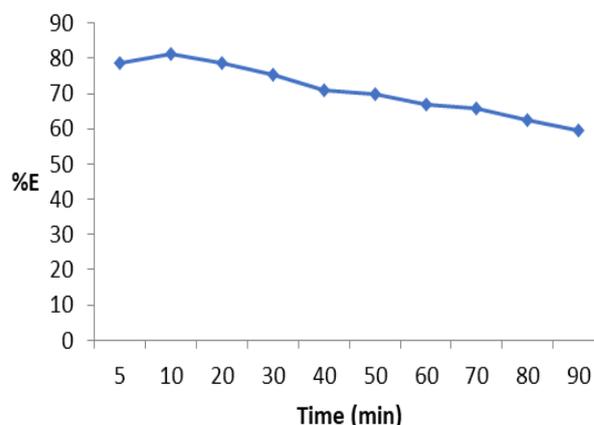


Figure 7. Profile for Co(II) Equilibration Time

For the extraction of Co(II), an equilibration time of 10 min was established. This time was employed in subsequent extraction of Co(II). The percentage Co(II) extracted at different time interval is shown in Figure 7.

3.5. Effect of pH on the Extraction of Fe(III) and Co(II)

The effect of pH on the extraction of metal ions under study, Fe(III) and Co(II), in buffer solution was carried out with 8.0 x 10⁻³% H₃L in dichloromethane and chloroform, respectively. The extraction of Fe(III) and Co(II) with H₃L was studied as a function of pH in the range 1-13. The percentage extracted at different pH is shown in Figures 8 and 9. From the results in Figure 8, a quantitative extraction (96%) was observed at pH 6. Low extraction observed between pH 1-4 is likely due to incomplete dissociation of the ligand leading to poor formation of chelate. It could also be due to competition between the proton (H⁺) and Fe³⁺ for azomethine ligation sites which are unfavorable for the formation of the complex. Quantitative extraction at pH 6 is likely due to the formation of complex completely extractable into the organic phase.

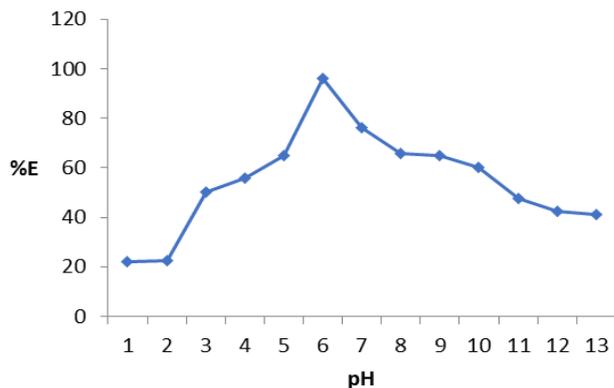


Figure 8. Profile for the Extraction of Fe(III) in Buffer Media

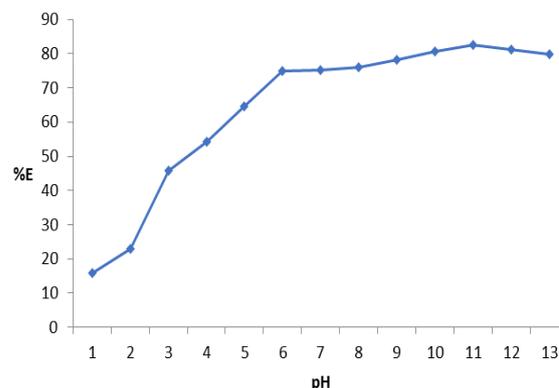


Figure 9. Profile for the Extraction of Co(II) in Buffer Media

Also, between pH 7-13 a decrease in amount of Fe(III) extracted was observed. Low extraction at this pH range is likely due to ease of hydrolysis of the metal ion and masking effect of buffer contributes in diminishing the extraction of the metal [14]. The extraction of Co(II) showed increase in the amount extracted between pH 9-13 with a maximum extraction (82.5 %) at pH 11 (Figure 9). Low extraction at pH 1-8 could be due to the competition between the protons and Co(II) ion for ligand coordination sites.

3.6. Effect of Acidity

Variation of acid concentrations with the percentage of Fe(III) extracted is displayed in Figure 10. The result shows that the acid concentration 10^{-3} - 10^{-2} supports the formation of extractable ionic complex. Also, it shows that there is a decrease in the amount of Fe(III) extracted as the acidity increases. Increase in extraction up to 96% in 10^{-3} HClO₄ was observed. This was achieved by replacement of the attached proton on the ligand coordination site by Fe(III) ion.

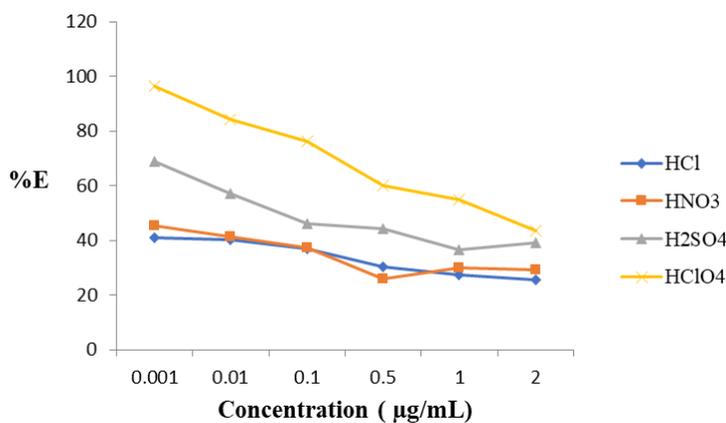


Figure 10. Profile for the Extraction of Fe(III) from Various Acid Media

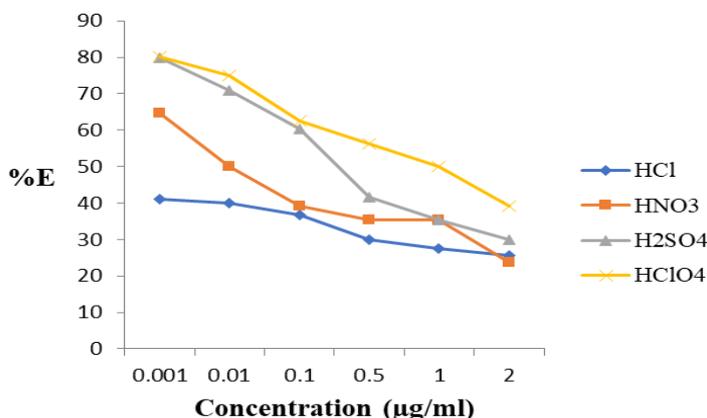


Figure 11. Profile for the Extraction of Co(II) in Various Acid Media

The extraction of Co(II) is displayed in Figure 11. The result shows that the acid concentration 10^{-3} - 10^{-2} also supports the formation of extractable ionic complex. In acid concentration 10^{-3} H₂SO₄ up to 80.2% of Co(II) was extracted. It also shows that the percentage extracted decreases with increase in acidity. Low extraction was observed in HCl than in any other acid. Increased extraction in acid concentration 10^{-3} may likely be due to the replacement of attached proton on the ligand by Co(II) for ligand coordination sites. Low extraction in HCl could be as a result of the formation of non-extractable complex [CoCl₄]²⁻ which could diminish the extraction of the metal at high chloride concentration.

4. Conclusion

The ligand was successfully synthesized, characterized and was used for liquid-liquid extraction of Fe(III) and Co(II). It has been established that Fe(III) was quantitatively extracted at pH 6 within 5 min and Co(II) at pH 11 within 10 min using H₃L. The established procedure was applied in the recovery of Fe(III) and Co(II) in a steel sample and up to 96.0 and 82.5%, respectively was extracted. Thus, H₃L is a promising extractant for Fe(III) and Co(II) ions.

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