SUST Journal of Natural and Medical Sciences (JNMS)vol. **16** (1) 2015
ISSN (Print): 1858-6805 e-ISSN (Online): 1858-6813

SUST
Journal of Natural and Medical Sciences

Journal homepage: http://journals.sustech.edu/

Preparation, Identification, and Investigationthe Extractability of Stearohydroxamic Acid towards Molybdenum (VI)

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Article history: Recieved: 16.12.2013
Accepted: 16.01.2014

ABSTRACT

The stearohydroxamic acid was prepared from stearic acid by the reaction of its corresponding methyl ester with hydroxylamine.The hydroxamic acid was identified by the melting point, its characteristic color testing, elemental analysis, FT-IR,^{1}H-NMR and ^{13}C-NMR spectroscopy. The extractive property of the prepared stearohydroxamic acid in chloroform towards aqueous solutions of Mo (VI) at different pH was investigated . The results showed that the optimum was 4 and the percentage of extraction was 93%.

KEYWORDS: Hydroxamic acids, extraction, hydrogen ion-concentration.

المستخلص

تم تحضير حمض استياروهيدروكساميك من حمض الاستياريك بتفاعل استرالميثيل مع هيدروكسيل امين. تم التعرف على حمض الهيدروكساميك الذي تم تحضيره عن طريق نقطة الانصهار، الكشف اللوني، تحليل العناصر ، طيف الأشعة تحت الحمراء، والرنين النووي المغناطيسي (^{1}H ، ^{13}C) . درست الخاصية الاستخلاصية لحمض الهيدروكساميك المذاب في الكلوروفورم تجاه المحلول المائي للموليبدنيوم (VI)عند قيم مختلفة للرقم الهيدروجيني . أوضحت النتائج ان أفضل رقم هيدروجيني للاستخلاص هو 4 وأعلي نسبة إستخلاص كانت 93%.

INTRODUCTION

Hydroxamic acid and their derivatives with the general formula R-CO-NHOH and R-CO-NR`OH have wide applications due to their biological activities and chelating properties. These compounds are weak organic acids with low toxicity [(1)]. In 1869,H.Lossen[(2)] reported that the reaction betweendiethyloxalateandhydroxylamineyi elded new compound named oxalohydroxamic acid [(3)]. The structural formula of the hydroxamic acid was studied by W.Lossen[(4)] and found that, each of the hydrogen atoms in hydroxylamine has a different substitution value, or else the constitution of base change when its hydrogen atoms are replaced by radicals, so that the three nitrogen valences acts in different manner[(5)].

Complexation of metal ions by hydroxamic acids is a basis of large number of analytical determinations [(6)]. The best known of these complexes is that formed with Fe(III) whose beautiful purple color forms the basis for the sensitive qualitative and quantitative determination of carboxylic acids and their derivatives[(6)].The ferric hydroxamate complex is formed by the following reaction:

$$3RCONHOH + FeCl_3 \rightarrow (RCONHO)_3Fe + 3HCl$$

Molybdenum (VI) in acidic medium form yellow chelate complexes with hydroxamic acids. This complex is

extractable in chloroform and the intensity of the color is directly proportional to the concentration of Mo (VI) [6]. One of the methods for determining Mo (VI) in aqueous layer or solutions is the thiocyanate method.

The objectives of the present study are to prepare stearohydroxamic acid, and study its extractability to Mo (VI) from aqueous solution at different pH.

MATERIALS and METHODS

The equipmts that were used include

pH-metter. (Jenway ,Model 3030), Melting point apparatus (Mettler), UV-Vis spectrophotometer, (Perkin Elmer 550), IR- spectrophotometer, (FTIR- 8400S, Shimadzu), NMR Spectrophotometer,^{1}H and ^{13}C were recorded at 400 and 75 MHZ respectively, on (a Bruker AV-400 spectrometer (USA). Chemical shift for ^{1}H and ^{13}C spectrum were recorded in ppm relative to residual proton of $CDCl_3$(1H 7.28 , ^{13}C 77 ppm).

The reagents are : Stearic acid (BDH Reagent).Methanol (BDH AnalarGrade).Sulphuric acids (BDH Analar Grade).Potassium hydroxide (Analar Grade).Hydroxylamine hydrochloride (BDH Reagent).Sodium hydroxide (AnalarGrade). Sodium chloride (Merck Analar Grade). Sodium metal (BDH Reagent).

Preparation of Methylstearate

0.2 mole (56.9g) stearic acid were refluxed with excess methanol(63mL) and 0.04 mole (2.2mL) of concentrated sulfuric acid for 24 hours. The ester was left forone day,then neutralized with methanolic potassium hydroxide (0.08mole) (4.5g) potassium hydroxide in 100 mL methanol) cooled and filtered off.

$$C_{17}H_{35}COOH + CH_3OH \xrightarrow[\text{reflux(24hours)}]{H_2SO_4} C_{17}H_{35}COOCH_3 + H_2O \quad (i)$$

Preparation of hydroxylamine in methanol

13.9 g (0.2 mole) hydroxylamine hydrochloride was added to 4% methanolic sodium hydroxide. The sodium chloride was filtered off, leaving solution of hydroxylamine in methanol.

$$H_2NOH.HCl \xrightarrow[CH_3OH]{Na\ \ OH} H_2NOH.CH_3OH + NaCl + H_2O \quad (ii)$$

Preparation of hydroxamic acid

Products (i) and (ii) were reacted in the presence of 0.05 mole sodium methoxide for 36 hours. Large volume of waterwasadded to the product , while it was warmed , the lighter organic layer separated , washed with H_2O and dried .

$$C_{17}H_{35}CO_2CH_3 + H_2NOH \xrightarrow[\text{reflux(36hrs)}]{CH_3ONa} C_{17}H_{35}C(=O)NHOH + CH_3OH$$

StHXA

Extraction of stearohydroxamic acid (SHXA)

Series` of Mo (VI) solution were prepared by transferring 5.0 ml of $1.0 \times 10^{-4} gmL^{-1}$ Mo (VI) solution to a 25 ml volumetric flask and were diluted to the volume with buffer solution (pH ranging from 1.0 to 6.0) the solution was transferred to a separatory funnel and was extracted with an equal volume (25 mL), of 0.25 $^{W}/_{V}$Stearohydroxamic acids (SHXA), in chloroform, with

vigorous shaking for 2 minutes.A yellow color was absorbed in the organic layer of all the mixtures i.e. at different pH. The two layers were separated; the aqueous layer and the organic layer [7].

The aqueous layer

Five mL of aliquots from eachseparated aqueous layerwere transferred to series of 100 separatory funnels. To each solution 2.0 ml of concentrated hydrochloric acid, 1.0 ml of 1.0% ferrous sulphate solution and 3.0 ml of 10.0% potassiumthiocyanate solution were added. The solution was shaken gently and then 3.0 ml of 10% Tin (II) chloride solution was introduced bringing the total volume to 25mL with distilled water. The golden yellow solution was extracted subsequently with three (10, 10 and 5 ml) portions of a solvent mixture of 1:1.amyl alcohol and carbon tetrachloride. The extracts were combined and poured through a filter paper (to remove water droplets), in to a 25-mlvolumetric flask and completed to the mark with the same solvent mixture. The absorption spectra of the solution were recorded at 465 nm in 1-cm cells.[7]

RESULTS and DICUSSION

characterization of stearohydroxamic acid

The melting point of stearohydroxamic was found to be 104^{o}C which is quite close to that reported in literature (106^{o}C) [7].

FT-IR spectra (KBr disc): of stearohydroxamic, showed the following absorphon bands (figure1):

For (O-H) at 3448.49cm^{-1}, for (N-H) at 3766.72cm^{-1}, ^{1}for (CH_2 or CH_3) at 2920.03cm^{-1}- 2850.59cm^{-1}, for (C=O) at 1743.53cm^{-1},for (N-O) at 985.56 - 918.05 cm^{-1},for (C-N) at 1168.78 cm^{1}. Which are close to that reported to that values recorded [7].

^{1}H-NMR .spectrum (solvent $CDCl_3$) showed(Fig: 2) chemical shifts δ=0.88ppm triplet for (CH_3), δ= 1.16ppm , 1.2 multiple doublet, δ=2.3pp triplet for (CH_2), 3.7ppm single for (N-H) , 7.26ppm single for (O-H).

^{13}C-NMR spectrum: showedδ=14ppm for (CH_3), δ=22ppm, d= 24ppm, δ=29ppm, δ= 31ppm, δ= 34ppm, δ= 51ppm. δ= 77ppm for (CH_2), δ= 174ppm for (C=O), see (figure3)

Table1: Elemental analysis of SHXA

From experiment		From empirical formula	
N%	3.57	N%	4.68
C%	72.21	C%	72.24
H%	12.59	H%	12.37
O%	11.18	O%	10.70
S%	0.00	S%	0.00

The FT-IR spectra of the hydroxamic acid prepared show the most characteristic bands associated with hydroxamic acid functional group that is due to OH, C=O, N-O , CH and C-N. The fundamental frequencies (cm^{-1}) of the various groups are summarized in the following table:

Table 2: The FT-IR absorption frequencies (cm^{-1}) of hydroxamic acid

Acid	O-H	C=O	N-H	CH	N-O	C-N
Stearohydroxamic acid	3448.49	1743.53	3766.72	2920.03-2850.59	985.56-918.50	1168.78

H-N-OH
|
R-C=O

The R group of the acid cause hypochromic effect on N – O group and hypschromic effect on C=O group [8]. The broadness of the hydroxyl absorption bands and thehypochromic shift in the C=O frequencies are indicative of the occurrence of intra and intermolecular hydrogen bonding[8]. The semi-solid states of this acid are found capable to form intermolecular and intramolcular hydrogen bondings involving the carbonyl and N–hydroxyl groups, respectively[8].These hydrogen bondings allow this acid to exhibit very good chemical stability in the semi- solid states.

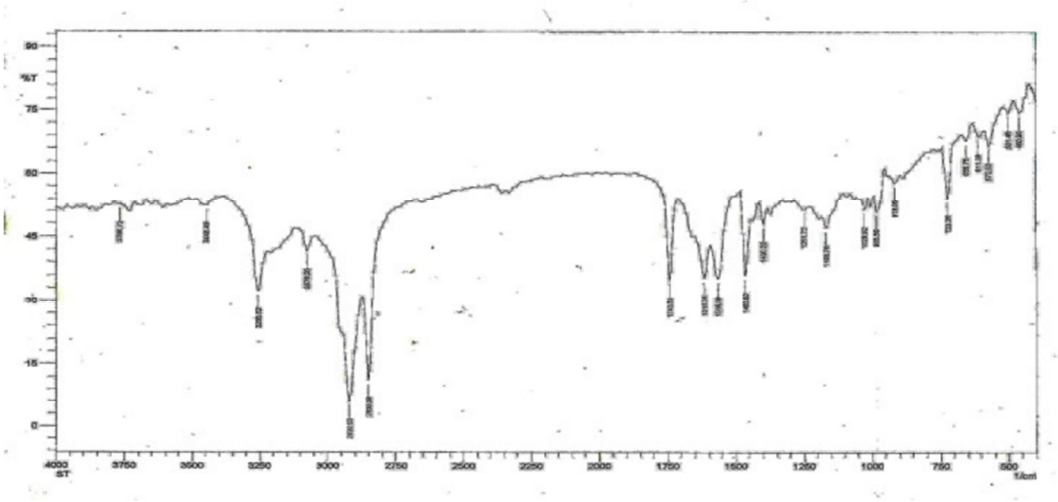

Figure 1: I.R Spectrum of Stearohydroxamic acid

The ^{1}H NMR spectra of the stearohydroxamic acid show the characteristic of the proton of the hydroxyl group attached to the nitrogen atom in the range 7.2 ppm.The protons of aliphatic CH_3appear in the range of 0.86 – 0.87 ppm. Where as that of CH_2 group appear in the range of 1.1- 3.6ppm[9].

Table 3: ^{1}H NMR spectral date of substituted hydroxamic acid

Acid	δppm	Hydrogen	Multiplicity	Assignment
Stearohydroxamic acid	0.86	3	Triplet	CH_3 proton
	7.2	1	singlet	O-H proton
	3.67	1	singlet	N-H proton

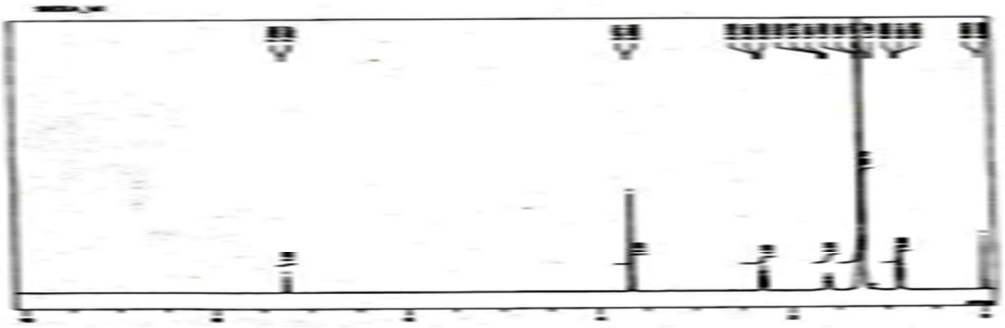

Figure2: ^{1}H NMR Spectrum of Stearohydroxamic acid

The ^{13}C NMR spectra exhibit absorption signal due to carbonyl (C=O) nearly 174 ppm. The chemical shift of aliphatic carbon appears in the range of 14.37 – 77 ppm [8].

Table 4: ^{13}C NMR data of substituted hydroxamic acid

Acid	^{13}C NMR data
Stearohydroxamic acid	δ14 C of CH_3, δ (22-77) C of CH_2, δ174 C of C=O.

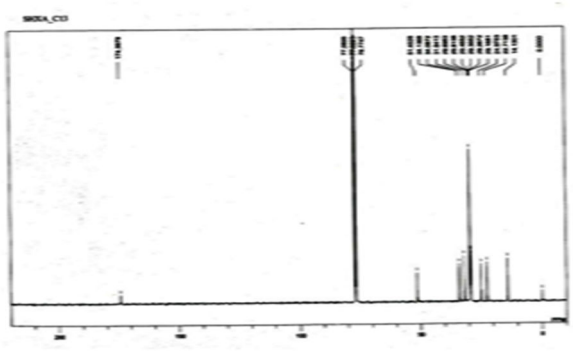

Figure3: ^{13}C Spectrum of Stearohydroxamic acid

Table 5: Results of extraction of Mo (VI) with 0.25% $^{w}/_{v}$SHXAin Chloroform

pH	Absorbance of aq at 460 nm	Conc (ppm)	Unextracted%	Extracted%
1	0.242	8.06	20.15	79.85
2	0.184	6.13	15.33	84.67
3	0.151	5.03	12.58	87.42
4	0.085	2.83	7.08	92.92
5	0.135	4.50	11.25	88.75
6	0.210	7.00	17.50	82.50

3.2 extractability of stearohydroxamic acid

The quantitative test to evaluate the maximum extractability of Molybdenum withstearohydroxamic acidwas carried out at different pH (1.0 to 6.0). The results are listed in Table 5. The high extraction of the complex of Mo (VI) with these acid at pH 4 in the moderate acid. Due to the varied substituent effect at the different fregments of the molecules.

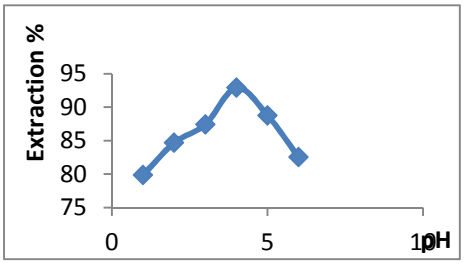

Figure 4: Extraction curve showing distribution of Mo (VI) as function of pH for SHXA

CONCLUSION

In the present study, the stearohydroxamic acid (SHXA) was prepared from the reaction of the methyl ester derivatives of stearic acid with hydroxylamine. This acid is found to be semi-solid at room temperature, soluble in chloroform, and has characterized by the following colour reaction:

1. With Ferric choloride in choloroform they give blood - red colour.
2. With Vanadium (V) solution they give reddish – violet colour.

the stearohydroxamic acid (SHXA) in chloroform form color chelate complexes with a number of metal ions. stearohydroxamic acid react with Mo (VI) to give a yellow color complex.

In addition, the FI – IR & NMR spectroscopic results confirm the successful preparation of the acid. The extractability of the stearohydroxamic acid in chloroform towards aqueous solution of Mo (VI) was examined at different pH. It is found that the optimum pH for extraction of Mo (VI) is pH 4.0 which gave 93%.

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