SPECTROPHOTOMETRIC DETERMINATION OF THE STOICHIOMETRIES, STABILITY CONSTANTS AND FREE ENERGIES OF ZINC (II) AND VANADIUM (V) COMPLEXES OF ANTHRANILIC ACID.

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MAY, 2019.

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A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL, FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI.

IN PARTIAL FULFILLMENT OF THE REQUIREMENTSFOR THE AWARD OF MASTER OF SCIENCE (M. Sc.) DEGREE IN INORGANIC CHEMISTRY.

MAY, 2019.

CERTIFICATION

This is to certify that this research work, 'SPECTROPHOTOMETRIC DETERMINATION OF THE STOICHIOMETRIES AND STABILITY CONSTANTS OF ZINC (II) AND VANADIUM (V) COMPLEXES OF ANTHRANILIC ACID, was carried out by Eze, Edith Ogochukwu (Reg. No. 20114773648), in partial fulfillment for the award of Master of Science (M.Sc.) Degree in Inorganic Chemistry in the Department of Chemistry, Federal University of Technology Owerri.

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DEDICATION

This research work is dedicated to the loving memory of my dear mother, Late Ezinne Salome U. Eze, who slept in the Lord on 13th November, 2016.

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ABSTRACT

This research work describes a simple and selective spectrophotometric methods for the determination of the stoichoiometries and the stability constants of zinc (II) and vanadium (V) complexes of anthranilic acid using Job's method of continuous variation and Yoe-Jones mole ratio method. Zinc (II) ion formed a colourless complex with anthranilc acid at pH 4, and vanadium (V) formed a golden-yellow complex at pH 6. The complexes showed maximum absorbance at 309 nm for zinc (II) and 326.5 nm for vanadium (V). The zinc (II) ion formed a 1:2 metal to ligand mole ratio complex with anthranilic acid (HA), while vanadium (V) ion formed a 1:1 metal to ligand mole ratio complex with anthranilic acid. That is, for Zn^{2+}/A^{-} complex, ZnA_2 is formed and V^{5+}/A^{-} complex, VO_2A is formed.The stability constants, (Log K), molar absorptivity and free energies of the formation of Zn (II) and V (V) anthranlilate complexes were 5×10^5, (5.71), 7.58×10^4 and -32.58 kJ/mol for zinc (II) anthranilate and 6.61×10^4, 6.67, 4.7×10^6 and -38.07 kJ/mol for vanadium (V) anthranilate, respectively. It was found that the vanadium (V) ion formed more stable complex with anthranilic acid with Log K value of 6.67 compared to zinc (II) complex with Log K value of 5.71. The negative values obtained for the free energies of both complexes showed that the reactions were spontaneous, feasible and irreversible and that stable complexes were formed. Anthranilic acid is a bidented ligand and as such formed a 4-coordinate bis-chelate with each of the metals; square planar geometry is being suggested for each of the chelate complexes, bearing in mind that anthranilic acid is a strong ligand.

Key Words: Spectrophotometric Techniques, Stoichometry, Complex, Ligand, Stability Constant Absorbance, pH, Molar Absorptivity, Free Energy.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND INFORMATION

Several instrumental analytical methods are available for the determination of stoichiometries and the stability constants of metal complexes. These methods are; electrochemical oxidation reduction, ion-chromatography, conductometry, potentiometry, atomic emission or absorption, spectrophotometric method. Among these methods, spectrophotometric method of determination based on UV-Vis absorption is probably the most often used because of its simplicity, sensitivity, accuracy and rapidity (Ogwuegbu, Oforka and Spiff, 1996; Pabilane, Delaand Marie, 2011). Also, absorbance measurements can be made without perturbing the equilibrium of the system being examined.

Complexes are formed when neutral molecules or ions called ligands are joined to a central metal atom or ion through coordinate covalent bond. Metal complexes can be neutral, positively charged or negatively charged. When the complex is charged, it is stabilized by neighboring counter-ions. Ligands are complexing agents which are bonded to the central metal atoms or ions to form stable complexes. (Cotton,Wilkinson and Carlos, 1999). The complexing agent used in this work is anthranilic acid.Its molecule consists of a benzene ring with two adjacent functional groups, a carboxylic acid and an amine. It binds or coordinates to the central metal atom through the two binding sites, the oxygen atom of the carboxylate group ($-COO^-$), and the nitrogen atom of the amine group (NH_2).

In this work, the stoichiometries and the stability constants of zinc (II) and vanadium (V) complexes of anthranilic acid were determined by spectrophotomeric technique using Job's method of continuous variation and Yoe-Jones mole ratio method.

1.1.2 Spectrophotometry

Spectrophotometry is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength or wave number. The basic principle is that each compound absorbs or transmits light over a certain range of wavelengths. Spectrophotometric method is the most important for the determination of metals in alloys, minerals and complexes, owing to its selectivity. It has the advantage of having calibration graphs that are linear over a wider range when compared with atomic emission spectroscopy, atomic absorption spectroscopy and similar techniques. A very extensive range of concentrations of substances (10^{-2}–10^{-8} M) may be covered (Dehahay, 1967). The basis of spectrophotometric methods is the simple relationship between the color of a substance and its electronic structure. A molecule or an ion exhibits absorption in the visible or ultra-violet region when the radiation causes an electronic transition in molecules containing one or more chromophoric groups (Blaedel and Meloche, 1964). Quantitative determination of a sample by measurement of light absorption is based on the two fundamental laws. These laws are the Lambert's Law and Beer's law (Whitten, Davis, Peck and Stanley, 2004). The Beer-Lambert law states that the amount of light absorbed or transmitted by a solute in a transparent solvent is proportional to the number of absorbing molecules in the light path. Spectrophotometry found it usefulness in its application to quantitative analysis in various scientific fields, such as physics, materials science, chemistry, agriculture, pharmaceutical, medicine, biochemistry, microbiology, molecular biology, forensics, textile industries, etc.

1.1.3 Coordination Complexes

A coordination complex or metal complex is one in which a central atom or ion, usually metallic is joined to one or more molecule(s) or ion(s), called ligand or

complexing agents through coordinate covalent bond. In such a complex the central atom acts as an electron-pair acceptor (Lewis acid)and the ligand as an electron-pair donor(Lewis base). The central atom and the ligands coordinate to constitute the coordination sphere, (Ogwuegbu and Chileshe, 2000; Housecroft, Alan and Sharpe, 2008; Zumdahl, 2007). Examples of ligands are halide ions, carbon monoxide, ammonia, cyanide ion, ethylenediamine, ethylenediaminetetraacetate ion (EDTA), anthranilic acid ($C_7H_7NO_2$), etc.

The complexation reaction of metal ion and the ligand in an aqueous solution is expressed by the following equation:

$$M^{n+} + nL \rightleftharpoons ML_n \qquad (1.1)$$

Where M^{n+}, L, ML_n are metal ion, ligand and metal complex respectively.

1.1.4 Coordination Number

Coordination number is the number of donor atoms surrounding the central metal atom. Coordination number can vary from as low as 2 to as high as 16 or more. The coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by the electronic factors such as charge, which depend on the electronic configuration of the metal ion. Some ligands contain more than one donor atom. Ligands that coordinate through two bonds are called bidentate ligands. Those that contain one donor atom are called monodentate ligands while those with more than one donor atom are referred as polydentate ligands. Anthranilic acid (AH), ethylenediamine (en) and oxalate ion (ox) are bidentate ligands. Bidentate and polydentate ligands are often called chelating ligands.

These competing effects are ionic potential which is defined as the charge to radius ratio (q/r). The bigger the charge on the central ion, the more attraction there will be

for negatively charged ligands. However, the bigger the charge, the smaller the ion becomes which then limits the number of groups able to coordinate.

1.1.5 Chelate and Chelating Agents

A chelate is a chemical compound formed from a metal ion and a chelating agent. A chelating agent is a multi-dentate ligand that can form several bonds to a single metal ion. Chelating agent are organic or inorganic compounds capable of binding metal ions to form complex ring-like structure called chelates. Chelating agents possess "ligand" binding atoms that form either two covalent and one co-ordinate or two co-ordinate linkages in the case of bidentate chelates. Bidentate or multidentate ligands form ring structures that include the metal ion and the two-ligand atoms attached to the metal (Anderson, 1999). Examples of chelating ligands include anthranilic acid and EDTA, an excellent chelating ligand because it has six donor atoms.

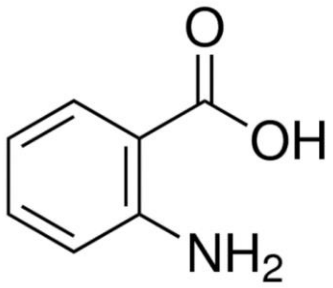


Figure 1.1: Anthranilic Acid

Anthranilic acid ($C_6H_4(NH_2)COOH$) is one of the best compound used by Carl Julius Fritzche (1808-1871) in the laboratory in St. Peterburg by degrading ancient dye indigo. It is a white solid amino acid in pure form whereas commercially available in yellow form. Its molecule consists of a benzene ring with two adjacent functional groups, a carboxylic acid and an amine (Sheibley, 1943). Anthranilic acid is a bidentate ligand, with two binding sites to the central metal ion. Complexes formed by chelating ligands often have additional stability over those of non-chelating

ligands (Atkins, Overton, Rourke, Weller and Armstrong,2010). This is known as chelate effect.

Virtually all metalloenzyme activities feature metals that are chelated, usually to peptides or cofactors and prosthetic groups. Such chelating agents include the porphyrin rings in hemoglobin and chlorophyll. Many microbial species produce water-soluble pigments that serve as chelating agents, termed siderophores. For example, species of *Pseudomonas* are known to secrete pyocyanin and pyoverdin that bind iron. Enterobactin, produced by *E. coli*, is the strongest chelating agent known.

All biochemicals exhibit the ability to dissolve certain metal cations. Thus, proteins, polysaccharides, and polynucleic acids are excellent polydentate ligands for many metal ions. Organic compounds such as the amino acids(e.g. glutamic acid and histidine), organic diacids such as malate, and polypeptides such as phytochelatin are also typical chelators.

In medicine, chelating agents are used to detoxify poisonous metal agents, such as mercury, arsenic, and lead, by converting them to a chemically inert form that can be excreted without further interaction with the body. It is also used indrug production example, antibiotic drugs of the tetracycline family, are chelators of Ca^{2+} and Mg^{2+} ions. They play important role in oxygen transport and photosynthesis. Chelators are also used in the production of nutritional supplements, fertilizers, as water softener and in chemical analysis. Also, they are used in the manufacture of commercial products such as shampoo and food preservatives. Industrially, chelates are used as catalysts.

1.1.6 Stoichiometry

Stoichiometry involves using relationships between reactants and/ or products in a chemical reaction to determine desired quantitative data. It is essentially the

measurement of elements or the study of chemical quantities consumed or produced in a chemical reaction.The essence of stoichiometry involves comparing how many moles of chemicals are present (Pabilane, Dela and Marie, 2011).Chemical reactions combine in definite ratios of chemicals. Since chemical reactions can neither create, nor destroy matter, the amount of each element must be the same throughout the overall reaction.Mole ratios are the central step in performing stoichiometry because they allow us to convert moles of one substance to moles of another substance. The coefficients in a balanced equation can be used as mole ratios which can act as conversion factors to relate the reactants to the products.

1.1.7 Stability Constant

Stability constant also known as formation constant or binding constant is equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. The stability constant(s) provide the information required to calculate the concentration(s) of the complex(es) in solution. The complexation reaction of metal ion and the ligand in an aqueous solution is usually a substitution reaction.

We assume that the chemical equation for the formation of the complex is given below as:

$$M + nL \rightleftharpoons ML_n \qquad (1.2)$$

Where M, L, n and ML_n are the metal, ligand, number of mole of ligand and the complex formed respectively. Generally the stability constant K_{stab} of the complex can be expressed

$$K = \frac{[ML_n]}{[M][L]^n} \qquad (1.3)$$

Thus by knowing the values of [M], [nL], and [ML_n], the value of the stability constant, K of the complex ML_n, can be computed.

Factors affecting the formation of stable metal complexes

i. Nature of the Metal Ion

The ionic size and ionic charge of the metal ion influence the type bond formed between the metal ion and the ligand. The tendency towards covalent character increases with increase in oxidation state of the metal while strength of the coordination bond increases with increasing charge on the metal ion and decrease with increasing radius (Fajan's rule). This is because the greater the charge, the stronger is the power of attraction for electrons. More generally, in examination of stability constant by Ahrland, Chatt and Davies, metal ions could be described as class A if they formed stronger complexes with ligands whose donor atoms are N, O or F than with ligands whose donor atoms are P, S or Cl and class B if the reverse is true, (Ahrland, Chatt and Davies,1958).Later, Pearson proposed the theory of hard and soft acids and bases (HSAB theory). In this classification, class A metals are hard acids and class B metals are soft acids. Some ions, such as copper are classed as borderline. Hard acids form stronger complexes with hard bases than with soft bases. In general terms hard-hard interactions are predominantly electrostatic in nature whereas soft-soft interactions are predominantly covalent in nature.

ii. Chelate Effect

Formation of a ring increases the stability of a complex as well as the value of the stability constant. Ring size, which is the number of members forming the chelate ring affect stability. If the number is too small (<4) or too large (>7), the probability of ring closure is reduced for non-conjugated ligands, the most stable chelate rings are those with five membered followed by six with usual preferred sequence 4<<5 >6

> 7 or larger. For conjugated ligand, the most stable chelate rings are those with six membered followed by five with usual preferred sequence being 4< 6 > 5 >7 or larger (Ogwuegbu andChileshe, 2000). The higher the number of lone pair donor atoms on the ligand, the more a stable complex is formed. The more the rings present in a complex the more is the stability it acquires.

iii. Nature of Ligand

The properties of a ligand affect the stability of the complex it forms with metal ions. These include the geometry (chemical composition) of the ligand and the basicity of its donor atoms, i.e. tendency of the ligand to donate a pair of electrons through the donor atoms. Donor atoms such as O, N, P or S may be present in a ligand or a combination of these atoms may be found in a chelating ligand. The more basic the ligand, the more stable the complex it forms with a metal. For transition metals, the stability of the complexes formed with ligands possessing these donor atoms increases in the order O < N < S < P. Ligands with highly polarizable (large) donor atoms form complexes of greater stability especially if the donor atoms have suitable accessible vacant d-orbital with which some of the d–electrons from metal ion can back bond.

iv. Steric Effect

When a bulky group is either attached to or is present near a donor atom of a ligand, repulsion between the donor atom of the ligand and the bulky group is produced and this mutual repulsion weakens the metal-ligand bonding and hence makes the complex less stable. The effect of the presence of bulky group on the stability of a complex is commonly called steric hindrance.

v. Crystal Field Effect

Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the charge to radius ratio. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block. For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t_2g orbitals before filling the eg orbitals since for octahedral complexes, the t_2g subset are directed in between the incoming ligands whilst the eg subset are directed towards the incoming ligands and cause maximum repulsion. For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be: Mn(II) < Fe(II) < Co(II) < Ni(II) > Cu(II) > Zn(II) Apart from the position of Cu(II), this corresponds to the Irving-Williams series. The discrepancy is once again accounted for by the fact that copper (II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory, (Irving and Williams, 1953).

Applications of coordination complexes

Coordination compounds and complexes are distinct chemical species in that their properties and behavior are different from the metal atom/ion and ligands from which they are composed. Coordination compounds have uses in both nature and in industry.Application of coordination compounds in different industries such as mining and metallurgy, medical sciences, analytical chemistry, pharmaceutical, environmental, biochemistry and industrial processes has been of great importance (Ogwuegbu andEhirim, 2010).

Some of the commonly known complex compounds found in nature are haemoglobin, chlorophyll, and vitamin B-12. There are numerous other coordination compounds that are produced and consumed by our body during many biological processes. Photosynthesis in plants requires chlorophyll for the process; chlorophyll is a magnesium-porphyrin complex. Many enzymes that catalyze the life processes within our body are coordination complexes, carboxypetidase is one such coordination compound that acts as an enzyme and catalyses the process of digestion.

A brief survey of some of the industrial uses of coordination compounds include;

i. Industrial Catalysts:

One major application of coordination compounds is their use as catalysts, which serve to alter the rate of chemical reactions. Certain complex metal catalysts, for example, play a key role in the production of polyethylene and polypropylene. Also, vanadyl acetylacetonate complex can be used as a catalyst in the hydrogen peroxide oxidation of anthracene to produce anthraquinone.

ii. Dyes and Pigments:

Coordination compounds have specific colours and hence are used in industries for intense colorations. Phthalocyanine is a class of coordination complexes that are vastly used in dyes and pigments industry to impart specific coloration to fabrics. Prussian blue is also a pigment that found wide use in paint industry, in the production of blue and black ink.

iii. Analytical Chemistry:

Colour Tests: Since many complexes are highly coloured they can be used as colorimetric reagents e.g. formation of red 2,2'-bipyridyl and l,l0-phenanthroline complexes as a test for Fe(II)

Gravimetric Analysis: Here chelating ligands are often used to form insoluble complexes e.g. $Ni(DMG)_2$ and $Al(oxine)_3$

Complexometric Titrations and Masking Agents: An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution, e.g. Zn^{2+}, Pb^{2+}, Ca^{2+},Co^{2+}, Ni^{2+}, Cu^{2+}, etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+} in the presence of Pb^{2+}. Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.

iv. Extraction and Separation of Metals:

Several important hydrometallurgical processes utilize metal complexes. Nickel, cobalt, and copper can be extracted from their ores as ammine complexes using aqueous ammonia. Differences in the stabilities and solubilities of the ammine complexes can be utilized in selective precipitation procedures that bring about separation of the metals. The purification of nickel can be effected by reaction with carbon monoxide to form the volatile tetracarbonyl nickel complex, which can be distilled and thermally decomposed to deposit the pure metal. Aqueous cyanide solutions usually are employed to separate gold from its ores in the form of the extremely stable dicyanoaurate(−1) complex. Cyanide complexes also find application in electroplating.

v. Sequestering Agents:

Related to their use as masking agents is the use of ligands for "sequestering" i.e. for the effective removal of objectionable ions from solution in industrial processing, e.g. EDTA is used to "soften" water. The addition of EDTA to water is used in boilers etc., to prevent "scaling" or buildup of insoluble calcium salts.

vi. Bio-Inorganic Chemistry:

Naturally occurring complexes include haemoglobin, chlorophyll, vitamin B_{12} etc. EDTA and other complexing agents have been used to speed the elimination

of harmful radioactive and other toxic elements from the body (e.g. Pb^{2+}). In these cases soluble metal chelate complexes are formed.

vii. Chemo-Therapy:

The platinum complex cis-$[Pt(NH_3)_2Cl_2]$ known as cisplatin is used as an antitumor agent in the treatment of cancer.

viii. Electroplating:

Many complexes are used as electrolyte in electroplating. For silver plating, the complex $K[Ag(CN)_2]$ is used.

ix. Photography:

Developed film is fixed by washing it with a solution of sodium thiosulphate. i.e. AgBr forms a soluble complex with sodium thiosulphate in photography (Cotton, Wilkison and Gaus, 1996).

The stoichiometry and stability constant of complexes are often estimated from the measurement and treatment of analytical data using a wide selection of traditional methods. These methods include the Job's (Job, 1928),Yoe and Jones (Yoe and Jones, 1944), Harvey and Manning (Harvey and Manning, 1950), Holme and Langmyhr (Holmes and Langmyhr, 1966), Rose and Drago (Rose and Drago, 1959), Bent and French (Bent and French, 1941) methods as well as stoichiometric (Garcia, Ramirez and Ceba, 1979) and non-stoichiometric (Nevado, Ramirez and Ceba,1981) dilution methods. The traditional methods are based on the graphical representation of curves derived from more or less complicated functions, obtained by means of the experimental measurement of analytical signals from a chemical system in equilibrium. Of the above, Job's and Yoe-Jones methods are the most widely used due to the simplicity of their theoretical foundation and their straight-forward experimental application .They are based on the study of a graphical representation of analytical signals versus ligand mole fraction (Jobs method) or mole ratio (Yoe-Jones method). In the representation the analytical signal increases with the ligand mole

fraction (or mole ratio) until a maximum is reached; at this point the analytical signal diminishes (Jobs method) or it is maintained constant (Yoe-Jones method). The maximum of the curve corresponds to the maximum formation of complex and it is indicated to be the stoichiometry of the complex.

In this experiment, the stoichiometries and the stability constants of the complex formation of Zn (II) and V(V) with anthranilic acid were studied using spectroscopic methods.

1.2 PROBLEM STATEMENT

Determination of trace metals is of interest because while some are essential nutrients, some others are toxic. Anthranilic acid is known to be a good complexing agent and has found extensive applications as an analytical reagent. The use of anthranilic acid as a spectrophotometric reagent in the determination of the stoichiometries and the stability constants of Zn (II) and vanadium (V) complexes is a challenging problem.

1.3 OBJECTIVES OF STUDY

The main objective of study is to determine the stoichiometries, the stability constant and free energies of zinc (II) and vanadium (v) complexes of anthranilic acid using spectrophotometric method.

The specific objectives of the study are to:

i determinethe effect of variation of pH on the formation of the complexes at equimolar concentration of the metal ions and ligand.

ii determine the number of anthranilic acid anions that are bonded to V(V) and Zn(II) ion in the formation of V(V) and Zn(II) anthranilate complexes using Job's continuous variation and Yoe-Jones mole-ratio methods.

iii evaluate the interaction of V(V) and Zn(II) ions with anthranilic acid ligand to ascertain the stability constant of their various complexes in order to measure the ability to act as a chelating agent in samples containing these metal ions.

iv determine the free energies of the V (V) and Zn (II) anthranilate complexes formed.

1.4 JUSTIFICATION OF STUDY

Formation of coloured complexes or precipitates by Zn(II) or V(V) metal ions with anthranilic acid may be used as a special test for these metal ions in samples where they are present.

The difference in ability of the anthranilic acid to form stable metal complexes with Zn(II) and V(V) ions may be applied in the separation of these metal ions in a mixture or compound.

The values of the stability constant can also be used in the evaluation of the selectivity of the ligand in the removal, separation and extraction of metals from mixture of other metals.

1.5 SCOPE OF STUDY

This present work focuses on the use of spectrophotometric technique to determine the stoichiometries and stability constants of Zn (II) and V (V)complexesof anthranilic acid. The effect of the variation of the pH on the complex formation, the wavelength of maximum absorption λ_{max} of the metal complexes and the free energies of the complexes were determined.

CHAPTER TWO

LITERATURE REVIEW

2.1 COORDINATION CHEMISTRY OF ZINC (II) WITH ANTHRANILIC ACID

Bina, Singh, Goyal and Tando (1980) reported that zinc and cadmium anthranilates do not extract into non-polar solvents alone in the pH range 4.5-6.5. But their extraction is synergistically enhanced in presence of N bases, apparently by displacement of coordinated water. The synergistic effect varies with the bases in the order P-picoline > pyridine > quinoline. The values of extraction constants suggested that cadmium forms more stable complexes than zinc.

Kiran (2012) reported that Zn(II) formed a yellow complex with 3-hydroxybenzylaminobenzoic acid at pH 5.0. The complex has a wavelength of maximum absorption at 460 nm and the molar absorptivity was $1.2x10^4$ $Lmol^{-1}cm^{-1}$. The proposed method was applied for the determination of Zn (II) in water and industrial effluent samples.

Taghreed, Khalid, Amer and Aliea (2013) investigated the mixed ligand complexes of Co (II), Ni (II), Cu (II) and Zn (II) with anthranillic acid and tributylphosphine which have shown profound activity against *Staphylococcus*, *Klebsiella spp*. and *Bacillas*. Furthermore, the rhodium complexes with (N-phenyl) anthranillic acid ligands are used as catalysts for the hydrogenation. Several other mixed ligands complexes with anthranilic acid were reported to have antifungal and antibacterial potential.

Dhiraj and Biswajit (2014) studied Zn(II) and Cd(II) complexes of a Schiff base derived from 3-amino-2-phenylquinazolin-4(3H)-one and 2-(2-formylphenoxy)

acetic acid were pre-pared and characterized by elemental and different spectroscopic (IR, UV–Vis and NMR) analyses. The elemental analysis indicated the formation of the complexes: $[ML(AcO)]\cdot H_2O$, where M stands for Zn(II) or Cd(II) and L stands for the Schiff base. The molar conductivities of the prepared complexes revealed their non-electrolytic nature. The complexes were also investigated for their antimicrobial activities using the turbidimetric assay method.

Suresh and Prakash (2010), reported a novel bidentate Schiff base, synthesized from 1-phenyl 2, 3-dimethyl-4-aminopyrazol-5-one (4-aminoantipyrene) and vanillin forms stable complexes with transition metal ions such as Cr (III), Mn (II),Co (II), Ni (II), Cu (II), Zn (II) and Cd (II). Their structures were investigated by elemental analysis, infraredspectroscopy, electronic spectroscopy, NMR spectroscopy; thermo gravimetric analysis and electron spin resonance spectroscopy. On the basis of the studies the coordination sites were proven to be through oxygen of the ring C = O and Nitrogen of the azomethine CH = N group. The microbiological studies revealed the anti bacterial nature of the complexes.

2.1.1 Coordination Chemistry of Zinc (II) with other Ligands

The spectophotometric determination of Zn (II) with thiocyanate and rhodamine 6G was studied by Prassada and Ramakrishina (1980). The method was based on the reaction of rhodamine 6G with tetrathiocyanatozincate (II) anion to form a pink coloured product. The zinc content was as low as 0.2 – 0.5 µg in 10 ml of sample can be readily determined. This method is precise and has been applied for the determination of zinc in synthetic matrics and soil samples.

A spectrophotmetric method has been developed to determine the formation constant of complexes (1:1), both protonated and normal types, with a knowledge of any molar absorptivities, and applied to study Zn(II) and La(III) complexes of 4-(2-

pyrdylazo) resorcinol (PAR or H_2R). This method is based on indirect estimation of the complexes, MHR and MR, by measuring absorbance at the peak of the ligand which decreases with increase in the metal concentration at a constant pH. The results showed that both MHR and MR complexes of Zn (II) and La (III) were formed at pH 6. Their formation constants were determined by graphical analysis. This method is simple and applicable to study many other complexes of similarly coloured reagents (Emiko, 1983).

A spectrophotometric determination of Zinc (II) thiozonate complex in anionic micellar media of dodecylsulphate salt has been reported. Beer's law is obeyed in the concentration range of $1.5x10^{-5}$ – $1.5x10^{-4}$ M. the wavelength of maximum absorbance was at 540 nm at pH 5 and the metal to ligand mole ratio was 1:2. This method has been applied for the determination of Zn (II) in pharmaceutical and vegetable samples. The molar absorptivity, critical micelle concentration, dithiozone and metal ion concentration were studied and discussed (Shar and Bhanger, 2000),

Sancho, Blanco, Ferretti, Jubert and Castro (2006) investigated the stability of the complex formed by one molecule of 1,2-dihydroxybenzene and one molecule of zinc acetate in solutions with different permittivity and temperature was investigated by means of spectroscopic and chromatographic methods. The Becke hybrid three-parameter nonlocal exchange functional combined with the Lee-Yang-Parr dynamic correlation functional method (B3LYP/6-31G(d)) and the isodensity polarized continuum model (IPCM) were used in the calculations. It was assumed that the formation of the complex takes place by a reaction between ions of opposite charges. It was also proposed an equation to explain the changes of the constant of the complexation equilibrium with the permittivity of the reaction medium. The calculations allowed us to prove that the increase of the hydrogen-bond donor ability of the solvents favours a higher thermodynamic stability of the reactants with respect

to the complex and, as a result, a decrease of the corresponding equilibrium constants. The non-planar structure proposed for the complex is consistent with the experimentally observed hyperchromic shift. The plane, in the complex molecule, containing the aromatic ring is tilted by approximately 18º with respect to that of the zinc and oxygen atoms. It was concluded that the formation of the complex is an endothermic process.

The spectrophotometric determination of Zn (II) using 2-benzoylpyridine thiosemicarbazone (BPT) as an analytical reagent was studied. The metal ion in aqueous medium formed a yellow coloured complex with BPT at pH 6.0 showing maximum absorbance at 430 nm. Beer's law was obeyed in the range 0.26-2-61 µg/ml. the composition of the complex was determined by Job's and mole ratio methods and was found to be 1:1 metal to ligand ratio and the stability constant was $2.4x10^6$ by job's method. The method is applied for the determination of Zn (II) in pharmaceutical and biological samples (Nagarjuna, Vasudeola and Hussain, 2011).

Reza, Abbas, Yaser, Morteza, Karim and Naser (2012), reported the synthesis and complexation properties of a new compound, 1,3-bis[5-(2-hydroxyphenyl)-4-phenyl-1,2,4-triazole-3-yl-thio]propa ne (BTP), towards certain transition metal ions, (M(II) where M = Zn, Cu, Ni) in acetonitrile is reported. A hard-modeling strategy was applied to UV-Visible spectroscopy data obtained from monitoring the reaction between BTP and the selected metal ions to determine the concentration profiles of each species and the corresponding stability constant(s) of the complex(es). The stability constants of complexes are always defined in terms of their free metal, free ligand and complexed forms. These constants are influenced by parameters such as the type of metal, ligand, counterion or solvent. In this study, the formation constants of the complexes were determined for the synthesized ligand with several metallic cations in acetonitrile solvent by UV-Vis spectrophotometry.

Tanzul and Jamaluddin (2013) investigated the spectrophotometric study of Zn in some real, environmental, biological, pharmaceutical, milk and soil samples using 5, 7-dibromo-8-hydroxyquinoline as an analytical reagent, (DBHQ). DBHQ formed a pale yellow chelate with Zn in an acidic medium. The wavelength of maximum absorbance was 391 nm. The molar absorptivity and sandell's sensitivity were found to be $1.62x10^{5}Lmol^{-1}cm^{-1}$ and 10 μg cm^{-2} respectively. The stoichiometric composition of the chelate is 1:2 (Zn: DBHQ). 3-hydroxybenzylaminobenzoic acid has been synthesized and used as a reagent for the determination of zinc (II) in various water samples.

Zewdu, Tesfahun, Ephrem, Girma and Solomon (2015) studied the heterocyclic ligand (L), 3-(2-hydroxy phenyl)-2-iminothiazolidin-4-one, was synthesized by the cyclocondensation of o-hydoxy phenyl chloroacetamide with potassium thiocyanate. The stoichiometries of the titled complexes were first determined by spectrophotometric mole ratio method which gave rise to the M:L ratio of 1:4 in case of Zn(II) and Cd(II) and 1:2 in case of Hg(II) ions respectively. Using these predetermined M:L ratios, complexes of the formulas [Zn-L_4], [Cd-L_4] and [Hg-L_2] were prepared accordingly using precursor of the corresponding metal salts with the title ligand in ethanol medium. The synthesized compounds were characterized by elemental analysis, FTIR, ^{1}H and ^{13}CNMR, UV-Vis and conductometric measurement. Stability constants (K_s) of these complexes were investigated by spectrophotometric mole ratio method. The FTIR, ^{1}H NMR and ^{13}C NMR data revealed that the studied ligand function as monodentate ligand interacting through phenolic oxygen as donor with Zn(II) and Cd(II) and as bidentate ligand interacting through phenolic oxygen and nitrogen atom with Hg(II). The synthesized complexes show conductivity values in the range of 122-133 $\mu Smol^{-1}cm^{2}$ in DMSO at 298 K which confirms the electrolytic nature of the complexes. The stability constants

decreased with increased temperature, confirming that these metal complexes are not stable at higher temperature. Sufficiently large negative values of ΔG of complex confirm the spontaneous formation of the title complexes. Furthermore, it was noted that the spontaneity of the reaction increased with temperature. The stability constant of these complexes follow the sequence Zn(II)>Cd(II)>Hg(II). Therefore, the overall result is complying very well with the Irving-William series of stability constants of metal complexes.

2.2 COORDINATION CHEMISTRY OF VANADIUM(V) WITH ANTHRANILIC ACID

Bendor, Jungreis and Jungreis (1966), reported that the Schiff base formed from salicylaldehyde and anthranilic acid has been found to be a specific and sensitive reagent for the spectrophotometric determination of vanadium (V). This reagent forms a violet ester with vanadic acid (at pH = 1) extractable with benzene. The determination can be carried out in the presence of many diverse ions, and all but ferric ions do not interfere. Phosphoric acid is used both for masking the iron III and to make the extraction easier. The limit of identification is 10 μg vanadate/1 ml.

Arya and Sarin (1990), reported the extractive spectrophotometric determination of vanadium with anthranilic acid in the presence of pyridine. Vanadium (III) gave a greenish-yellow complex with anthranilic acid in the presence of pyridine. The comples is extractable with chloroform and is used for photometric determination of vanadium by measuring the absorbance at 390 nm against a reagent blank. Beer's law holds good in the range 1-20 μg V/ml. Moderate amount of Pb(II), Ca(II), Sr(II), Ba(II), Cd(II), Mg(II), Mn(II), Ni(II), Co(II), Cu(II),, Zn(II) and limited amount of W(IV), Al(III), Th(IV), Zr(IV), Sn(II), Sb(III), Ti(IV), Fe(III) and Cr(VI)can be tolerated. U(VI) and Mo(VI) interfere.

Comparative studies of the reaction of 7-arylazo-8-hydroxyquinoline-5-sulphonic acid (Azoxine S) dyes with vanadium(IV), show that 2:1 yellow, water-soluble complexes are formed over the pH range 2.5-6, and that the phenyl derivative is the most suitable for spectrophotometric determination of 0.2-1.4 ppm of vanadium(IV). The colour is formed instantaneously and is stable for about 8 hr. The molar absorptivity at lambda(max), 400 mmu;, is 1.15 x 10(4), and the equilibrium constant for complex formation is of the order of 10(2). These dyes can also be used as indicators in the direct complexometric determination of vanadium(IV). The interference of a number of anions and cations is reported by (Goyal and Tandon,1967).

2.2.1 Coordination Chemistry ofVanadium (V) with other Ligands

Vanadium (V) complexes have been found to act as catalysts in oxidation reactions of various substrates using peroxides. The catalytic oxidation by Schiff-base complexes of vanadium with dioxygen has also been reported.Vanadium (V) forms many stable complexes with oxalates, tartrate, EDTA, and a few other ligands. The crystal structure determination of oxalate and EDTA complexes reveals octahedral structure (Sharpless and Michaelson,1973).

Nageswara and Adinarayana (1981) developed a method for the direct spectrophotometric determination of vanadium (V) using gallacetophenone oxime. The reagent forms a yellow-green complex in acid medium. The colour is stable for 20 hours. The system obeys Beer's law over the concentration range 0.5 to 6.0 μg/ml. The molar absorptivity and Sandell sensitivity are 8.6×10^3 $1mole^{-1}cm^{-1}$ and 0.0058 μgcm^{-2} respectively. The effect of foreign ions was also studied. The stoichiometry is established as 1:2.

Khalid, Aldher and Bashir(1985), reported a new chromogen, thiophene-2-hydrazide, for the determination of trace amounts of vanadium in aqueous solution has been developed. The intense yellow, water-soluble, stable and binary complex, formed in acidic medium, is suitable for the determination of 0.5–5 p.p.m. of vanadium ion, with a molar absorptivity of 12.1×10^3 mol^{-1} cm^{-1}, at 410 nm, relative error –0.6 to +4.0% and relative standard deviation 0.3–0.8%, depending on the concentration level of the determinant. Moreover, the colour formation is very fast. Interferences due to foreign ions have been examined.

Ahmed and Banerjee (1995), reported an ultra-sensitive and highly selective non-extractive spectrophotometric method for the rapid determination of vanadium(v) at trace levels using 5,7-dibromo-8-hydroxyquinoline (DBHQ) as a new spectrophotometric reagent (lambda max = 400 nm) in slightly acidic solution (0.00015-0.016 mol^{-1} sulfuric acid). The reaction is instantaneous and the absorbance remains stable for over 48 h. The average molar absorption coefficient and Sandell's sensitivity were found to be 6.1 x $10^{(3)}$ l mol^{-1} cm^{-1} and 0.015 micrograms cm^{-2} of V (V), respectively. Linear calibration graphs were obtained for 0.1-20 micrograms ml^{-1} of Vv: the stoichiometric composition of the chelate is 1:3 (V:DBHQ). Large excesses of over 50 cations, anions and complexing agents (e.g., tartrate, oxalate, citrate, phosphate, thio-urea, SCN^-) do not interfere in the determination. The method was successfully used in the determination of vanadium in several Standard Reference Materials (alloys and steels) as well as in some environmental waters (potable and polluted), biological samples (human blood and urine), soil samples and complex synthetic mixtures. The method has high precision and accuracy (s = +/- 0.01 for 0.5 micrograms ml^{-1}).

Vachirapatama, Dieinoski, Townsend and Haddad (2002) reported the separation and determination of the vanadium (V) ternary complex formed with 4-(2-

pyridylazo)resorcinol (PAR) and hydrogen peroxide using ion-interaction reversed-phase high-performance liquid chromatography on a C18 column has been investigated. The optimal mobile phase was a methanol-water solution (32:68, v/v) containing 3 mM tetrabutylammonium bromide, 5 mM acetic acid and 5 mM citrate buffer at pH 7, with absorbance detection at 540 nm. The stoichiometry of the ternary complex of vanadium at pH 6 in 10 mM acetate buffer using the mole ratio and Job's method by HPLC indicated that the mole ratio of V(V):PAR:H_2O_2 was 1:1:1. The optimal conditions for precolumn formation of the ternary complex were 10 mM acetate, 7 mM H_2O_2, 0.3 mM PAR, and pH 6. The method gave relative standard deviations of retention time, peak area and peak height for the ternary complex of 0.187, 0.45 and 0.57%, respectively. The detection limit (at a signal-to-noise ratio of 3) for V (V) was 0.09 ng/ml in the digested sample using a 100-µl injection loop (or 0.09 µg/g in the solid fertilizer sample). The method was applied to the analysis of fertilizers (phosphate rocks and nitrogen, phosphorus and potassium fertilizer). The results for vanadium obtained by the HPLC method agreed well with those from magnetic sector inductively coupled plasma MS analysis.

A novel, rapid, highly sensitive and selective spectrophotometric method for the determination of traces of vanadium (V) in environmental and biological samples, pharmaceutical and steel samples was studied. The method is based on oxidation of 2,4- dinitro phenyl hydrazine(2,4-DNPH) by vanadium (V) followed by coupling reaction with N-(1-naphthalene-1-yl)ethane-1,2-diamine-dihydrochloride (NEDA) in acidic medium to give red colored derivative or on oxidation of 4-Amino Pyridine by vanadium (V) followed by coupling reaction with NEDA in basic medium to give pink colored derivative. The red colored derivative having an λ_{max} 495 nm which is stable for 8 days and the pink colored derivative with 525 nm is stable for more than 7 days at 35°C. Beer's law is obeyed for vanadium (V) in the concentration range of

0.02 - 3.5 μg mL^{-1} (red derivative) and 0.03 – 4.5 μg mL^{-1} (pink derivative) at the wave length of maximum absorption. The optimum reaction conditions and other analytical parameters were investigated to enhance the sensitivity of the present method. The detailed study of various interferences made the method more selective. The proposed method was successfully applied to the analysis of vanadium in natural water samples, plant material, soil samples, synthetic mixtures, pharmaceutical samples and biological samples. The results obtained were agreed with the reported methods at the 95 % confidence level (Krishna, Subrahmanyam, Dilip and Chiranjeevi, 2006).

Gavazov, Vanya and Patronov (2006), studied a new ternary complex of vanadium (V) with 4-(2-pyridylazo)-resorcinol (PAR) and thiazolyl blue (MTT) using an extraction-spectrophotometric method. The complex absorbs light at 560 nm with a molar absorptivity coefficient of $3.4x10^4$ L mol^{-1} cm^{-1} at the optimum extraction conditions: pH=5.8 ± 0.7, CPAR=$1.2x10^{-4}$ mol L^{-1}, CMTT=$1.0x10^{-4}$ mol L^{-1}, extraction time - 2 min. Beer's law is obeyed up to 1.5 μg V(V) mL^{-1}. The following constants have been calculated: the distribution constant (Log K_D=1.61), the association constant (Log β=15.9), the extraction constant (Log K_{ex}=17.5) and the recovery factor (R=97.49%). The composition of the complex has been found to be V (V) : PAR:MTT=1:2:3. The effect of foreign ions has been studied and a sensitive, selective and precise extraction-spectrophotometric method for the direct determination of vanadium (V) and indirect determination of vanadium (IV) has been proposed.

Narayana, Reddy Adi-Narayana, Sarala and Varada (2008), developed a highly sensitive spectrophotometric method for the determination of micro amounts of vanadium(V) in environmental and alloy samples by using 3,4-dihydroxybenzaldehydeisonicotinoylhydrazone (3,4-DHBINH). The vanadium (V)

showed maximum absorbance at wavelength 360 nm. The metal ion gives a yellow colored complex with 3, 4-DHBINH in acetate buffer of pH 5.5 with 1:1 (metal:ligand) composition. The method obeys Beer's law in the range 0.5–5.3 μg mL^{-1} of vanadium(V). The molar absorptivity and Sandell's sensitivity were found to be 1.29×10^4 L mol^{-1} cm^{-1} and 0.003949 μg cm^{-2} respectively. The correlation co-efficient of the V(V)-3, 4-DHBINH complex was 0.992 which indicated an excellent linearity between the two variables. The repeatability of the method was checked by finding the relative standard deviation (RSD) as 0.424% ($n = 5$), and its detection limit 0.01677 μg mL^{-1} of vanadium (V). The instability constant of the method was calculated by Asmus' method as 4.1666×10^{-3}. The proposed method was successfully applied to the determination of vanadium (V) in environmental samples (water and soil) tobacco leaves and alloy samples.

Srilalitha, Raghavendra, Seshagiri and Ravindranath(2010) proposed a spectrophotometric method for the micro determination of vanadium (V) using salicylaldehyde acetoacetic acid hydrazone (SAAH) as a reagent. The method was based on the formation of 1:2 complex between the metal and SAAH. Beer's law was applicable in the range of 0.243-2.438 5g/ml. The optimum conditions for the determination were established. The method detection limit, limit of quantification, molar absorptivity, Sandell's sensitivity and stability constant (β) were reported. The method is free from common interferences. The method was successfully applied for the determination of vanadium (V) in tap water samples, plant tissues and alloys.

Swetha, Raveendra and Krishina (2013) determined trace amount of vanadium (V) in aqueous DMF medium with 5-bromosalyicylaldehyde isonicotinoyl hydrazone, (5-BrSAINH). Vanadium (v) formed a brown coloured soluble complex with 5-BrSAINH in the pH range 1.0 – 5.0. The complex showed maximum absorbance at 400 nm and 1:1 (M:L) mole ratio. Beer's law was obeyed in the range 0.51-5.1μgmL^{-1}

of V (V). The molar absorptivity and Sandell's sensitivity for the colored solution were found to be 1.25 x 10^4 $Lmol^{-1}cm^{-1}$ and 4.0 x10^{-3}μgcm^{-2}, respectively. The stability constant of the complex was determined as 2.70 x 10^8 by Job's method. The developed methods have been employed for the determination of vanadium (V) in water, human hair and rice samples.

The simultaneous spectrophotometric determination of vanadium (V) ions using Cinnamaldehyde-4-hydroybenzoylhydrazone (CMHBH) as a chromogenic reagent was studied. The reagent (CMHBH) gave a green coloured complex with vanadium (V) in the presence of micellar medium (C-TAB) 5% at wavelength 400 nm and pH 4.0 and the stoichiometry was 1:1 (M:L). The molar absorptivity, sandell's sensitivity and the stability constant were found to be 4.36 x10^4 L $mol^{-1}cm^{-1}$ 0.0011 and 10x10^6 respectively (Gopala and Kethani, 2013).

Kasim and Zainab (2014) reported a new thiazolylazo reagent, 7-(6-bromo-2-benzothiazolylazo)-8-hydroxyquinoline, (7-(6-BrBTA8HQ)), used as a reagent in spectrophotometric determination of vanadium (V). Vanadium and (7-(6-BrBTA8HQ)) formed a dark orange coloured complex with mole ratio (1:2). The molar absorptivity of the complex was 1.9737x10^3 $LMol^{-1}cm^{-1}$ at wavelength 634 nm. Beer's law was obeyed in the range 1 – 14 ppm and the stability constant was 0.1088x10^{10} L^2mol^2.

Complex formation of vanadium (V) with 2,6-dithiolphenol (DTP) and hydrofob amins by spetrophotometry was investigated. The extraction of mixed ligand complexes was maximal at pH 3.5 – 4.9 and wavelength 590 nm. The Beer's law was applicable in the range 0.05 -16.00 / ml. The procedure has been developed for the extraction-spectrophotometric determination of vanadium in soils, oil and oil products. (Kerim and Naila, 2015).

2.3 ANTHRANILIC ACID METAL COMPLEXES

Majumdar and Sen (1960) reported the spectrophotometric determination of platinum using anthranilic acid as a reagent. Anthranilic acid gave a reddish violet complex having maximum absorbance at 500 nm and pH 5.0. The composition studies showed a 1:1 complex with the reagent and the dissociation constant of the complex is $2.6x10^4$.

Ramakrishna and Murthy (1980) reported the spectrophotometric determination of uranium with anthranilic acid and rhodamine 6G. The reaction of the uranium-anthranilic acid complex to form an ion-association complex with Rhodamine 6G provides a means for its estimation. The anionic primary complex is suggested to be a mixed-ligand complex of uranium with anthranilic acid and its oxidation products. The method is sensitive ($\epsilon = 6.25 \times 10^4$ 1.mole^{-1}.cm^{-1} at 575 nm) and fairly selective, and obeys Beer's law for 0.04–4.00 ppm of uranium. It has been applied to analysis of monazite sand.

Norman, William and Karl (1982) reported that anthranilic acid has been anchored to polystyrene, and rhodium, palladium, platinum and ruthenium complexes of this modified polystyrene have been prepared. These catalysts will reduce a variety of olefinic and aromatic hydrocarbons, and also nitrile, nitro and carbonyl functional groups, being present in either ketones or aldehydes.

Al-noor, Dawood and Malih (2012), reported the synthesis,(Spectroscopic and Antibacterial) Studies of Tin (II) and Lead - (Anthranilic Acids and Nicotinamide) Complexes. The research includes the synthesis and identification of two types complexes of the Ligand anthranilic acid (AH) and Nicotinamide (NA) with Pb (II) and Sn(II). 1-The mixed Ligand complexes of composition , [$M(A)_2$ $(NA)_2$] Where AH = Anthranilic acid = $C_7H_7NO_2$ M(II) = Pb (II) and Sn(II) 2-The mono Ligand

Complexes of AH or NA with Pb (II) and Sn(II) The results showed that the deprotonated ligand (anthranilic acid) to anthranilate ion (A^-) by using (NaOH) coordinated to metal ions as bidentate ligand through the oxygen atom of the carboxylate group ($-COO^-$), and the nitrogen atom of the amine group (NH_2), where the nicotinamide coordinated as a monodentate through the nitrogen atom. The complexes of the ligand with metal ions (for mono complexes) were studied in ethanol and /or water in order to determine the M : L ratio in the complex following the continues variation method (Job's method). A series of solutions were prepared having a constant concentration (10^{-3} M) of the metal ion and (L).The M : L ratio was determined from the relationship between the absorption of light and the molar ratio of M : L.The results of complexes formation in solution =1: 2.

Amr, Manal, Moustafa and El-Medani (2014) investigated thhe complexes of Sm(III) and Tb(III) with 2-aminobenzoic acid (anthranilic acid, AA) and 2-amino-5-chlorobenzoic acid (5-chloroanthranilic acid, AACl). The complexes were synthesized and characterized based on elemental analysis, IR and mass spectroscopy. The data are in accordance with 1:3 [Metal]: [Ligand] ratio. On the basis of the IR analysis, it was found that the metals were coordinated to bidentate anthranilic acid via the ionised oxygen of the carboxylate group and to the nitrogen of amino group. While in 5-chloroanth-ranilic acid, the metals were coordinated oxidatively to the bidentate carboxylate group without bonding to amino group; accordingly, a chlorine-affected coordination and reactivity-diversity was emphasized. Thermal analyses (TGA) and biological activity of the complexes were also investigated. Density Functional Theory (DFT) calculations at the B3LYP/6-311++G (d,p)_ level of theory have been carried out to investigate the equilibrium geometry of the ligand. The optimized geometry parameters of the complexes were evaluated using SDDALL basis set. Moreover, total energy, energy of HOMO and

LUMO and Mullikan atomic charges were calculated. In addition, dipole moment and orientation have been performed and discussed.

Temitope and Temitope (2015), carried out synthesis of Schiff base ligand derived from 2-aminobenzoic acid and *p*-hydroxybenzaldehyde with metal ions in an alkaline aqueous medium. The reaction yielded the metal (II) complexes of the hydrolysed Schiff base product, identified as metal (II) complexes of 2-aminobenzoic acid. These compounds were characterized by physical and spectroscopic techniques. The elemental analysis indicated the ligand to metal ratio as 2:1 in the complexes with general molecular formula $M(L)_2$ (L = 2-aminobenzoic acid; M = Mn, Co, Ni, Cu and Cd). IR data showed the ligand coordinated to the metal ion through the carboxylate oxygen and the amine nitrogen. The compounds were screened for *in-vitro* antimicrobial activity against chosen strains of bacteria and fungi.

Rabiul, Mohammad, Abdulsalam and Mohammad (2015), reported the synthesis, characterization and microbial evaluation of nickel complexes of Schiff bases mono / diketone with anthranilic acid. On the basis of analytical data, four co-ordinate geometry was proposed for the nickel (II) complex formed and the complexes possess 1:1 stoichiometry. The bio-efficacy of the complex was examined against the growth of bacteria and fungi in vitro to evaluate their antimicrobial potential.

George, Varghese and Kulkarni (2015), investigated a simple, selective and sensitive Spectrophotometric method developed for the determination of osmium (VIII) using anthranilic acid as a reagent in the presence of TritonX-100. The molar absorptivity and Sandell's sensitivity of the violent coloured species are 3.02×10^4 $Lmol^{-1}cm^{-1}$ and 3.5 ng cm^{-2} respectively. Beer's law is obeyed between 0.5 – 5.5 μg mL^{-1} of Os (VIII) at 500 nm. The stoichiometry of the complex is found to be 1:2 (metal : ligand). Calibration graph for the first order derivative spectrophotometric determination of

Os (VIII) is derived by measuring derivative amplitude at 525 nm with a linear range 0.25 – 5.5 μg mL^{-1}. The detection limit and quantitative limit of first order derivative spectrophotometry are found to be 0.075 and 0.25 μg mL^{-1} respectively. The metal ions which are normally associated with osmium in catalyst and alloy samples do not interfere. The proposed method has been successfully applied for the trace level determination of osmium in various synthetic mixtures containing commonly associated metal ions and corresponding to the alloy composition.

Md. RabiulHasan,Md. AbdusSalam and Mohammad (2016), reportedthe nickel(II) complexes of the dibasic tridentate Schiff bases *viz.* Sal-Anthra$\underline{H_2}$, HNP-Anthra$\underline{H_2}$, HAP-Anthra$\underline{H_2}$, HPP-Anthra$\underline{H_2}$, Acac-Anthra$\underline{H_2}$, Etac-Anthra$\underline{H_2}$, and Bzac-Anthra$\underline{H_2}$, have been synthesized and characterized by IR, ^{1}H NMR, mass and electronic spectra, and magnetic and conductance studies. On the basis of analytical data, four-coordinate geometry was proposed for the prepared nickel(II) complexes. The complexes have been found to possess 1:1 stoichiometry. The bio-efficacy of the prepared complexes has been examined against the growth of bacteria and fungi *in vitro* to evaluate their antimicrobial potential.

2.3.1 Application of Complexes of Anthranilic Acid

The mixed ligand complexes of Co (II), Ni (II), Cu (II) and Zn (II) with anthranillic acid and tributylphosphine have shown profound activity against *Staphylococcus*, *Klebsiella spp.* and *Bacillas*. Furthermore, the rhodium complexes with (N-phenyl) anthranillic acid ligands are used as catalysts for hydrogenation.Several other mixed ligands complexes with anthranilic acid were reported to have antifungal and antibacterial potential.

Foye, Lemke and Williams (1995) reported that anthranilic acid or 2-aminobenzoic acid is a good analytical reagent for the spectrophotometric determination of metal

ions. Anthranilic acid dyes in various conditions have shown significant biological activity especially against bacteria *S. aureus* and *E. coli*.

Dileep, Haque Misra and Chandra (2011) reported that anthranilic acid is very useful in synthesis of heterocyclic systems and other molecules. It serves as an excellent biochemical precursor to aromatic amino acids and it also forms an important part of several alkaloids. The acid and its derivatives are useful in various applications such as sunscreen production, perfumery and monitoring of glycosylation of proteins anti-convulsant and anti-inflammatory activity of 2-aminobenzoic acid and its derivatives while some transition metal anthranilates have demonstrated ability for hydrogenation.

Zheng and Ma (2016), reported that metal complexes of anthranilic acid derivatives that constitute a novel class of non-sugar-type α-glucosidase inhibitors were synthesized and assessed *in vitro* for inhibitory activity. All of the Ag(I) complexes inhibited α-glucosidase at the nanomolar scale, while 3,5-dichloroanthranilic acid silver(I) was the most potent (IC_{50} = 3.21 nmol/L). Analysis of the kinetics of enzyme inhibition indicated that the mechanism of the newly prepared silver complexes was noncompetitive.

2.4 METHOD OF CONTINUOUS VARIATIONS (JOB'S METHOD)

This method is used to determine the composition of a complex which is formed by two reacting species. It is most effective to be applied when only a single complex is formed in the solution. Job's method is based on the concept that equimolar solution of metal-ion and ligand are mixed gradually by using different volume ratio. As the concentration of metal ion increase, the concentrations of ligand will decrease. It maintains the total number of mole reactants to be constant in a series of mixture of reactants. The absorbance of each solution is then measured and plotted vs. the

volume fraction of one of the reactants (M or L) as shown in Figure 1.2 below. For example, the volume fraction of the metal is given by:

$$V_M / (V_M + V_L) \qquad 2.1$$

Where V_M is the volume of the metal cation solution and V_L is the volume of the ligand solution. Assuming the complex absorbs more than the reactants, a maximum occurs at a volume ratio V_M/V_L corresponding to the combining ratio of cation and ligand in the complex. At other volume ratios, one of the reactants is a limiting reagent, (Job, 1928; Ogwuegbu, Oforka and Spiff, 1992).

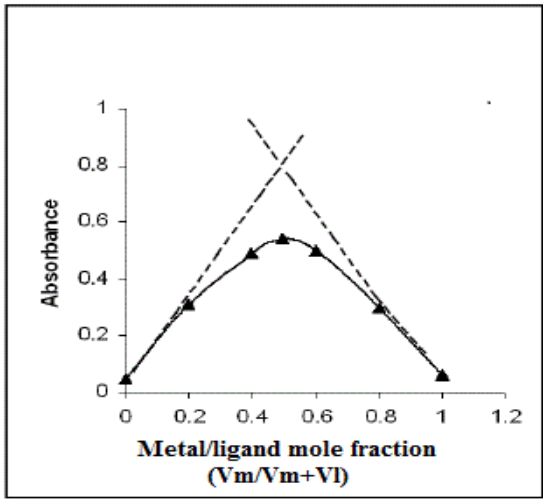


Figure 2.1: Job's plot for a 1: 2 metal-ligand complex

Source: Job (1928).

2.5 MOLE-RATIO METHOD (YOE-JONES METHOD)

Mole-ratio method is an alternative to the method of continuous variations for determining the stoichiometry of metal-ligand complexes. In this method, a series of solutions is prepared in which the concentration of one usually, the moles of metal, is held constant, while the other reactant is varied. The absorbance of each solution is measured and plotted vs. the mole ratio of the reactants. The mole ratio method can be used for complex reaction that occurs in a stepwise pattern, provided that the

molar absorptivities of the metal-ligand complexes differ, and the formation constants are sufficiently different.

Figure 2.2 below show typical results of, (a) the mole-ratio plot for the formation of a 1:1 complex in which the absorbance is monitored at a wavelength where only the complex absorbs. (b) the mole-ratio plot for a 1:2 complex in which all three species – the metal, the ligand, and the complex – absorb at the selected wavelength; and (c) the mole-ratio plot for the step-wise formation of ML and ML_2(Vosbargh andCooper, 1941; Skoog, West and Holler, 1988; Ogwuegbu *et al.*, 1992).

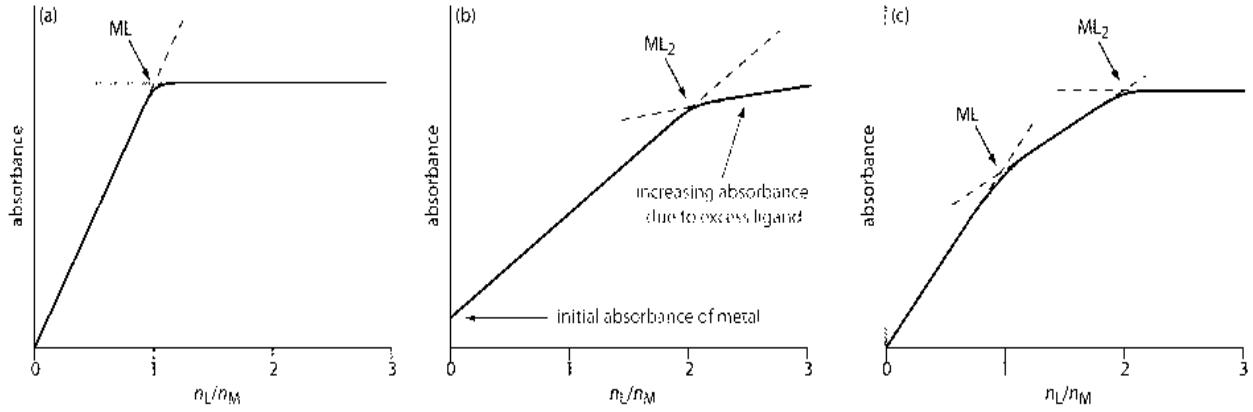


Figure 2.2: Yoe-Jones mole ratio plot

Source: Yoe and Jones (1944).

2.6 FORMATION OF METAL–ANTHRANILIC ACID (LIGAND) COMPLEX

$$2AH + 2KOH \longrightarrow 2K^+ A^- + 2H_2O \qquad (2.2)$$

$$\underset{\text{reflux}}{MCl_2} + 2K^+ A^- \xrightarrow{E\ to\ H} M(A)_2 + 2KCl \qquad (2.3)$$

Where M is the metal ion Zn(II) or V(V); AH = ($NH_2C_6H_4COOH$)

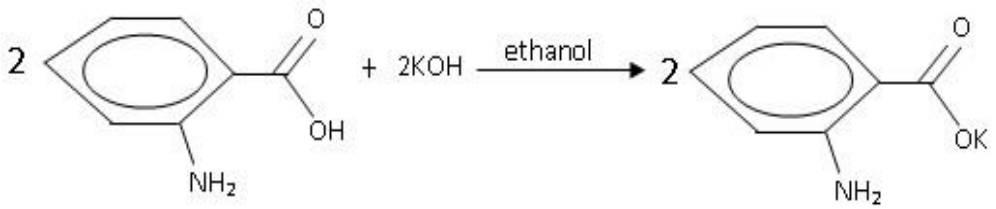


Figure 2.3: Schematic Representation of the Formation of Potassiumanthranilate (K^+A^-).

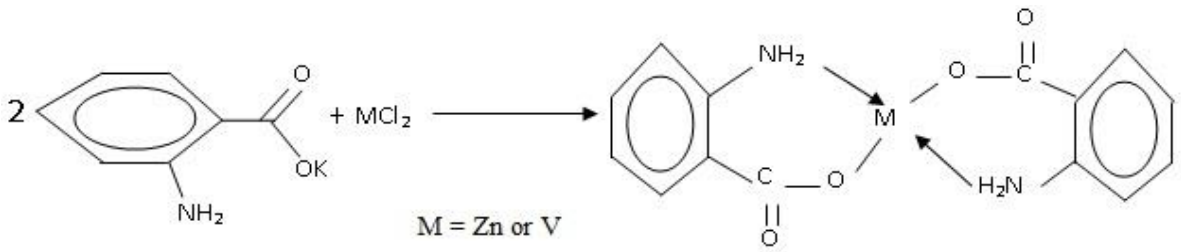


Figure 2.4: Schematic Representation of the Formation of Anthranilic Acid Metal Complex, (M(A)2)

CHAPTER THREE

MATERIALS AND METHOD

3.1 REAGENTS

All chemicals used in this work were of analytical grade and were used as supplied. Vanadium (V) oxide and Zinc (II) tetraoxosulphate (VI) were used to produce the metal V (V) and Zn (II) ions. Anthranilic acid ($C_7H_7NO_2$) was the ligand used. Other chemicals include ethanol, KOH, distilled water and buffer solutions were prepared from the following reagents: potassium chloride (KCl) and hydrochloric acid at pH (1.0-2.0), potassium hydrogen phthalate ($KHC_8H_4O_4$) and Hydrochloric acid (HCl) at pH (3.0–4.0), acetic acid (CH_3COOH)and sodium acetate (CH_3COONa) at pH (5.0 – 6.0) , Sodium hydroxide (NaOH) and potassium dihydrogen phosphate (KH_2PO_4) at pH (7.0), borax and HCl at pH (8.0 – 9.0) and bicarbonate ($NaHCO_3$) and sodium bicarbonate (Na_2CO_3) at pH (10.0).

3.2 APPARATUS / EQUIPMENT

A Shimadzu 1800 UV-visible spectrophotometer, Hanna 209 pH meter. Other apparatus used were 10ml and 100ml measuring cylinders, beakers, conical flasks, measuring cylinder and volumetric flasks.

3.3 PROCEDURE

3.3.1Preparation of Stock Solutions

Stock solution of 0.01 M of Zn (II) ion in 100 ml volumetric flask was prepared by dissolving 0.2875 g of $ZnSO_4.7H_2O$ (App. A) in buffer solution(pH 1- 10) to generate the Zn^{2+} that reacted with the anthranilic acid anion, A^-.

Stock solution of 0.01 M of V (V) was prepared by dissolving 0.11698 g of NH_4VO_3 in 10 ml of 1 M conc. HCl to generate the VO_2^+ that reacted with the anthranilic acid anion, A^-. This solution was made up to 100 ml by the addition of appropriate buffer solution,(Bieluonwu, 1995).

Similarly, the stock solution of 0.01 M anthranilic acid, $C_7H_7NO_2$ in 100 ml volumetric flask was prepared by dissolving 0.137 g of anthranilic acid in an ethanoilic KOH solution.

The absorbances of the stock solutions of vanadium (V) anthranilate and Zinc (II) anthranilate were measured between wavelengths 200-700 nm.

3.3.2 Preparation of Working Solution

1.0×10^{-5} M dilute solutions of the metal ions Zn (II) and V (V) ions and the ligand (anthranilic acid) were prepared by appropriate serial dilution of the stock solution. 10 cm^3 of the stock solutions were each diluted and made up to 1000 cm^3 to obtain the working solutions of Zn (II) and V (V) ions respectively.

3.4 DETERMINATION OF WAVELENGTH OF MAXIMUM ABSORPTION, λ_{max} OF THE LIGAND AND METAL COMPLEXES

The UV-visible absorption spectra of the complex solutions were obtained between wavelength ranges of 200 – 700 nm. The wavelength for which there was strong absorbance (λ_{max}) was recorded.

3.5 DETERMINATION OF THE OPTIMUM pH RANGE FOR THE FORMATION OF ANTHRANILIC ACID-METAL COMPLEXES

The effects of variation of pH on the formation of the complexeswere studied to ascertain the optimum pH for formation of complex. The UV- visible absorption spectra of 1:1 molar mixtures Zn^{2+}:A^- and V^{5+}:A^- (metal:ligand) were recordedover a

pH range of 1.0-10.0 (App. B). Plots of absorbance against pH were obtained as shown in Figures 4.3 and 4.4.

3.6 DETERMINATION OF THE STOICHIOMETRIES OF THE COMPLEXES

The stoichiometries of the complexes were determined using Job's method of continuous variation and Yoe - Jones mole ratio method as reported by (Ogwuegbu *et al.*, 1992; Juan, Eva and Lui, 2003; Ombarka and Gichumbi, 2011).

3.6.1 Job's Method of Continuous Variations

In this method, various volumes of solutions of 1×10^{-5} M of the metal and ligand ions were prepared according to Job's method (Job, 1928), such that the total volume of the mixture were kept constant at 10 ml having metal to ligand at ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1. The spectra of these complexes were determined at a particular wavelength for which there is a strong absorbance. The absorbance at wavelength of maximum absorbance (λ_{max}) were plotted against the composition or metal:ligand mole fraction to give the Job's plot. The linear portions of the plot were extrapolated and the intercept represent the metal:ligand mole ratio or the empirical formula of the complex.

3.6.2 Yoe- Jones Mole-Ratio Method

In this method, a series of solutions of 1×10^{-5} M of the metal and ligand ions were prepared in which the volume of one reactant was held constant while that of the other varied. The metal / ligand solutions were mixed at volume ratios 1:1, 2:1, 3:1, 4:1, 5:1. The absorbance of the complexes were recorded at wavelength of maximum absorbance and plotted against metal / ligand volume ratio. The mole ratio corresponding to the combining ratio was obtained at the intercept of the two extrapolated lines.

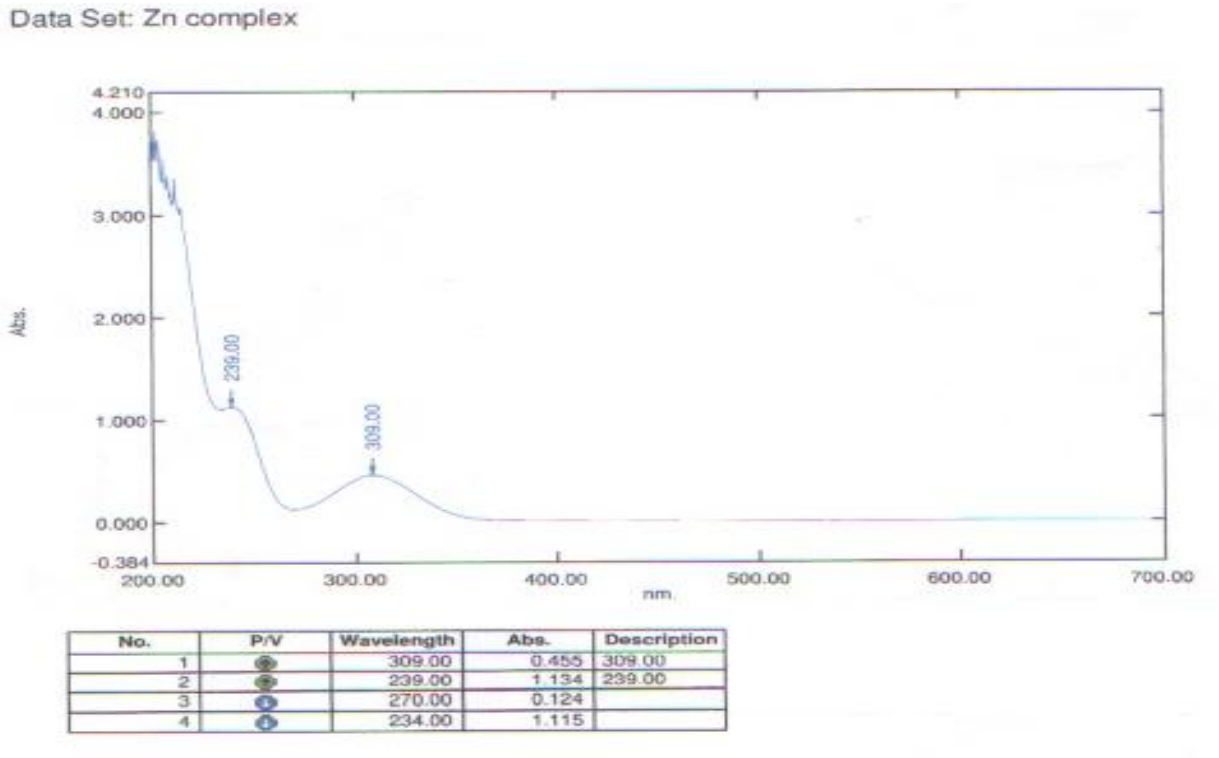
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 DETERMINATION OF WAVE-LENGTH OF MAXIMUM ABSORPTION, λ_{max} OF Zn^{2+}/A^- COMPLEXES.

The plot obtained for the determination of the wave-length of maximum absorption of Zn^{2+}/A^- is given in Fig. 4.1 as a plot of absorbance versus wavelength.



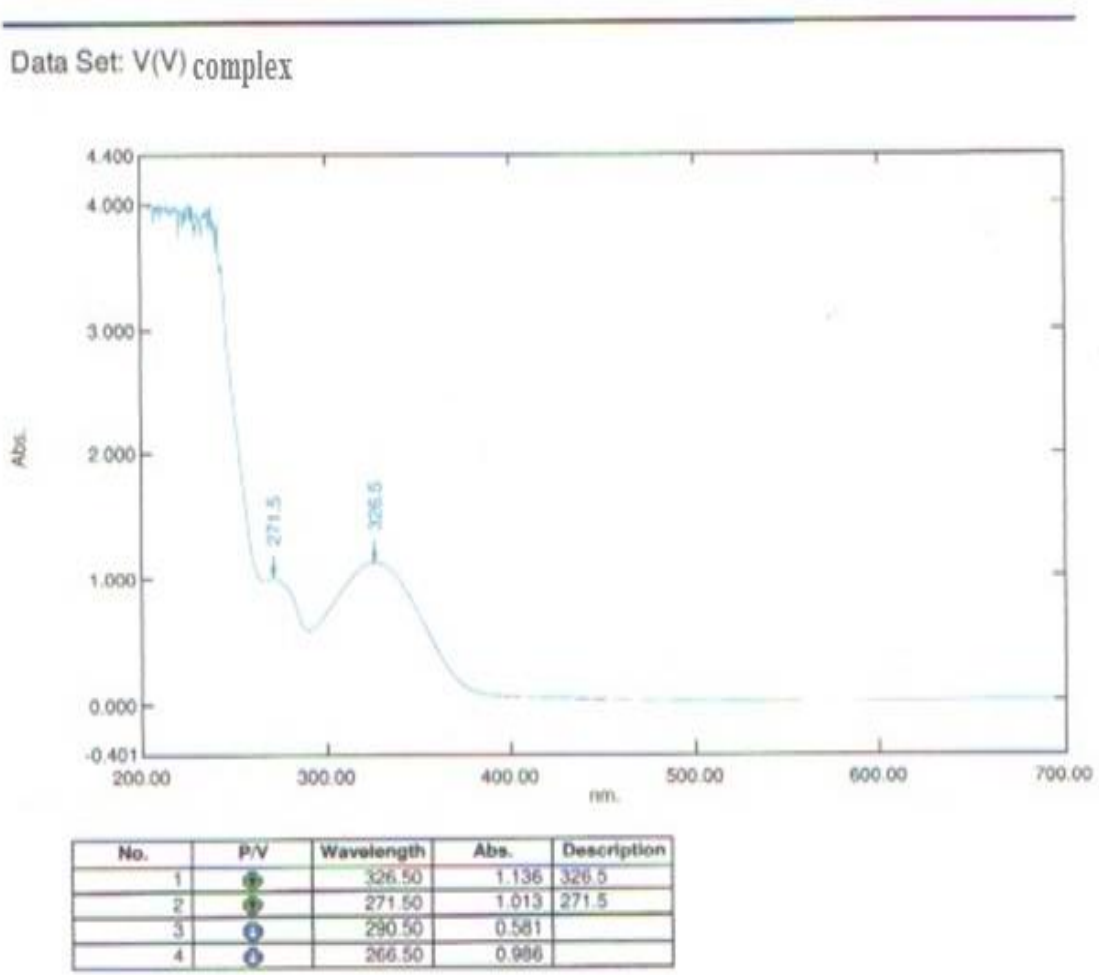
No.	P/V	Wavelength	Abs.	Description
1		309.00	0.455	309.00
2		239.00	1.134	239.00
3		270.00	0.124	
4		234.00	1.115	

Figure 4.1: UV-visible spectrum of Zn^{2+}/A^- Complex at pH 4.

The absorption spectrum in Figure 4.1 showed that Zn^{2+}/A^- maximum absorbance occurred at 309 nm and pH 4. Zn (II) has a d^{10} configuration, hence Zn (II) complex are not expected to show d-d transitions (Housecroft and Sharpe, 2008). It formed a colourless complex with anthranilic acid. The absorption at 309 nm in the spectrum of Zn (II) complex is due to ligand-metal charge-transfer.

4.1.2 DETERMINATION OF WAVELENGTH OF MAXIMUM ABSORPTION, λ_{max} OF V^{5+}/A^- COMPLEX.

The plot obtained for the determination of the wave-length of maximum absorption of $V^{5+}/A^-$is given in Figure 4.2 as a plot of absorbance versus wavelength.



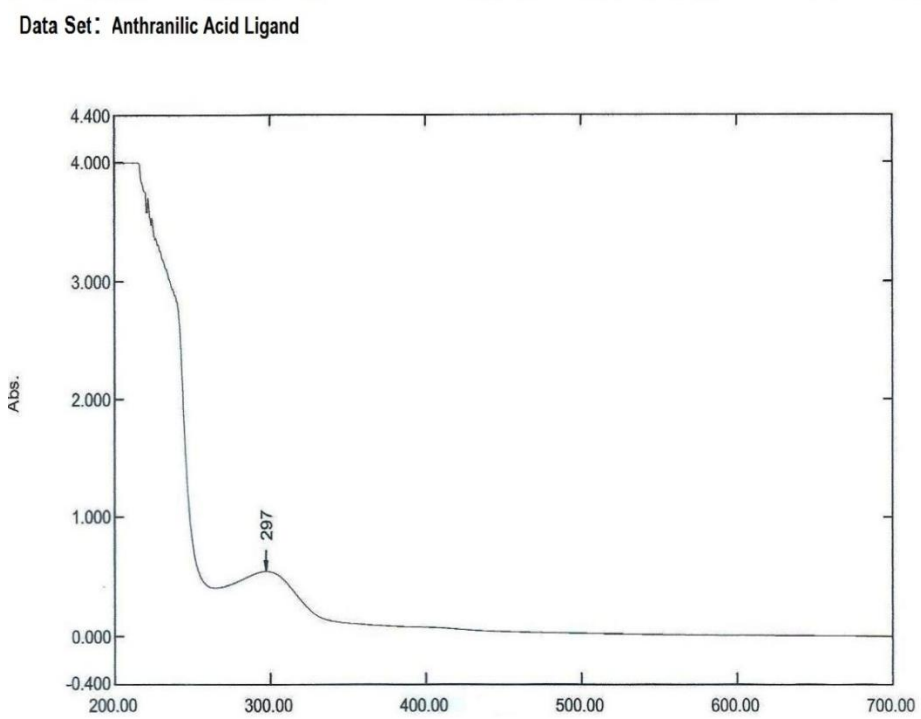
No.	P/V	Wavelength	Abs.	Description
1		326.50	1.136	326.5
2		271.50	1.013	271.5
3		290.50	0.581	
4		266.50	0.986	

Figure 4.2: UV-visible spectrum of V^{5+}/A^- at pH 6.

The absorption spectrum in Figure 4.2 showed that V^{5+}/A^-maximum absorbance occurred at 326.5 nm and pH 6. Vanadium (V) formed a golden-yellow complex with anthranilic acid because of d-d transition.

4.1.3 DETERMINATION OF WAVELENGTH OF MAXIMUM ABSORPTION, λ_{max} OF ANTHRANILIC ACID LIGAND

The plot obtained for the determination of the wave-length of maximum absorption of anthranilic acid ligand is given in Figure 4.3 as a plot of absorbance versus wavelength.



No.	P/V	Wavelength	Abs.	Description
1	↑	297.00	0.547	297
2	↓	264.00	0.407	

Figure 4.3: UV-visible spectrum of anthranilic acid ligand

The absorption spectrum in Figure 4.3 showed that anthranilic acid ligand maximum absorbance occurred at wavelength 297 nm.

4.1.4 DETERMINATION OF THE OPTIMUM pH FOR THE FORMATION OF ANTHRANILIC ACID METAL COMPLEXES

(i) Data and the Plot Obtained for the Determination of Optimum pH for the Formation of Zn^{2+}/A^- Complex.

The data and the plot obtained for the determination of the effect of pH on the formation of Zn^{2+}/A^- complex $[Zn^{2+}]=[A^-]=1x10^{-5}$ M, λ_{max} = 309 is given on Table 4.1 and Figure 4.4 respectively.

Table 4.1: Data Obtained for the Determination of the Effect of pH on the Formation of Zn^{2+}/A^- Complex $[Zn^{2+}]=[A^-]=1x10^{-5}$ M

pH	Absorbance
1	0.112
2	0.103
3	0.191
4	0.356
5	0.119
6	0.218
7	0.121
8	0.131
9	0.120
10	0.123

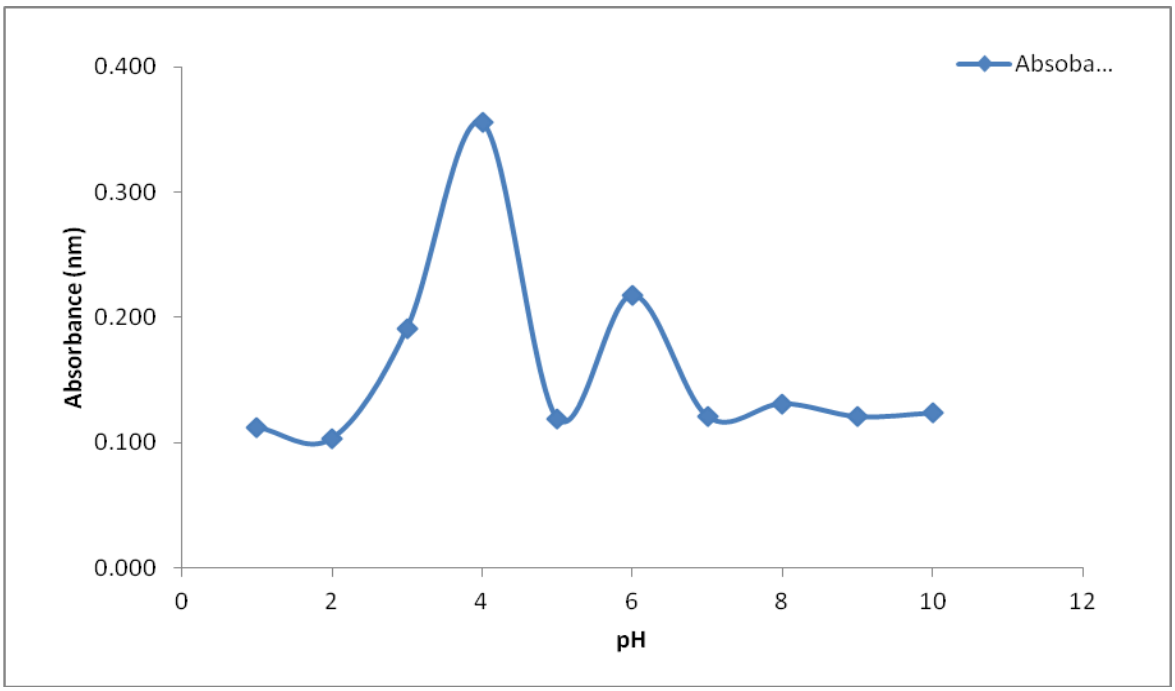


Figure 4.4: **Plot of absorbance of Zn^{2+}/A^- complex against the pH, $Zn^{2+}]=[A^-]=1x10^{-5}$, λ_{max}= 309**

Figure 4.4 shows the graphical representation of the data obtained in Table 4.1 which shows the effect of pH on the formation of Zn^{2+}/A^-. From Figure 4.4 above, the pH at which there was maximum formation of Zn^{2+}/A^- complex was at pH 4. However, there was also a related peak at pH 6, this observed peaks could be ascribed as non-bonding to anti-bonding (n - π*) for pH 6 while the higher absorption at pH 4 could be as a result of bonding to anti-bonding (π - π*).

(ii) Data and the Plot Obtained for the Determination of Optimum pH For the Formation of V^{5+}/A^- Complex.

The data and the plot obtained for the determination of the effect of pH on the formation on the formation of V^{5+}/A^- complex, $[V^{5+}]=[A^-]=1x10^{-5}$M, λ_{max} = 326.5 isgiven on Table 4.2 and Figure 4.5 respectively.

Table 4.2: Data obtained for the Determination of the Effect of pH on the Formation of V^{5+}/A^- Complex $[V^{5+}]=[A^-]=1x10^{-5}M$

pH	Absorbance
1	0.074
2	0.149
.3	0.255
4	0.331
5	0.268
6	0.422
7	0.106
8	0.199
9	0.125
10	0.056

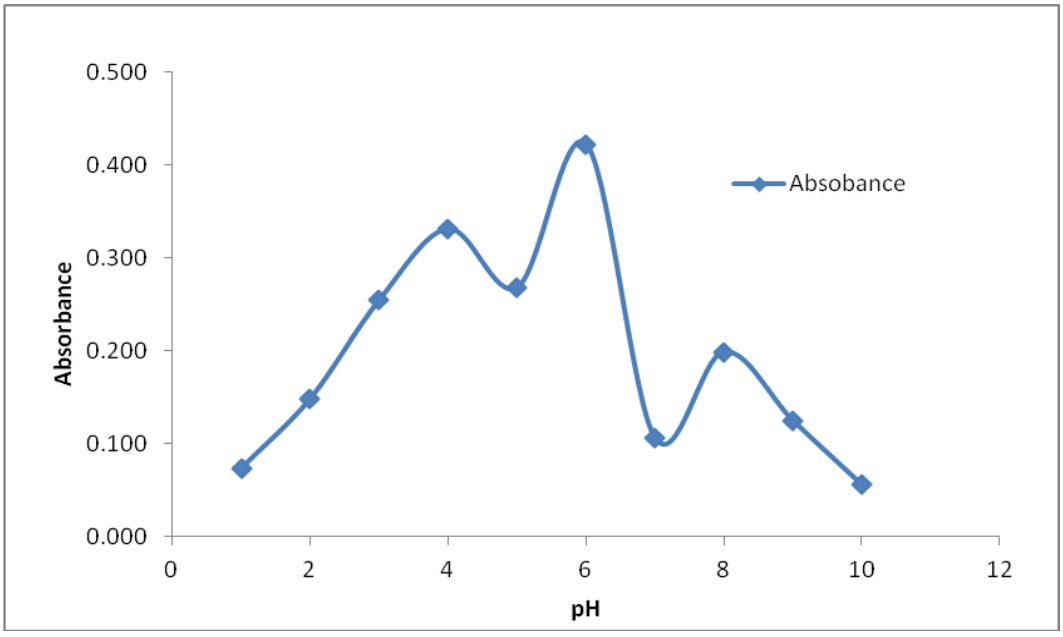


Figure 4.5: Plot of absorbance of V^{5+}/A^- complex against the pH, $[V^{5+}]=[A^-]=1x10^{-5}M$, λ_{max} = 326.5.

From the Figure 4.5 which shows the graphical representation of the data obtained in Table 4.2 for the effect of pH on the formation of V^{5+}/A^-, the pH at which there was maximum formation of V^{5+}/A^-complex was at pH 6. Although there were other peaks

showing absorbances at pH 4 and pH 8. The absorbance at pH 8 is lacking in zinc, this means that the two metals can be separated from their mixture using anthranilic acid at pH 8.

4.1.5 DETERMINATION OF THE STOICHIOMETRIES OF Zn^{2+}/A^- AND V^{5+}/A^- COMPLEXES BY CONTINUOUS VARIATION METHOD

(i) Determination of the Stoichiometry of Zn^{2+}/A^- Complex.

The UV-visible data obtained for the determination of Zn^{2+}/A^- complex using Job's method of continuous variation is given on Table 4.3.

Table 4.3: Uv-visible data for absorbance of the various mixtures of Zn^{2+}/A^- complexes by Job's continuous variation method at λ_{max} 309 nm, $[Zn^{2+}] = [A^-] = 1x10^{-5}$ M, pH 4.

Metal volume, V_m (cm^3)	Ligand volume, V_l (cm^3)	$V_m/(V_l + V_m)$ (mole fraction)	Absorbance
1.0	9.0	0.1	0.061
2.0	8.0	0.2	0.142
3.0	7.0	0.3	0.187
4.0	6.0	0.4	0.211
5.0	5.0	0.5	0.186
6.0	4.0	0.6	0.164
7.0	3.0	0.7	0.138
8.0	2.0	0.8	0.103
9.0	1.0	0.9	0.068

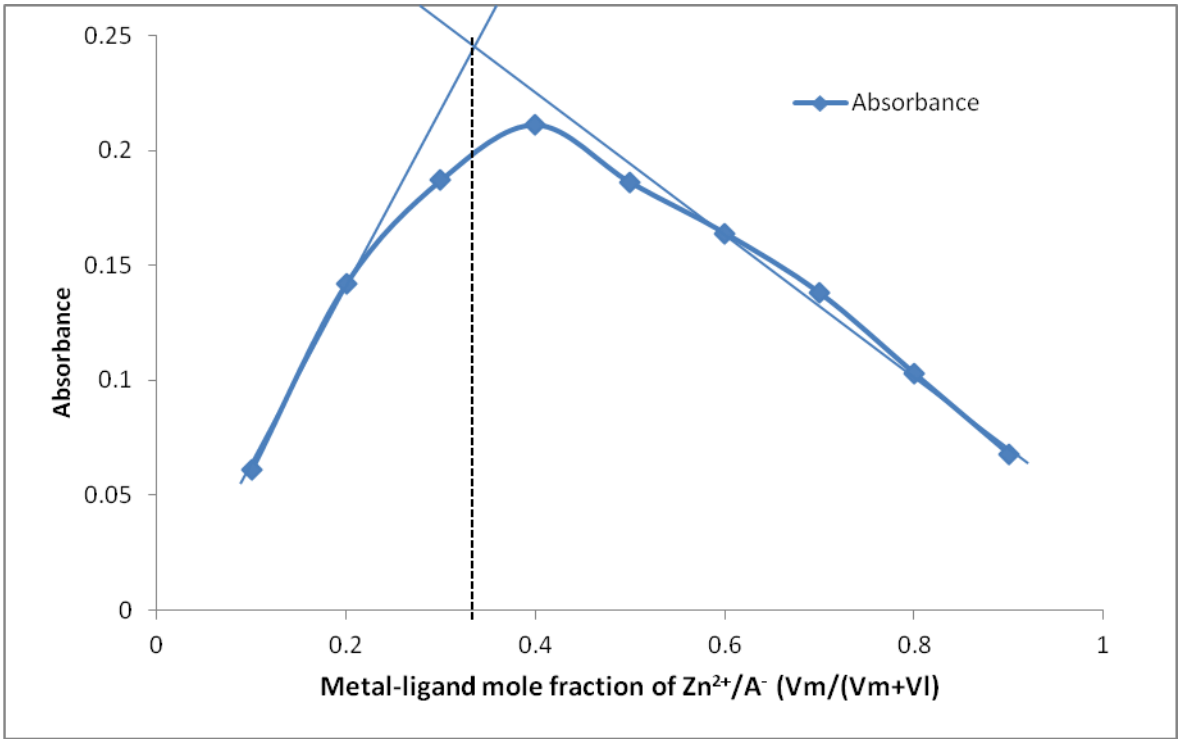


Figure 4.6: Job's plot for Zn^{2+}/A^- complex at λ_{max} 309 nm and pH 4. $[Zn^{2+}] = [A^-] = 1 \times 10^{-5}$ M.

Figure 4.6 showed the graphical representation of the data in Table 4.3 and this is the Job's plot for the determination of the stoichiometry of Zn^{2+}/A^-. From Figure 4.6 above, the intersect of the two straight lines occurred at 0.37 of metal ion concentration to the total metal and ligand concentration, indicating the formation of 1:2 metal to ligand complex for Zn^{2+}/A^-. Similar result has been obtained thiozonate by (Shar *et al.*, 2001), using micellar media of dodecylsuphate salt.

(ii) Determination of the Stoichiometry of $V^{5+/}A^-$ Complex.

The UV-visible data obtained for the determination of V^{5+}/A^- complex using Job's method of continuous variation is given on Table 4.4

Table 4.4: Uv-visible data for absorbance of the various mixtures of V^{5+}/A^- complexes by continuous variation method at λ_{max} 326.5 nm, $[V^{5+}] = [A^-] = 1x10^{-5}$ M at pH 6.

Metal volume, V_m (cm^3)	Ligand volume, V_l (cm^3)	$V_m/(V_l+V_m)$ (mole fraction)	Absorbance
1.0	9.0	0.1	0.112
2.0	8.0	0.2	0.304
3.0	7.0	0.3	0.448
4.0	6.0	0.4	0.579
5.0	5.0	0.5	0.546
6.0	4.0	0.6	0.383
7.0	3.0	0.7	0.267
8.0	2.0	0.8	0.128
9.0	1.0	0.9	0.042

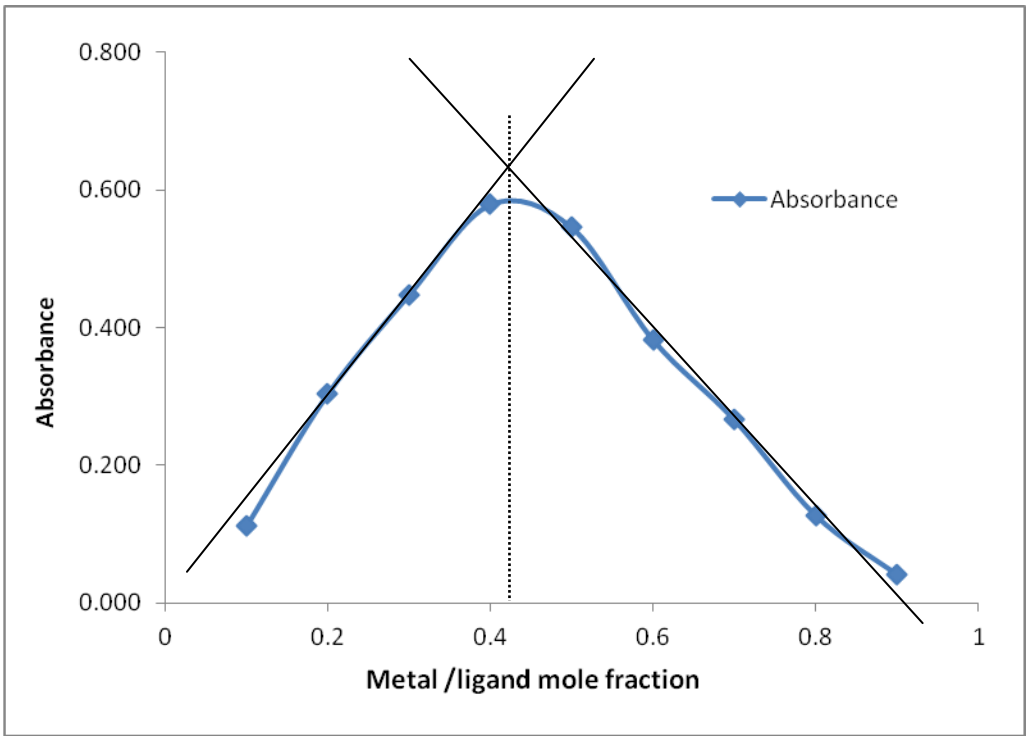


Fig. 4.7: Job's plot for V^{5+}/ A^- complex at λ_{max} 326.5 nm and pH 6. $[V^{5+}] = [A^-] = 1 \times 10^{-5}$ M.

Figure 4.7 shows the graphical representation of the data in Table 4.4 and this is the Job's plot for the determination of the stoichiometry of V^{5+}/A^-. From Figure 4.7 above, the intersect of the two straight lines occurred at 0.42 of metal ion concentration to the total metal and ligand concentrations, indicating the formation of 1:1 metal to ligand complex for V^{5+}/A^-, (Note: VO_2^+ = V(V) = V^{5+}). The result obtained is in line with those obtained by previous researcher, Gopala *et al.*, 2013; Swetha *et al.*, 2013).

4.1.6 DETERMINATION OF THE STOICHIOMETRIES OF Zn^{2+}/A^- AND V^{5+}/A^- COMPLEXES BY MOLE RATIO (Yoe-Jones) METHOD

(i) Determination of the Stoichiometry of Zn^{2+}/A^- Complex.

The UV-visible data obtained for the determination of Zn^{2+}/A^-complex using Yoe-Jones mole ratio method is given on Table 4.5.

Table 4.5: Uv-visible data for absorbance of the various mixtures of Zn^{2+}/A^- complexes by mole ratio method at λ_{max} 309 nm, $[Zn^{2+}] = [A^-] = 1x10^{-5}$ M at pH 4.

Metal volume, V_m (cm^3)	**Ligand volume, V_l (cm^3)**	**(V_m/V_l)**	**Absorbance (nm)**
1.0	1.0	1.0	0.109
2.0	1.0	2.0	0.314
3.0	1.0	3.0	0.348
4.0	1.0	4.0	0.350
5.0	1.0	5.0	0.352
6.0	1.0	6.0	0.352

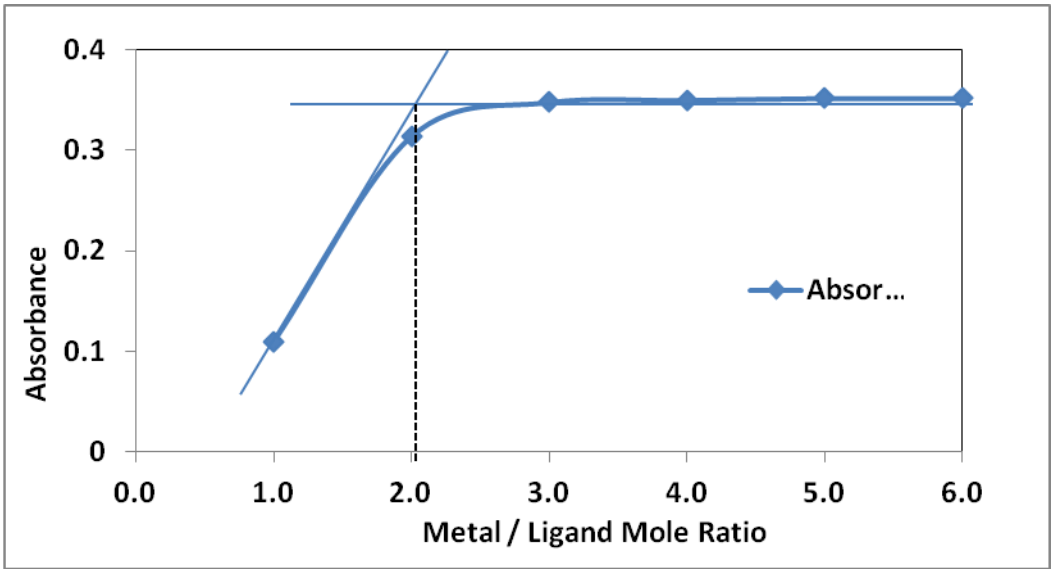
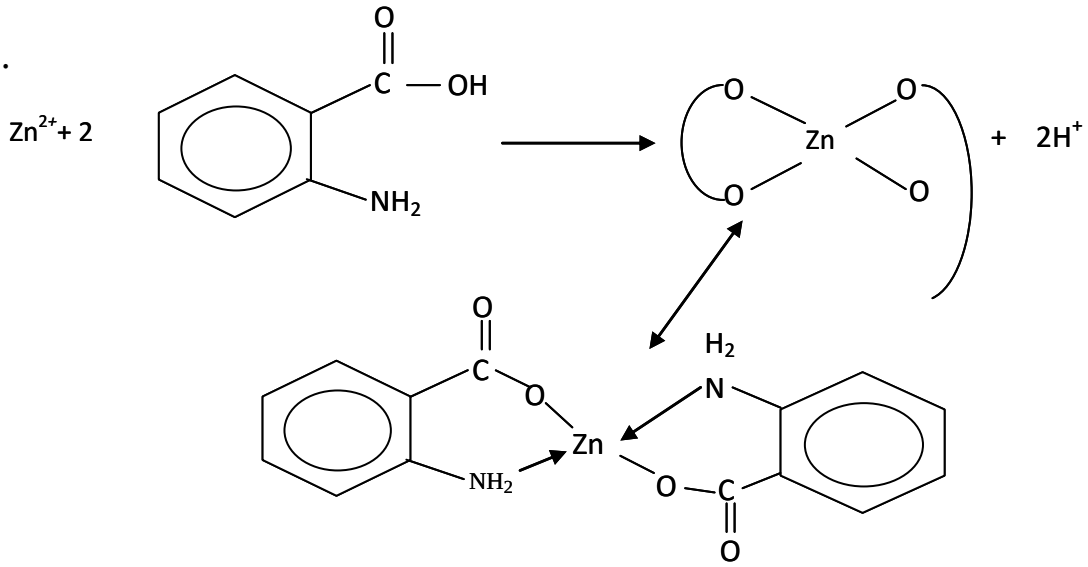


Figure4.8: Yoe-Jones plot for Zn^{2+}/A^- complex of λ_{max} 309nm and pH 4 $[Zn^{2+}]=[A^-]=1 \times 10^{-5}$ M.

Figure 4.8 shows Yoe-Jones mole ratio plot for the determination of the stoichiometry of Zn^{2+}/A^- complex. From Figure 4.8 above, the intersect of the two straight lines shows the formation of 1:2 metal to ligand mole ratio, giving a complex with the formula $[Zn(A)_2]$. Thus:

$$Zn^{2+} + 2AH \longrightarrow Zn(A)_2 + 2H^+$$

i.e.



1:2 zinc-anthranilic acid compound is formed, which is a 6-membered chelate of square planar geometry, since AH^- is a strong ligand.

(ii) Determination of the Stoichiometry of V^{5+}/A^- Complex.

The UV-visible data obtained for the determination of V^{5+}/A^-complex using Yoe-Jones mole ratio method is given on Table 4.6.

Table 4.6: Uv-visible data for absorbance of the various mixtures of V^{5+}/A^- complex by mole-ratio method at λ_{max} 326.5 nm, $[V^{5+}] = [A^-] = 1x10^{-5}$ M at pH 6.

Metal volume, V_m (cm^3)	**Ligand volume, V_l (cm^3)**	**(V_m/V_l)**	**Absorbance (nm)**
1.0	1.0	1.0	0.239
2.0	1.0	2.0	0.347
3.0	1.0	3.0	0.432
4.0	1.0	4.0	0.454
5.0	1.0	5.0	0.456
6.0	1.0	6.0	0.458

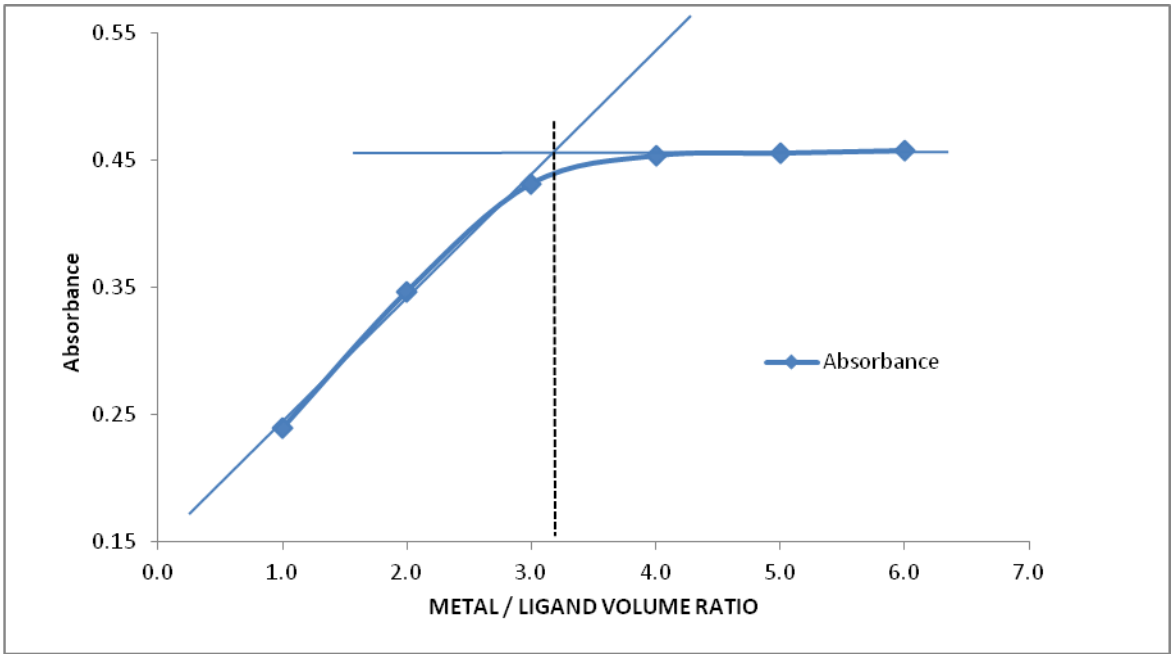


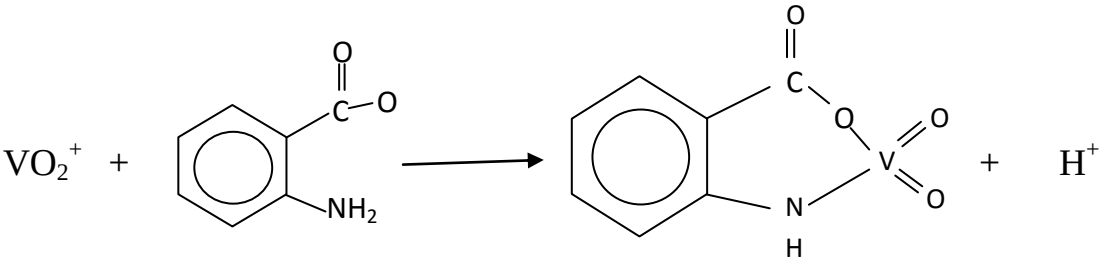
Figure 4.9: Yoe-Jones plot for the determination of the stoichiometry of V^{5+}/ A^- complex at λ_{max} 326.5 nm and pH 6 $[V^{5+}] = [A^-] = 1 \times 10^{-5}$ M.

Figure 4.9 shows Yoe-Jones mole ratio plot for the determination of the stoichiometry of V^{5+}/A^- complex. From the Figure 4.8 above, the intercept of the two straight lines shows the formation of 1:1 metal to ligand mole ratio, giving a complex with the formula $[VO_2A]$. Thus the result of Yoe-Jones mole ratio method is in agreement with the Job's continuous variation method and those obtained by previous researchers (Salalitha*et al.*, 2010;Temitope*et al.*,2015).

Thus;

$$VO_2^+ + AH^- \longrightarrow VO_2A + H^+$$

i.e.



Mole ratio is 1(V):1(A), a 6-membered chelate complex is formed. The structure of the VO_2^+/A^- suggests a square planar geometry since AH (anthranilic acid) is a strong ligand, with one displaceable hydrogen atom.

4.1.7 DETERMINATION OF THE STABILITY CONSTANT OF Zn^{2+}/A^- AND V^{5+}/A^- COMPLEXES.

(i) Determination of the Stability Constant of Zn^{2+}/A^- Complex.

Data for the determination of stability constant of Zn^{2+}/A^- complex is given on Table 4.7.

Table 4.7: **Data for the determination of the stability constant of Zn^{2+}/A^- complex, λ_{max} = 309 nm, $[Zn^{2+}] = [A^-] = 1 \times 10^{-5}$ M, pH = 4.**

Zn^{2+}/A^- (cm^3)	$X(10^{-5})$ M/dm^3	$Y(10^{-5})$ M/dm^3	$XY\ (10^{-10})$	Absorbance (A)	XY/A (10^{-10})
1:9	1	9	0.09	0.061	1.4754
2:8	2	8	0.16	0.142	1.1268
3:7	3	7	0.21	0.187	1.1230
4:6	4	6	0.24	0.211	1.1374
5:5	5	5	0.25	0.186	1.3441
6:4	6	4	0.24	0.164	1.4634
7:3	7	3	0.21	0.138	1.5217
8:2	8	2	0.16	0.103	1.5534
9:1	9	1	0.09	0.068	1.3235

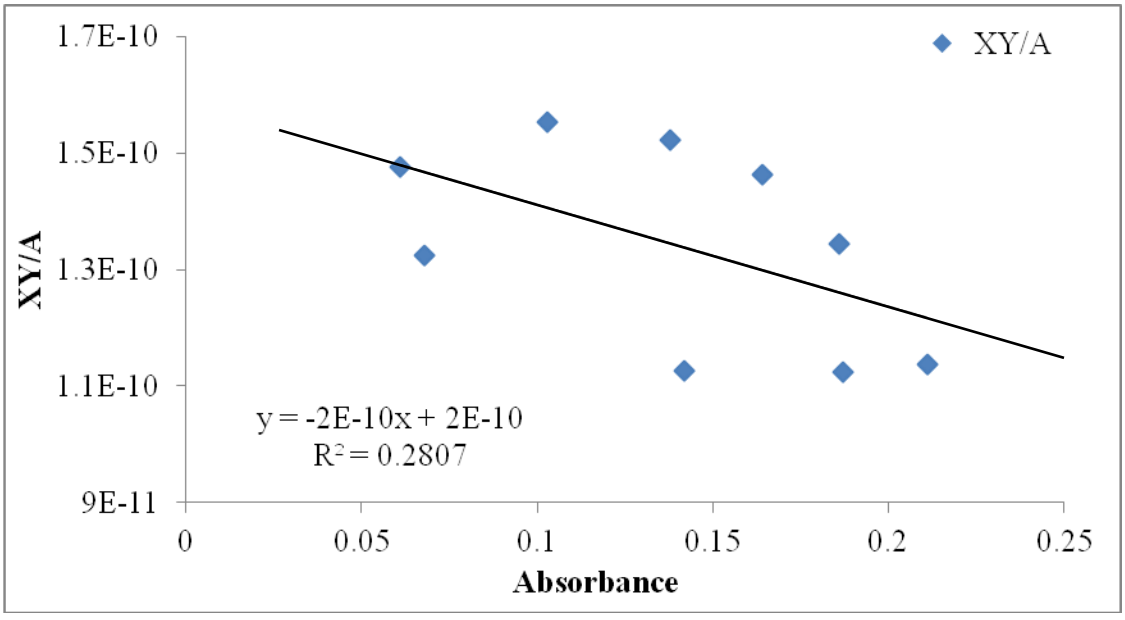


Figure 4.10: Plot of XY/A versus Absorbance for the determination of the stability constant for Zn^{2+}/A^- complex at $[Zn^{2+}] = [H^-] = 1 \times 10^{-5}$ M, pH = 4.

Figure 4.10 above shows the plot of XY/A against A for the determination of Zn(II) anthranilate complex. From Figure 4.9, using regression method, the slope of the graph was determined to be -1.74 x 10^{-10}, (App. C). Molar absorptivity,ε, was determined as 7.58 x 10^{4}. Substituting the values of el and X+Y into Job's equation, gave stability constant values for $[Zn(A)_2]$as 5.08 x 10^{5} and Log K value of 5.71. Since K>1 shows that the formation of product is favored. The free energy of the reaction given by the equation ΔG = -RT lnk, ΔG was determined to be -32.58 $KJmol^{-1}$.

(ii) Stability Constant Determination for V^{5+}/A^{-} Complex

Table 4.8: Data for the determination of the stability constant of V^{5+}/A^{-} complex at λ_{max} = 326.5 nm, $[V^{5+}] = [A^{-}] = 1 \times 10^{-5}$ M, pH = 6

V^{5+}/A^{-} (cm^3)	X(10^{-5}) M/dm^3	Y(10^{-5}) M/dm^3	XY (10^{-10})	Absorbance (A)	XY/A (10^{-10})
1:9	1	9	0.09	0.112	0.8036
2:8	2	8	0.16	0.304	0.5263
3:7	3	7	0.21	0.448	0.4688
4:6	4	6	0.24	0.579	0.4145
5:5	5	5	0.25	0.546	0.4579
6:4	6	4	0.24	0.383	0.6266
7:3	7	3	0.21	0.267	0.7865
8:2	8	2	0.16	0.128	1.2500
9:1	9	1	0.09	0.042	2.1429

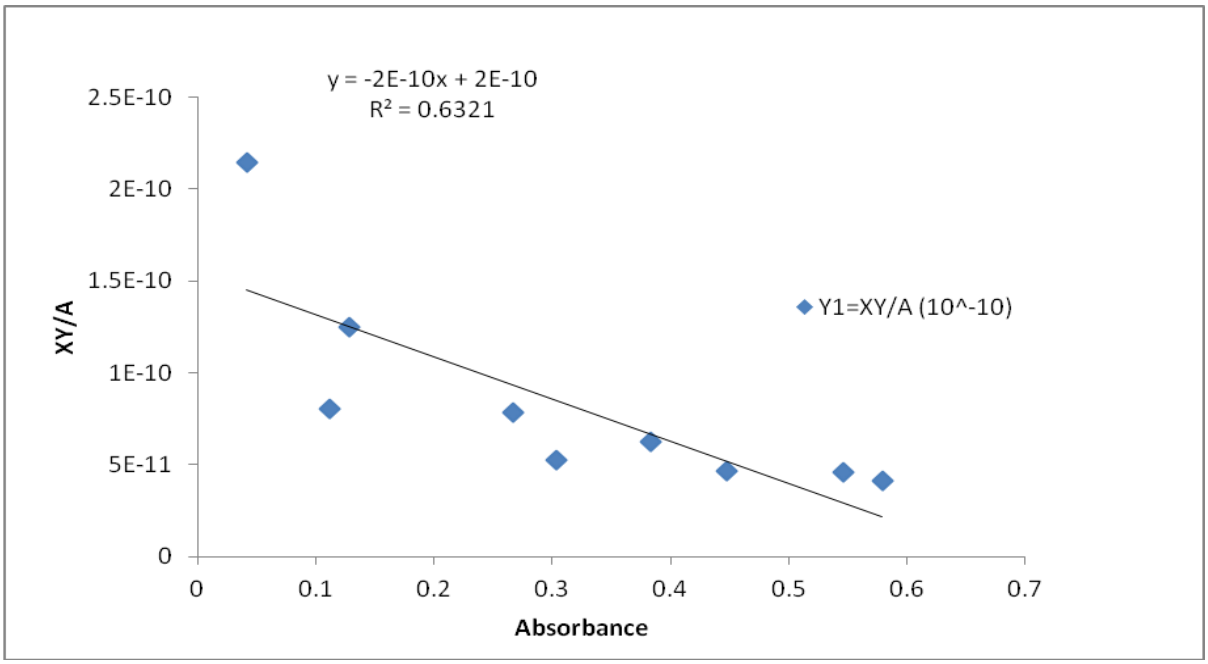


Figure 4.11: Plot of t XY/A versus Absorbance for the determination of the stability constant for V^{5+}/A^- complex at $[V^{5+}] = [A^-] = 1x10^{-5}$ M at pH 6.

Figure 4.11 above showed the plot of XY/A against A for the determination of V (V) anthranilate complex. From Figure 4.10, the slope of the graph was determined to be -2.29 x 10^{-10}. The molar absorptivity,*e*, was determined to be 6.6069 x 10^4 substituting in the values of el and (X + Y) into Job's equation gave the stability constant K for $[VO_2A]$ complex to be 4.698 x 10^6, Log K = 6.67 and ΔG was determined to be -38.07KJ/mol.

4.2 DISCUSSION

From the results obtained, zinc (II) ion formed a colourless complex with anthranilc acid at pH 4 and vanadium (V) formed a golden-yellow complex at pH 6. The complexes showed maximum absorbance at 309 nm for zinc (II) and 326.5 nm for vanadium (V). The zinc (II) ion formed a 1:2 metal to ligand mole ratio complex with anthranilic acid (HA), while vanadium (V) ion formed a 1:1 metal to ligand mole ratio complex with anthranilic acid. That is, for Zn^{2+}/A^-complex, ZnA_2 is formed and

V^{5+}/A^- complex, VO_2A is formed. The stability constants, (Log K), molar absorptivity and free energies of the formation of Zn (II) and V (V) anthranlilate complexes were 5 x 10^5, (5.71), 7.58 x 10^4 and -32.58 kJ/mol for zinc (II) anthranilate and 6.61x 10^4, 6.67, 4.7x 10^6 and -38.07 kJ/mol for vanadium (V) anthranilate, respectively.

The values obtained for the stability constant of the complexes have been found to be greater than zero, which is perhaps one of the most convincing pieces of evidence for the existence of the complex species in solution.

Comparing the stability of these complexes, it was found that the vanadium (V) ion formed more stable complex with anthranilic acid with Log K value of 6.67 compared to zinc (II) complex with Log K value of 5.71. The higher stability constant value for vanadium (V) complex can be attributed to the smaller ionic radius value of Vanadium (V) ion compared to of zinc (II). The smaller the ionic radius, the more stable the complex formed and vice versa. This implies that vanadium (V) ion formed more stable complex than zinc (II) ion. This means that V (V) will have greater stability than Zn (II) since the ligand will have a stronger electrostatic attraction with the ion thus giving intense charge transfer spectra.

Also the higher stability constant observed in vanadium (V) complex can be attributed to higher oxidation state of +5 in vanadium compared to +2 oxidation state of zinc (II) ion. Stability constant is affected by the charge on the central metal ion. Greater the charge on the metal ion, greater is the stability of the complex ion. The larger the oxidation state, the more stable the complex (Weissten, 2007). Stability of less electropositive metal results from covalent contribution to metal-ligand bond. This involves transfer of electron density from the metal to the Ligand via Pi-bonding (Basolo, 1972). This is called back-bonding.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The present work used anthranilic acid as a spectrophotometric reagent for the determination of zinc (II) and V (V) ions. The method of UV- visible spectrophotometry has been successfully employed for the determination of the stoichiometries and stability constants of Zn (II) and V (V) complexes of anthranilic acid. The experiment using Job's method of continuous variation and Yoe-Jones mole ratio method showed that the stoichiometries for the Zn(II) /$A^-$was 1:2 and V(V) /A^- was 1:1, i.e., [$Zn(A)_2$] and [VO_2A]. The golden-yellow colour of the complex solution is an indication of the generation of VO_2^+ cation in the working solution since the colour of the aqueous solution of VO_2^+ is usually yellow.

Vanadium (V) anthranilate was found to be more stable than zinc (II) anthranilate. The stability constants obtained indicate that anthranilic acid is a good chelating agent for Zn (II) and V (V), and hence can be used as analytical reagent inchemical industries.

5.2 RECOMMENDATIONS

During this research work, it was felt that there were so many points and number of questions which were unsolved and unanswered. This opens new doors for further researches. Some selected points are as follows, which are not undertaken because it was beyond the scope of the study.

i. The kinetics of formation of these complexes may be studied. The determination of rate of formation at different temperatures as this may help in drawing the mechanism during complex formation.

ii. The complexation reactions of Zn (II) and V (V) with anthranilic acid were studied but characterizations were beyond the scope of this study. So, further work could be done in the area of characterization.

iii. IR and NMR analyses would be desirable in other to check the structures of the complexes and to confirm the coordination points of the ligand.

iv. Finally, complexation studies with other biologically important trace elements may also be taken into consideration.

5.3 CONTRIBUTIONS TO KNOWLEDGE

i. **Stability constant:** The stability constants values obtained for Zn (II) anthranilate, $Zn(A)_2$ and V (V) anthranilate, VO_2A showed that anthranilic acid is a good complexing reagent and can form stable complexes with the metals studied, and hence can be used for the extraction and separation of these metal ions (Zn^{2+} and V^{5+}) in samples, containing them, (for example, alloys, ore minerals, etc).

ii. **Stoichiometries:** The actual number of species present in the solutions of Zn^{2+} and V^{5+} complexes of anthranilic acid were determined using Job's and Yoe- Jones methods. The stoichiometries were found to be 1:2 and 1:1 metal ligand complexes for Zn (II) and V h(V) ions respectively. These complexes were also found to be thermodynamically stable having high values of ΔG with negative sign; hence anthranilic acid is a good analytical reagent and can be used in identification and determination of these metal ions in solution.

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GLOSSARY

AH:	Anthranilic Acid
Zn^{2+}:	Zinc(II) ion
V^{5+}:	Vanadium (V) ion
$KZn(II)/A^-$:	Stability constant of Zinc (II) anthranilate complex
$KV(V)/A^-$:	Stability constant of V(V) anthranilate complex.
A:	Absorbance
ε:	Molar absorptivity extinction coefficient
l:	Pathlength in the cell (1 cm)
x:	The concentration of metal ion (Zn^{2+} or V^{5+}) added to the complex solution.
Y:	The concentration of anthranilate ion, added to the complex solution.
b:	Slope of the graph.
a:	intercept at Y-axis.
n:	Number of data points
X_1:	Absorbance (A)
$\sum X_1$:	Total sum of x
Y_1:	$^{xy}/_{A}\ (Y\ axis\ data)$
$\sum X_1 Y_1$:	Summation of the products of X_1 and Y_1
$\sum X_1^2$:	Summation of the square of the X_1.
$(\sum X_1)^2$:	Square of the total sum of X_1
$\bar{X}$:	Mean of the values of sum X_1
T:	Temperature
R:	Rate Constant (8.314 $mole^{-1}K^{-1}$)
K:	Stability constant
pH:	Hydrogen ion concentration
ΔG:	Gibb's free energy.
PPM:	Part per million

APPENDIX A

PREPARATION OF STOCK SOLUTIONS

The stock solutions of the metal ions (Zn(II) and V(V)) and the ligand (anthranilic acid) by the product of their molar mass, molarity (0.01) and volume of the solution.

- **Preparation of 0.01 M solution of $ZnSO_4.7H_2O$**

Reacting mass (g) = Molarity (M) x Volume (V) x Molar mass

Where Volume (V) of solution in litre, Molarity is in mole and Molar mass is in g/mol.

Therefore, 100 cm^3 of 0.01 M $ZnSO_4.7H_2O$,

Molar mass of $ZnSO_4.7H_2O$ = 287.53 g/mol

$$\text{Reacting mass (g)} = 0.01\ \text{mol/L} \times 0.1\ \text{L} \times 287.53\ \text{g/mol}$$

$$g_{ZnSO4.7H2O_4} = 0.28753\text{g}$$

- **Preparation of 0.01 M solution of NH_4VO_3**

Therefore, 100 cm^3 of 0.01 M $ZnSO_4.7H_2O$,

Molar mass of $ZnSO_4.7H_2O$ = 287.53 g/mol

$$\text{Reacting mass (g)} = 0.01\ \text{mol/L} \times 0.1\ \text{L} \times 116.98\ \text{g/mol}$$

$$g_{NH4VO3_{\Delta\Delta}} = 0.11698\ \text{g}$$

- **Preparation of 0.01 M solution of Anthranilic acid, $C_6H_4(NH_2)(CO_2H)$**

Molar mass of $C_6H_4(NH_2)(CO_2H)$ =137.14 g/mol

100 cm^3 of 0.01 M $C_6H_4(NH_2)(CO_2H)$

Reacting mass (g) = 0.01 M/L x 0.1 L x 137.14 g/mol

= 0.13714 g $C_6H_4(NH_2)(CO_2H)$

PREPARATION OF WORKING SOLUTION

The working solutions were prepared by serial dilution method.

- **Preparation of 250 cm^3 of 0.01 M of Zn(II) ion**

$C_1V_1 = C_2V_2$

$C_1 = 0.01$ M $V_1 = X\ cm^3$

$C_2 = 1 \times 10^{-5}$ M, $V_2 = 1000\ cm^3$

$\therefore\ 0.01M \times X cm^3 = 250\ cm^3 \times 1 \times 10^{-5}$ M

$$\therefore X\ cm^3 = \frac{100 cm^3 \times 1 \times 10^{-5} M}{1 \times 10^{-2}\ M}$$

$$= 0.25\ cm^{3}`$$

0.25 cm^3 of 1×10^{-2} M stock solution was made up to 250 cm^3 with distilled water.

- **Preparation of 250 cm^3 of 0.01 M of V(V) ion**

$$X\ cm^3 of\ 1 \times 10^{-2} M\ of\ V(V)\ ion = \frac{250\ cm^3 \times 1 \times 10^{-5}}{1 \times 10^{-2}}$$

$$= 0.25\ cm^3$$

0.25 cm^3 of 1×10^{-2} M stock solution was made up to 250 cm^3 with distilled water.

- **Preparation of 250 cm^3 of 0.01 M of $[C_6H_4(NH_2)(CO_2)]^-$ ion**

$$X\ cm^3 of\ 1 \times 10^{-2} M\ of\ [C_6H_4(NH_2)(CO_2)] - = \frac{250\ cm^3 \times 1 \times 10^{-5} M}{1 \times 10^{-2} M}$$

$$= 0.25\ cm^3$$

0.25 cm^3 of 1×10^{-2} M stock solution of anthranilic acid in ethanolic KOH solution was made up to 250 cm^3 with ethanolic KOH solution.

APPENDIX B

PREPARATION OF BUFFER SOLUTIONS

HCI – KCI Buffer of Clark Lubs for PH 1and2

- **Preparation of 0.2M of HCI**

  0.2 M KCl was prepared by dissolving 14.91 g reagent grade KCl with distilled water and solution made up to 1 litre.

  0.2 M solution of HCl was prepared by diluting 320 ml concentrated reagent grade HCl with distilled water and the solution made up to 1 litre with distilled water.

- **For pH 1.1**

  47.3 ml of 0.2 ml HCI was added to 2.7 M KCl and made up to 100ml with water.

- **pH 2**

  6.0 ml of 0.2 M HCI was added to 44. 1 ml 0.2 M KCI and the mixture was made up of 100 ml.

- **pH 3**

  4.5 ml of 0.2 M HCl was added to 45.5 ml of 0.2 M KCl and was made up to 100 ml of distilled water.

- **Acetate buffer**

  0.2 M solution of acetic acid was prepared by dissolving 11.55 ml of acetic acid in 1 litre of distilled water and 0.2 M solution of sodium acetate was prepared by dissolving 16.4 gof CH_3CO_2Na in 1 litre of distilled water.

- **pH 4**

  41.0 ml of 0.2 M solution of acetic acid was mixed with 9.0 ml of 0.2 M solution of sodium acetate and the mixture was made up to 100 ml with distilled water.

- **pH 5**

  14.8 ml of 0.2 M solution of acetic acid was mixed with 35.2 ml of 0.2 M solution of sodium acetate and the mixture was made up to 100 ml with distilled water.

- **Citrate - Phosphate Buffer**

  0.1 M solution of acetic acid 19.21 g of acetic acid was dissolved in 1000 ml of water.

  0.2 M solution of disbasic sodium phosphate (Na_2HPO_4) was prepared by dissolving 28.39 g of reagent grade of Na_2HPO_4 in 1000 ml of distilled water.

- **pH 6**

  17.9 ml of 0.1 M citric acid was mixed with 32.1 ml of 0.2 M solution of Na_2HPO_4 and the mixture made up to 100 ml with distilled water.

- **pH 7**

  6.4 ml of 0.1 M solution of acetic acid was mixed with 43.6 ml 0.2 M solution of Na_2HPO_4 and the mixture was made up to 100 ml distilled water.

- **pH 8**

  2.65 ml of 0.2 M was added to 47.35 ml of 0.2 M $Na_2HPO_4.12H_2O$and the mixture was made up to 100 ml distilled water.

- **Preparation of Carbonate - Bicarbonate Buffer**

  0.2 M solution of anhydrous sodium carbonate was prepared by dissolving 21.2 g of reagent grade anhydrous sodium carbonate and diluting to 1 litre with distilled water.

  0.2 M solution at sodium bicarbonate was prepared by dissolving 16.8 g reagent grade sodium bicarbonate and diluting to 1 litre with distilled water.

- **pH 9**

  Buffer at pH 9 was prepared by mixing 4.0 ml of anhydrous sodium carbonate and 46.0 ml of sodium bicarbonate and the solution was made up to 200 ml with distilled water.

- **pH 10**

  Buffer at pH 10 was prepared by mixing 27.5 ml of anhydrous sodium carbonate and 22.5 ml of sodium bicarbonate and the solution diluted to 100 ml with distilled water.

APPENDIX C

DATA TREATMENT

Calculation of the Stability Constant of the Complexes and the Free Energies of the Complexes

The equation for the formation of the complexes can be written as:

$$Zn^{2+} + n(AH) \rightleftharpoons Zn(AH)n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$V^{5+} + n(AH) \rightleftharpoons V(AH)n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$\frac{KZn^{2+}}{AH^{-}}^{n} = \frac{[complex]}{[Zn^{2+}][AH^{-}]^{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

$$\frac{KV^{5+}}{AH^{-}}^{n} = \frac{[complex]}{[V^{5+}][AH^{-}]^{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where n is the number of moles of anthranilate ion, $[Zn^{2+}]$, $[V^{5+}]$ and [AH]refer to the concentration of these free species.

A = log [lo/l] = εl (complex) …….……..……..5

A = absorbance, lo = incident light intensities.

L = transmitted light intensities

ε = extinction (absorption) coefficient of the complex.

L = the pathlength in the cell (1cm).

To determine the stability constant, the concentration of the complex is first determined by means of equation 5

$$KZn2 + \Big/_{AH} = \frac{[complex]}{[Zn^{2+}][AH]} = \frac{[complex]}{[X-(complex)][y-(complex)]} \ldots\ldots\ldots 6$$

$$KV^{5+} \Big/_{AH} = \frac{[complex]}{[V^{5+}][AH]} = \frac{[complex]}{[X-(complex)][y-(complex)]} \ldots\ldots\ldots 7$$

Where X is taken to be the concentration of metal ion $[Zn^{2+}]$ or $[V^{5+}]$added to the solution and Y is the concentration of anthranilic acid added. Substituting A/el for the complex in equations (6 and 7) yield.

$$k = \frac{\frac{A}{\varepsilon l}}{\left[X - \frac{A}{\varepsilon l}\right].\left[Y - \frac{A}{\varepsilon l}\right]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 8$$

Rearranging equation 8 above, we have:

$$K(X - A/\varepsilon l) = A/\varepsilon l \ \ldots\ldots\ldots\ldots\ldots\ldots 9$$

$$K(xy - Ax/\varepsilon l - Ay/\varepsilon l + A^2/(\varepsilon l)^2) = A/\varepsilon l \ \ldots\ldots\ldots\ldots 10$$

Dividing through by KA

$$\frac{Xy}{A} = \frac{X}{\varepsilon l} - \frac{y}{\varepsilon l} + \frac{A}{(\varepsilon l^2)} = \frac{1}{k\varepsilon l} \ldots\ldots\ldots\ldots\ldots\ldots 11$$

$$\frac{Xy}{A} = \frac{1}{k\varepsilon l} + \frac{X}{\varepsilon l} + \frac{y}{\varepsilon l} = \frac{A}{(\varepsilon l)^2} \ldots\ldots\ldots\ldots\ldots\ldots 12$$

$$\frac{Xy}{A} = \frac{1}{\varepsilon l\left[\frac{1}{k} + (x + y)\right]} - \frac{A}{(\varepsilon l)^2} \ldots\ldots\ldots\ldots\ldots\ldots 13$$

Equation (13) is the Job's equation.

$$\frac{xy}{A} = \frac{1}{\varepsilon l}\left[{}^{1}/_{k} + (x + y)\right] - {}^{A}/_{(\varepsilon l)^2}$$

The total concentration (x + y) is constant (Job's method). A plot of $\frac{xy}{A}$ in fig. 4.9 and 4.10 gave a graph, the slope of the yield el and the intercept of the graph at y axis equal to $\frac{1}{\varepsilon l}\left[{}^{1}/_{k} + (x + y)\right]$, K will then be calculated when εl and x+y values are substituted.

DETERMINATION OF THE STABILITY CONSTANT OF Zn^{2+}/AH^{-} COMPLEX

Zn^{2+}/AH^{-} (cm^3)	$X(10^{-5})$ m/dm^3	$Y(10^{-5})$ m/dm^3	XY (10^{-10})	Absorbance (A)	XY/A (10^{-10})
1:9	1	9	0.09	0.061	1.4754
2:8	2	8	0.16	0.142	1.1268
3:7	3	7	0.21	0.187	1.1230
4:6	4	6	0.24	0.211	1.1374
5:5	5	5	0.25	0.186	1.3441
6:4	6	4	0.24	0.164	1.4634
7:3	7	3	0.21	0.138	1.5217
8:2	8	2	0.16	0.103	1.5534
9:1	9	1	0.09	0.068	1.3235

Determination of x in 1: 9; $1/10 \times 1x10^{-5} = 1.0 \times 10^{-6}$ M

Determination of y in 9 : 1; $9/10 \times 1x10^{-5} = 9.0 \times 10^{-6}$ M

Determination of x in 2 : 8; $2/10 \times 1x10^{-5} = 2.0 \times 10^{-6}$ M

Determination of y in 8 : 2; $8/10 \times 1x10^{-5} = 8.0 \times 10^{-6}$ M

Where 1×10^{-5} M is the working concentration of the reactant in the plot of Xy/A against A shown in figure 4.9 and 4.10, using statistical method (regression method) to determine the slope and the intercept of the graph.

$$b = \text{slope of the graph} = \frac{\Sigma X_1 Y_1 - \Sigma X_1 Y_1}{n\Sigma X_1^2 - (\Sigma X_1)^2}$$

Intercept at y-axis, $a = \bar{y} - b\bar{x}$

Where n = number of data points

$\bar{x} =$ mean of values of X_1

$\bar{y} =$ mean of values of Y_1

Zn^{2+}/AH (cm^3)	$X_1 = A$	$Y_1 = XY/A$	$X_1Y_1 = XY$ (10^{-10})	$X_1^2 = A^2$
1:9	0.061	1.47541	0.09	0.003721
2:8	0.142	1.126761	0.16	0.020164
3:7	0.187	1.122995	0.21	0.034969
4:6	0.211	1.137441	0.24	0.044521
5:5	0.186	1.344086	0.25	0.034596
6:4	0.164	1.463415	0.24	0.026896
7:3	0.138	1.521739	0.21	0.019044
8:2	0.103	1.553398	0.16	0.010609
9:1	0.068	1.323529	0.09	0.004624
	$\Sigma X_1 = 1.26$	**$\Sigma Y_1 = 12.06877$**	**$\Sigma XY = 1.65$**	**$\Sigma X_1^2 = 0.199144$**

Let X_1 = absorbance (A) and

$$Y_1 = XY/A$$

$$\overline{X} = \frac{1.26}{9} = 0.14$$

$$\Sigma XY = 1.65$$

$$\overline{Y}_1 = \frac{12.06877}{9} = 1.340975$$

$$(\Sigma X_1)^2 = 1.5876$$

Slope of the graph

$$b = \frac{n\Sigma_1 Y_1 - \Sigma X_1 \Sigma Y_1}{n\Sigma X_1^2 - (\Sigma X_1)^2}$$

$$= \frac{9 \times 1.65 - 1.26 \times 12.06877}{9 \times 0.199144 - 1.5876}$$

$$b = -1.74244 \times 10^{-10}$$

From Job's equation (13), the slope of the graph = $-\frac{1}{(\varepsilon l)^2}$ where $l = 1cm$

Therefore, the slope of the graph =

$$\frac{-1}{-1.74244 \times 10^{-10}}$$

$$= 5.7392103 \times 10^{9}$$

$$\varepsilon^2 = \sqrt{5.7392103 \times 10^{9}}$$

$$\varepsilon = 75758.5$$

$$a = Y - b\bar{x}$$

$$= 1.340975 - (-1.7424 \times 10^{-10}) \times 0.14$$

$$a = 1.584911 \times 10^{-10}$$

$$a = \frac{1}{\varepsilon}\left[\frac{1}{k} + (x + y)\right]$$

$$1.584911 \times 10^{-10} = \frac{1}{75758.5}\left[\frac{1}{k} + 1 \times 10^{-5}\right]$$

$$1.584911 \times 10^{-10} = \left[\frac{1.31998 \times 10^{-5}}{k} + \frac{1.31998 \times 10^{-10}}{1}\right]$$

$$1.584911 \times 10^{-10} - 1.31998 \times 10^{-10} = \frac{1.31998 \times 10^{-5}}{k}$$

$$= 2.6 \times 10^{-11} = \frac{1.31998 \times 10^{-5}}{k}$$

$$k = \frac{1.31998 \times 10^{-5}}{2.6 \times 10^{-11}}$$

$$k = 507692.308$$

$$k = 5 \times 10^{5}$$

$$\text{Log } k = 5.70560058$$

$$= 5.71$$

Determination of the free energy of the reaction for the formation of Zn^{2+}/AH^{-}

$$\Delta G = -RT \ln k$$

Where R = 8.314 mol^{-1} k, T = 25^0C = 273 + 25 = 298k

$$\therefore \Delta G = -2.303 \times 8.314 \times 298 \times 5.71$$

$$= -32580.394$$

$$= -32.58 kJ/mol$$

APPENDIX D

DETERMINATION OF THE STABILITY CONSTANT OF V^{5+}/AH^- COMPLEX

V^{5+}/AH^- (cm^3)	$X(10^{-5})$ M/dm^3	$Y(10^{-5})$ M/dm^3	XY (10^{-10})	Absorbance (A)	XY/A (10^{-10})
1:9	1	9	0.09	0.112	0.80357
2:8	2	8	0.16	0.304	0.52632
3:7	3	7	0.21	0.448	0.46875
4:6	4	6	0.24	0.579	0.41451
5:5	5	5	0.25	0.546	0.45788
6:4	6	4	0.24	0.383	0.62663
7:3	7	3	0.21	0.267	0.78652
8:2	8	2	0.16	0.128	1.25000
9:1	9	1	0.09	0.042	2.14286

Determination of x in 1:9, $^1/_{10}$ x 1 x 10^{-5} = 1 x 10^{-6} M

Determination of y in 1:9, $^9/_{10}$ x 1 x 10^{-5} = 9 x 10^{-6} M

Where 1.0 x 10^{-5} M is the working concentration of the reactants. In the plot of Xy/A against A shown in figure 4.10, using statistical method or regression to determine the slope and the intercept of the graph.

$$b = \text{slope of the graph} = \frac{n\Sigma X_1 Y_1 - \Sigma X_1 \Sigma Y_1}{n\Sigma X_1^2 - (\Sigma X_1)^2}$$

$$\text{Intercept at } Y - \text{axis} = a = \overline{Y} - b\,\overline{X}$$

Where n = number of data points (g)

$\overline{X}$ = mean of values of X_1

$\overline{Y}$ = mean of values of Y_1

V^{5+}/AH^{-} (cm^3)	$X_1 = A\ (10^{-10})$	$X_1Y_1 = XY$ (10^{-10})	$Y_1 = \frac{XY}{A}\ (10^{-10})$	$X_1^2 = A^2$
1:9	0.112	0.09	0.80357	0.012544
2:8	0.324	0.16	0.52632	0.104976
3:7	0.579	0.21	0.46875	0.335241
4:6	0.546	0.24	0.41451	0.298116
5:5	0.448	0.25	0.45788	0.200704
6:4	0.312	0.24	0.62663	0.097344
7:3	0.202	0.21	0.78652	0.040804
8:2	0.108	0.16	1.25000	0.011664
9:1	0.032	0.09	2.14286	0.001024
	ΣX_1 =2.663	**ΣXY =1.65**	**ΣY_1 =8.760505255**	**ΣX_1^2=1.102417**

Let X_1 = Absorbance

$Y_1 = \frac{XY}{A}$

$$\bar{X} = \frac{2.809}{9} = 0.312111$$

$$\bar{Y} = \frac{7.477026299}{9} = 0.8307807 \times 10^{-10}$$

$$(\Sigma X_1)^2 = (2.809)^2 = 7.890481$$

Slope of the graph;

$$b = \frac{n\,\Sigma X_1 Y_1 - \Sigma X_1 \Sigma Y_1}{n\,\Sigma X_1^2 - (\Sigma X_1)^2}$$

$$= \frac{9 \times 1.65 - 2.809 \times 7.477026299}{9 \times 1.175147 - 7.890481}$$

$$b = -2.290889365 \times 10^{-10}$$

From Job's equation (13), the slope of the graph = $-\frac{1}{(\varepsilon l)^2}$ but $l = 1cm$

$$= \frac{-1}{-2.290889365 \times 10^{-10}}$$

$$\varepsilon^2 = 4365116952$$

$$\varepsilon = \sqrt{4365116952}$$

$$\varepsilon = 66069.03172 = 6.6069 \times 10^{4}$$

$$a = \bar{Y} - b\bar{x}$$

$$a = 0.8307807 \times 10^{-10} - (-2.29089 \times 10^{-10}) \times 0.312111$$

$$= 1.54579 \times 10^{-10}$$

$$a = \frac{1}{\varepsilon l}\left[\frac{1}{k} + (x + y)\right]$$

Where $x + y = 1 \times 10^{-5}$, the concentration of the solution

$$a = \frac{1}{\varepsilon}\left[\frac{1}{k} + (x + y)\right]$$

$$1.54579 \times 10^{-10} = \frac{1}{66069.03}\left[\frac{1}{k} + 1 \times 10^{-5}\right]$$

$$1.54579 \times 10^{-10} = \left[\frac{1.51357 \times 10^{-5}}{k} + \frac{1.51357 \times 10^{-10}}{1}\right]$$

$$1.54579 \times 10^{-10} - 1.51357 \times 10^{-10} = \frac{1.51357 \times 10^{-5}}{k}$$

$$= 3.222 \times 10^{-12} = \frac{1.51357 \times 10^{-5}}{k}$$

$$k = \frac{1.51357 \times 10^{-5}}{3.222 \times 10^{-12}}$$

$$k = 4697610.18$$

$$k = 4.7 \times 10^{6}$$

$$\text{Log } k = 6.67187$$

Determination of the free energy of the reaction for the formation of Zn^{2+}/AH^{-}

$$\Delta G = -RT \ln k$$

Where R = 8.314 mol^{-1} k, T = 25^{0}C = 273 + 25 = 298 k

$$\therefore \Delta G = -2.303 \times 8.314 \times 298 \times 6.67$$

$$= -38068.718$$

$$= -38.07 \text{ kJ/mol}$$