# LIQUID-LIQUID SOLVENT EXTRACTION OF FE (III) USING 1, 5-DIMETHYL- 2-PHENYL-4-[(E)-(2,3,4-TRIHYDROXYLPHENYL)DIAZENYL]-1,2-DIHYDRO-3H-PYRAZOL-3-ONE.

## I.J. Opara. P.O. Ukoha and *N.R. Ekere

Department of Pure & Industrial Chemistry, University of Nigeria, Nsukka, Nigeria
Accepted:26/08/2016
*Corresponding author: nwachukwu.ekere@unn.edu.ng

## Abstract

*The work reports the synthesis and use of an azo ligand, 1,5-dimethyl- 2- phenyl-4-[(E)-(2,3,4-trihydroxylphenyl) diazenyl]- 1,2-dihydro-3H-pyrazol-3-one ($H_3L$) in solvent extraction studies of its Iron (III) complex. Extraction studies at pH range 1-13, indicates that quantitative extraction of Fe (III) using $8.0\times10^{-3}$ % $H_3L/CH_2Cl_2$ is observed at pH 6. Fe(III) was quantitatively extracted at pH 6 up to 98.75% as well as in 0.001 M $HClO_4$ up to 96.25% within five minutes. Extraction up to 96.25 % was observed with $10^{-3}$ M $HClO_4$ and it was observed that as the concentration of various mineral acids increases the amount extracted decreases. $10^{-3}$ M $KClO_4$ and $Na_2SO_4$ proved to be good salting out agents for the extraction of Fe (III). The ligand has potentials for use in large scale environmental clean-up of iron overload and other analytical determinations of Iron (III) ions.*

**Keywords**: Iron (III), liquid-liquid, extraction, chelation, $H_3L$, synthesis, ligand, spectrophotometry.

## Introduction

Separation of solute between two immiscible liquid phases in solvent extraction is based on solubility differences [1]. The simplest extraction procedure possible and the technique most employed in the laboratory analytical separations involve the bringing of a given volume of solution into contact with a given volume of solvent until equilibrium has been attained, followed by separation of the liquid layers [1]. If necessary, the procedure may be repeated after the addition of fresh solvent. Batch extraction is most widely where a large distribution ratio for the desired separation is readily obtainable. [1] Solvent extraction of metals is widely being used in treatment of waste waters and hydrometallurgical operations [12]. Due to the fact that salts are mainly insoluble in organic solvents, the extraction process requires the introduction of an extractant that will combine with the metal ion to form an organic soluble species.

Among the classes of extractants used in liquid-liquid extraction processes, chelating extractants stand out as very useful [2]. Chelating extractants contain donor atoms such as nitrogen, sulphur or oxygen as the basic atom capable of forming bidentate complexes with metal ions. Examples of some chelating reagents are dithizone, cupferron, acetylacetone, thenoyltrifluoroacetone, 4-acyl-5-pyrazolones and derivatives of 5-isoxazolones, etc. Some commercially useful chelating extractants are substituted 2-hydroxybenzophenone oximes and the substituted 8-hydroxyquinolines [3].

Iron is the fourth most abundant element in the earth's crust. Oxidation states (+2) and (+3) are very common for iron. The best known reaction of aqueous iron(III) is with thiocyanate to form an intense red colour and it is therefore of use in the detection and quantitative estimation of trace quantities of iron(III) .[2] In water, ferric iron forms compounds that are often insoluble, at least near neutral pH and hydrolyses water to produce iron(III) oxide-hydroxides and hydrogen ions in solution which causes lowering of the pH [4].

Iron (III) form a variety of cationic, neutral and anionic complexes with different ligands. The complexation of Fe(III) with 4-nitrobenzene -1,2-diol (4-nitro catechol, 4NC) has been studied for treating iron overload in environmental samples [4].

Solvent extraction of iron using neutral extractants, such as ketones, amines and tributylphosphate and with cationic reagents such as quaternary ammonium ions have been reported [5 – 8]. Furthermore, liquid-liquid extraction of iron as Iron (III) chloride complex into 1,2-Dichloroethane (1.2-DCE) by [2.2.2] and [2.2.1] cryptands has been carried out. [8 ,10] Y.A. El-Nadi and N.E. El-Hefny reported the removal of iron from Cr-electroplating solution by extraction with di(2-ethylhexyl)phosphoric acid in kerosene [11]. Liquid-liquid extraction followed by spectrophotometric determination of iron using Acetophenone 2',5' - dihydroxy thiosemicarbazone (ADHTS) at the pH 3.6 with n-Butanol as solvent has been reported [12].

Separation of iron(III) in aqueous solutions containing Mn(II), Ni(II), Co(II) and Cu(II) by solvent extraction and transport through polymer inclusion membranes (PIMs) processes was carried out by Beata and co workers [13].

This paper was aimed at synthesizing 1,5-dimethyl-2-phenyl-4-[(E)-(2,3,4-trihydroxylphenyl) diazenyl]-1,2-dihydro-3H-pyrazol-3-one ($H_3L$) and using it to extract Fe(III) from aqueous solution at various extraction conditions.

## Materials and Method

The pH values of buffer solutions and sample solutions were checked with universal pH indicator

paper and Jenway 3510 pH meter. Ground – glass-stoppered bottles of 20 cm$^3$ capacities were used for all equilibration and a multifix mechanical shaker type M80 with left-right directional revolution speed control and timer units was used for all the shakings. Melting point was determined with Fisher-Johns melting point apparatus.

For spectral properties aunthenticationh, VIS Spectrophotometer (S23A Medifield) and UV-Visible Spectrophotometer (Model: Jenway 6305) were used. The infrared spectra were measured with Shimadzu spectrophotometer while conductivity of the ligand and the complexes were measured with LF – 90; W TW conductivity meter.

### Reagents
The reagents were of analytical grade used without further purification. The reagents were supplied by Sigma Aldrich, England.

### Preparation of Metal Stock Solution
### Iron (III) solution
Standard iron (III) solution (10 µg/ml) was prepared by dissolving 0.05g of iron (III) chloride hexahydrate FeCl$_3$ in 1 liter of distilled water.

### Preparation of pH Solution
Standard solutions covering pH range 1-13 with standard of the following acids/ salts systems ; hydrochloric acid / potassium chloride , hydrochloric acid / potassium hydrogen phthalate, potassium hydrogen phthalate/ sodium hydroxide, and boric acid/ sodium hydroxide were prepared following the Clark and Lubb's procedure. [14] They were standardized using a universal indicator paper and Jenway 3510 pH meter.

### Preparation of Acids, Salting out Agents and Masking Agents
Solutions of.2.0 M Hydrochloric acid( HCl); 2.0 M Sulphuric acid (H$_2$SO$_4$) ; 2.0 M Nitric acid (HNO$_3$) and 2.0 M Hypochlorate acid (HClO$_4$) were each prepared in a 100 cm$^3$ standard flask according to classical method. Also, 2.0 M NaCl; 2.0 M Na$_2$SO$_4$; 2.0 M KNO$_3$; 2.0 M KCN; 2.0 M EDTA and.2.0 M Potassium hydrogen phthalate solutions were similarly prepared for salting out and masking interfering metallic ions.

### Spectrophotometric reagent
Exactly 7.61 g of ammonium thiocyanate was weighed and dissolved in 50 % (w/v) of acetone and made up to the mark in a 100 cm$^3$ standard flask to give a 2.0 M Potassium thiocyanate.

### Synthesis of 1,5-dimethyl-2-phyenyl-4[(E)-(2,3,4-trihydroxy phenyl)diazenyl]-1,2- dihydro 3H-pyrazole-3-one [H$_3$L]
The ligand was synthesized following the Heinosuke Yasuda method [15] and successfully used by Agbo and Ukoha [16]. It was done by dissolving 4-aminoantipyrine in dilute hydrochloric acid and diazotizing with sodium nitrite solution below 5 $^0$C with hand stirring. The resulting 4-aminoantipyrine 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 washed with ethanol and stored in a desiccators over CaCl$_2$. A $8.0\times10^{-3}$ g of ligand was weighed and dissolved in dichloromethane and made up to mark in a 100 ml standard flask. This was used to synthesize the Fe (III) complex as described in literature [15].

### Stoichiometric Studies
The stoichiometric studies were carried out by employing Job's continuous variation method of analysis [17].

### Extraction Procedures
The following extraction variables were considered for effective extraction procedure. Solutions of both organic and aqueous phases were allowed to equilibrate at room temperature $27\pm1^0$C before mixing for extraction.

### Equilibration Time
The equilibration time of metal complex was investigated in buffer solution.10 µg/ml of Fe (III) standard solution (1 ml) was put into different extraction bottle. A volume of 1.5 ml of buffer (pH 6.0) added and made up to 5 ml with distilled water. Equal volume (5 ml) of $8.0\times10^{-3}$ % solution of H$_3$L in dichloromethane was added into each bottle. The bottles were shaken and one bottle removed after each of desired time interval of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 minutes. The two phases were centrifuged and separated. The amount extracted in the organic phase and the amount unextracted in the aqueous phase were determined spectrophotometrically with 1.0 M potassium thiocyanate /acetone

### Extraction from Buffer Solution
A volume of 1 ml of 10 µg/ml of Fe (III) ions was put into different extraction bottles to cover a pH range 1-13. Exactly 1.5 ml of the buffer solution of known pH was added into each bottle and adjusted to the appropriate pH using either dilute hydrochloric acid or ammonium solution. The content was made up to 5.0 ml with the buffer solution and 5.0 ml of $8.0\times10^{-3}$ % H$_3$L in dichloromethane was added to each extraction bottle. The phases were equilibrated, centrifuged and separated. The amount of metal ion extracted into the organic and aqueous phases were determined spectrophotometrically.

### Extraction from Acid Media
1 ml of 10 µg/ml solution of metal ion under study was pipetted into different extraction bottles and the appropriate volume of the acid (H$_2$SO$_4$, HCl, HNO$_3$ or HClO$_4$) 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 $8.0\times10^{-3}$ % H$_3$L ligand in solvent was added and the mixture equilibrated for the appropriate time determined. The amount of metal extracted and unextracted was determined spectrophotometrically.

### Extraction in presence of salting-out agents
A volume of 1 ml of 10 µg/ml solution of Fe (III) ion was pipetted into different extraction bottles.

Appropriate volume (5 to 10 ml) of salting out agent ( $KNO_3$, $Na_2SO_4$, $KClO_4$ or NaCl) was added to cover the concentration range 0.001-1.0 M in $HNO_3$, $H_2SO_4$, $HClO_4$ or HCl respectively at the acid concentrations that gave partial extraction all in 5 ml final solution. A 5 ml of $8.0 \times 10^{-3}$ % $H_3L$ in dichloromethane was added into each bottle and the phases equilibrated for the 5 minutes. The phases were centrifuged, separated and the amount of metal ions in each phase was determined spectrophotometrically.

**Measurement of Distribution Ratio (D)**

The distribution ratio of the metal was calculated as the ratio of the concentration of the metal ion in the organic phase to that in the aqueous phase.

**Results and Discussions**

**Physical characterization, spectroscopic data and stoichiometric ratio studies of the Ligand ($H_3L$) and its Fe (III) Complex**

The results authenticated the structures of 1, 5-dimethyl- 2- phenyl-4-[(E)-(2,3,4-trihydroxylphenyl) diazenyl]- 1,2-dihydro-3H-pyrazol-3-one ($H_3L$) and the complex as earlier reported [16]. The structures for the ligand and complex are shown in Figures 1 and 2.
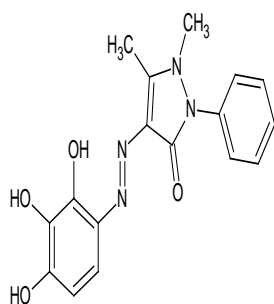


1,5-dimethyl-2-phenyl-4-[(*E*)-(2,3,4-trihydroxyphenyl)diazenyl]-1,2-dihydro-3*H*-pyrazol-3-one
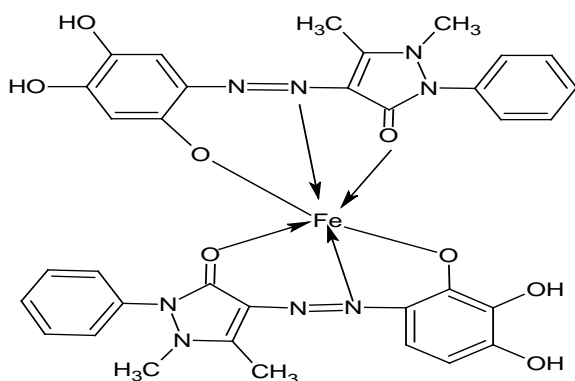
**Figure 1: Structure for $H_3L$**



**Figure 2: Structure of [Fe ($H_2L$)$_2$]$^+$**

**Effect of equilibration time on solvent extraction of Fe (III)**

The equilibration time of Fe (III) ions was carried out with $8.0 \times 10^{-3}$ % $H_3L$ in dichloromethane and the percentage extracted at different time intervals are presented in the Table 2 .

**Table 2: Amount of Fe (III) extracted into the organic phase at various time intervals**
**Initial concentration = 10 µg/ml**

| Time (min) | Fe(III) in organic phase ( µ/ml) | Fe(III) in aqueous phase (µg/ml) | Percentage extracted %E | Distribution ratio (D) |
|---|---|---|---|---|
| 5 | 9.99 | 0.01 | 99.90 | 999 |
| 10 | 8.75 | 1.25 | 87.50 | 7.00 |
| 20 | 8.38 | 1.62 | 83.50 | 5.15 |
| 30 | 7.50 | 2.50 | 75.00 | 3.00 |
| 40 | 6.94 | 3.06 | 69.30 | 2.27 |
| 50 | 7.63 | 2.37 | 76.00 | 3.21 |
| 60 | 7.75 | 2.25 | 77.50 | 3.14 |
| 70 | 6.56 | 3.44 | 65.60 | 1.91 |
| 80 | 6.31 | 3.69 | 63.00 | 1.71 |
| 90 | 6.19 | 3.81 | 61.80 | 1.62 |

An equilibration time of 5 min was established for extraction of Fe(III) ions from aqueous solutions and this value was subsequently utilised in further extractions.

The effect of pH on the extraction of the metal ions in buffer solution was carried out with $8.0 \times 10^{-3}$ % $H_3L$ in dichloromethane. The results shown in Figure 3 indicate that between pH 1- 4, the amount of Fe(III) extracted was between 21.25 to 56.60 % and reached a peak at pH 6 with 98.75 % extraction. Low extraction between pH 1-4 may be 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 $Fe^{3+}$ for azomethine ligation site which is unfavourable for the formation of the complex. Also between pH 7-13 a decrease in amount of Fe(III) extracted was observed. Poor extraction at this pH range is likely due to ease of hydrolysis of the metal ion and masking effect of buffer contribute in diminishing the extraction of the metal. [18]
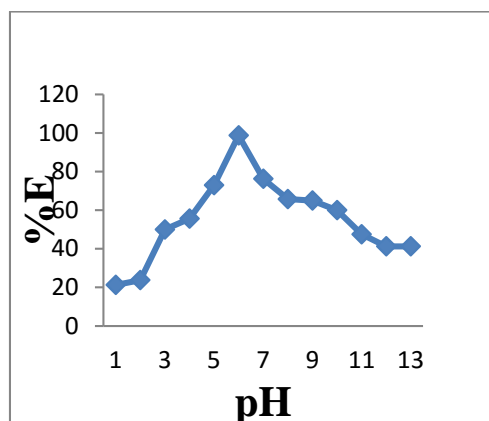


**Figure 3: Profile for extraction of Fe(III) in buffer media**

The effect of acidity on the extraction of Fe(III) at various acid concentration is shown in Figure 4. At an acid concentration of $10^{-3}$ - $10^{-2}$ M, the formation of extractable ionic complex is favoured and there was a decrease in the amount of Fe(III) extracted as the acidity increases. This was by replacement of the attached proton on the ligand coordination site by Fe(III) ion.
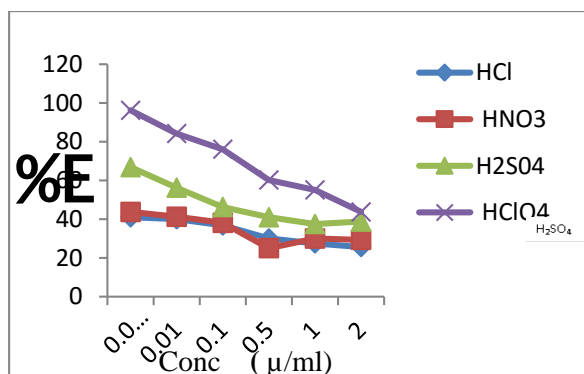


**Figure 4: Profile for extraction of Fe(III) in various acid media.**

The effect of salting-out agents on the extraction of Fe(III) ions at varying concentration of salting out agents is presented in Figure 5. HCl / NaCl system showed an enhancement in extraction from 25.60 in 2.0 M to 55.50 % on addition of 0.001 M NaCl. This may likely be due the formation of extractable specie that is soluble in the organic phase. In $H_2SO_4$ / $Na_2SO_4$ system, enhancement of the extraction from 37.5 -75.60 % on addition of 0.01 M $Na_2SO_4$ was achieved. This may likely be due to the lowering of the activity of water consequent on hydration of the added salt so that formation of extractable species is facilitated. The amount extracted decreases with increase in concentration of $Na_2SO_4$. In $HClO_4$ / $KClO_4$ system enhanced from 43.75 to 93.70 % on addition of 0.001 M $KClO_4$ was observed. This may likely be the increase in the dielectric constant of the aqueous media which makes the complex less ionic, hence more soluble in the organic phase. In $HNO_3$ / $KNO_3$ system enhanced extraction from 25- 45.6 % was observed. Generally it was observed that the amount of the metal ion extracted was higher at lower concentration of the salting –out agents. Thus, 0.001 M $KClO_4$ and 0.01 M $Na_2SO_4$ are good salting out agent for the extraction Fe(III) ions.
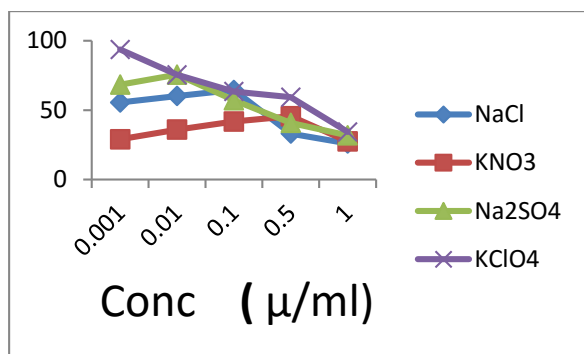


**Figure 5: Salting out agents for Fe(III) extraction with $H_3L/CH_2Cl_2$**

In conclusion, extraction studies at pH range 1-13, indicates that optimum quantitative extraction of Fe(III) using $8.0\times10^{-3}$ % $H_3L$ in $CH_2Cl_2$ is observed at pH 6. Extraction up to 96.25 % was also observed with $10^{-3}$ M $HClO_4$. It was observed that as the concentration of various mineral acids increased the amount extracted Fe(III).ions decreased. $10^{-3}$ M $KClO_4$ and $Na_2SO_4$ proved to be good salting out agents for the extraction of Fe(III) ions whereas 1,5-dimethyl-2-phenyl-4-[(E)-(2,3,4-trihydroxylphenyl)diazenyl]-1,2-dihydro-3H-pyrazol-3-one ($H_3L$) has high potentials for removal of iron overload in the environment successfully.

**References**
1. F.W Fifield & D. Kearly. (1990), Principle and Practice of Analytical Chemistry. London: Blackie Academic and Professional. 76 – 86.
2. Z. Marczenko (1976), Spectrophotometric Determination of Elements. Britain: John Wiley and sons. 230 – 240.
3. K. Gavazor, T. Stefanova & T. Oncheva (2013). Liquid-liquidExtraction Spectrophotometric Characterization of a New Tenary ion Association Complex of Iron(III). J Chem Technol Metall.; 8(6): 624-681.
4. D.J Garole, & V J Garole.(2012), An Extractive Spectrophotometric Method for the
5. Determination of F(III) using 4-methyl 2,3-Pentanedione dioxime. Derphama Chemica.;4 (1).: 282-287.
6. M.S Lee & K J Lee (2005). Separation of Iron by Extraction Hydrometal.. 80:163-170.
7. A.V.L.N.H Hariharan, ; C.H Sudhakar,& A.Srinivasanaidu. (2011), Solvent Extraction of Iron(III) by tri-n-octyl Phosphine Oxide. J Chem Pharm Res.; 3(4): 945-950.
8. A.V.L.N.H Hariharan., C.H.Sudhaka & R.B.Venkaleswara (2013) Solvent Extraction of Iron(III) with Tetra butyl ammonium bromide from Aqueous Solutions. Int J Bioanal Chem. 3(3):78-81
9. G.I. Astrid, & B .Tamhins (2013), Extraction and Formation of Iron(III) Thiocyanate Complexes : Application for Spectrophotometric Determination of Iron. Croatica Chemical ACTA CCACAA;76(4) : 323-328
10. B. Ismael, A. Razzauk & M.G. Jalhoom (2014). Extraction of Fe(III) as Chloride Complex by Cryptands. Int J Anal Bioanal Chem.; 4(1): 15-19.
11. W.U. Feng & D. Nansheng (2000). Photochemistry of Hydrolytic Iron(III) Species and Photo-induced Degradation of Organic Compound. A Mini-Review, Chemosphere.; 41: 1137- 1143.
12. Y.A. El-Nadi & N.E. El-Hefny (2011). Removal of Iron from Cr-Electroplating Solution by Extraction with di(2-ethylhexyl) Phosphoric acid

in Kerosene. Chem Engnrg Process . 49: 159-164.

13. P.S Navarkar, R.S Lokhande,  S.M.Pitale, S.P. Janwadkar, P.K Rana, & D.K. Yadav (2012)

14. Liquid–Liquid Extraction and Spectrophotometric Determination of Iron using  Acetophenone 2,5-Dihydroxy Thiosemicabazone (ADHTS) as a New Analytical  Reagent. Int J Pharm Sci Res.; 3(9):459-463.

15. B. Pospiech, W. Walkowiak & M.J. Wozniak (2005) Application of TBP in Selective Removal of Iron (III) in Solvent Extraction and Transport through Polymer Inclusion Membranes Processes: Physicochemical Problems. Min Process,39: 89-98.

16. I.M. Kolthoff, E.B. Sandell, E.J. Mecham & S.P. Eastein (1960). Quantitative Chemical Analysis. London.: Macmillian. 56 – 76.

17. Y. Heinosuk (1967), Infrared analysis of 2-pyrazolin-5-one Derivatives, Applied Spectroscopy. 23: 969- 674.

18. N. Agbo & P.O. Ukoha (2010). Synthesis, Characterization and Biological Activities of Some Azo Ligands and their Metal Complexes 1: 1, 2 –dihydroxy -1,5-dimethyl -4-[(E)- (2,3,4-trihydrophenyl) -3H- Pyrazol- 3-one (H3L) and its Co(II), Fe(III)and Os(III) Complexes. Int  J Chem. 20: 217-225.

19. P. Job (1936), Analytical  Chemistry. 16: 97- 104.

20. P.O. Ukoha, L.N. Obasi & F.I. Nwabue (2013), Solvent Extraction of Copper(II) and Silver (1) Complexes of Bis(4-hydroxypent -2-ylide2e) Diaminoethane: Separation  of Ag(I) from Cu(II) .Int J Chem. 22. 15-24.