



Sudan University of Science and Technology
College of Graduate Studies



**Synthesis and Solvent Extractive Properties of Two Aliphatic
Hydroxamic Acids at Different Levels of Acidity**

تحضير ودراسة الخواص الإستخلاصية لإثنين من الأحماض الهيدروكسيميية الأليفاتية في
مستويات مختلفة من الحموضة

**A thesis Submitted for Fulfillment of the requirements of the
Degree of Master of Science in Chemistry**

By:

Nanda Ibrahim Abd elwahab Mohammed

(B.Sc. Honors - SUST)

Supervisor:

Dr: Elmugdad Ahmed Ali

September 2016

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

(وَقُلْ اَعْمَلُوا فَسَيَرَى اللّٰهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ وَسَتُرَدُّونَ اِلَى

عَالَمِ الْغَيْبِ وَالشَّهَادَةِ فَيُنَبِّئُكُمْ بِمَا كُنْتُمْ تَعْمَلُونَ)

صدق الله العظيم

سورة التوبة الآية (105)

Dedication

To my Dear Husband

And To my Parents.

Acknowledgements

Firstly thanks to Allah almighty for given the strength to complete this research.

Thanks expended to my supervisor **Dr.Elmugdad Ahmed Ali** for his guidance, encouragement and spiritual support throughout this work.

I am grateful to all the staff of chemistry department, college of science, Sudan University of Science and Technology for their help and useful advice. Thanks also expended to any one supporting and help me during this research.

Abstract

The main aim of this work is to prepare and study the extractive ability of some hydroxamic acid (stearohydroxamic acid (StHA) and succinohydroxamic acid (SHA)).

The two compounds were prepared by coupling esters with free hydroxylamine at alkaline media. The two prepared compounds were identified by the color test with vanadium and ferric solution, their m.p and infrared. The infrared spectra of (StHA) and (SHA) gave the fundamental frequencies (in cm^{-1}) of OH, C=O, C- N and N-O groups at 3257-3434, 1616-1635 , 1267-1274, and 977- 993, respectively.

The extractibility of the prepared hydroxamic acid towards the studied metal ions (Fe^{3+} and Cu^{2+}) were found as follows:

Stearohydroxamic acid was found to have a maximum extraction for Fe (III) 96.4% at pH 5 and Cu (II) 99.8% at pH 4.

Succinohydroxamic acid was found to have a maximum extraction for Fe (III) 31.1 % at pH 4 and Cu (II) 2.02 % at pH 3.

The extractive proprieties of these compounds toward the metal ions Fe^{3+} and Cu^{2+} were studied at different pH levels using atomic absorption spectroscopy.

المستخلص

الغرض الأساسي من هذا البحث هو تحضير ودراسة الخواص الإستخلاصية لبعض الأحماض الهيدروكسيميية (حمض إستييارو هيدروكسميك وحمض سكسينوهيدروكسميك)

تم تحضير المركبين عن طريق إقتران الإستر المقابل مع الهيدروكسيل أمين في الوسط القاعدي. تم التعرف علي (، عن طريق قياس III المركبات الناتجة عن طريق الإختبارات اللونية بإستخدام محلول الفاندييوم ومحلول الحديد) نقطة الإنصهار و طيف الأشعة تحت الحمراء.

طيف الأشعة تحت الحمراء لحمض إستييارو هيدروكسميك وحمض سكسينوهيدروكسميك اعطي الإمتصاصات 1616 – 1635 ، 3257 – 3434 عند N-O و C-N ، C=O ، OH) لمجوعات الـ cm^{-1} الأساسية بالـ علي التوالي . 977 – 933 و 1267 – 1274 ،

عند II)) والنحاس III) وجد أن القدرة الإستخلاصية القصوي لهذه الأحماض تجاه الأيونات قيد الدراسة (الحديد) مختلف القيم الهيدروجينية كما يلي :

% عند الأس الهيدروجيني 96.4) كانت III أعلي نسبة إستخلاص بواسطة حمض إستييارو هيدروكسميك للحديد (4% عند الأس الهيدروجيني 99.8) كانت II وللنحاس 5)

% عند الأس الهيدروجيني 31.1) كانت III أعلي نسبة إستخلاص بواسطة حمض سكسينوهيدروكسميك للحديد (3% عند الأس الهيدروجيني 2.02) كانت II وللنحاس 4)

(عند مختلف قيم الأس II) والنحاس III) تمت دراسة الخواص الإستخلاصية لهذه الأحماض تجاه أيونات الحديد) الهيدروجيني بإستخدام جهاز الإمتصاص الذري.

List of content:

Contents	Page
الآية	i
Dedication.	ii
Acknowledgements.	iii
Abstract (English).	iv
المستخلص	v
List of content	vi
List of Abbreviations and nomenclature.	x
List of tables.	xii
List of graphs.	xiii
List of histograms.	xiv
Chapter one:	
Introduction:	
1. Introduction.	01
1.1 Organic reagents in analytical chemistry.	01
1.2 Chemistry of hydroxamic acids.	02
1.2.1 Structure and bonding.	02
1.2.2 Synthesis of hydroxamic acids.	06
1.2.3 Nomenclature of hydroxamic acids.	07
1.2.4 Detection of hydroxamic acids.	08
1.2.5 Properties of hydroxamic acids.	08
1.2.6 Reactions of hydroxamic acids.	09
1.2.6.1 Hydrolysis.	09
1.2.6.2 Nucleophilic reactions.	09
1.2.6.3 Lossen rearrangement.	10

1.2.6.4 Oxidation and reduction.	11
1.2.7 Industrial uses and Biological activity.	11
Contents	Page
1.2.8 Stearic acid.	13
1.2.9 Succinic acid.	13
1.2.10 Thio-hydroxamic acid.	14
1.2.11 Analytical applications of hydroxamic acids.	15
1.2.11.1 Qualitative organic analysis.	15
1.2.11.2 Gravimetric methods.	15
1.2.11.3 Colorimetric applications of hydroxamic acid.	16
1.2.11.4 Titremetric and Paper Chromatographic Applications.	17
1.2.11.5 Hydroxamic acid chelating exchange resins.	18
1.2.12 Hydroxamic acid complexes.	18
1:3 Solvent extraction.	21
1.3.1 Theory of extraction.	21
1.3.2 Distribution Ratio (D).	22
1.3.3 Extraction efficiency (E).	23
1.3.4 Chemical interactions in the aqueous phase.	24
1.3.5 Chemical interactions in organic phase.	24
1.3.6 Extraction Systems.	25
1.3.6.1 Types of inorganic extractable complexes.	25
1.3.6.1.1 Coordination complexes.	25
1.3.6.1.2 Ion association complexes.	26
1.3.7 Methods of Extraction.	27
1.3.7.1 Batch extraction.	27
1.3.7.2 Continuous extraction.	29

1.3.7 Discontinuous counter- current extractions.	30
1.3.8 Choice of solvent.	30
1.4. Transition metals used in this research.	31
1.4.1. Copper.	31
Contents	Page
1.4.1.1. Occurrence.	13
1.4.1.2. Properties.	31
1.4.1.3. Copper compounds.	32
1.4.2. Iron.	34
1.4.2.1. Occurrence.	34
1.4.2.2. Properties.	34
1.4.2.3. Iron compounds.	34
1.5.Objective of this work	37
Chapter Two	
Materials and Methods	
2. Materials and methods.	38
2.1 Materials.	38
2.2 Methods.	39
2.2.1 Preparation of hydroxamic acid.	39
2.2.1.1 Preparation of stearohydroxamic acid.	39
2.2.1.2 Preparation of succinohydroxamic acid.	40
2.2.2 Preparation of some solutions.	42
2.2.2.1 Preparation of stock solutions.	42
2.2.2.2 Preparation of standard buffer solutions	43
2.2.3 Preparation of standard metals solution.	44
2.2.3.1 Preparation of 1000 ppm Copper solution.	44

2.2.3.2 Preparation of 1000 ppm Iron solution.	44
2.2.4 Preparation of hydroxamic acid solution in organic solvent.	45
2.2.4.1 Stearohydroxamic acid.	45
2.2.4.2 Succinohydroxamic acid.	45
2.2.5 General Extraction procedure.	45
2.2.5.1 Extraction Iron (III)	45
Contents	Page
2.2.5.2 Extraction Copper (II)	53
Chapter Three. Results and Discussion.	60
References.	63
Appendix	
Infrared spectra for stearohydroxamic acid	69
Infrared spectra for succinohydroxamic acid	70
Atomic absorption spectrophotometer instrument	71
Atomic absorption spectrophotometer diagram	72

List of Abbreviations and Nomenclature:-

Abbreviations:

1. cm: centimeter (10^{-2} of a meter).
2. dm: decimeter (10^{-1} of a meter).
3. g: gram.
4. L: liter.
5. mg: milligram (10^{-3} of gram).
6. mA: milliamper.
7. min: minute.
8. ppm: part per million.
9. °C: degree centigrade.
10. uv: ultra violet.
11. i.r: infrared.
12. nm: nano meter (10^{-9} of a meter).
13. λ : wave length.
14. M: molar.
15. d: density
16. mol: mole.
17. mmol: millimole.
18. A.R: analytical reagent.
19. G.P.R: general purpose reagent.
20. M.pt.: melting point.
21. M.W: molecular weight.
22. AAS: atomic absorption spectrophotometer.
23. conc: concentration.

Nomenclature:

1. StHA: stearohydroxamic acid.
2. SHA: succinohydroxamic acid.

List of tables:

Table	Description	Page
Table 1	Intermediate compounds of prepared hydroxamic acids.	41
Table 2	hydroxamic acid prepared.	41
Table 3	Standard calibration curve for Fe.	47
Table 4	Extraction of iron using StHA.	48
Table 5	Extraction of iron using SHA.	48
Table 6	Standard calibration curve for Cu.	54
Table 7	Extraction of copper using StHA.	56
Table 8	Extraction of copper using SHA.	56

List of graphs:

Graph	Description	Page
Graph 1	Calibration curve for atomic absorption spectrophotometric determination of Fe (III) with hydroxamic acids.	48
Graph 2	Extraction curve showing distribution of Fe (III) as a function of pH for StHA.	50
Graph 2	Extraction curve showing distribution of Fe (III) as a function of pH for SHA.	51
Graph 4	Calibration curve for atomic absorption spectrophotometric determination of Cu (II) with hydroxamic acids.	55
Graph 5	Extraction curve showing distribution of Cu (II) as a function of pH for StHA.	57
Graph 6	Extraction curve showing distribution of Cu (II) as a function of pH for SHA.	58

List of Histograms:

histogram	Description	Page
Histogram 1	Extraction distribution of Fe (III) as a function of pH for hydroxamic acid	52
Histogram 2	Extraction distribution of Cu (II) as a function of pH for hydroxamic acid	59

1. Introduction:

1.1 Organic reagents in analytical chemistry:

Organic reagents are important in analytical chemistry because of the inherent sensitivity and selectivity of their reactions with metal ions. Much of the early work in the field was empirical, being directed toward a search of specific, or at least highly selective, reagent for metals. Selectivity often can be achieved for a particular purpose by controlling variables such as pH, reagent concentration, organic oxidizing or reducing agents.

Organic reagents are used as indicators, precipitants, masking agents, photometric reagents and some finding use in gas chromatography as volatile metallo-organic compounds, (Laitinen 1960).

To achieve adequate selectivity in analytical work it is frequently necessary to exploit differences in physical or chemical properties among reaction products. Some of the most common properties and their applications are as follows:

- a) Differences in solubility; these may be made the basis for gravimetric methods of analysis. Trace constituents may be concentrated by co-precipitation, or alternatively by partitioning into water immiscible solvent, by following the practice of solvent extraction.
- b) The production of a characteristic color; which is utilized as:
 - (i) Reagent in qualitative testing, or in spot test.
 - (ii) Indicators, in end-point detection in titrimetric methods of analysis.
 - (iii) Direct spectrophotometric determination of the species giving rise to the color.

Organic reagents have simplified the determination of micro-amounts of elements. Precipitates formed in gravimetric analysis are voluminous, easy to wash and filter and the gravimetric factors, very favorable. Organic precipitates are generally more specific than inorganic ones. A number of organic precipitates have been developed for gravimetric analysis. Typical examples are: 8- hydroxyquinoline, which has long being used to separate aluminum as specific reagent, 1-nitroso-2-naphthol which precipitate cobalt and dimethylglyoxime for nickel, (Erdey 1965).

The most important organic reagents are those forming chelate complexes, which involve the formation of one ring or more including the metal atom. Such chelates are more stable than the corresponding coordination compounds involving no ring formation and even greater stability is imparted by structures involving two or more fused chelates.

In fact there is no known specific reagent; however by the right choice of masking agent and judicious conditioning of the reaction environment, the reagent can be made very selective or even specific. Moreover, selectivity of reactions often increases as the functional groups which form chelates through two oxygen atoms are changed to choose chelating through one oxygen and one nitrogen atom and further when chelation is through two nitrogen atoms, (Welcher 1947).

1.2 Chemistry of hydroxamic acids:

1.2.1 Structure and bonding:

Hydroxamic acids are class of organic acids of general formula $R_2C=NOH$. The first hydroxamic acid prepared was oxalohydroxamic acid, which isolated by (Lossen 1869) from the reaction product of ethyl oxalate and hydroxylamine, (Bary, Synder & Casba 1973) .They are characterized by a remarkable versatility as reactants in inorganic and