The syntheses of Salicylichydroxamic acid as extracting agent for some transition metals

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Abstract:

This research is aimed to synthesis and characterize of salicylichydroxamic (SHA), by using some analytical tools, in order to be used for extraction heavy metals ions . Extraction of heavy metals plays an important role in biological fields. The extraction was carried out by using n-butanol alcohol. Salicyhydroxamic acid reagent showed highly efficiency for extraction of Fe^{+3} in 1M Hcl and Cr(VI) in 4 pH with extraction percentages (92.0%) and (83.3%)respectively. The obtained results were tabulated, graphicrlated and interoperated by statistical analysis.

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Introduction:

Hydroxamic acid:

hydroxamic acid is Analytical reagent allowed to use a large number of organic legends to form metal complexes. The hydroxamic acid was prepared firstly in 1869 by H. Lossen when he produces oxalhydroxamic acid from reaction between diethyl oxalate acid and hydroxylamine yield. Also, he found that the reaction between benzyl chloride and hydroxyl ammonium chloride give mixture of benzohydroxamic acid, benzoyl, benzohydroxamate and dibenzoyl benzo-hydroxamate ⁽¹⁾.

when heated the benzoyl benzohydroxamate above melting point, liberated phenyl isocynate and benzoic acid.

The potentialities of the metal chelates of hydroxamic acids as extracting have been fully recognized and some very useful separation and extractions have been achieved. They have also received a considerable attention as reagents for gravimetric and Spectrophotometric analysis of metals.

They are also known as constituents of growth factors, food additives, antibiotics, tumour inhibitors, antifungal and anti malarial ⁽²⁾.

proper evaluation of analytical methods involving organic reagent it is very important to know the nature selectivity or specificity of reaction with the metal ions. The hydroxamic acid have a large area of research and development, both from theoretical and technological, that activation due to there's electrons distribution.

Structure:

The structure of hydroxamic acid determined at the first by Lossen, when he was observing that product obtained by the reaction of an isohydroxamic acid and benzoyl chloride was different from the product produced by the reaction of benzohydroxamic acid and anisoyl chloride. It was at that time the Werner, Tiemann and the others determined structure of hydroxamic acid in tautomeric forms, ketoform and enolform.

When alkyl or aryl group are release hydrogen atom from nitrogen atom the N- substituted hydroxamic acid obtained is formed below :

On the other hand, Hydroxamic acid tautomeric ketoform are substituted by alkyl or aryl group when hydrogen atom in hydroxyl group replaced and compound O-alkyl or aryl hydroxamic acid formed.

O-alkylhydroxamic acid

But when the alkyl or aryl group are attached the hydrogen atom at hydroxyl group in the enolform structure the O, O dialkyl or aryl hydroxamate obtained such as:

Preparation of hydroxamic acid:

Hydroxamic acid synthesis is described by Yale ⁽¹⁾. Method of preparation hydroxamic acid is similar to amides. Most used the acylation of hydroxylamine derivatives.

The acylating agents include free carboxylic acids carboxylic ester, acid chlorides and anhydrides. The reaction is generally carried out in basic media ⁽³⁾.

Where X refer to OH group, OR group, OCOR group or halides.

Salicylhydroxamic acid and derivatives:

Salicylhydroxamic acid is an aromatic organic compound can be use as analytical reagent, in metal complex formation in biological activity.

Plodder S. N and Adhiya J. N ⁽⁴⁾ used this reagent to determine Al^{3+} ion at pH 6.0 – 7.5, Ga ion at pH 5.5 – 6.5 and In ion at pH 4.5 – 5.0 and also used for separation some metal ions ⁽⁵⁾.

Experimental

1. Instrumentation:

- (I) UV/VIS spectrophotometer Jenway 6305.
- (ii) I.R. Spectrophotometer, Perkins Elmer 1330.
- (iii) pH meter, Jenway model2S.U.K.
- (iv) Melting point apparatus.
- (v) Soxhlet apparatus.

2. Preparation of Methyl salicylate:

The preparation of methylsalicylate undergoes the esterfication of salicylic acid reactions, which prepared by coupling reaction between salicylic acid and methanol according to the following equation:

Procedure:

A 28 g (0.2 mole) of salicylic acid were added to 8.10 cm³ (0.2 mole) of methanol were mixed well and placed in the round-bottom volumetric flask (500 ml). An accurate 8ml of concentrated sulphuric acid were added cautiously with shaking

to the mixture. The obtained mixture refluxed on water bath for five hour. Moreover, an excess 3ml of methanol was added during refluxing of the mixture. After removal of excess methanol, the residue was poured into 250 cm³ of water contained in separatory funnel and extracted with 15 cm³ of carbon tetrachloride. The rejected, methyl salicylate solution was returned to the separatory funnel and shaken with strong solution of sodium hydrogen carbonate (NaHCO₃) until acid free is obtained.. The obtained yield is washed with sufficient amount of distilled water and dried over anhydrous magnesium sulphate (MgSO₄). The yield is found to be 25.2 g with yield percentage (82.9%) and identified with it is m.p, IR. Obtained data :- table (1)

3. Preparation of Salicylhydroxamic acid:

3-1 Procedure:

Salicylhydroxamic acid synthesis is carried out by the coupling reaction of methylsalicylate and hydroxylamine hydrochloride according to the following equation:

Dissolve 14 g (0.2 moles) of hydroxylamine hydrochloride in 200 ml of concentrated sodium hydroxide 12 % and cooled to the room temperature, then 15.2 g (0.1 mole) of methylsalicylate were added in small portions with vigorous shaking after each addition to ensure complete dissolution. The mixture was allowed to stand for three days until the solution become stow brown, then acidified, washed with dilute Hcl and re crystallized from distilled water containing few acetic acid, the yield is found to be 13.03 g with yielding percentage 84 %, and its identified with mp is 170⁰C and with it is m.p , IR and elemental analysis. The obtained data are recorded in tables (2), (3) respectively

4. Determination of the Nitrogen in the Salicylhydroxamic acid:

A 0.4 g of the reagent was taken in Kjeldahl apparatus, 20.0ml concentrated sulphuric acid, 10 g potassium sulphate and traces of manganese dioxide were added to the flask. The mixture was digested on heating mantle in the fume chamber until the organic matter was destroyed and the solution was clear. The contents were cooled and diluted with 50 ml distilled water, then a few anti pumping granules were added and a drop of screen methyl orange indicator was also added. The excess acid was neutralized with 4 M Sodium hydroxide. A 50 ml of 0.1 M hydrochloric acid were placed in the receiver flask. The tip of the

condenser was adjusted so that it just dipped in the acid solution. The contents were heated for boiling gently until 2/3 of the original solution was distilled off. The excess acid was titrated with 0.10 M standard Sodium hydroxide. The volume of the Sodium hydroxide that neutralized the excess acid was determined and the process was done triplicated for each acid.

$$N = \frac{(M_a \times V_a) - (M_b \times V_b)}{\text{weight of the sample}} \times 1.4$$

Where: M_a and V_a molarity and volume of standard hydrochloric acid.

M_b and V_b molarity and volume of Sodium hydroxide, respectively the result is:

The N % of SHA was found to be 8.93 %, (Theoretical is 8.80 %). Table (4)

5. Preparation of Standard solutions:

5-1. Preparation of the standard solutions of Potassium Chloride:

A 7.46g KCl was dissolved in distilled water and transferred to 1000ml volumetric flask, and the volume was completed to the mark with distilled water. The result is the solution of 0.1M concentraon of KCl. A Also 0.2M KCl solution was prepared by dissolving 14.91g of KCl in 1000cm³ distilled

water, and the volume was completed to the mark with distilled water.

5-2. Preparation of standard solution of Hydrochloric acid:

The standard Solution of hydrochloric acid 0.1M was prepared by transferring 8.6ml of concentrated hydrochloric acid to 100ml volumetric flask. Then used distilled water to complete to the mark.

And 0.2M of HCl acid was prepared by the same way except that 17.2ml of concentrated HCl acid were taken.

5-3: Preparation of Sulphuric acid solutions:

To prepare 1M, 2M sulphuric acid were diluting respectively 5.3ml, 10.8ml of concentrated H_2SO_4 to 100ml volumetric flask.

5-4. Preparation of standard solution of Sodium hydroxide:

Prepared 0.1M of sodium hydroxide by dissolving 4.00g in distilled water and transferred to 1000ml volumetric flask. Then completed to the mark with distilled water.

6. Preparation of the Buffer solution:

All the buffer solution prepared were checked with pH-meter and adjusted to the required pH, with few drops of either dilute hydrochloric acid or sodium hydroxide solution.

6-1. Preparation of the pH 1 and pH 2:

The pH 1, was prepared by adding, 670ml of 0.2M HCl with 250ml of 0.2 M KCl solution and diluted to 1000ml with distilled water. And pH 2 was prepared by adding 65ml of 0.2M HCl with 250 ml of 0.2 M KCl solution and diluted to 1000ml with distilled water.

6-3. Preparation of acetate buffers solution with pH (3 – 8):

A series of acetate buffer solutions from pH 3.00 to pH 8.00 were prepared from acetic acid and Sodium acetate. The pH values were prepared closely adjusted by addition of the acid or the sodium salt using pH-meter, according to the PH needed.

7-. Preparation of stock standard solutions:

All reagents use are analytical standard salts

7-1. Preparation of stock Iron (III) solution:

The standard ferric solution 0.01M concentration was prepared by dissolving 1.6221g of Ferric Chloride (FeCl_3) anhydrous LR, in distilled water and replaced in volumetric flask

1000 ml, and then added 10 ml of concentrated hydrochloric acid, the volume was completed to the mark with distilled water.

7-2. Preparation of stock Chromium (VI) solution:

The standard chromium (VI) solution (0.01M) was prepared by dissolving 2.9418g of potassium dichromate ($K_2Cr_2O_7$) in distilled water, replaced to volumetric flask 1000 ml and then completed to the mark with distilled water.

7-3. Preparation of standard solution of Salicylhydroxamic acid 0.02M in organic solvent:

A 1.531g of Salicylhydroxamic acid was dissolved in 500ml butan-1-ol, and used for each extraction.

8. Complexation and extraction of Iron (III) with Salicylhydroxamic acid:

A 10 ppm of Ferric (III) was prepared by diluting 2ml for stock solution of iron (III) to 200 ml with distilled water.

9- pH effect on extraction of Fe(III)-SHA complexes:

In ten series of separatory funnels 100-ml capacity pipetted 5.0 cml of 10 ppm Fe (III) solution, 5.0ml of 1M, 2M, 3M hydrochloric acid and buffer solution from pH 1 to pH 6 were added to each. And then added 10cm³ of salicylhydroxamic with concentration 2×10^{-2} M in organic solvent of each series. After addition separatory funnel were shaken gently two layers

were allowed to separate, and separated the organic and aqueous layers, organic layer were analyzed. The optimum absorbance was obtained for reading of the concentration in table (5) and plotted against the wavelength as shown in fig(1)

10-Preparation the standard Iron (III) solution for calibration curve:

The standard solution for calibration curve was prepared by pipetting in the series of volumetric flasks 100ml 5.00, 10.00, 15.00, 20.00, 25.00, and 3.00 ml of 10 ppm Ferric solution. And then added 5.00 ml concentrated hydrochloric acid of each and also added 10.00 ml of 10.0% potassium thiocyanate and completed the volume to the mark with distilled water. The optimum absorbance was reading for the concentration plotted against the wavelength are shown in Fig (2) and Table (6).

11. Complexation and extraction of Chromium (VI) with Salicyl-hydroxamic acid:

11-1:-The pH effect on extraction of Cr(VI)-salicylhydroxamic acid complex:

In the series of ten separatory funnel 100ml capacity pipetted 5.00ml of 10 ppm Cr (VI) solution, 5.00ml of 4M, 3M, 2M and 1M sulphuric acid and buffer solutions of pH 1 to pH 6.

Then 10.00 ml salicylhydroxamic acid 1×10^{-2} M in organic solvent were introduced, to each series And shake the mixture gently for short time two layers were allowed to separate, organic phase and aqueous phase kept for analysis. The result as shown in table (7) and fig (3).

12-Preparation the standard solution of Cr (VI) ion for calibration curve:

Standard solution of Cr(VI)ion for calibration curve was prepared by pipetting 5.00 ml, 10.00 ml, 15.00 ml, 20.00 ml, 25.00 ml and 30.00 ml of 10ppm Cr(VI) solution in 100.00 ml volumetric flask, then 5.00 ml of 1M sulphuric acid was added and 1.00 ml of 1% ethanol solution of diphenylcarbazide was introduced. The solution was completed to mark with distilled water, and left for few time for complete colour development. The optimum absorbance obtained for the reading at 540 nm, the result are shown in Table (8) plotting the absorption against concentration is shown in Fig (4).

Results and discussion

The salicylhydroxamic acid as a ligand is synthesized by coupling reaction between the hydroxylamine and methylsalicylate in presence of Sodium hydroxide. The methylsalicylate itself was prepared, the yield is

Found to be 82.9% is 25.20 g. but the ligand yield is
found to be 13.03 g(84 %), and mp is 170°C.

Table (1) I.R. spectral data of Characteristic functional groups of methylsalicylate⁽⁶⁾.

Group frequency	Absorption in cm ⁻¹	
	Found	Literature
O – H	3215	3100 – 3600
C = O	1680	1560 – 1760
C – O	1200	1100 – 1300
Aryl C – H	2900	2600 – 3000
1350	1300 – 1500
C≡C	775	700 – 800

Table (2)

I.R. spectra; Characteristic functional groups of S.H.A acid

Group frequency	Absorption in cm^{-1}	
	Found	Literature
O – H	3215	3100 – 3600
C = O	1680	1560 – 1760
C – O	1200	1100 – 1300
Aryl C – H	2900	2600 – 3000
N – H	1500	1460 – 1560
C $\equiv$ C	775	700 – 800
C – N	1180	1100 – 1300
N – O	900	850 – 950

Uv absorption of S.H.A in 95% ethanol:

C=O absorbed 260nm, and aryl group absorbed 290nm.

Table (3) the elemental results:-

Compound	Carbon %		Nitrogen%		Hydrogen %	
	Found	Theoretical	Found	Theoretical	Found	Theoretical
Salicylhydroxamicacid	52.7	52.8	8.75	8.80	8.16	8.18

Table No (4):

**Nitrogen contents of the salicylhydroxamic acids
prepared :**

Compound	Nitrogen %	
	Found	Theoretical
salicylhydroxamic	8.93	8.80

Table No (5)
pH and con.of HCl effect on Iron(III) extracted by
S.H.A.

HCl	pH	Absorption nm	Concentration ppm	Extraction %
4M		0.182	3.31	66 %
3M		0.189	3.44	68 %
2M		0.201	3.67	73 %
1M		0.254	4.62	92 %
		0.228	4.47	89 %
	1	0.246	4.15	83 %
	2	0.234	4.25	85 %
	3	0.203	3.67	73 %
	4	0.199	3.61	72 %
	5	0.167	3.04	61 %
	6	0.108	1.16	35 %
	7			

Fig (1):

pH effect on Iron(III) extracted by S.H.A.

Table No (6): The standard calibration curve of Iron (III) extraction.

Concentration ppm	Absorption nm	Extracted ppm	Extracted %
5	0.062	3.60	72 %
10	0.128	6.90	69 %
15	0.164	11.63	77 %
20	0.282	17.85	89 %
25	0.211	21.45	85 %
30	0.203	24.90	83 %

The standard calibration curve of Iron (III) extraction.

Fig 5-2:

Table No (7):

pH and con. of H_2SO_4 effect on Chromium(VI) extraction by S.H.A.

H_2SO_4	pH	Absorption nm	Concentration ppm	Extraction%
4M	1	0.018	7.00	70%
3M		0.167	6.51	65%
2M		0.144	5.61	56%
1M		0.130	5.06	50.6%
		0.139	5.42	54.2%

2	0.151	5.89	58.9%
3	0.189	7.37	74%
4	0.203	8.33	83.3%
5	0.180	7.02	70.2%
6	0.143	5.57	55.7%

pH effect in chromium(VI) extraction by S.H.A.

Fig (3): pH effect in chromium(VI) extraction by S.H.A.

Table No (8):

The standard calibration curve of chromium (VI) extraction.

Volume of stock 10 ppm cm ³	Dilute conc ppm	Absorption nm
5	0.50	0.028
10	1.00	0.081
15	1.50	0.137
20	2.00	0.223
25	2.50	0.294
30	3.00	0.346

Fig (4) : The standard calibration curve of chromium (VI)

13-1Evaluation Statistical Analysis

1. Iron results:

(i). The mean and standard deviation:

$$\text{The mean } X = \sum x_i / n$$

$$= 23.19/6 = 3.87$$

x_i	$(x_i - x)$	$(x_i - x)^2$
4.15	0.28	0.078
4.47	0.60	0.360
4.25	0.38	0.144
3.67	- 0.20	0.040
3.61	- 0.26	0.068
3.04	- 0.83	0.689
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23.19		1.379

(ii).Standard deviation (s):

$$S = \sqrt{\sum (x_i - x)^2 / n - 1}$$

$$= \sqrt{1.379/5}$$

$$= 0.276$$

(iii).Relative standard deviation:

$$\text{R.S.D} = s/x \times 100$$

$$= 0.276/3.87 \times 100$$

$$= 7.13 \%$$

(iv).The confidence limit = $x \pm ts/\sqrt{n}$

$$\begin{aligned}\text{In } 90 \% &= 3.87 \pm 2.015 \times 0.276 / 2.449 \\ &= 3.87 \pm 0.227\end{aligned}$$

In 90% confidence the true value were felled on range between

$$3.643 - 4.097.$$

$$\begin{aligned}\text{In } 95 \% &= 3.87 \pm 2.571 \times 0.276 / \sqrt{6} \\ &= 3.87 \pm 0.2897\end{aligned}$$

We confidence 95% the true value were felled on the range between 3.580– 4.159.

$$\begin{aligned}\text{In } 99\% &= 3.87 \pm 4.032 \times 0.276 / 2.449 \\ &= 3.87 \pm 0.454\end{aligned}$$

We confidence in 99% the true value was found on the range 3.416 – 4.324.

(v).The beast linear by least squares methods:

$$Y = mx + b$$

$$m = \frac{\sum x_i y_i - (\sum x_i \sum y_i) / n}{\sum x_i^2 - (\sum x_i)^2 / n}$$

X_i	y_i	$(x_i)^2$	$x_i y_i$
4.15	0.228	17.223	0.946
4.47	0.246	19.981	1.100

4.25	0.234	18.063	0.995
3.67	0.201	13.469	0.718
3.61	0.199	13.032	0.718
3.04	0.167	9.242	0.508
_____	_____	_____	_____
23.19	1.275	91.01	5.01

$$\sum x_i^2 = 91.01 \quad (\sum x_i)^2 = 537.776 \quad (\sum x_i \sum y_i) = 29.567$$

$$\sum x_i y_i = 5.01$$

$$m = \frac{5.01 - 29.567/6}{91.01 - 537.776/6} = 0.056$$

$$b = y - mx$$

$$b = 0.213 - 0.056 \times 3.87 = -0.004$$

$$y = 0.056 x - 0.004$$

The Chromium results:

(i).The mean and standard deviation:

$$\begin{aligned} \text{The mean } X &= \sum x_i / n \\ &= 39.60 / 6 \\ &= 6.6 \end{aligned}$$

$$X_i \quad (x_i - x) \quad (x_i - x)^2$$

5.42	- 1.18	1.39
5.89	- 0.71	0.50
7.37	0.77	0.59
8.33	1.73	2.99
7.02	0.42	0.18
5.57	- 1.03	1.06
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39.60		6.71

(ii). Standard deviation (s):

$$\begin{aligned}
 S &= \sqrt{\sum(x_i - \bar{x})^2 / n - 1} \\
 &= \sqrt{6.71 / 5} \\
 &= 1.158
 \end{aligned}$$

(iii). Relative standard deviation:

$$\begin{aligned}
 \text{R.S.D} &= s/\bar{x} \times 100 \\
 &= 1.158 / 6.60 \times 100 \\
 &= 17.5\%
 \end{aligned}$$

(iv). The confidence limit

$$\begin{aligned}
 &= \bar{x} \pm ts/\sqrt{n} \\
 \text{In 90\%} &= 6.60 \pm 2.015 \times 1.158 / \sqrt{6} \\
 &= 6.60 \pm 0.953
 \end{aligned}$$

The range of confidence 90% between 5.647 – 7.553

$$\text{In 95\%} = 6.60 \pm 2.571 \times 1.158 / \sqrt{6}$$

$$= 6.60 \pm 1.216$$

The range of confidence limit in 95% between 5.384 – 7.816

$$\text{In } 99\% = 6.60 \pm 4.032 \times 1.158 / \sqrt{6}$$

$$= 6.60 \pm 1.907$$

The confidence limit range between 4.693 – 8.507

(v).The best linear by least squares methods:

$$Y = mx + b$$

$$m = \frac{\sum x_i y_i - (\sum x_i \sum y_i) / n}{\sum x_i^2 - (\sum x_i)^2 / n}$$

X_i	y_i	$(x_i)^2$	$x_i y_i$
5.42	0.139	29.38	0.75
5.89	0.151	34.69	0.89
7.37	0.189	54.32	1.39
8.33	0.203	69.39	1.69
7.02	0.180	49.28	1.26
5.57	0.143	31.02	0.80
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39.60	1.01	268.08	6.78

$$6.78 - 40.00 / 6$$

$$m = \frac{\quad}{\quad}$$

$$268.08 - 1568.16 / 6$$

$$= 0.017$$

$$b = y - mx$$

$$= 0.168 - 0.017 \times 6.60$$

$$= 0.056$$

$$y = 0.017x + 0.056$$

13-2 Discussion

The pH effect in extractions:-The Iron(III) was extracted at the best yield in 1M of Hydrochloric acid. The extraction decrease when the pH value increase.

-The high concentration of Chromium(VI) was extracted in pH 4.

Calibrations curve: In the standard calibration curve of Iron (III), absorbance were plotted against concentration, when the axis's point linked the curve had produced. Because some results deviated from the line due to the deviation from direct proportionality between absorbance and concentration encountered as produce from intermolecular force. In addition adherence in dilute concentration the interaction between iron ion electromagnetic radiation increase but in higher concentration were decrease. The other reasons were due to the complex formation there are two type of species at the solvent, Iron (II) complex were found as well as Iron(III) but Iron(III) complex as more complexation formed.

The Chromium calibration curve were produced straight line because the direct proportionality between concentration and absorbance.

The evaluations:

1. Iron:

-Standard deviation was 0.276 and the R.S.D was 7.13%.

- the confidence limit in 90 % = 3.87 ± 0.227

In 95 % = 3.87 ± 0.2897

In 99 % = 3.87 ± 0.454

The values in out of this ranges had never null according to Q test, may produced form random error.

2. Chromium:

- Standard deviation was 1.158 and the R.S.D 20.33%.

- the confidence limit in 90% = 6.60 ± 0.953

In 95% = 6.60 ± 1.216

In 99% = 6.60 ± 1.907

We observed all the results on the confidence 99% in closely to true value.

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