Spectrophotometric Study of Stability Constants of Fe (III), Co (II) and Cu (II) Complexes of Salicylhydroxamic Acid at Room Temperatures

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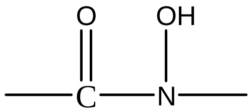
Abstract: ***Complexation of Fe (III), Co (II), Cu (II) with salicylhydroxamic acid have been studied spectrophotometrically at absorption maximum for Fe - hydroxamate, Co- hydroxamate, and Cu- hydroxamate, of 520, 510 and 640nm respectively. The complexations were carried out at temperatures 25°C at the wavelengths of the respective complexes. The stoichiometry of the complexes were determined using Job's continuous variation method and the value was found to be 1:2 metal to ligand ratio for Fe (III) and Co (II) and 1:1 for Cu (II). Stability constants (K) values were calculated using the continuous variation method and found to be in the order 5.9 x 10^3, 5.2 x 10^3 and 1.4 x 10^3 for Fe - hydroxamate, Co- hydroxamate, and Cu- hydroxamate respectively.***

Keywords: Iron (III), Cobalt (II), Copper (II), Spectrophotometric, Stability constant

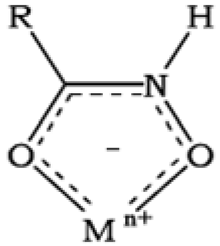
1. Introduction

The interest in studying stability parameters has expanded greatly of ligands of organic compounds of all types, mono, bi, and tri dentate. This is because of free electronic doubles in them and the formation of the coordination bond (the Ligand-metal bond), organic ligands are compounds that are slightly soluble in water due to the nature of their covalent bonds, and they have multiple advantages that made their use widely spread and received various applications and uses in various fields such as medicine, technology and science and gave results of great importance (1, 2). These ligands were used in analytical chemistry, in the field of quantitative and qualitative estimation of the minimal concentrations of many metal ions and in different models (2). Ahydroxamate as they are characterized by their easy preparation, stability and high sensitivity to the transition metal ions (3, 4). Stability constants of metal ion complexes of various ligands and especially chelating ligands using different methods such as spectrophotometric and potentiometric techniques have been determined (5). The complex stability depends on several factors such as ligand type, metal ion type, and solvent (6). About more than 100 years ago, Lossen discovered the hydroxamic acids (7). They are a class of a week organic acids of general formula RC (=O) N (R') OH (8). They have been classified as primary (I), secondary (III) and cyclic they can be represented in two tautomeric forms keto, andenol. Bothtautomers may exist as Z (zusammen) or E (entgegendiastereomers, hydroxamic acids are important chelating agents, towards a very great number of metal ions. They have bidentate functional group.

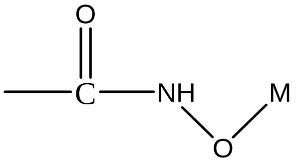


$-C(=O)-N(OH)-$

The complex formation between a metal and hydroxamic acid Usually take place with the replacement of hydroxylamine hydrogen by the metal ion and ring closure through the carbonyl- oxygen chelate (9), producing highly stable complexes.



a hydroxamic acid can also act as a monodentate ligand through its nitrogen atom. As shown in the figure below;



On acid hydrolysis of free hydroxamic acids, hydroxylamine and the parentcarboxylic acid are formed (10). Metal ions bound to hydroxamates also hydrolyze (11). The Stoichiometry, preparation and characterization of hydroxamic acid metal complexes had been extensively sutdued (12-16)In this study, we discuss the complexation reaction between hydroxamic acid and some metal by applied continuous variation method. The applied of continuous variations method is attributed to Job (17). In this method, A series of solutions are prepared where in the concentration of one reactant is systematically increased while the other is decreased, the combined concentration staying constant throughout. Solution absorbances are subsequently recorded at an appropriate wavelength.

2. Materials and Methods

2.1 Chemicals

Chemicals used in this study includes

Salicylic acid, LOBAchemie, India. Methanol, lOB Achemie, India. Sulfuric acid, LOBA chemie, India. Carbon tetrachloride, LOBA chemie. India. Hydroxylamine hydrochloride, LOBA chemie, India. Sodium hydroxide, CDH, China. Ferric chloride, CDH, China. cobalt nitrite, China. Copper sulfate, LOBA chemie, India. Ethanol, Alwatanya ltd. company for distillation, Sudan. Sodium hydrogen carbonate. Magnesium sulfate.

2.2 Instruments

- FTIR spectrophotometer, 84005, Shimatzu, Japan.
- pH/ion meter, 555, Corning pinnacle, Switzerland.
- UV/Vis. spectrophotometer, 6505, Jenway, England
- Melting point electrical, type (Gallenkamp, England)

2.3 Methods

2.3.1 Preparation of salicylhydroxamic acid (SHA):

Salicylohydroxamic acid was preparedin two simple steps, step one the reaction of salicylic acid with methanol and step two by the coupling of methyl salicylate and free hydroxylamine, acidified by 2M H_2SO_4, the precipitate which was formed is filtered, recrystallized form water acetic acid mixture.

2.3.2. Characterization of salicylhydroxamic acid

1) m.p 169C$^{\circ}$
2) IR. Spectrum, the spectra showing absorption bands: 3288.4 cm^{-1} (OH), 1614.17 cm^{-1}
3) NMR.Aromatic ring appear at (6.82-7.83). (IV) Mass spectra.

2.3.3 Preparation of buffer solutions

1) 0.1M (hydrochloric acid, potassium hydrogen phthalate) was prepared and mixed to obtain a solution of pH 3
2) 0.1M of (Sodium hydroxide, potassium hydrogen phthalate) was prepared and mixed to obtain a solution of pH 6, 7.

2.3.4 Preparation of iron stock solution (0.013M)

1 cm of 1000ppm ferric chloride was diluted and, then transferred to 100cm^{3}volumetric flask 5cm^3 of buffer solution (PH=3) was added to the solution then diluted to the volume mark with distilled water.

2.3.5 Preparation of salicylhydroxamic acid stock solution (0.013M)

0.02g of salicylhydroxamic acid was weighed and dissolved in 1.0 cm³ ethanol, then transferred to 100cm³ volumetric flask, 5cm³ of buffer was added (pH =3), the volume was completed up to the mark with distilled water.

2.3.6 Preparation of iron salicylhydroxamate complex

A series volumes (0, 1, 2, 3, 4, 5, 6, 7, 8, 9cm3) of the Fe (III) solutions and (9, 8, 7, 6, 5, 4, 3, 2, 1 and 0cm3) of the ligand were added, keeping the mole fraction of the solution and the pH constant. The absorbances of the solution was taken at the wavelength of maximum absorbance of the complex which was determined by the wavelengths from 520nm.

2.3.7 Preparation of cobalt nitrite stock solution (0.013M)

1 cm of 1000ppm cobalt nitrate was diluted and, then transferred to 100cm^{3}volumetric flask, 5cm^3 of buffer solution (PH=7) was added, to the solution then diluted to the volume mark with distilled water.

2.3.8 Preparation of salicylhydroxamic acid stock solution (0.013M):

0.02g of salicylhydroxamic acid was weighed and dissolved in 1.0 cm³ ethanol, then transferred to 100cm³ volumetric flask, 5cm³ of buffer was added (pH =7), the volume was completed up to the mark with distilled water.

2.3.9 Preparation of cobalt salicylhydroxamate complex: (0.013M)

A series volumes (0, 1, 2, 3, 4, 5, 6, 7 8, 9cm3) of the Co (II) solutions and (9, 8, 7, 6, 5, 4, 3, 2, 1 and 0cm3) of the ligand were added, keeping the mole fraction of the solution and the pH constant. The absorbances of the solution was takenat the wavelength of maximum absorbance of the complex which was determined by the wavelengths from 510 nm.

2.3.10. Preparation of copper sulphate stock solution (0.013M):

1 cm of 1000ppm copper sulphate was diluted and, then transferred to 100cm^{3}volumetric flask, 5cm^3 of buffer solution (PH=6) was added to the solutionthen diluted to the volume mark with distilled water.

2.3.11. Preparation of salicylhydroxamic acid stock solution: (0.013M):

0.02g of salicylhydroxamic acid was weighed and dissolved in 1.0 cm³ ethanol, then transferred to 100cm³ volumetric flask, 5cm³ of buffer was added (pH =6), the volume was completed up to the mark with distilled water.

2.3.12. Preparation of copper salicylhydroxamatecomplex (0.013M):

A series volumes (0, 1, 2, 3, 4, 5, 6, 7 8, 9cm3) of the 0.01M of Cu (II) solutions and (9, 8, 7, 6, 5, 4, 3, 2, 1 and 0cm3) of the ligand were added, keeping the mole fraction of the solution and the pH constant. The absorbances of the solution was taken at the wavelength of maximum absorbance of the complex which was determined by the wavelengths from 640nm.

3. Results and Discussion

3.1 Calculation of stability Constant for Metal Complex (13)

To achieve this objectives continuous variation was used to find the ratio of ligand to metal and also benefit from it in calculating the stability constant by taking the resulting absorption values of the solutions of mixing the ligand with the metal ion that wanted to perform stability, and therefore it was used (18):

$M + n L \_\_\_\_\_\_\_\_ ML_n$

$K = \frac{[ML]}{[M][L]}$

K= Stability constant

n =number of ligand

$\alpha = \frac{A_{m} - As}{Am}$ Absorbtion of complexes

A_m = The highest absorbance of complex

As= The less highest absorbance of complex

α =The degree of bonding between the ligand and ion

C= Concentration of complex

Were (n=1)uses this relation;

$K = \frac{(1 - a)}{a2.C}$

Were (n=2)uses this relation;

$K = \frac{(1 - a)}{4a^3 C2}$

When stability values are found, it is easy to calculate the change in free energy from relation;

$\Delta G = - RT \ln K$

Table 1: M/M+L values

M\ M + L	Fe (III)	Co (II)	Cu (II)
0.1	0.011	0.039	0.023
0.2	0.016	0.063	0.026
0.3	0.012	0.082	0.044
0.4	0.018	0.075	0.045
0.5	0.019	0.050	0.051
0.6	0.022	0.053	0.047
0.7	0.024	0.047	0.040
0.8	0.019	0.043	0.033
0.9	0.017	0.041	0.024
0.00	0.00	0.00	0.00

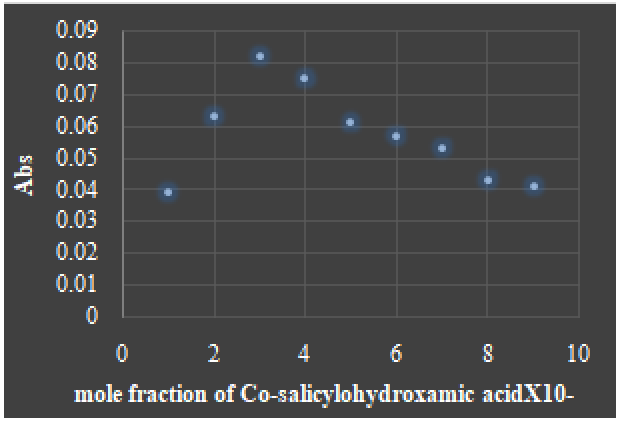


Figure 1: Mole fraction of Co.Salicylichydroxamic acid

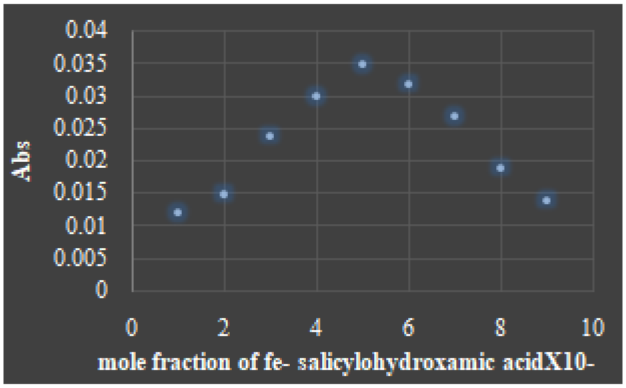


Figure 2: Mole fraction of Fe.Salicylichydroxamic acid

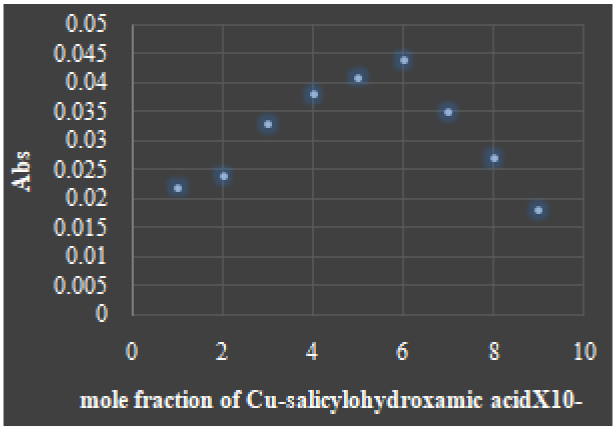


Figure 3: Mole fraction of Cu. Salicylichydroxamic acid

Table 2: Stability constant of metal ions complexes at room temperature

Metal ion complex	A_m	A_s	a	K	ΔG- $KJ.mol^{-1}$
Fe (III)	0.024	0.011	0.5	5.9×10^3	21.1
Co (II)	0.082	0. 039	0.52	5.2×10^3	21
Cu (II)	0.051	0.023	0.49	1.4×10^2	12.2

4. Discussion

Salicylhydroxamic acid was prepared by react the ester with hydroxylamine. The acid was recrystallized and identified by M.pt, complex-color test and IR spectra, nmr and mass spectra. Iron salicyl hydroxmate, cobalt salicyl hydroxmate, copper salicylhydroxmate complexes were prepared in the solution.

Based on complex formation, following continuous variation method; iron shows 1:2 stoichiometric ratio at pH3. Cobalt shows 1:2 stoichiometric ratio at pH 7 and copper shows 1 :1 stoichiometric ratio at pH 6The higher value of K, for this compound can be attributed to resonance, from the benzene rings where there could be delocalization of electrons between the ligand-metal π-bonding thereby providing extra stability for the chelates and also, formed a five member ring - when associated with metallic ion, complexes of iron and cobalt and copper hydroxamate have small size more stable ion but the iron ion more stable than the other metal ions, and this is due to that The extra charge carried by the positive Iron ion gave it high ability to attract uniform ligand. In addition To the size of the metal ion, it plays a role in the stability of the complex state. Thus, they are arranged as follows: Fe > Co> Cu in which low stabilities of Cu – hydroxmate was observed. A negative value of ΔG^o point is evidence of reaction spontantaneous (meaning higher energy loss to obtain more stable compounds).

5. Conclusion

Complexes resulting from the coordination of the metal ions with the ligand (hydroxamic acid) are thermodynamically stable. Based on complex formation, following continuous variation method; iron shows 1:2 stoichiometric ratio at pH3.cobalt shows 1:2 stoichiometric ratio at pH 7 and copper shows 1 :1 stoichiometric ratio at pH 6The higher value of K, for this compound can be attributed to resonance.

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