SUST
Journal of Natural and Medical Sciences
Journal home page:
http://Scientific-journal.sustech.edu/

DEANSHIP OF SCIENTIFIC RESEARCH

Stoichiometry Study of Iron and Vanadium Salicylhydroxamate Complexes

Randa, B. A.,[1]* Elmugdad, A. A.[2]

Azal Pharmaceutical industries,
SUST, department of chemistry, e.mail: elmugdad@hotmail.com
Corresponding Author: e.mail: randab.ahmed@gmail.com

Abstract
Salicylhydroxamic acid was synthesized by coupling methyl salicylate with free hydroxylamine. The compound was recrystallized in water/acetic acid mixture and identified by m.p., iron and vanadium color test and IR spectra [showing absorption bands 3295 cm^{-1} (--OH), 1610 cm^{-1} for C=O and 910 cm^{-1} for N-O. Iron and vanadium salicylhydroxate complexes were prepared by reacting salicylhydroxamic acid with the corresponding metal salt in aqueous media, filtered, purified and dried, showing the characteristic colors. Their purity of complexes was tested by their linear relationship of concentration and absorbance. Stoichiometry of iron and vanadium with the ligand is measured at different pH values. The results show 1:1, 1:2, 1:3 for iron and 1:2, 1:3 for vanadium.

**Keywords:** Hydroxamic acid, Ligand, Spectra, oxo-vanadate.

المستخلص

تم تحضير سالسيلات الميثيل عبر الأسترة الحمضية لحمض السالسيليك في ميثانول. تم تحرير هيدروكسيل أمين الطليق بمعالجة هيدروكلوريد هيدروكسيل أمين بإضافة كمية مكافئة من محلول هيدروكسيد صوديوم. تم تركيب حمض سالسيل هيدروكسميك بخلط هيدروكسيل امين الحر مع ستر سالسيلات ميثيل. وتم التعرف والتحقق من الحمض بقياس نقطة الانصهار وطيف الأشعة تحت الحمراء. وحضرت معقدات حمض سالسيل هيدروكسميك مع الحديد والفانيديوم وأظهرت المعقدات الألوان المميزة. أظهرت تحاليل الطيف فوق البنفسجي والمرئي علاقة خطية بين الامتصاص وتراكيز لمعقدات. تبين من قياسات العلاقة الكمية الحسابية للنسب التي تتكون بها المعقدات بين اللاقط وأيون المعدن عند مختلف قيم قيم الأس الهيدروجيني، أن الحديد يظهر العلاقات 1:1، 1:2 و 1:3 ، بينما يظهر الفانيديوم 1:2 و 1:3

Introduction

Stoichiometry is the science of measuring the quantitative proportions or math ratios in which chemical elements stand to one another [1]. It is defined as the constrains placed on the composition of a closed system by the requirement for conservation of the amount of each atomic species and of electronic charge. These constrains take the form of linear conservation equation, which may be expressed in the form of either linear algebraic atom or charge balanced equation or chemical equation [2].

Hydroxamic acids are organic molecules containing the -CO-N-O- group(s) [3]. They are a class of organic acids of general formula RC (=O) N (R') OH, that have very important role in biological systems [4].
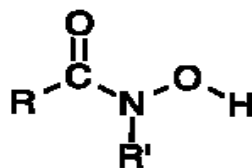
The first hydroxamic acid, oxalohydroxamic acid, was synthesized by H. Lossen [5].Shortly thereafter, W. Lossen [6] discovered a rearrangement reaction of O-acyl derivatives of hydroxamic acids, which now bears his name:
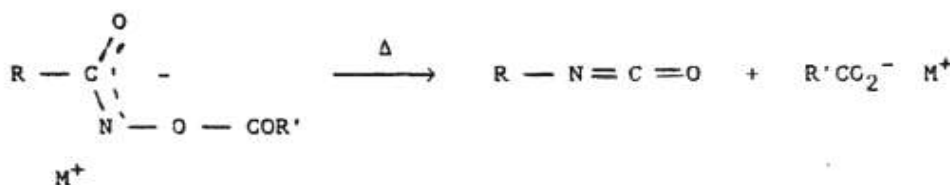
Hydroxamic acids are among the most well studied compounds due to their significance in so many fields [7] that can act as O--O donor ligands with high affinities for hard cations such as Fe^{3+} [8, 9, 10].

The salicylhydroxamic acid molecule possesses, apart from the reactive grouping of the hydroxamic acid, one more functional group (-OH) in a position favorable for chelation.
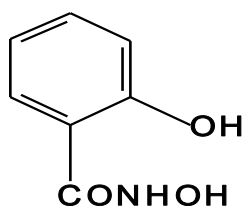
Salicylhydroxamic acid has a salicylate and hydroxamic acid moieties, it is a potent chelating agent for Fe^{+2}, V^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2}, etc. [11].
Compounds containing the hydroxamic group [C (QO)–N (–H)–O–H)] act as chelating agents for metal ions [12].

Hydroxamic acids act as bi-dentate ligands. They exist in two tautomeric forms (eno- and keto-) of the acid; the structure of their metal complexes may represent in three different forms as shown below:

(I)   (II)   (III)
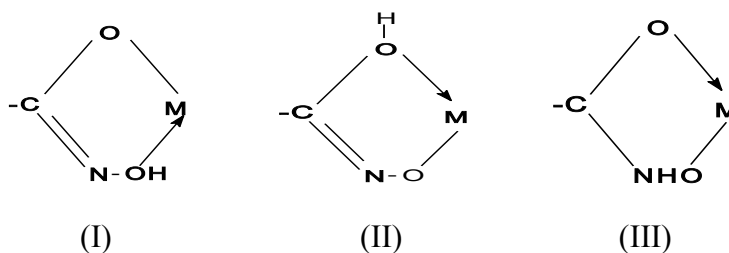
Other possible structures are excluded, as they would lead to the formation of unstable four member rings involving the metal nitrogen linkage [13]. The complex formation is believed to take place by replacement of the hydroxyl amino hydrogen by the metal ion and ring closure through the carbonyl oxygen. The resultant complex is generally neutral and forming a precipitates or soluble colored complex in aqueous solution, providing a methods for gravimetric analysis or solvents extraction with spectrophotometric finish. The most characteristic reaction is the intense violet color produced by ferric chloride and purple color with vanadium (V). Since it is known

that derivatives of the general formula RCONHOR' or RC (OH) =NOR' do not give color reactions with ferric chloride, while compounds of the structures do. It is
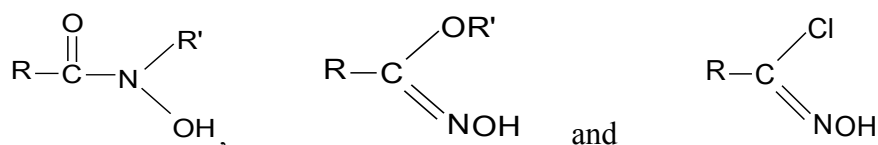
apparent that the =NOH grouping is necessary for the formation of the coordination compound.

Complexes of monohydroxamic acids with Fe (III), Co (II) and Cu (II) are shown to co-ordinate via oxygen atoms of the ligand [14].
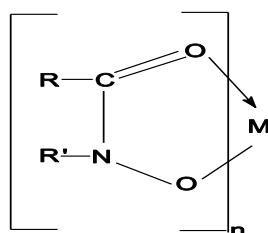
(n=oxidation state of metal)

Copper (II) forms square planar complexes and vanadium (V) forms oxo-complexes. The best known of these complexes is that, with Fe (III) the beautiful purple color of

this compound forms the basis for the sensitive qualitative and quantitative determination of hydroxamic acids and their derivatives (15, 16).
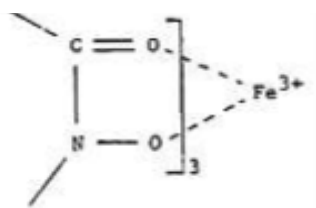
Hydroxamic acids, RCONHOH, form highly stable complexes with vanadium (V) in 1:1, 1:2 and 1:3 molar ratios. The stability constants of the complexes were determined through spectrophotometric and potentiometric methods at various pH values and found in agreement. The hydroxamates are of interest due to their ability to form stable transition metal complexes through the formation of a five membered chelate ring [17]. Even in acid media iron (III) forms intensely colored complexes with this ligand which are useful for spectrophotometric analysis. The ability of hydroxamic acids to chelate metal ions has also found pharmaceutical applicat-ions[16].

Stoichiometry is determined by different methods: mole ratio, slope ratio and continuous variations (job's method).

Mole ratio method determines the concentration of metal ion is held fixed, while the concentration of the reagent (ligand) increased stepwise. One the graph of absorbance vs. moles of reagent added, the intersection of the extrapolated linear segments determines the ratio: moles of reagent / moles of metal.

In slope ratio method, two series of solutions are prepared. In the first series various amounts of metal ion are added to a large excess of the reagent, while in the second series different quantities of reagent are added to a large excess of metal ion. The absorbance of the solutions in each

series is measured and plotted vs. the concentration of the variable component.

The discovery of continuous variations method is attributed to Job [18]. Who first applied it to complex formation; it is a simple and effective approach to the determination of chemical reaction.

In this method, cation and ligand solutions with identical analytical concentrations are mixed in such a way that the total volume and the total moles of reactants in each mixture is constant but the mole ratio of reactants / varies systematically (for example, 9:1, 8:2, 7:3, …, 1:9). The absorbance of each solution is then measured at a suitable wavelength and corrected for any absorbance that the mixture might exhibit if no reaction had occurred. The corrected absorbance is plotted against the volume fraction of one reactant, that is, $V_M/ (V_M+V_L)$, where V_M is the volume of cation solution and V_L is the volume of the ligand solution.

The resulting curve will show a maximum at the mole fraction corresponding to that in the complex. When the curvature is pronounced and the maximum is not apparent, the apex may be obtained by drawing tangents [19].

Experimental and Results
Reagents:
(i) Salicylic acid, LOBA chemie, India.
(ii) Methanol (dried), LOBA chemie, India.
(iii) Sulfuric acid, LOBA chemie, India.
(iv) Carbon tetrachloride, LOBA chemie, India.
(v) Hydroxylamine hydrochloride, LOBA chemie, India.
(vi) Sodium hydroxide, CDH, China.
(vii) Ferric chloride, CDH, China.
(viii) Ammonium metavanadate, CDH, China.
(ix) Copper sulfate, LOBA chemie, India.
(x) Ethanol, Alwatanya ltd. company for distillation, Sudan.
(xi) Sodium hydrogen carbonate.
(xii) Magnesium sulfate.

Instruments
1. FTIR spectrophotometer, 84005, Shimatzu, Japan.
2. pH/ion meter, 555, Corning pinnacle, Switzerland.
3. UV/Vis. spectrophotometer, 6505, Jenway, England.

Preparation of salicylhydroxamic acid (SHA)
Salicylohydroxamic acid was prepared by coupling of methyl salicylate and free hydroxylamine left overnight, acidified, the precipitate formed is filtered, recrystallized form water acetic acid mixture and identified.

Characterization of salicylhydroxamic acid
(i) m.p 170^0C (lit. $168\text{-}170^0C$)
(ii) i.r. Spectrum (KBr); the spectra showing absorption bands: 3288.4 cm^{-1} (OH), 1618.17 cm^{-1}

Quantitative Evaluation of complex formation
Linear relationship between metal complexes concentration and absorbance

Preparation of stock solution of salicylhydroxamic acid
0.01M of salicylhydroxamic acid was prepared by weighing 0.15314 g, dissolved in 5ml of ethanol, transferred to 100 ml volumetric flask, the volume was completed to the mark with distilled water.

Preparation of stock solution of metals
0.01M stock solutions of Fe (III), V (V) and Cu (II) were prepared. 0.0290 g $FeCl_3$, 0.0230 g NH_4VO_3 and 0.25 g $CuSO_4$ were weighed out accurately, dissolved in distilled water, transferred into 100 ml volumetric flasks, completed up to the mark with distilled water.

Preparation of standard solution of complexes
2, 4, 6, 8, 10, 12 ppm standard solutions of metal were prepared by taking 0.2, 0.4, 0.6, 0.8, 1, 1.2 ml of metal stock solution into 10 cm^3 volumetric flask, then 1 ml of

0.01M salicylhydroxamic acid was added, the volume was completed to the mark with distilled water.
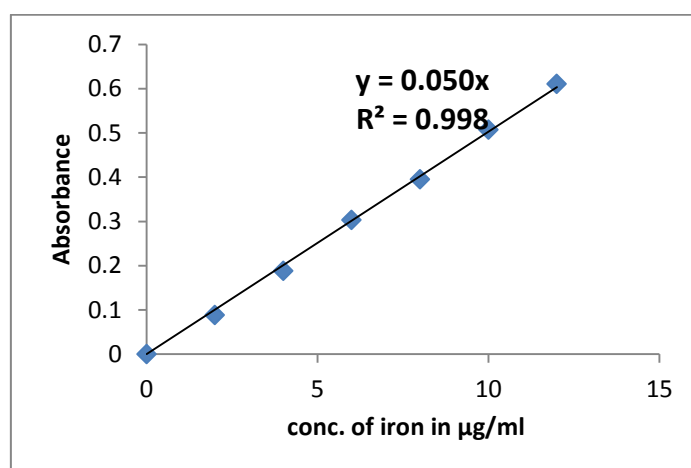
Preparation of blank solution
$1cm^3$ of 0.01M salicylhydroxamic acid was taken, transferred to $10 \ cm^3$ volumetric flask and completed up to the mark with distilled water.
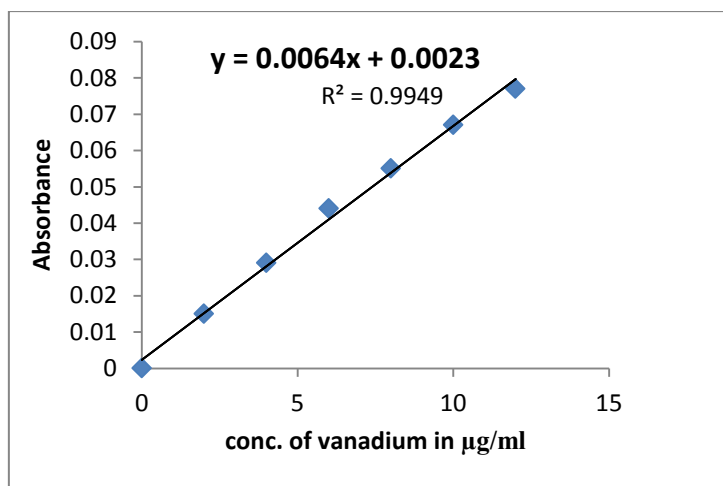
λ$_{max}$ determination

$1cm^3$ of 0.01M salicylhydroxamic acid was taken into $10 \ cm^3$ volumetric flask, and then $1 \ cm^3$ of $FeCl_3$ was added and completed up to the mark with distilled water.

The same method was repeated for vanadium.

Instead for copper the standard solutions of 20, 40, 60, 80, 100, 120 ppm were prepared.

Calibration curve of iron salicylhydroxamate complex

Calibration curve of vanadium salicylhydroxamate complex

Determination of stoichiometry of complexes using continuous variation method

Preparation of buffer solutions

(i) Chloride buffer: 50 cm^3 of 0.2M potassium chloride was mixed with 41.4cm^3 of 0.2M hydrochloric acid to obtain a solution of pH 1.5
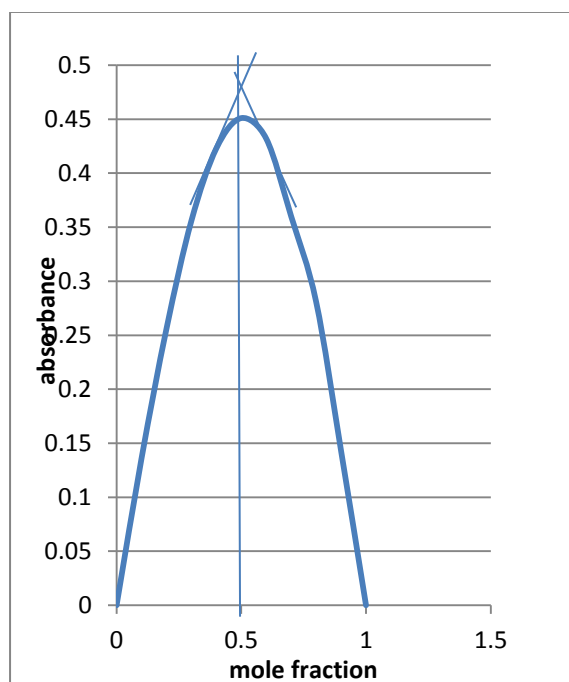
(ii) 0.04M of (phosphoric acid, boric acid and acetic acid) was prepared and mixed to obtain a solution of pH is equal 2.

For higher acidity drops of acetic acid was added.

Effect of pH on stoichiometry of iron salicylhydroxamate complex at pH 1.5

Preparation of ferric chloride stock solution (0.013M):

0.0106g of ferric chloride (0.000653mole) was weighed and dissolved in small amount of distilled water, then transferred to 50 cm^3 volumetric flask,5 cm^3 of buffer (pH = 1.5) was added, the volume was completed up to the mark with distilled water.

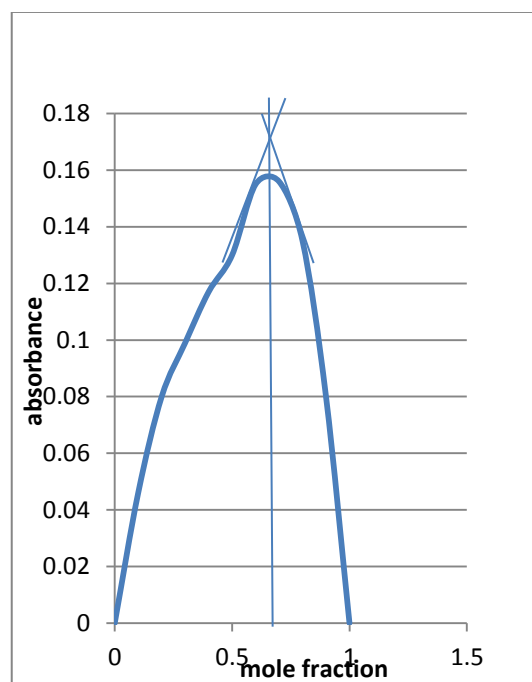### Preparation of salicylhydroxamic acid stock solution (0.013M)

0.01g (0.000653mole) of salicylhydroxamic acid was weighed and dissolved in 1.0 cm^3 ethanol, then transferred to 50cm^3 volumetric flask, 5cm^3 of buffer was added (pH =1.5), the volume was completed up to the mark with distilled water.

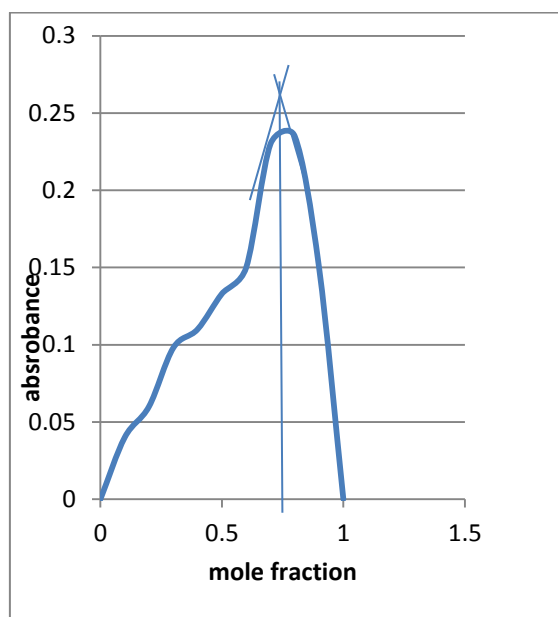### Preparation of Iron salicylhydroxamate complex

A series of solutions of different mole fractions of the two constituents were prepared, 0:10, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1 and 10:0 cm^3 salicylhydroxamic acid (ligand): ferric ion. The total volume of the prepared complex and the pH were kept constant.

The λ_{max} was determined; the absorbance of each solution was recorded at the wavelength of maximum absorbance.

The same method was used for determination of stoichiometry of complexes with pH= 2.5and 3.5, λ_{max} = 400 and 390 respectively.

Stoichiometric curve of iron complex at pH 1.5

Stoichiometric curve of iron complex at pH 2.5

Stoichiometric curve of iron complex at pH 3.5

Determination of vanadium salicylhyd-roxamate complex (at pH=5)

Preparation of ammonium-metavanadate stock solution

0.0078g of ferric chloride (0.000653mole) was weighed and dissolved in small amount of distilled water, then transferred to 50cm³ volumetric flask, 5cm³ of buffer was added (pH= 5), the volume was completed up to the mark with distilled water.

Preparation of salicylhydroxamic acid stock solution

0.01g (0.000653mole of iron) of salicylhydroxamic acid was weighed and dissolved in 1cm³ ethanol, then transferred to 50cm³ volumetric flask, 5cm³ of buffer was added (pH=5), the volume was completed up to the mark with distilled water.

Preparation of vanadium salicylhydr-oxamate complex

A series of solutions of different mole fractions of the two constituents were prepared, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1cm³ salicylhydroxamic acid (ligand): ammonium metavanadate (metal). The total volume of the prepared complex and the pH were kept consistent.

λ_{max} determination

$\lambda_{max.}$ was determined using the solution having the highest concentration, and found to be 520 n.m.
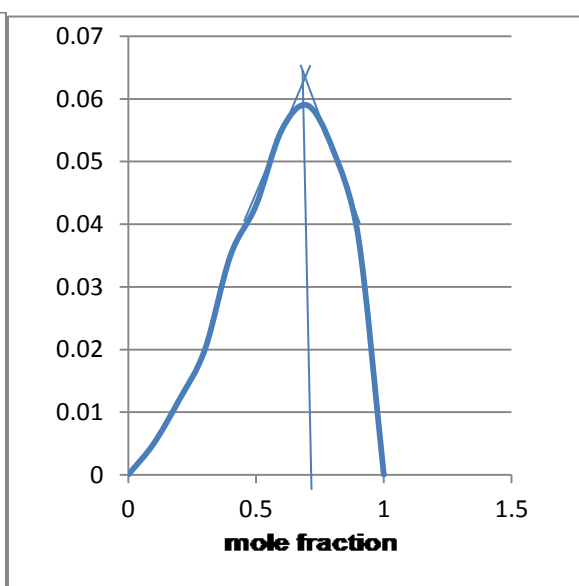
The λ_{max} was determined; the absorbance of each solution was recorded at the wavelength of maximum absorbance.

The same method was used for determination of stoichiometry of complex with pH 6.5 and

λ_{max} = 520 nm. (Dark blue) color was observed for both pH values.
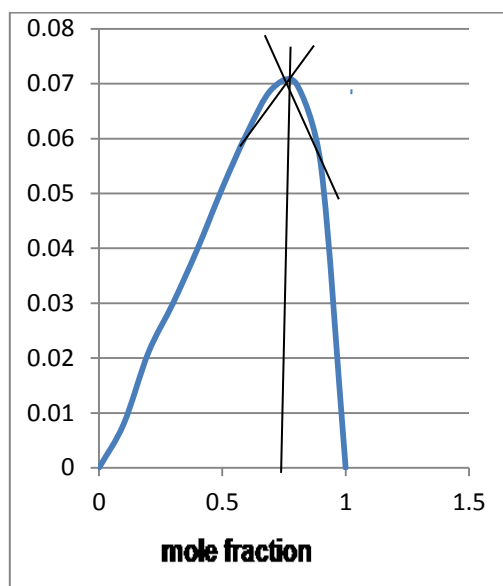
Stoichiometry curve of vanadium complex at pH 5

Stoichiometry of vanadium complex at pH 6.5

Discussion

Salicylhydroxamic acid was smoothly prepared through the ester route method. The acid was recrystallized and identified by M.pt, complex-color test and IR spectra. Iron salicylhydroxmate (violet), vanadium salicylhydroxmate complexes were prepared in aqueous acidic media. The complexes were air dried to form defined beautiful crystals.

UV-Visible spectroscopic measurements of the ligand with iron and vanadium complexes at different concentrations show strict linearity. This confirms that the ligand and the metal cations are complexed uniformly. The complexes for both cations were formed at pH values which are later selected for stoichometric study.

Based on complex formation, following continuous variation method; iron shows 1:1, 1:2 and 1:3 stoichiometric ratios at pH 1.5, 2.5 and 3.5 respectively. Vanadium shows 1:3 and 1:2 stoichiometric ratios at pH 5 and 6.5 respectively. Aquo-chemistry of Vanadium (V) with hydroxamate depends upon pH. At low pH non oxo-vanadium coordination complex is formed.

As the pH increases oxo coordination is restored. 1:1 stoichiometry is not present for vanadium; this may rest on the fact that it forms only octahedral stable complexes. This could be explained by its coordination number 6 leaving for 1:2 and 1:3 stoichiometry ratios.

All of the vanadium ions are in the +5 oxidation state as the VO^{3+} unit and are related by a pseudo-three-fold axis. The salicylhydroxamic acid is triply deprotonated; therefore, this trianionic ligand is coordinated as a salicylhydroximate rather than the doubly deprotonated salicylhydroxamate. Although all four oxygen and nitrogen atoms. Are bound to vanadium, an individual ligand donates only two heteroatoms to each independent vanadium (V). The deprotonated hydroxamate nitrogen and phenolate oxygen bind to vanadium atom while the two remaining oxygen atoms bind to the second vanadium. This bonding repeats throughout the cluster forming a triangular unit with a [-V-N-O-] core.

References

1. H. Latinen, "Chemical Analysis;" Mc Graw-hill, new York, (1960).

2. W. Smith and R. Missen, What is Chemical stoichiometry; chem. eng edu., 13, 26-32, (1979).

3. E. Lipczynska-kochany, The photolability of hydroxamic acids and its importance to the human environment; J. The Science of the Total Environment, 100, 469-482, (1991).

4. P. Gans, A. Sabatini, A. Vacca and M. Iuliano, D. Tommaso, The formation of iron (iii)-salicylhydroxamic acid complexes; Talanta, 43, 1739-1753, (1996).

5. H. Lossen, (1869). Ueber die Oxalohydroxamsaure; J. Justus Liebigs Ann. Chem., 150, 314-322.

6. M. Fox, Organic heterogenous photocatalysis, Chemical conversion sensitized by irradiated semiconductors; J. Acc. Chem. Res., 16, 314-121, (1983).

7. M. Khalil and F. Hassabelnaby, Potentiometric Investigation on Mixed-Ligand Complexes of some Lanthanide and Actinide Cations with Hydroxamic Acids and Diamines; Jordan Journal of Chemistry 2 (3), 275-285, (2007).

8. E. Muri, M. Nieto, R. Sindelar and J. Williamson, Hydroxamic acids as pharmacological agents; J. Current Med. Chem. Vol.9, 1631-1653, (2002).

9. P. Desaraju and A. Winston, Synthesis and iron complexation studies of bis-hydroxamic acids; J. Coord. Chem. Vol.14, 241-248, (1986).

10. M. Carrott, O. Fox, C. Maher, C. Mason, R. Taylor, S. Sinkov, and G. Choppin Solvent extraction behavior of plutonium (IV) ions in the presence of simple hydroxamic acids. Solv. Extr. Ion Exch. Vol. 25, 723-746, (2007).

11. A. Majumdar and B. Singh Electrochromatography in the separation of ions: Separation of alkaline earth metals; Anal. Chemica Acta., vol. 20, 275–277, (1959).

12. A. Kaczor, J. Szczepanski, M. Vala and L. Proniewicz, (2005). Matrix-isolation and computational study of salicylhydroxamic acid and its photochemical degradation; Journal of Phys. Chem. Chem. Phys., vol. 7, 1960–1965.

13. B. Gipson, F. Petell, C. Kinner and W Shive.; (1963). J. Org. chem., 28, 1425.

14. D. Brown, D. Keith and W. Glass, (1979). Iorg. Chim. Acta, 35, 5.

15. A. Windston, D. Varaprasad, J. Metterville and H. Rosenkrantz,.; (1985). Evaluation of polymeric hydroxamic acid iron chelators for treatment of iron overloaded; J. Pharmacol. Exp. Ther., 232, 644 – 649.

16. M. Miller, (1989). Syntheses and therapeutic potential of hydroxamic acid based chromophores and analogues; Chem. Rev., 89, 1563-1579.

17. K. Ali, N. Fatima, Z. Maqsood and S. Kazmi, (2004). Journal of the Iranian Chemical Society; Complexation of vanadium (IV) with Hydroxamate Chelators and Their Stability Relation with pH., Vol. 1(1), 65-70.

18. P. Job, (1928). Ann. Chim, 9 (113).

19. D. Skoog, D. West, F. Holler and S. Crouch, (2004). "Fundamentals of Analytical Chemistry"; Thomson, 8th Edditon.