STUDIES IN METAL CHELATE COMPOUNDS
(METAL CHELATES OF 8-HYDROXYQUINOLINE-5-SULPHONIC ACID DERIVATIVES & ALUMINON)

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in this thesis entitled, "Studies in Metal Chelate Compounds (Metal Chelates of 8-Hydroxyquinoline-5-Sulphonic Acid Derivatives & Aluminon)" was carried out by Shri Balraj K. Avinashi, under my guidance and supervision during the period of September, 1967 to March, 1971.

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CHAPTER I

INTRODUCTION

Historically few branches of chemistry have received as much concentrated study with such fruitful results, as the area encompassed by coordination chemistry. The field of coordination chemistry has grown in the past few decades from a readily defined and limited area into what is now, one of the most active fields in inorganic chemistry. The rapid and fascinating strides made in this field during half a century have largely been responsible for renaissance in inorganic chemistry. This science is, even now, in a state of rapid advance, probably similar to that experienced in organic chemistry, nearly hundred years ago. The kind of compounds with which it is concerned is so varied that it can be easily expected that future progress is likely to pick up greater pace and for the beginning as well as established scientists, coordination chemistry will be an extremely attractive field of research.

Metal chelate compounds

A chelate may be defined as a compound possessing a cyclic structure arising from the union of a metal ion with an electron donor (chelating agent) which is a neutral molecule or a charged species, with two or more points of attachment. In ordinary complexes, as apart from a chelate compound or metal chelate, the ligand is monofunctional, and no ring formation takes place. The ring formation is a special characteristics of chelate compounds and the term chelate (chele meaning Crab's claw) was introduced in coordination chemistry by Morgan (1) as early as in 1920, to designate such cyclic structures. Usually rings containing five or six members, including the metal ion, are more stable.

The formation of inner complex compounds also involves a ring structure which was noted by various investigators including Werner (2), Ley (3) and others, who found that these structures are exceptionally stable, insoluble in water but frequently soluble in non-polar solvents and are often intensely coloured. But Feigl (4) asserts that there is a tendency to exaggerate these properties of the inner complexes. The chemical and physical properties of the metal chelates in general, resemble those of the simple complexes and differ only in a qualitative way. Although chelates are now considered to be a distinct class of compounds with characteristic behaviour, they can, at best, be regarded as belonging to a special type, under the general class of metal complexes. Thus, all chelates are complex compounds but all complex compounds are not necessarily chelates.

For the formation of a chelate, a ring formation is an essential condition. In case of bidentate chelates, the concerned bonds may either be (i) covalent bonds, (ii) one covalent bond-one coordinate bond or (iii) both coordinate bonds. In fact, in the earlier stages, the nature of the linkages has been used as a basis for classifying chelate compounds. Covalent bonding is produced by the replacement of a proton in an organic group. Functional groups of this type are sometimes called acidic groups because of the fact that hydrogen may be replaced from them. Coordinate linkages, without the replacement of hydrogen, are formed by the donation of an electron pair.

With the discovery of compounds, in which the metal atom is linked to the organic molecule, through three or more groups, it became necessary to look more closely into these compounds. It was Morgan (1) who called these compounds tridentate, quadridentate, quinquidentate and sexadentate accordingly as they functioned through three, four, five or six groups, respectively. Since polydentate molecules may be attached to the central metal atom through two kinds of functional groups, acidic and coordinating, to form covalent and coordinate linkages, the logical classification should follow the number and kind of attachment involved. Such a classification has been developed by Diehl (5), according to which, the rings may be closed in the case of a tridentate chelate either by (i) three covalent linkages, (ii) two covalent and one coordinate bond, (iii) one covalent and two coordinate bonds or (iv) by three coordinate bonds, and so on for quadridentate, quinquidentate and sexadentate. However, there is no way of distinguishing a coordinate covalent bond from any other covalent bond present, once the chelate is formed.

Theories of chelation

Of the more modern theories advanced to explain the bond structures in metal complexes and chelates, the simplest approach is based on valence bond theory. It assumes that the association results from the overlap of an orbital of the ligand containing an unshared pair of electrons with hybridized orbitals of the metal ion. This may be thought of either as a sharing of the electron pair between the metal ion and ligand or as a partial donation of the ligand electron to the metal ion. From the point of view of depicting the bonding in terms of the electron configuration of the metal ion, it is profitable to consider that the ligand electron pairs enter the metal ion orbitals, while still maintaining the electronic configuration originally present in the ligand. The main features of valence bond theory are (i) the formation of directional bonds through the overlap of atomic orbitals (ii) the formation of hybridized bonds by mixing of atomic orbitals, that are capable of forming stable bonds. Covalent σ bond is formed through the overlap of a filled orbital of the central metal, while in a π bond there is overlapping of a vacant ligand orbital with a central metal orbital, containing available d-electrons.

Usually, σ and π bonds occur simultaneously and produce a stronger bond than either would do alone. Two types of π bonds are commonly recognized: either a combination of

σ (ligand → metal) and π (metal → ligand) or σ (ligand → metal) and π (ligand → metal). The former are generally formed with the metal ion in a low oxidation state (many electrons) and an unsaturated ligand, while the latter type is prevalent with saturated ligands and the metal in a high oxidation state.

The valence bond theory has however been found to be highly inadequate in explaining some of the magnetic properties and spectral properties (6).

In the molecular orbital theory, the formation of molecular orbital is assumed rather than the simple overlap of the orbitals of the reactants. The configuration of the molecules is then obtained by introducing electrons to the lowest orbital of the molecular frame work. As the lower energy levels are occupied, the entering electron goes to a higher excited level. These electrons oppose bond formation and are known as antibonding electrons. Electrons occupying a lower energy level are the bonding electrons, while those not participating in the bond formation are known as nonbonding electrons. The energy separation between the nonbonding and the lowest of the antibonding orbitals, is the ligand field separation. The introduction of electrons into the antibonding orbitals has the effect of weakening the bonding orbitals.

The crystal field theory revived from the early work of Van Vleck (7) deals with the electrostatic interaction of the ligand ions with the central ion and the consequent effect of the field on the energy of metal d-orbitals. This theory has been extended by Schlapp and Penny (8) to include neutral polar ligand which are covalently bonded to the central metal atom and consequently is now called the ligand field theory. Orgel (9,10) has worked it out to interpret certain aspects of the transition metal chemistry. It considers the influence of the electrostatic fields due to the ligand, on the five d-orbitals of a transition metal atom. If a ligand possessing an electrostatic field approaches a metal ion or atom, the energies of the degenerate d-orbitals (in ligand field free state) become distinguishable, and the orbitals lying in the directions of the ligand acquire a higher energy. The strength of the electrostatic field of the ligand is influenced mainly by two factors, viz., the charge density of the cental metal ion and the nature of the ligand itself. If the approaching ligand has a weak electrostatic field, then the splitting of the orbital degeneracy is small, and if the field is a strong one, then the splitting is large. So that when a transition metal is introduced into the field of octahedral symmetry, the electrons preferentially fill up the lower energy level first. The ligand field theory has been found to be more valuable for describing metal-ligand interaction and has been very helpful particularly in explaining the magnetic susceptibility and the visible absorption spectra of the metal complexes particularly of the transition metals of the first long period.

The importance of metal chelates

Metal chelates are of tremendous practical importance in addition to the theoretical interest associated with them. The application of metal chelates is manifold in various chemical, biological and technical fields. It finds use in practically all spheres of human activity.

The metals which are essential for plant and animal nutrition, are known to form chelates in the organism (11). Chlorophyll, the green pigment, practically omnipresent in plants, contains two closely related coloured substances, both of which are magnesium chelates. Hemin, the red colouring matter of the blood is an iron chelate (12). In the functioning of enzymes the vitally important intermediate compounds are known to consist of chelate compounds. The use of metal ion buffer is also of very great biological importance. The concentration of free metal ion in the system is maintained at a fairly constant level in a required range, in the presence of suitable chelating agent.

An important use of chelating agents is in water softening. Ion-exchange resins have been developed based on the coordination phenomena, which yield deionized water, with a purity almost equivalent to distilled water. The formation of metal lakes in mordanting is well known in the textile industry. Coordination and chelation also play an important role in the electrodeposition of metals and in leather industry.

Chelating agents which form water soluble chelates are called sequestering agents and are used in aqueous solution for the removal of objectionable metal ions. Chelating agents such as EDTA have been known to be used to speed up the elimination of harmful radioactive metal from the body.

Chelates in chemical analysis

A new use of chelating agent has been suggested by Schwarzenbach (13) for the direct determination of metals in solution. He found that a number of chelating agents change colour according to the metal ion concentration, which make direct metal titrations possible.

There are numerous uses of metal chelates in the chemical laboratory, both in qualitative and quantitative analysis. The different organic compounds show specific reactions with inorganic ions, resulting in the formation of a coloured precipitate or lake, due to the formation of chelate compounds and are used in the identification of ions even on the micro scale and forms the basis of 'spot methods' (14) for their identification.

Chelating agents, having specific reactivity with several ions, leading to the formation of sufficiently insoluble inner complex compounds, are used in gravimetric procedures as precipitating agents. The formation of the coloured chelates by metals with various chelating agents has received considerable attention in recent years. It forms the basis of colorimetric analysis by the measurement of intensity of colour of the solution. The procedure involving the measurement of intensity of the colour is termed as photometric method of determination. Almost all metals can be determined colorimetrically with organic reagents and Sandell has estimated that in case of at least three fourths of the metals, organic reagents are superior to inorganic reagents because of their selectivity or sensitivity.

The advent of excellent and relatively cheap spectrophotometers has not only given a great impetus to the methodology and technique of photometric determination, but also has extended the scope of colorimetric analysis by enabling the analyst to work in the entire range of the specturm from ultraviolet to infra red.

The formation of metal chelates involves the replacement of hydrogen ions by a metal ion from the acid form of a chelating agent (15). The conventional type of organic acids, particularly those containing the carboxylic group, however have a limited application in analytical chemistry. Of greater interest are the organic acids or compounds containing groups other than carboxyl and capable of releasing hydrogen ions, in solution, on subsequent replacement by metallic ions. Some organic compounds, not ordinarily considered as acids, yield small amounts of hydrogen ions due to keto enol isomerism when the equilibria are disturbed by the introduction of certain metallic ions that form stable chelates or complexes. The most common acidic group in organic compounds is the hydroxyl group (- OH) group. It does not ordinarily split off hydrogen ions, but it does so, frequently, on interaction with a metal ion to yield stable chelates or complexes through the coordination of phenolic oxygen (16). It is interesting to note that generally ligands have considerably lower reactivities when complexed, then when in their free state (17). A number of typical nonmetallic elements of group V, VI and VII are nitrogen, phosphorous, sulphur, oxygen and fluorine which also behave as suitable electron donors in chelate or complex formation.

The value of a reagent for its use as a satisfactory colorimetric reagent lies in its specificity and selectivity. Such reagents are difficult to be found. The value of a reagent may however be enhanced enormously by masking and unmasking agents. Masking agents can greatly increase the selectivity of reagents. Organic compounds which have received most attention as masking agents are aminocarboxylic acids. EDTA and other carboxylic acids ~~which~~ form stable, water soluble complexes with the alkaline earth elements and even to some extent with alkali metals. Because of high stability and water solubility of their complexes, these reagents are excellent for masking metal ions. Most obvious example of unmasking, is precipitation by pH adjustment (18). An interesting example to illustrate this phenomena is the demasking of zinc with formaldehyde from the cyanide solution of zinc and nickel.

In general, a reagent may be considered to be useful for spectrophotometric determination of the chelates if some of the requirements, listed below, are also met with, besides specificity:

(i) high sensitivity,
(ii) water solubility,
(iii) reproducibility, and
(iv) availability of other reagents.

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CHAPTER II

METHODS OF DISCERNING METAL CHELATE FORMATION IN SOLUTION

CHAPTER II

METHODS OF INVESTIGATION

In general, any property of a system which is related to the concentration of one of the species (hydrogen ion, metal ion, ligand or the chelate) involved in the formation of the chelate may be used to determine the formation of the complex. Some of the techniques which have been used for such studies are, absorption by ion-exchange (1,2,3), pH measurements (4), polarography (5,6), opticochemical methods (7,8), solubility (9), reaction kinetics (10), and electrical conductance (11). Among the numerous other methods oxidation reduction potentials, electrophoresis, isotopic metal or ligand exchange, liquid-liquid partition, dielectric polarization measurements, magnetic susceptibility, heat of mixing, volume changes, molar refraction, ultrasonic absorption, ultra-centrifugation, dialysis and light scattering are useful in specialised situations.

Absorptiometric measurements

The formation of a characteristic colour, is one of the important and distinguishing features of chelate compounds. Ley (11) used absorption spectra to distinguish between free metal ion and their chelates. The colour of the chelate compound is generally accepted, as being very significant, and the intensification of colours usually considered an indication that a chelate may have been formed.

Absorption of light has been extensively employed in recent years, for the study of coloured complexes in solution, mostly employing the spectrophotometric methods, where it is possible to employ an almost monochromatic light of a narrow band width. This fact is of great importance, since the Beer's Lambert law holds good only for the monochromatic radiations, where

$$E = \log(I_0/I) = \epsilon cd \qquad (2.1)$$

where E — Absorbance of the solution

I_0 — Intensity of the incident beam

I — Intensity of the transmitted beam

c — Concentration of the coloured substance in moles/liter

d — Depth of the solution traversed by light

ϵ — A constant, extinction coefficient, whose value for specialised units depends upon the solvent, the temperature as well as on the wavelength.

In cases of mixtures, the absorbance will be the sum of the absorbances due to each constituent.

Discerning composition of metal chelates

Numerous procedures are known which employ absorption measurements for the calculation of the composition of the complexes. A brief account of some of the better known methods may be profitably discussed.

Method of continuous variation

A useful and convenient method to determine the composition of the coloured chelates, in solution, has been the method of continuous variation, as introduced by Job (12). Although the principles of this method were worked out by Ostromisslensky (13) in 1910 and by Denison (14) in 1912, yet the credit of invention of the method is generally ascribed to Job. The method involves the use of an additive molecular property as a guide. Let us suppose that a complex is formed by the mixture of two solutions in the same solvent of two simple constituents A and B. Mixtures of these solutions in variable proportions are prepared in such a way that the total volume remains constant and the variation of the physical property (say absorbance) of the mixture in terms of the composition is studied. Frequently it so happens that the particular property chosen, becomes maximum or minimum, for a mixture of a particular composition. In such cases one is naturally led to admit that this particular composition where the property attains the maximum or minimum value, is the index of the formation of the complex, whose composition, must correspond to this maximum composition. Job chose molecular extinction coefficient as the property to be studied, in his studies and emphasized that the method is applicable to such systems where only one complex is formed. This then is method of continuous variation.

Vosburgh and Cooper (15) modified Job's method of continuous variation to study the composition, in cases, where more than one complex is formed, by conducting studies at several wavelengths. A more general treatment applicable in such cases is given by Katzin and Gebret (16). More recently Klausen (17) has described a method for determination of stability constants of complexes, in solution, based on the method of continuous variation and on computer calculated values of the maximum concentration for different total molar concentrations. This method can be used to differentiate between monomeric and dimeric complexes.

The method of continuous variation has been very popular for the studies of the composition of the complexes and inspite of the criticism of the method by a large number of workers (18,19,20,21,22,23) ~~and~~ it is agreed by all concerned that the results are reliable when absorbance measurements are used as the property.

Mole-ratio method

In the mole-ratio method of Yoe and Jones (24), a series of solutions of mixtures is prepared containing a constant amount of the metal ion to that of the reagent. The curve of absorbance plotted against the concentration ratio rises linearly from the origin when both the reactants are colourless and breaks sharply to a horizontal straight line at the molar ratio of the component in the complex. However, a complex that undergoes appreciable dissociation in solution gives a continuous curve, which only becomes approximately parallel to the molar ratio axis when an excess of the variable component is added. This method is more useful for very stable complexes.

Slope-ratio method

In the slope-ratio method of Harvey and Manning (25), to find out the composition of the complex, the stoichiometry is arrived at by comparing the slopes of the two straight line plots of the absorbance of the solutions obtained by varying the concentration of the first one and then the other component, in the presence of large excess of the second component. This method is applicable only if the system conforms to Beer's law and is more useful for the study of less stable complexes.

Other methods

Numerous other methods based on absorptiometric measurements have been employed for the study of the complexes. Molland (26) has worked out a method which is applicable in cases involving more than one central ion in the reaction. The method of proportional absorbances developed by Budesinsky (27) in recent years, is applicable for establishing the existence of binuclear complexes formed in solution. Method of Frank and Oswalt is effective in identification of 1:1 complexes. Logarithmic method (28,29) and the method of isobestic points (30) have also been applied in many cases. Methods applied for the investigation of the stepwise formation of complexes include those of Bjerrum (31), Newman and Hume (32), Janssen (33), Yatsimirskii (34) and Nickless and Anderson (35).

The method of continuous variation, is by far, the simplest and most trustworthy of the methods, particularly, if optical data is used as the guiding property, and has therefore been extensively used as one of the methods of investigation.

DETERMINATION OF STABILITY CONSTANT

The evaluation of stability constant is useful for understanding the characteristics of a chelate (or a complex). The quantitative measurements of the tendency towards formation of a complex species in aqueous solution is represented by the formation (stability) constant, the magnitude of which gives a quantitative measure of the relative stability of various complexes.

In general, a complex may be defined as a species formed by the association of two or more simpler species, each capable of independent existence. If two species M and L coexist in solution, they may interact to form one or more complexes of general formula M_mL_n. Although M, L and M_mL_n are usually solvated, it is customary not to take the solvent into account. This is justified because the reactants are present in low concentration and the concentration (activity) of the medium (usually water) remains constant throughout the series of measurements. Many examples of the existence of polynuclear complexes have been reported, but it has been found that only mononuclear complexes are formed in a large majority of systems.

Most mononuclear complexes formed in aqueous solution belong to one of the following two main types:

(1) Brönsted acids, in which hydrogen ions act as ligands and are associated with a neutral or anionic central group. These species can be represented as LH_y.

(2) Metal complexes, including ion pairs, which usually consist of one or more neutral or anionic ligands coordinated to a central metal ion (ML_n).

The formation of a mononuclear complex ML_n can be represented as:

$$M + L \rightleftharpoons ML \qquad {}^{T}K_1 = \frac{\{ML\}}{\{M\}\{L\}} \qquad (2.2)$$

$$ML + L \rightleftharpoons ML_2 \qquad {}^{T}K_2 = \frac{\{ML_2\}}{\{ML\}\{L\}} \qquad (2.3)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots \qquad \cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots \qquad \cdots\cdots\cdots\cdots\cdots\cdots$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad {}^{T}K_n = \frac{\{ML_n\}}{\{ML_{n-1}\}\{L\}} \qquad (2.4)$$

$$M + nL \rightleftharpoons ML_n \qquad {}^{T}\beta_n = \frac{\{ML_n\}}{\{M\}\{L\}^n} \qquad (2.5)$$

where the quantities $\{ML_n\}$, $\{M\}$, and $\{L\}$ represent the activity of the complex, metal ion and the ligand respectively, $^TK_1$, ..., ^TK_n are the successive stepwise stability constants (stepwise activity quotients) and $^T\beta_n$, is the activity quotient, overall stability constant or the thermodynamic equilibrium constant. n represents the number of the ligand species which combine per metal ion. From the equations (2.4) and (2.5):

$$\{M\ L_n\} = {}^T\beta_n\ \{M\}\{L\}^n = {}^TK_n\{M\ L_{n-1}\}\{L\}$$

Thus, $^T\beta_0 = {}^TK_0 = 1$ and $^T\beta_1 = {}^TK_1$

The overall and stepwise stability constants are related by the expression:

$$^T\beta_n = {}^TK_1 \cdot {}^TK_2 \cdot {}^TK_3 \cdots {}^TK_{n-1} \cdot {}^TK_n = \sum_0^n {}^TK_n \qquad (2.6)$$

In the above description, the equilibrium constants have been expressed in terms of activity coefficients, which depend only on the nature of the reactants and the products. But it is convenient to determine the concentration of the reacting species and the resulting complex, rather than their activities. It is possible to keep the activity coefficient, γ, of each species constant throughout a series of measurements by the use of a medium with constant ionic strength(36). In such cases, the concentration of the complex $\{ML_n\}$ and the reactants may be expressed in terms of the corresponding concentration quotients, and the stoichiometric stability constant can then be expressed as:

$$K_n = \frac{[M\ L_n]}{[M\ L_{n-1}][L]} = \frac{\{M\ L_n\}}{\{M\ L_{n-1}\}\{L\}} \cdot \frac{\gamma_{M\ L_{n-1}}\gamma_L}{\gamma_{M\ L_n}}$$

(in which concentration = activity/activity coefficient, i.e.γ)

or $$K_n = {}^{T}K_n \cdot \frac{\gamma_{ML_{n-1}}\ \gamma_L}{\gamma_{ML_n}} \qquad (2.7)$$

and similarly,

$$\beta_n = \frac{[M\ L_n]}{[M][L]} = {}^{T}\beta_n \frac{\gamma_M\ \ \gamma_L}{\gamma_{M\ L_n}} \qquad (2.8)$$

where square brackets indicate equilibrium concentration, K_n represents stepwise stoichiometric stability constants and β_n is the overall stoichiometric stability constant. γ_{ML_n}, γ_M, γ_L are the activity coefficients of the complex, metal ion and the ligand respectively.

The above described stoichiometric stability constants can be calculated by knowing the concentration of the complex, free ligand and the metal ion present in the system with the help of various methods available. In fact, the stoichiometric stability constants are the thermodynamic constants which are valid for particular ionic strength of the solution.

The thermodynamic stability constants (${}^{T}\beta_n$, ${}^{T}K_n$, etc.) which are more important from the thermodynamic and the structural point of view, can further be calculated by substituting the appropriate values of the activity coefficients, which are seldom available in the equations (2.7) and (2.8). Preliminary values of the activity quotient may also be calculated using approximate activity coefficients and then extrapolating to zero ionic strength to give a more reliable value (37,38).

In another method, a series of values of stoichiometric stability constants, corresponding to the different ionic strengths may be extrapolated to zero ionic strength either by graphical method (39,40) or by the least squares treatment using Debye-Huckel type relation (41,42).

The values of the thermodynamic stability constants obtained by extrapolation to infinite dilution are more reliable than the values calculated from the measurements at a single ionic strength, for they are less dependent on the choice of the parameters in equations for activity coefficients. However, unless measurements are made in very dilute solutions, the extrapolation method cannot give thermodynamic constants which are entirely independent of assumptions about activity coefficient (43). Until more information about activity coefficients, both for single and mixed electrolytes is available, values of thermodynamic stability constants should, therefore, be treated with caution. However, it is always convenient to determine the stoichiometric stability constants at a definite ionic strength which serves for most of the purposes of the stability constants (44). Rossotti and Rossotti (45) have expressed this idea very aptly by saying that, "It is better to obtain reliable values of the stoichiometric constant, than less certain values of the thermodynamic constant, which are useful for practical purposes".

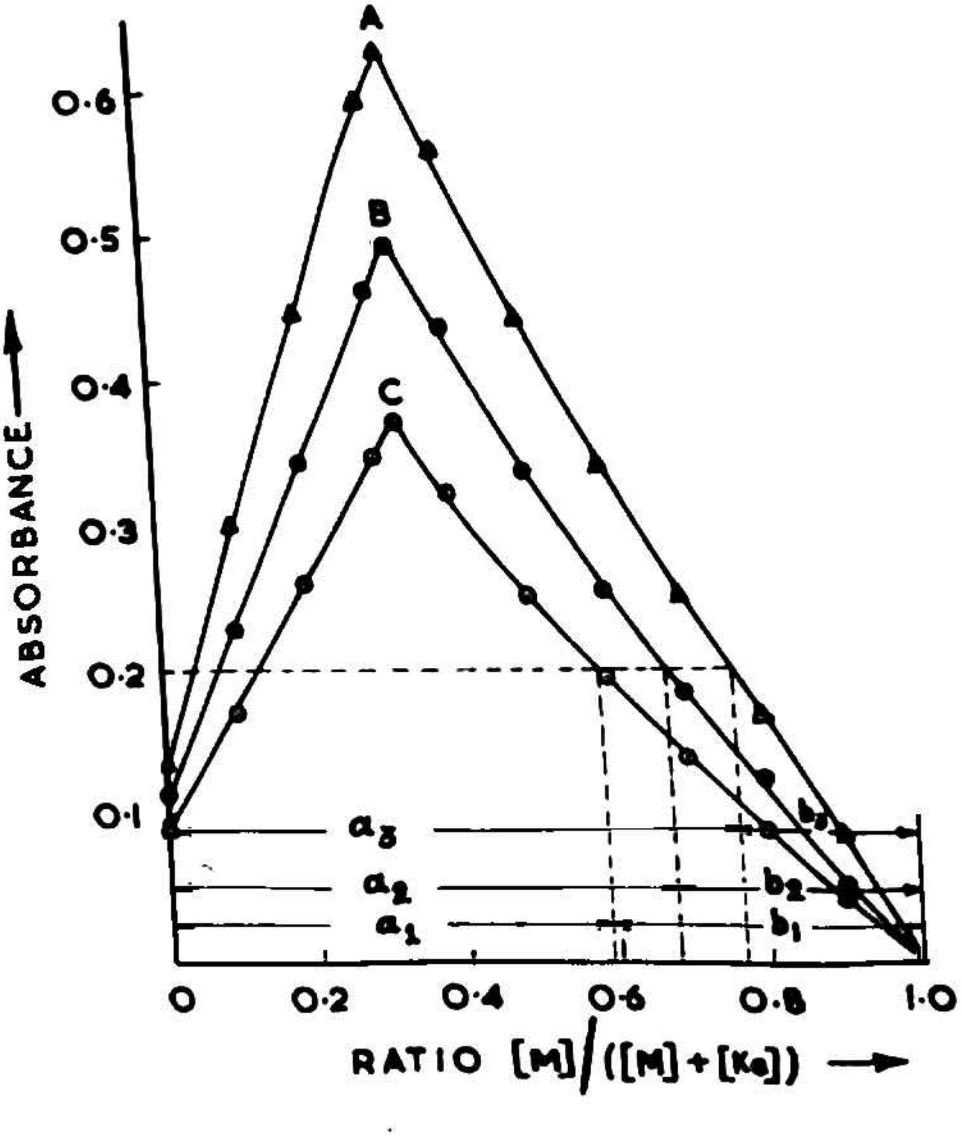
A critical description of the various methods used for determination of stability constants have been provided in various publications of Rossotti and Rossotti (45), Martell and Calvin (46), Chaberek (47), M.M. Jones (48) and Yatsimirskii (49).

Although several methods based on absorptiometric measurements are available for the determination of stability constants, yet, in the following account, the various methods, used in this work, for calculating the stability constant are briefly described:

1. Banerji and Dey method

Among the procedures adopted for the determination of stability of coloured complexes, a convenient method is that described by Anderson and coworkers (50,51) which is based on the comparison of the composition of mixtures having identity of colours, i.e., the same absorbance values. Anderson and coworkers (51,51b) have concluded as a result of comparative study of various methods of determination of the formation constants, that their method yields more reproducible results. The method however, suffers from a limitation that both the interacting solutions forming the complex should be colourless. Banerji and Dey (52) modified the method to calculate the stability of complexes, in solution, where one of the reactants may be coloured. This method has been found to be useful and applicable under a wider variety of conditions.

P·I·F·I



CALCULATION OF STABILITY CONSTANTS BY BANERJI AND DEY METHOD.

The results obtained from the method of continuous variation, using equi-molecular solutions, was adopted and the absorbance of mixtures of varying composition, at a fixed wavelength was measured. In a graph, the observed absorbance (and not the difference in absorbance) is plotted against $[M]/[M]+[Ke]$, where $[M]$ is the concentration of the metal ion and $[Ke]$ that of the chelating agent. A graph, as shown in the P.1.F.1, is obtained for a 1:2 type complex.

Usually, the metal ions are colourless at the wavelength used for the studies. Hence, in the procedure adopted, with the progressive increase of $[M]$, $[Ke]$ decreases and it may reasonably be assumed that in the descending portions of the curves, where $[M]$ is in large excess as compared to $[Ke]$, most of the chelating agent is bound up in the complex. Therefore, in these portions of curves, the absorbance due to free chelating agent is negligible and does not contribute to the absorbance of the system. The observed absorbance, therefore, is due to the colour of the complex alone, when the measurements are being made at or near the region of maximum absorption of the chelate. It would therefore be reasonable to assume that in curves A, B and C, where the absorbance is the same (say 0.200), the respective amounts of the complex formed in each case are identical.

In a complex forming reaction of the type:

$$nM + nKe \rightleftharpoons M_m Ke_n$$

the formation constant K is given by:

$$K = \frac{x}{(a-x)\ (b-nx)^n} \qquad (2.9)$$

where 'x' is the concentration of the complex at equilibrium, and 'a' and 'b' are the initial concentration of the metal ion and the chelating agent.

Where m = n = 1, the formation constant K is given by:

$$K = \frac{x}{(a-x)\ (b-x)}$$

Taking two concentration a_1, a_2 and b_1, b_2 of the reactants giving the same absorbance of the mixture, that is, the same value of 'x', we have

$$K = \frac{x}{(a_1-x)\ (b_1-x)} = \frac{x}{(a_2-x)\ (b_2-x)}$$

$$\text{or} \qquad x = \frac{a_1b_1 - a_2b_2}{(a_1+b_1) - (a_2+b_2)} \qquad (2.10)$$

In a system where m = 1 and n = 2, the formation constant K is given by:

$$K = \frac{x}{(a-x)\ (b-2x)^2}$$

Taking two mixtures having the identical absorbance as in the previous case, we have,

$$K = \frac{x}{(a_1-x)\ (b_1-2x)^2} = \frac{x}{(a_2-x)\ (b_2-2x)^2}$$

or

$$x = \frac{-\left[\text{[illegible]} - b_1^2 + \text{[illegible]}\right] \pm \sqrt{\begin{array}{l}\left[\text{[illegible]} - b_1^2 + \text{[illegible]}\right]^2 \\ -\left[\text{[illegible]}\left\{(a_1 + b_1) - (a_2 + b_2)\right\} \\ \left(\text{[illegible]}\right)\right]\end{array}}}{\text{[illegible]}\left\{(a_1 + b_1) - (a_2 + b_2)\right\}} \qquad (2.11)$$

Thus, from a knowledge of two initial concentrations of a and b, the value of x can be calculated and the value of K can be obtained by substitution.

2. Job's method (using non-equimolecular solutions)

In this method, the volume of the metal ion is plotted against the Δ - absorbance and the stability constants are obtained from the expressions given below:

$$K = \frac{\left(n - (n+1)x\right)\,(p-1)^{n}}{c^{n}\,p^{n-1}\left[(p+n)x - n\right]^{n+1}} \qquad (2.12)$$

Thus for 1:1 complex,

$$K = \frac{(1-2x)\ (p-1)}{c\left[(p+1)x-1\right]^{2}}$$

and for 1:2 complex,

$$K = \frac{(2-3x)\ (p-1)^{2}}{c^{2}\,p\left[(p+2)x-2\right]^{3}}$$

where c = concentration of the metal ion

$$p = \text{A ratio} = \frac{\text{chelating agent concentration}}{\text{metal ion concentration}}$$

$$x = \left[\frac{\text{Total volume} - \text{Peak volume}}{\text{Total volume}}\right] \text{ of metal ion} \qquad (2.12b)$$

3. Mole-ratio method

The stability of the complex can also be calculated from the mole-ratio curve, through a calculation of the degree of dissociation, as proposed by Harvey and Manning (24). α - the degree of dissociation is given by the equation:

$$\alpha = \frac{(E_m - E_s)}{E_m} \qquad (2.13)$$

where E_m is the absorbance of the undissociated complex (in presence of excess of chelating agent) and E_s is the absorbance of the dissociated complex (at equilibrium).

After calculating the value of α, K is determined from the equation given below:

$$K = \frac{1 - \alpha}{n^n . \ \alpha^{n+1} . c^n} \qquad (2.14)$$

where c is the concentration of the complex.

Thus for 1:1 complex; $K = (1-\alpha)/\alpha^2 c$ and

for 1:2 complex; $K = (1-\alpha)/4\alpha^3 c^2$.

4. Molecular extinction coefficient method

The molecular extinction coefficient, a specific extinction coefficient for a concentration of one gram mole of the complex per liter and a path length of one cm is expressed as:

$$\epsilon = D/c.t = D/c \text{ (when } t = 1 \text{ cm)} \qquad (2.15)$$

(a) whether a substance will precipitate out from solution, and if so, to what extent? Will other substances separate under the same conditions? If so, can we change conditions by using complexing agents or controlling the acidity of the solution to obtain a selective separation? (b) What are the characteristics of reaction that are of practical use in methods of determination? (c) What is the nature and extent of any side reaction ? (d) What are the criteria for selection of suitable indicators for titrimetry?

Similarly, in trying to interpret the physical, chemical or biological properties of a metal chelate system (in solution), it is essential to know the stability constants, because each species that is present makes a significant contribution to these properties.

The stability constants of metal chelates are related to thermodynamic properties such as free energy change (ΔF^o), heat-content or enthalpy change (ΔH) and entropy change (ΔS) of the system. A knowledge of these properties is important for getting a complete idea of the reaction and provides information regarding the nature of the bonding between the metal and the ligand.

The change in free energy of formation of the complex can be calculated from the relation:

$$\Delta F^o = \Delta G^o = -RT\ln K \qquad (2.16)$$

where ΔF^o or ΔG^o is the change in free energy of formation, R is the gas constant, T, the absolute temperature at which the work had been carried out and K, the formation constant.

The equation $\Delta F = -RT\ln K$ is known as Van't Hoff Isotherm. Differentiating equation (2.16), with respect to temperature, we get,

$$\frac{d}{dt}(\Delta F^{o}) = -R\ln K - RT\frac{d}{dt}\ln .$$

Upon multiplying throughout by T and substituting ΔF^{o} for $-RT\ln K$, it is seen that,

$$T\frac{d}{dt}(\Delta F^{o}) = \Delta F^{o} - RT^{2}\frac{d}{dt}\ln K \qquad (2.17)$$

Gibbs-Helmholtz equation for the special case in which the substances are all in their standard states, is

$$T\frac{d}{dt}(\Delta F^{o}) = \Delta F^{o} - \Delta H^{o} \qquad (2.18)$$

Combination of equation (2.17) with equation (2.18) gives

$$\frac{d}{dt}\ln K = \frac{\Delta H^{o}}{RT^{2}}$$

$$\frac{d}{dt}\ln K = \frac{\Delta H}{RT^{2}} \quad \text{(because } \Delta H^{o} \text{ can be easily replaced by } \Delta H\text{)} \qquad (2.19)$$

Equation (2.19) is popularly known as Van't Hoff Isochore or Van't Hoff equation.

For applying this isochore to any particular reaction, it is essential to integrate it. If ΔH remains constant over a range of experimental temperatures (say 20°C - 50°C), we can have on integration,

$$\ln K = \int \frac{\Delta H}{RT^2} dt = \frac{-\Delta H}{RT} + \text{a constant}$$

If we integrate the above expression between two temperature T_1 and T_2 at which the equilibrium constants are K_1 and K_2 respectively, we have

$$\ln K_2 - \ln K_1 = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or
$$\frac{\ln K_2}{\ln K_1} = \frac{\Delta H}{R} (T_1 - T_2)/T_2T_1$$

or
$$\log K_2 - \log K_1 = \frac{-\Delta H}{2.303\ R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Thus knowing the equilibrium constant at different temperatures, by plotting log K against 1/absolute temperature, it is possible to calculate ΔH of the reaction by using the following equation:

$$\Delta H = \frac{2.303\ R\ (\log K_2 - \log K_1)\ T_1T_2}{T_2 - T_1} \qquad (2.20)$$

From the knowledge of enthalpy change, the entropy change of the reaction can further be calculated from the relationship:

$$\Delta F^o = \Delta G^o = \Delta H - T\Delta S \qquad (2.21)$$

IONIZATION CONSTANTS

Ionization constant refers to constants which are used to measure the strength of acids and bases. They reveal the proportions of the different ionic species into which a substance gets divided at any chosen pH. This kind of information is useful in many ways. For example, different ionic species have different absorbances. The different ionic species of a given substance differ in physical properties and in some cases chemical and biological properties as well (53). Ionization constants, by defining the pH range in which a substance is least ionized, indicate the conditions under which it can be isolated with a maximum yield and this has a great value in preparative chemistry. They are often used to help diagnose the structure of newly isolated substances and can help to confirm the identity of two substances which cannot be differentiated by melting point determinations.

Conductometry is probably the oldest method used for the determination of the ionization constant, and is especially useful for very weak acids. with a little care, the method is capable of yielding excellent results.

A more convenient method for the determination of ionization constants is by using potentiometry. However, spectrophotometry is particularly suitable for sparingly soluble substances and also for work at very high and very low pH values, which are beyond the range of the glass electrode. It can however be used only for substances which absorb ultraviolet or visible light and the relevant ionic species must show absorption maxima at different wavelengths.

Whereas the potentiometric method of determination of the ionization constant, measures the hydrogen ions not bound by the unknown species, the spectrophotometric method measures the spectral shift produced when the unknown species bind the hydrogen ions. Raman spectra and nuclear magnetic resonance permit the determination of the ionization constants of such strong acids as nitric acid and tri-fluoro-acetic acid (54).

Another method consists in the determination of increase in aqueous solubility of unknown species at different pH (55). Although the method cannot claim the accuracy of earlier ones, it is useful in cases where a substance is [1] too insoluble in water for potentiometric and conductometric determination or [2] has no useful ultraviolet spectra.

Substituent groups can change the electron density on an acidic group by polar interactions. Many authors have attempted to divide polar interactions into inductive effects, displacement of electrons along the molecular chain or ring at direct or electrostatic field effects which occur, at least in part, through the solvent (56-61). The distinction is however a fruitless one, because there is no way to estimate one type of interaction independently of the other. Commonly these changes in acid strengths are treated by considering them as arising from the polar effect, resonance effect, hydrogen bonding and steric hindrance. Often more than one of these considerations play a significant role in determining the acid strength of a molecule and it is difficult to find examples which illustrate just one of them. The effects of substituents can also be treated by a "linear free energy" relationship. The most generally used form of this expression is the modified Hammet equation

$$pK_a = \rho \sigma \qquad (2.22)$$

where the substitution constant σ measures the ability of the substituent to either withdraw electrons from the ring or donate them by induction and resonance. It depends primarily on the position of the substitution because resonance is more important at the para position than at the meta position. It is assumed to be independent of temperature and the solvent. ρ is the reaction constant which is the same for all substituents but depends on the solvent, the temperature and nature of the acid group.

The Hammet equation is a land mark in the development of physical organic chemistry. With it, one can store and correlate a large quantity of equilibrium. The sign and magnitude of ρ have proved useful in characterising the nature of reactions and in speculating their mechanism.

Most of the ligands, which are used for forming the metal chelates, may be regarded as complexes containing hydrogen or hydroxyl ions. A knowledge of their dissociation constants is necessary for calculating the stability constants.

Acid dissociation constants, K^a, are equilibrium constants for reactions of the type:

$$LH_N \rightleftharpoons LH_{N-1} + H^+ \qquad (2.23)$$

Since the acid dissociation constant of the fully saturated proton complex, LH_n, is usually designated by the subscripts 1,2,3, etc.

$$K_1^a = \frac{[LH_{N-1}][H^+]}{[LH_N]} = \frac{1}{K_N^H}$$

where K_N^H is the Nth stepwise acid association (formation) constant.

Similarly for the next dissociation step,

$$K_2^a = \frac{[LH_{N-2}][H^+]}{[LH_{N-1}]} = \frac{1}{K_{N-1}^H}$$

and in general

$$K_{N+1-n}^a = \frac{[LH_{n-1}][H^+]}{[LH_n]} = \frac{1}{K_n^H} \qquad (2.24)$$

The values of acid dissociation constants are generally quoted in terms of pK^a values which are related to the dissociation or the association constant as follows:

$$pK_{N+1-n}^a = -\log K_{N+1-n}^a = \log K_n^H \qquad (2.25)$$

DETERMINATION OF THERMODYNAMIC IONIZATION CONSTANTS

The method of J. Philip (62) has been employed for the spectrophotometric determination of thermodynamic ionization constants of the ligands used in our work.

First of all, the spectra of fully protonated form (in 0.1N HCl), the partially protonated form (in a buffer solution - say of pH 5.5) and completely unprotonated form (in 0.1N-NaOH) of the ligand is recorded over a wide range of wavelength. If a significant difference in the absorbance between the different ionic species, is observed, one can proceed with the determination of the ionization constants.

The approximate ranges are then determined in which pK values of the ligand may lie, applying half equivalence point method. Then buffers of various pHs in those ranges and of known ionic strengths are prepared.

Subsequently the absorbance of a definite concentration of ligand is measured at a number of wavelengths (where peaks are recorded in the absorption spectra) in:

A. for determining pKNH

(1) in 0.1N HCl

(2) in buffers covering the pK value range

and (3) in buffer of 5.5 in which entire spectra has already been recorded.

B. for determining pKOH

(1) in buffer of 5.5, in which entire spectra had been recorded

(2) in buffers, covering the pK value range

and (3) in 0.1N NaOH

The value of pK can then be determined by applying the equation (62)

$$pK_c = pH + \log \frac{b-x}{x-a} \qquad (2.26)$$

where pH is that of the buffer, in which, absorbance x of the ligand has been measured (as obtained in step 2), a and b are absorbances of the same concentration of the compound in acidic and basic solutions.

Further the thermodynamic ionization constant (pK_a) can be then obtained by applying the expression:

$$pK_a = pK_c + \frac{I^{1/2}}{1 + I^{1/2}} \qquad (2.27)$$

where I is the ionic strength of the buffer, in which absorbance x of the ligand is measured.

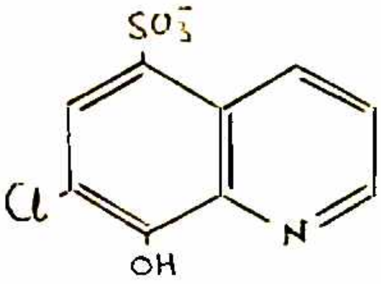
PART A

SPECTROPHOTOMETRIC INVESTIGATIONS

The introduction of 8-hydroxyquinoline for use as a reagent for the analysis of metal ions by Berg and Hahn (63) opened a new field in analytical chemistry. The ability of 8-hydroxyquinoline to form metal chelates is due to the peri position of phenolic hydroxyl group to the hetero atom nitrogen, forming of grouping N-C-C-O which can give rise to the formation of a five membered chelate ring, which is one of the more stable ring structures.

The selectivity of organic reagents is invariably related to the presence of certain salt forming groups and the coordinating atoms. A better understanding of the coordinating groups in -hydroxyquinoline and its analogues, will offer great help in carrying out systematic work towards a greater applicability and selectivity of these reagents. By condensation and substitution reactions, certain groups can be introduced into the molecule of this compound so as to modify their complex forming properties.

The present study is concerned with the determination of thermodynamic dissociation constants and stability constants of the chelates of, substituted 8-hydroxyquinolines, having the following structures:



(1) 7-chloro-8-hydroxyquinoline-5-sulphonic acid

(2) 7-bromo-8-hydroxyquinoline-5-sulphonic acid

Some of the aims of the work presented here in the realm of spectrophotometric investigations are:

(1) To study the composition of the metal chelates

(2) To determine the stability constants of the metal chelates

(3) To study the effective pH range for the stable existence of these chelates

(4) To find out the usefulness of these chelating agents for the spectrophotometric estimation of metals

(5) To find out the interferences in various foreign ions and their tolerance limit in the estimation of these metals

(6) To determine the thermodynamic ionization constants of these chelating agents

(7) To determine the thermodynamic functions as free energy of formation, enthalpy change and entropy change of the metal chelates formed

(8) To find out the effect of halogen substitution in the aromatic ring on the thermodynamic ionization constants of these chelating agents

(9) To find out the correlation between the thermodynamic ionization constant of the ligand and the stability constant, free energy of formation, enthalpy change and entropy change of its metal chelates.

(10) To study the variation of stability constant and the thermodynamic functions of the chelate with the properties of the metal like electronegativity and ionization potential

The ligands chosen for the studies have been prepared by the method used by Tiao-Hsu Chang et al (64).

EXPERIMENTAL DETAILS

In order to avoid duplication, a brief review is being made here of the details of the experimental methods adopted in these investigations, which are common to all the systems studied.

Instruments

All absorbance measurements were made with a Hilger Uvispek Spectrophotometer (Model H 700-380) using one cm matched quartz cell, equipped with thermoplates to stabilize the temperature of the cell holder. pH was measured on a Beckman pH meter (Model H2), with a glass-calomel electrode system. The individual solution and all other mixtures were kept in a Townson and Mercer precision thermostatic bath maintaining a constant temperature. The solutions were kept for about an hour to attain equilibrium, before absorbance measurements were made.

Materials

All the chemicals used throughout this work were of analytical and reagent grade purity. Double distilled water was used for making the solutions. The working solutions were prepared by appropriate dilution of the stock solution, with double distilled water.

The hydroxyquinoline derivatives were tested for their purity by usual methods.

Optimum conditions of study

The optimum conditions of study were worked out first, in order to ensure reproducible results.

Effect of pH

Measurements were made at a fixed pH (by employing suitable buffers) to avoid any error due to pH variations.

Effect of time

The complex formation was found to be instantaneous in most cases and the absorbance attained constancy within a short time (maximum an hour). It was also found that there was no significant change in absorbance values, even after [illegible] hours.

Effect of temperature

Temperature change had little effect on the absorbance of the complex, when the ligand is present in excess.

Order of addition of reagents

The order of addition of reagents did not have any effect on the absorbance of the chelates. However the ligand was taken first in all the cases and then the metal ion was added to it.

Nature of the complex species formed

The method of Vosburgh and Cooper (15) was used to ascertain that only one complex is formed in each case under the specified conditions. Several mixtures containing metal and ligand in ratios, 1:1, 1:2, 1:3 and 1:4 were prepared and then the absorbances were measured at different wavelengths. By the number of shifts in the λmax from the λ_{max} of the reagent itself, the number of complexes formed was ascertained.

Composition of the chelate

The empirical formula of the chelate, in solution, was determined by the following methods, using absorbance measurements:

(1) Continuous variation method
(2) Mole-ratio method, and
(3) Slope-ratio method

It was considered desirable to use several independent methods for establishing the composition because, to avoid arriving at, misleading results, which may occur by using only one method. It has been found that all different methods reported in this thesis give results which are in good agreement with each other, in almost all the cases. In case of continuous variation method, the results have been confirmed using both - equimolecular and non-equimolecular solutions.

Evaluation of stability constants

The apparent stability constants were determined by the methods already outlined, viz.,

(1) Method of Banerji and Dey
(2) Job's method, using non-equimolecular solutions (in some cases)
(3) Mole-ratio method, and,
(4) Molecular extinction coefficient method.

Evaluation of thermodynamic functions

The free energy of formation, enthalpy change and the entropy change, during the formation of a complex can be calculated by applying equations (2.16), [illegible] and [illegible].

Analytical applications

After the composition of the chelate has been determined, in order to study the analytical applications of the chelate, the following factors are looked into:

The effect of reagent concentration

The effect of the reagent concentration is studied with solutions containing a given amount of metal and varying amounts of a solution of the ligand. The pH values of the solutions are kept constant and the absorbance is measured at the λ max (using the same concentration of the reagent at that pH as blank). The number of moles of the ligand per mole of the metal ion are plotted against the absorbance and the moles of the reagent required for complexing a unit mole of the metal ion is thereby known. The same can also be found out from the mole-ratio curves, when the given amount of the metal is mixed with a varying amount of the ligand.

Beer's law and effective photometric range

The range of concentration for adherance to Beer's law, (in ppm) is determined by plotting a graph between absorbance of various mixtures, and the amount of metal ion (in ppm).

The effective photometric range is found by plotting the Ringbom plot, between the percentage transmittance and the ppm of the metal ion and noting the range in which the curve records a steep rise.

Sensitivity

The sensitivities of the colour reactions is also determined as defined by Sandell (65) in $\mu g/cm^2$ based on an absorbance of 0.001 unit.

Molecular extinction coefficient

The molecular extinction coefficient is calculated for each of the systems investigated.

Effect of diverse ions

The effect of diverse ions is examined in a solution containing a known amount of metal ion and diverse ion. The pH is adjusted to the required value. The tolerance limit is calculated in each case. The tolerance limit is defined as the concentration of the foreign ions which affects the absorbance of the system by less than ±3 per cent. Wherever possible, an attempt should be made to make use of masking agents for elimination of foreign ions.

Reproducibility and percentage error

The reproducibility and accuracy of the method is studied by analyzing solutions containing known amounts of the metal ion in ppm. To aliquot quantities of the metal ion solution, taken in 25 cc flask, excess of the reagent is added; the volume in each is made to 25 cc after adjustment of the pH. From the results obtained, the percentage error can easily be calculated.

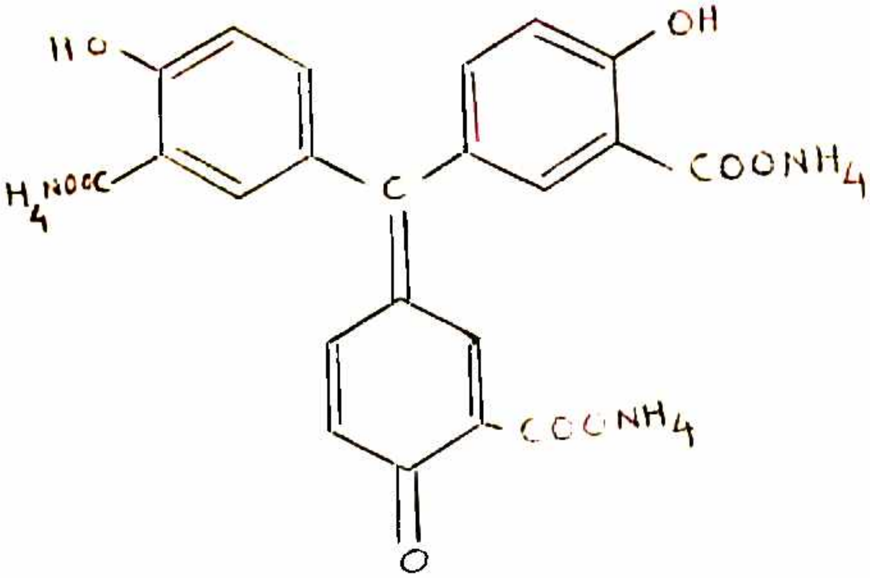
Thus the metal ion in the given alloys or ores, can easily be calculated.

PART B

POTENTIOMETRIC STUDIES

One of the important classes of organic dyes, which stand out prominently for their varied applications, is the hydroxytriphenylmethane group of dyes. Besides their use in dyeing, printing and chrome-mordanting, their other applications are manifold. A number of them possess the interesting property of forming coloured products with inorganic ions and this has largely been used in the field of inorganic analysis. The coloured metal chelates may be soluble or insoluble depending upon the concentrations, as well as on the nature of the metal ion. The colour reaction is specific or selective in many cases, and the dyes have found applications as metallochromic indicators in chelometric titrations, as spot reagents, and as colorimetric reagents for the detection and determination of microquantities of inorganic ions.

Aurintricarboxylic acid (triammonium salt) is an important dye of this group (Fig. 1)



Hammet and Sottery (66) in 1925, reported the formation of a red coloured compound between aluminium and ammoniumaurintricarboxylate (usually abbreviated as AAC), and on account of this reaction, the compound thought to be specific for aluminium, came to be known as aluminon. Mukherji and Dey (67) noted the colour reactions of various metals with aluminon. These authors further (68) found from electrical conductance studies that the reagent behaved as a colloidal electrolyte, and they suggested that physico-chemical measurements should preferably be carried out in extremely dilute solutions, when it behaves as a true solution.

Aluminon forms a number of chelates with several metal ions, and considerable work has been reported on the spectrophotometric investigations of these compounds.

It was thought profitable to determine the stepwise protonation constants of AAC and formation constants of its chelates with some of the di-, tri, and tetrapositive metal chelates, potentiometrically.

The most widely used and probably the most reliable method for the determination of stability constants of metal complexes is the potentiometric measurement of hydrogen ion concentration. This is based on the fact that pH of a solution is directly affected by complex formation, since most complexing agents are also acids (or bases) and the formation of the complex is accompanied by the displacement of a proton (decrease in pH) from the acidic ligand, or by a decrease in concentration of the base. The increased acidity is a result of competitive binding tendencies of the two Lewis acids (electron acceptors), viz., hydrogen and metal ions, for a Lewis base, i.e., the ligand. The magnitude of the observed pH change (or alkali needed to neutralise this pH change) is related to the metal-ligand binding tendency and may be used to determine the stability constants of various complexes formed in the system. The method was developed, mainly by Bjerrum (4), Calvin and Wilson (69), Fronaeus (70), Schwarzenback (71,72) and Irving and Rossotti (73). Bjerrum (4) introduced a function $\bar{n}$, which is defined as the average number of ligand molecules bound per metal ion, which is generally determined from the data obtained from the pH titration of the system containing known concentration of the metal and the ligand.

The $\bar{n}$ values and the corresponding negative log values of free ligand concentration (pL) at various pH values are calculated and then graphically plotted. From the values of $\bar{n}$ and pL, the values of the stability constants can be obtained by the methods such as curve fitting method (74), Bjerrum's spreading factor method, half - $\bar{n}$ method and mid-point method (4), Scwarzenbach's graphical method (75), Irving and Rossotti's correction term method, method of successive approximation, method of solution of simultaneous equations, interpolation at various $\bar{n}$ values method and ~~of~~ least square method (76).

In the present studies, we have employed the Bjerrum-Calvin pH-titration technique as described by Irving and Rossotti (45,73).

Titrations are carried out in aqueous media and sufficient ($HClO_4$ + $NaClO_4$) is added to give a definite overall ionic strength. The titrant is NaOH, which is used as primary standard.

A large number of titrations should be carried out maintaining different ionic strengths, employing different ligand concentration:metal ion concentration ratios, using different molar concentrations of ($HClO_4$ + $NaClO_4$) medium, and using various molar concentrations of the titrant.

We may assume a case for discussing the procedure, in which, $\mu = 0.02$, $T_L = 2.5 \times 10^{-3}M$, $T_m = 0.5 \times 10^{-3}M$, $E = 0.1M$ and $N = 0.1M$.

It is also assumed that the anion of the ligand (L) reacts with metal ion (M) to form the species ML and ML_2 and with protons (H) to form LH and LH_2. These reactions are represented by two chelate stability and dissociation constants. To determine a chelate stability constant, three titrations are carried out:

(a) Perchloric acid (E = 0.01M) is titrated against sodium hydroxide (N = 0.1M)

(b) Perchloric acid (E = 0.01M) plus ligand (T_L=2.5x10^{-3}M) is titrated against sodium hydroxide (N = 0.1M)

and (c) Perchloric acid (E = 0.1M) plus ligand (T_L=2.5x10^{-3}M) plus metal (T_M=0.5x10^{-3}M) is titrated against sodium hydroxide (N = 0.1M)

The initial volume of the titration solution in each case is kept constant (V_o = 100 mls). Say, volumes v', v'' and v''' of alkali are consumed in titration (a), (b) and (c) respectively to give identical values of pH.

A ligand-proton formation curve is then obtained by plotting the degree of formation ($\bar{n}_A$) (where $\bar{n}_A$ is the average number of protons bound per free ligand molecule) of the ligand-proton complex against pH, using the well-known relationship derived by Irving and Rossotti (76)

$$\bar{n}_A = y + \frac{(v' - v'')}{(V_o + v')} \cdot \frac{(N + E)}{T_L} \qquad (2.28)$$

and y the total number of dissociable protons per ligand added at the beginning of the titration. From this plot the acid dissociation constants of the ligand were obtained. These constants were then used in calculating the stability constants.

A complex ligand formation curve is then obtained by plotting the degree of formation of the complex ($\bar{n}$) (where $\bar{n}$ is the average number of ligands bound per metal ion) against the negative logarithm of the concentration of non-protonated ligand (pL) using the following relationships:

$$\bar{n} = \frac{(v''' - v'')\,[N+E+T_L(y - \bar{n}_A)]}{(V_o + v'')\,\bar{n}_A\,T_M} \qquad (2.29)$$

$$pL = \log_{10}\left\{\frac{(\beta_0^H + \beta_1^H[H] + \beta_2^H[H]^2)}{(T_L - \bar{n}\,T_M)}\left(\frac{V_o + v'''}{V_o}\right)\right\} \qquad (2.30)$$

where $\beta_0^H = 1$, β_1^H and β_2^H are the reciprocal acid dissociation constants of the ligand and are equal to $[LH]/[L][H]$ and $[LH_2]/[L][H]^2$ respectively. The chelate stability constants and acid dissociation constants can be read from the formation curves.

If the formation curves for the proton-ligand system extends between $\bar{n}_A = 0$ to 2, it shows two steps of dissociation and there will be accordingly two step-acid dissociation constants - $\log K_1^H$ and $\log K_2^H$, whose values can be obtained, by applying various computational methods.

We have employed, in the present studies, Bjerrum's half $\bar{n}_A$ method (4), Bjerrum's mid-point method (4) and Irving and Rossotti's (76) interpolation at various $\bar{n}$. values method.

Similarly, if the formation curves for the metal-ligand system is extended between the values of $\bar{n} = 0$ to 2, the existence of two steps in equilibria are indicated. There are two steps - chelate stability constants - $\log K_1$ and $\log K_2$, whose values can be obtained similarly, by using the computational methods mentioned above.

A brief outline of these methods is given as under.

According to Bjerrum's half $\bar{n}$ method,

$$\log K_n = pL_{n-1/2} \tag{2.31}$$

when $n = 1$, $\log K_1 = pL_{1/2}$ and

when $n = 2$, $\log K_2 = pL_{3/2}$

The values of $\log K_1$ and $\log K_2$ (and hence $\log \beta_2$), are obtained by reading the value of pL, corresponding to the points, where $\bar{n} = 0.5$, and 1.5 respectively. This equation is applicable where $K_1/K_2 \gg 10^{2.5}$.

For calculations by the mid-point method, it has been found that at the mid-point of the formation curve, when $\bar{n}=1$,

$$\log K_1 K_2 = 2\, pL_1 \tag{2.32}$$

For a system in which $N = $ [illegible], the following equation holds good

$$D = \frac{4.606}{\text{[illegible]}} \qquad (2.33)$$

Applying equations (2.32) [illegible] (2.33), we can calculate the values of log K_1 and log [illegible].

D in the equation (2.33) is the slope of the formation curve at the point where $\bar{n} = 1$. These equations are applicable only where K_1/K_2 lies between 10^3 and 10^{-2}. This condition has rarely been fulfilled in our studies; hence this method has not been applied frequently for calculating the stability constants.

To calculate log K_1 and log K_2 by Irving and Rossotti's method, use is made of the following relationships:

$$\log K_1 = pL_{1-d} + \log (1-d)/d \qquad (2.34)$$

$$\log K_2 = pL_{1+d} - \log (1-d/d \qquad (2.35)$$

where d is assumed to be equal to 0.1, 0.2, ..., 0.9 and values of log K_1 and log K_2 are accordingly calculated, by taking the average of values so obtained. The use of these equations over the whole range of formation curve ($0 < d < 1$) is justified only if $K_1/K_2 > 10^4$.

Further,

$$\log \beta_1^H = \log K_1^H;\ \log \beta_2^H = \log K_2^H + \log K_1^H \qquad (2.36)$$

and similarly $\log \beta_1 = \log K_1$ and $\log \beta_2 = \log K_1 + \log K_2$ (2.37)

The consumption of an excess of alkali in the chelation titration relative to the simple ligand titration is due to the ligand protons liberated during the complex formation. Despite the tendency of metal ions to hydrolyse in aqueous solutions, such effects have been ignored in this work since the chelates are stable in the pH ranges, in which studies have been carried out.

In some cases, the proton-ligand stability constants of AAC and stepwise stability constants of the complexes have been determined at various ionic strengths and the ionic strength has been adjusted by the addition of $NaClO_4$.

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CHAPTER III

THERMODYNAMIC IONIZATION CONSTANTS AND METAL CHELATES OF 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

Introduction

8-hydroxyquinoline has been a very important reagent in the analysis and estimation of a number of metal ions, since 1926. But it lacks selectivity and such, forms insoluble chelates with at least thirty metal ions. While researches on the use of 8-quinolinol in analytical separations and determinations have not yet been exhausted, the search for new, potentially useful reagents similar to 8-quinolinol but having greater selectivity, is being carried on, with even greater ardour.

The selectivity of organic reagents is invariably related to the presence of certain salt forming groups and the coordinatable atoms. Coordinating groups present in a reagent, affect its selectivity and so do, other atoms or groups present in the molecule. By means of substitution and condensation reactions, certain groups can be introduced into the molecule of these organic reagents, so as to modify their complex forming properties.

In 8-hydroxyquinoline, the phenolic hydroxyl group has a strong ortho-para - directing influence, as a result of which, substitutions in the 5 and 7 positions mostly occur, with the more active electron-seeking reagents substituting in both the positions. Generally, the 5-position is attacked first. Quinoline is reactive at the 2 and 4 position towards nucleophilic reagents. However, substitutions in the 2-position have been more effective. Correspondingly in 8-quinolinol too, substitutions in position 2 have been found very common. A number of substituted 8-quinolinols can often be used to advantage. The presence of the sulphonic acid group makes the reagent soluble in water. Albert and Magrath (1) made some colorimetric tests of 8-quinolinol-5-sulphonic acid with some metal ions and found that it forms soluble chelates with many metal ions and this led many workers to investigate its metal chelates in aqueous medium by various physico-chemical means regarding composition, stability, thermodynamic functions and analytical applications. More recently mixed ligand chelate studies employing this reagent have also been carried out.

Amongst the chloro substituted 8-hydroxyquinolines, considerable interest has been taken, in compounds like, 5-7-dichloro-8-quinolinol, 5-chloro-8-quinolinol, 7-chloro-8-quinolinol, 5-chloro-7-iodo-8-quinolinol, 7-chloro-5-iodo-8-quinolinol, 5-chloro-8-quinolinol-7-sulphonic acid and 7-chloro-8-hydroxyquinoline-5-sulphonic acid. The ability of the chloro substituted 8-quinolinols, to precipitate the metal ions from aqueous solutions have made these compounds very important from the point of view of gravimetric estimations of metal ions and the solubility of these metal chelates so precipitated, in organic solvents led many workers to investigate the utility of these compounds as spectrophotometric reagents.

Considerable interest has been evinced in studying the effect of substituents, on the ionization constants, chelate stability constants and thermodynamic functions of halo derivatives of 8-quinolinol and its sulphonates. Studies have been made on 7-chloro-8-hydroxyquinoline-5-sulphonic acid, which forms a good number of water soluble chelates, regarding (a) its ionization constants (b) composition, stability and molecular structure of its metal chelates (c) thermodynamic functions, associated with the formation of its metal chelates and (d) their use in the analysis of metal ions.

Richard Berg (2), while studying the influence of substituents on the insolubility and stability of metal complexes of 8-hydroxyquinoline derivatives, observed that 7-chloro-8-hydroxyquinoline-5-sulphonic acid in acetone-water solution containing a mineral acid, gave a greenish yellow precipitate with copper (1:200,000) and a greenish black precipitate with ferric salts (1:100,000). Jacob Molland (3) observed the possibility of colorimetric determination of iron with some 8-hydroxyquinoline derivatives, including, 7-chloro-8-hydroxyquinoline-5-sulphonic acid, which produces a dark green colouration with $FeCl_3$. He recommended the use of pthalate and borate buffers for the determination, as they did not influence the colouration. Harry B. Feldman and Arnet L. Powell (4) reported that 8-hydroxyquinoline-5-sulphonic acid and its derivatives displayed properties of indicators. On the basis of calculations of acid and basic dissociation constants, he found 7-chloro-8-hydroxyquinoline-5-sulphonic acid, as the most suitable indicator. Antonio Luis, Palomo Coll and Gabriel Palomo Coll(5), while studying the chemistry of Amebicides, reviewed the method of synthesizing the derivatives by halogenation, by the Skarup synthesis, or by the Gattermann-Sandmeyer synthesis and reported improvement in the procedures. The melting point of 7-chloro-8-hydroxyquinoline-5-sulphonic acid was reported by him to be 300°C. J. Buchi and P. Meier (6) reported the preparation and bacteriological testing of several 8:hydroxy alkoxy quinoline derivatives.

Tiao-Hsu Chang et al (7) prepared some of the derivatives of 8-hydroxyquinoline. They also reported the dissociation constants and chelate stability constants of Cd(II), Pb(II), Zn(II), Co(II) and Ni(II) chelates. The acid dissociation constants were found by NaOH titration at 25°C in 2M-NaCl and chelate stability constants were determined by metal perchlorate titration under the same conditions, using Bjerrum-Calvin plots. The acid dissociation constants of halo-substituted acids were found to be lower, owing to the inductive effect of aromatic halogen, which behaves as an electron attracting group. The order of inductive effect in these halo substituted 8-quinolinol sulphonates was found to be $Cl > I > Br$. The order of stability of the halo-substituted sulphonates was reported as $I > Br > Cl > H$. The order of decreasing stability of metal ions to form metal chelates as found by them was $Ni(II) > Co(II) > Zn(II) > Pb(II) > Cd(II)$. They further observed that the chelates of 8-quinolinol-5-sulphonic acid with metal ions were more stable than those of 8-quinolinol-7-sulphonic acid, while most of the chelates of 7-halo-8-quinolinol-5-sulphonic acid were less stable than those of corresponding 5-halo-8-quinolinol-7-sulphonic acid.

Hans Berge (8) reported the polarographic studies of complex equilibrium in dioxane-water mixtures and determined the stability constants via exchange equilibriums.

As no significant work seems to have been done on the chelates of Copper, Palladium, Uranium, Vanadium, Iron and Gallium, a systematic work was undertaken.

In order to reduce the bulk of the thesis, complete data on only one bipositive and one tripositive metal chelate has been presented along with the graphical representations. The data obtained in the detailed investigation of the other chelates have, however, been represented only graphically.

Preparation of 7-chloro-8-hydroxyquinoline-5-sulphonic acid

The compound has been prepared by the method used by Tiao-Hsu Chang et al (7). To 90 gm of 50% fuming sulphuric acid, 10 gm of 8-hydroxyquinoline was added drop by drop. The mixture after having been allowed to stand over night, was poured into ice-water, when crude precipitate of 8-hydroxyquinoline-5-sulphonic acid immediately separated. The precipitate of 8-hydroxyquinoline-5-sulphonic acid was collected and recrystallised from distilled water, to give pale yellow needles which crystallises with 2 molecules of water.

5 gm of 8-hydroxyquinoline-5-sulphonic acid was dissolved in 150 ml of 10% sodium hydroxide solution. The solution was magnetically stirred while a steady stream of chlorine gas was led through it for two hours. After the reaction was complete,

the solution was acidified. The precipitate was filtered and recrystallised from 500 ml of distilled water. The product, which consisted of yellow needles, containing two molecules of water, could be converted to deep brown anhydrous needles by heating in a drying oven at 120 °C for two hours. The yield was about 60%.

Colour formation with inorganic ions

The colour reactions of the reagent with some of the cations were studied and the results obtained have been recorded in Table 3.01.

Table 3.01: Colour reactions of metal ions with 7-chloro-8-hydroxyquinoline-5-sulphonic acid (CHQS)

Reagent - Light yellow in colour

Sl.No.	Metal	Colouration	Remarks
1	Hg^{2+}	Colour intensified	Sensitive with dilute solutions
2	Cu^{2+}	Slightly bluish coloured tinge developed	Sensitive with dilute solutions
3	UO_2^{2+}	Orange red	Very sensitive with dilute solutions
4	Fe^{3+}	Green	Most sensitive with dilute solutions
5	Cr^{3+}	Colour intensified	Sensitive with dilute solutions
6	Ti^{4+}	Colour intensified	Sensitive with dilute solutions
7	V^{5+}	Dark yellow	Sensitive with dilute solutions

THERMODYNAMIC IONIZATION CONSTANTS OF 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

The thermodynamic ionization constants of 7-chloro-8-hydroxy-quinoline-5-sulphonic acid have been determined in aqueous medium, using spectrophotometric methods, at 25°C.

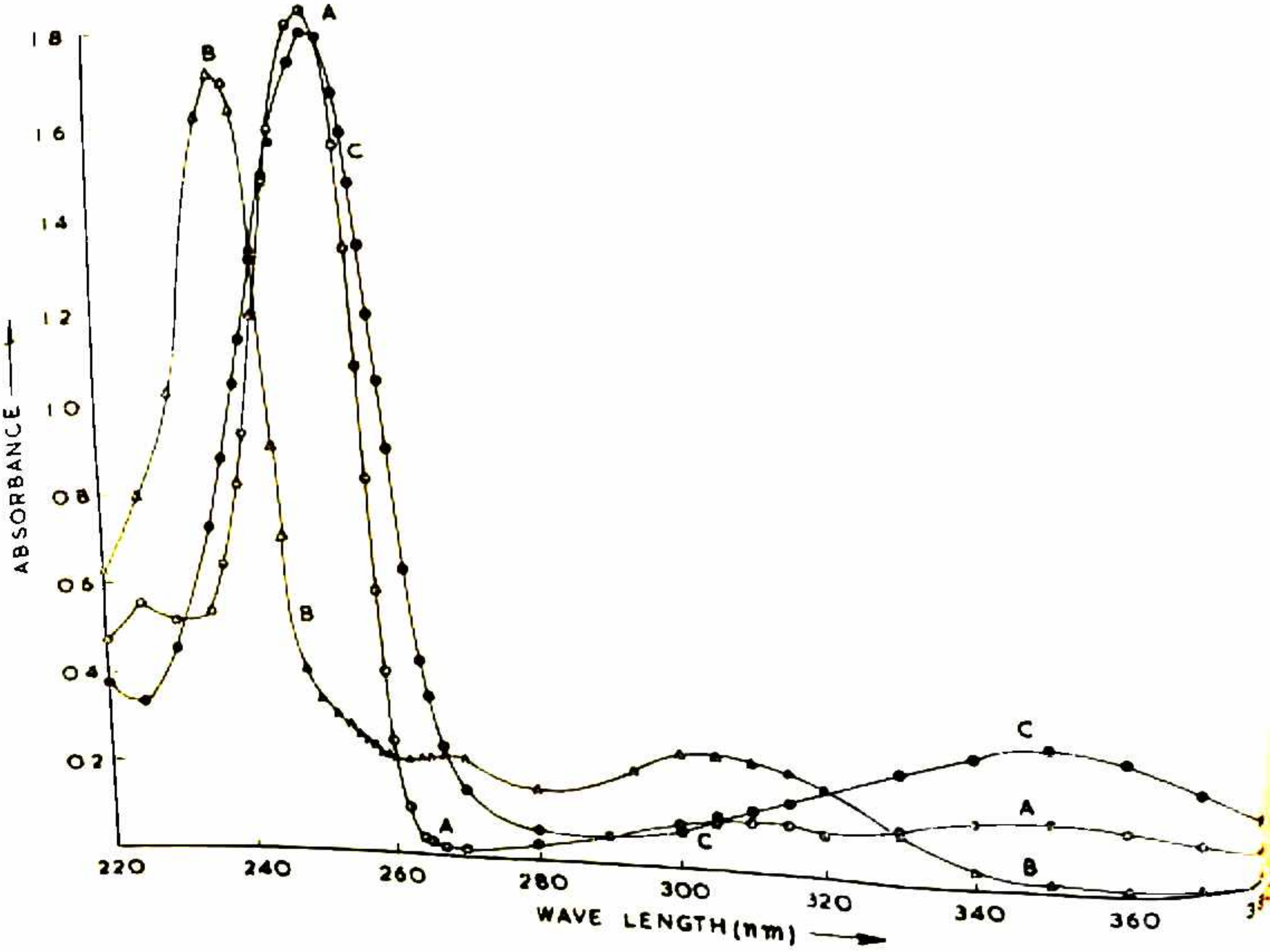
The instruments used for absorbance and pH measurements have been described earlier. 7-chloro-8-hydroxyquinoline-5-sulphonic acid was recrystallised twice from double distilled water and the spectra of the solutions were taken against a blank consisting of the aqueous buffer, acid or alkali used as solvent for the ligand. The other chemicals used were of A.R. quality.

All experiments were performed at 25 ± 0.1°C. The pH of the solutions were adjusted using chloro-acetic acid - KOH buffer, succinic acid - KOH buffer and KH_2PO_4 - Na_2HPO_4 buffer.

Spectral studies of 7-chloro-8-hydroxyquinoline-5-sulphonic acid

The spectra of fully protonated form in 0.1N HCl (Curve A), the partially protonated form in a buffer of pH 5.5 (Curve B) and completely unprotonated form in 0.1N NaOH (Curve C) of CHQS were taken in the range of 220 nm to 380 nm. The results have been presented in Table 3.11 and represented graphically in P.2.F.1.

P·2·F·1



1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
ABSORBANCE
A
B
C
A
B
C
A
C
B
220
240
260
280
300
320
340
360
3
WAVE LENGTH (nm)

Table 3.11: P.2.F.1.

Conc. of CHQS = 6×10^{-5} M

Curve A — CHQS in 0.1N HCl

Curve B — CHQS in buffer of pH 5.5

Curve C — CHQS in 0.1N NaOH

Wavelength (nm)	Absorbance		
	A	B	C
220	0.495	0.704	0.712
225	0.485	0.565	0.416
230	0.505	0.685	0.405
232	-	0.810	-
235	0.547	1.046	0.570
237	-	0.964	0.685
240	0.814	1.375	0.900
242	1.026	-	1.080
244	-	-	1.275
245	1.446	1.105	1.383
247	1.722	0.876	-
250	1.976	0.695	1.812
255	1.950	0.705	1.946
257	1.822	-	-
260	1.202	0.815	1.636
262	0.707	-	1.356
264	-	-	1.020
265	0.260	1.050	0.873
267	0.111	1.168	0.595
270	0.080	1.315	0.320
275	-	1.262	0.134
277	-	1.075	-
280	0.065	0.664	0.076
282	-	0.421	-
285	-	0.215	-
290	0.081	0.138	0.061
300	0.115	0.130	0.087
305	0.134	0.135	0.110
310	0.140	0.135	0.140
315	0.158	0.130	0.160
320	0.143	0.125	0.185
330	0.156	0.091	0.225
340	0.180	0.044	0.259
350	0.181	0.016	0.302
360	0.155	0.018	0.296
370	0.110	0.026	0.238
380	0.064	0.036	0.150

The results indicate the presence of different ionic species of CHQS which correspond to the neutralization reactions:

$$H_2A \rightleftharpoons HA^- + H^+ \qquad K_1 = [H^+][HA^-]/[H_2A]$$

$$HA^- \rightleftharpoons H^+ + A^{-2} \qquad K_2 = [H^+][A^{-2}]/[HA^-]$$

Thermodynamic ionization constants

The ionization constants of CHQS have been obtained, since there is a significant difference in the absorbance between the different ionic species. By measuring the absorbance of the compound in a buffer of known pH, the ionization constant of the compound can be obtained from the following equation (9):

$$pK_c = pH + \log \frac{b-x}{x-a}$$

where pH is that of the buffer and x is the absorbance of the compound in that buffer and a and b are the absorbances of the same concentration of the compound in acidic and basic solutions.

Further the thermodynamic ionization constant can be obtained by the equation :

$$pK_a = pK_c + \frac{I^{1/2}}{1 + I^{1/2}}$$

where I is the ionic strength of the medium in which the absorbance of the compound is measured. The value of 'x' has been determined using different buffers and wavelengths and the pK_{a1} and pK_{a2} obtained for 7-chloro-8-hydroxyquinoline-5-sulphonic acid have been represented in Tables 3.12 to 3.15.

Table 3.12: Conc. of CHQS = 6×10^{-5}M; λ = 250 nm
a = 1.976; b = 0.695; Temp. = 25°C.

Buffer	pH	x	pK_c	pK_a
Chloro-acetic acid - KOH buffer	2.8	1.550	3.1026	3.1935
Chloro-acetic acid - KOH buffer	3.2	1.247	3.0792	3.1701

Table 3.13: Conc. of CHQS = 6×10^{-5}M; λ = 255 nm
a = 1.950; b = 0.705; Temp. = 25°C

Chloro-acetic acid - KOH buffer	3.2	1.285	3.1406	3.2315

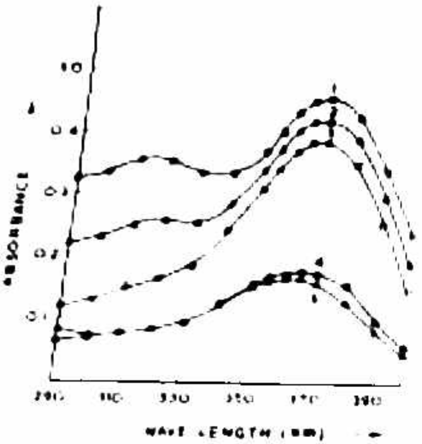
Table 3.14: Conc. CHQS = 6×10^{-5}M; λ = 270 nm
A = 1.315; b = 0.320;

KH_2PO_4 - Na_2HPO_4	7.2	0.825	7.2130	7.3039
KH_2PO_4 - Na_2HPO_4	7.4	0.715	7.2184	7.3093
KH_2PO_4 - Na_2HPO_4	7.6	0.600	7.1929	7.2838

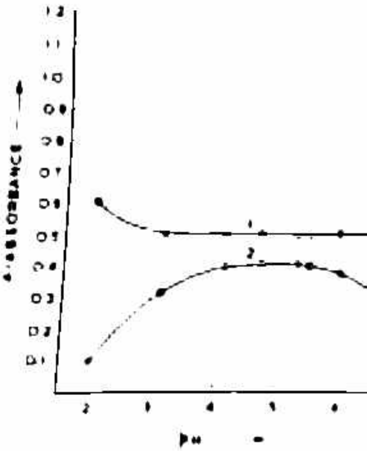
Table 3.15: Conc. of CHQS = 6×10^{-5}; λ = 275 nm
a = 1.262; b = 0.134

KH_2PO_4 - Na_2HPO_4	7.2	0.702	7.2060	7.2969
KH_2PO_4 - Na_2HPO_4	7.4	0.571	7.2010	7.2919
KH_2PO_4 - Na_2HPO_4	7.6	0.450	7.1901	7.2810

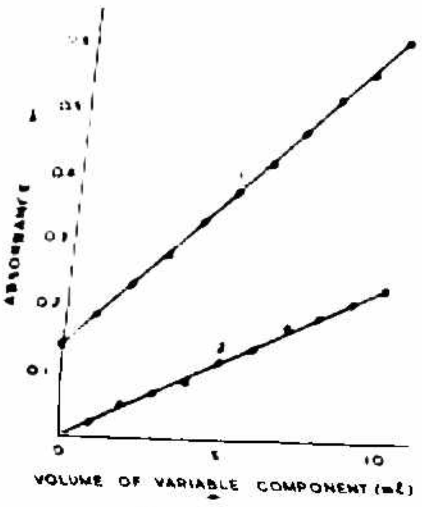
P-3 F-1



P-3 F-2



P-3 F-3



P-3 F-4

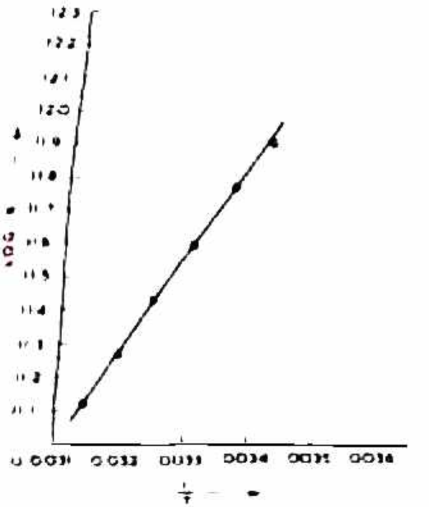
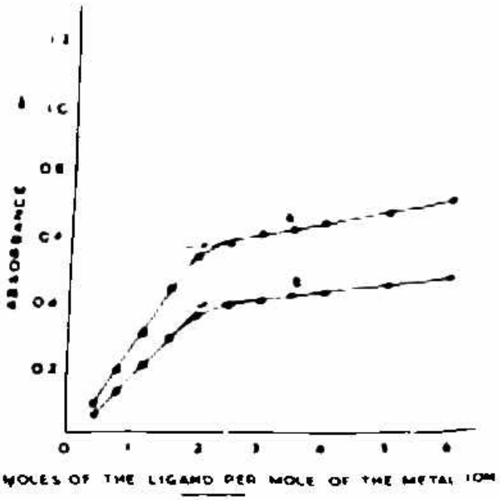
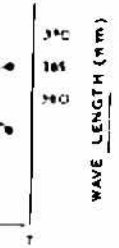
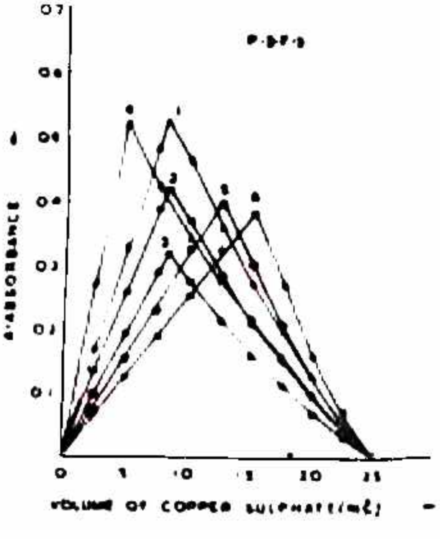


FIG. 4


ABSORBANCE
0.2
0.4
0.6
0.8
1.0
1.2
A
B
0
1
2
3
4
5
6
MOLES OF THE LIGAND PER MOLE OF THE METAL ION


390
365
340
WAVE LENGTH (nm)


A·ABSORBANCE
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
5
10
15
20
25
1
2
3
4
5
6
VOLUME OF COPPER SULPHATE(mL)

COPPER(II)-7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of the complex between bivalent copper and 7-chloro-8-hydroxyquinoline-5-sulphonic acid (abbreviated as CHQS) has been studied in aqueous medium. The chelate is stable in the pH range 3.1 to 6.6. The composition of the chelate, in solution, has been determined by three different methods and it has been found that a stable complex is formed between one mole of copper and two moles of 7-chloro-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by the method of Banerji and Dey, mole-ratio method and the method using molecular extinction coefficient. The effect of temperature on the stability and the thermodynamic functions such as free energy of formation, enthalpy change and entropy change during the chelate formation have also been investigated.

EXPERIMENTAL

A standard solution of copper was prepared from A.R. $CuSO_4 \cdot 5H_2O$ (B.D.H.) and the copper content was estimated. A purified sample of 7-chloro-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of ligand solution in double distilled water. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 20°C. The individual solutions and mixtures were kept in a thermostat maintaining a temperature of 20 ± 0.1°C, for one hour, to attain equilibrium. The pH of the solutions and mixtures was adjusted by the addition of suitable amount of sodium acetate - acetic acid buffer.

Absorption spectra of the complex in solution

To determine the nature of the complex in solution, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of copper and 7-chloro-8-hydroxyquinoline-5-sulphonic acid (CHQS) were prepared. The concentrations employed are recorded in Table 3.21.

Table 3.21:

Mixture	Conc. of Copper	Conc. of CHQS	Ratio
1	4×10^{-5} M	1.6×10^{-4} M	1:4
2	4×10^{-5} M	1.2×10^{-4} M	1:3
3	4×10^{-5} M	8×10^{-5} M	1:2
4	4×10^{-5} M	4×10^{-5} M	1:1
5	1.6×10^{-4} M	4×10^{-5} M	4:1

Absorbance of these mixtures at various wavelengths, from 290 to 400 nm, was measured. The results have been recorded in Table 3.22 and graphically represented in P.3.F.1; which shows that the λ_{max} of all the mixtures are in the spectral region of 365 nm. It is evident therefrom that only one complex is formed under the conditions of study.

Table 3.22

Wavelength (nm.)	Absorbance				
	1	2	3	4	5
290	0.325	0.220	0.121	0.066	0.084
300	0.335	0.231	0.131	0.070	0.076
310	0.355	0.251	0.153	0.080	0.080
320	0.356	0.260	0.165	0.084	0.084
330	0.336	0.256	0.184	0.095	0.095
340	0.335	0.286	0.244	0.125	0.012
350	0.370	0.341	0.311	0.158	0.155
355	0.403	0.374	0.343	0.170	0.165
360	0.432	0.404	0.368	0.175	0.169
365	0.450	0.418	0.385	0.179	0.167
370	0.455	0.420	0.385	0.175	0.160
380	0.424	0.390	0.349	0.158	0.129
390	0.339	0.298	0.255	0.103	0.085
400	0.239	0.193	0.149	0.059	0.049

Effective pH range

Solutions containing the same concentration (1.2×10^{-4} M) of the reagent and copper sulphate were prepared at different pH with dilute H_2SO_4 and NaOH and the ionic strength was maintained at 0.1, with $NaClO_4$. The complex showed λ_{max} at 365 nm in the pH range 3.1 - 6.6; and an almost constant absorbance in the range 4.1 - 5.5. To maintain uniform conditions of study, pH 5.3 was selected for subsequent studies. The results of the studies are recorded in Table 3.23 and graphically represented in P.3.F.2. Curve 1 shows the variation of λ_{max} with pH; whereas Curve 2 shows the variation of Δ - absorbance at 365 nm with pH.

Table 3.23

Wavelength (nm)	pH 2.0 A	pH 2.0 B	pH 2.0 C	pH 3.1 A	pH 3.1 B	pH 3.1 C	pH 4.1 A	pH 4.1 B	pH 4.1 C
350	0.381	0.346	0.035	0.421	0.184	0.237	0.424	0.084	0.340
355	0.393	0.330	0.063	0.454	0.179	0.275	0.460	0.084	0.376
360	0.390	0.298	0.092	0.473	0.173	0.300	0.484	0.089	0.395
365	0.375	0.276	0.099	0.479	0.162	0.317	0.488	0.094	0.394
370	0.349	0.223	0.126	0.464	0.153	0.311	0.475	0.099	0.376

Wavelength (nm)	pH 4.7 A	pH 4.7 B	pH 4.7 C	pH 5.3 A	pH 5.3 B	pH 5.3 C	pH 5.5 A	pH 5.5 B	pH 5.5 C
350	0.425	0.071	0.354	0.426	0.071	0.355	0.426	0.085	0.341
355	0.461	0.074	0.387	0.463	0.074	0.389	0.463	0.084	0.379
360	0.484	0.079	0.405	0.484	0.082	0.402	0.484	0.090	0.394
365	0.490	0.085	0.405	0.490	0.088	0.402	0.490	0.096	0.394
370	0.476	0.092	0.384	0.478	0.096	0.382	0.478	0.103	0.375

Wavelength (nm)	pH 6.0 A	pH 6.0 B	pH 6.0 C	pH 6.6 A	pH 6.6 B	pH 6.6 C
350	0.428	0.105	0.323	0.431	0.204	0.227
355	0.464	0.106	0.358	0.467	0.206	0.261
360	0.488	0.111	0.377	0.492	0.208	0.284
365	0.492	0.115	0.377	0.498	0.200	0.298
370	0.480	0.119	0.361	0.487	0.191	0.296

A, B and C are the absorbance values of the complex, ligand, and the difference in absorbance (A - B) respectively.

Stoichiometry of the components

Three methods were adopted for determination of the empirical formula of the complex in solution.

(1) Job's method

The composition of the complex was determined at 360 nm, 365 nm and 380 nm by Job's method of continuous variation, using both equimolecular and non-equimolecular solutions. Only representative results, obtained in case of studies at 365 nm, have been presented in Tables 3.24 through 3.29 and graphically represented in P.3F.3.

Table 3.24: Concentration of copper sulphate (c) = 2.0×10^{-4}M
Concentration of ligand (CHQS) (c') = 2.0×10^{-4}M
pH = 5.3 ± 0.1, $p = \frac{c'}{c} = 1$, $\lambda = 365$ nm,
$\mu = 0.1$ $NaClO_4$
(P.3.F.3 Curve 1)

Volume of CHQS (ml)	Volume of copper sulphate (ml)	Absorbance of		Difference (a-b)
		Mixture (a)	CHQS (b)	
25.00	0.00	0.136	0.136	0.000
22.50	2.50	0.300	0.128	0.172
20.00	5.00	0.444	0.115	0.329
17.50	7.50	0.589	0.105	0.484
16.67	8.33	0.624	0.100	0.524
15.00	10.00	0.556	0.090	0.466
12.50	12.50	0.440	0.079	0.361
10.00	15.00	0.339	0.064	0.275
7.50	17.50	0.252	0.055	0.197
5.00	20.00	0.170	0.041	0.129
2.50	22.50	0.090	0.031	0.059
0.00	25.00	0.000	0.000	0.000

Table 3.25: Concentration of copper sulphate (c) = 1.6 x 10^{-4}M

Concentration of the ligand (c')= 1.6 x 10^{-4}M

pH = 5.3 ± 0.1, p = c'/c = 1, λ= 365 nm

μ = 0.1 $NaClO_4$

(P.3.F.3 Curve 2)

Volume of CHQS (ml)	Volume of copper sulphate (ml)	Absorbance of Mixture (a)	Absorbance of CHQS (b)	Difference (a-b)
25.00	0.00	0.115	0.115	0.000
22.50	2.50	0.228	0.094	0.134
20.00	5.00	0.342	0.081	0.261
17.50	7.50	0.460	0.070	0.390
16.67	8.33	0.489	0.069	0.420
15.00	10.00	0.434	0.062	0.372
12.50	12.50	0.334	0.050	0.204
10.00	15.00	0.255	0.043	0.212
7.50	17.50	0.185	0.033	0.152
5.00	20.00	0.126	0.026	0.100
2.50	22.50	0.055	0.013	0.042
0.00	25.00	0.000	0.000	0.000

Table 3.26: Concentration of copper sulphate (c) = 1.2 x 10^{-4}M

Concentration of the ligand (c')= 1.2 x 10^{-4}M

pH = 5.3 ± 0.1, p = c'/c = 1, λ = 365 nm

μ = 0.1 $NaClO_4$

(P.3.F.3 Curve 3)

25.00	0.00	0.089	0.089	0.000
22.50	2.50	0.170	0.069	0.101
20.00	5.00	0.257	0.061	0.196
17.50	7.50	0.346	0.054	0.292
16.67	8.33	0.370	0.049	0.321
15.00	10.00	0.321	0.044	0.277
12.50	12.50	0.250	0.036	0.214
10.00	15.00	0.195	0.032	0.163
7.50	17.75	0.139	0.023	0.116
5.00	20.00	0.090	0.021	0.069
2.50	22.50	0.045	0.011	0.034
0.00	25.00	0.000	0.000	0.000

Table 3.27: Concentration of copper sulphate (c) = 3.2×10^{-4}M

Concentration of the ligand (c') = 1.6×10^{-4}M

pH = 5.3 ± 0.1, p = c'/c = 0.5, λ = 365 nm,

μ = 0.1 $NaClO_4$

(I.3.F.3 Curve 4)

Volume of CHQS (ml)	Volume of copper sulphate (ml)	Absorbance of Mixture (a)	Absorbance of CHQS (b)	Difference (a-b)
25.00	0.00	0.115	0.115	0.000
22.50	2.50	0.369	0.094	0.275
20.00	5.00	0.604	0.081	0.523
17.50	7.50	0.494	0.070	0.424
15.00	10.00	0.402	0.057	0.345
12.50	12.50	0.331	0.050	0.281
10.00	15.00	0.260	0.043	0.217
7.50	17.75	0.193	0.032	0.161
5.00	20.00	0.125	0.026	0.099
2.50	22.50	0.060	0.013	0.047
0.00	25.00	0.000	0.000	0.000

Table 3.28: Concentration of copper sulphate (c) = 1×10^{-4}M

Concentration of the ligand (c')= 2×10^{-4}M

pH = 5.3 ± 0.1, p = c'/c = 2.0, λ= 365 nm,

μ = 0.1 $NaClO_4$

(P.3.F.3 Curve 5)

25.00	0.00	0.137	0.137	0.000
22.25	2.25	0.204	0.128	0.076
20.00	5.00	0.270	0.115	0.155
17.50	7.50	0.333	0.103	0.230
15.00	10.00	0.404	0.076	0.328
12.50	12.50	0.464	0.064	0.400
10.00	15.00	0.354	0.050	0.304
7.50	17.50	0.246	0.036	0.200
5.00	20.00	0.160	0.030	0.130
2.50	22.50	0.075	0.016	0.059
0.00	25.00	0.000	0.000	0.000

Table 3.29: Concentration of copper sulphate (c) = 8 x 10^{-5} M
Concentration of the ligand (c') = 2.4 x 10^{-4} M
pH = 5.3 ± 0.1, p = c'/c = 3, λ=365 nm
μ = 0.1 $NaClO_4$
(P.3.F.3 Curve 6)

Volume of CHQS (ml)	Volume of copper sulphate (ml)	Absorbance of		Difference (a-b)
		Mixture (a)	CHQS (b)	
25.00	0.00	0.154	0.154	0.000
22.50	2.50	0.212	0.143	0.069
20.00	5.00	0.256	0.132	0.124
17.50	7.50	0.308	0.120	0.188
15.00	10.00	0.359	0.107	0.252
12.50	12.50	0.405	0.080	0.325
10.00	15.00	0.444	0.060	0.384
7.50	17.50	0.318	0.046	0.272
5.00	20.00	0.194	0.032	0.162
2.50	22.50	0.094	0.020	0.074
0.00	25.00	0.000	0.000	0.000

The peaks are observed at the metal:ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from copper and CHQS in such a way that the mole-ratio of copper to CHQS varied from 1:0.4 to 1:6.0. The absorbance of these mixtures was measured, using water as blank, at 360 nm, 365 nm and 380 nm. Some of the representative results, obtained in case of studies performed at 365 nm, have been presented in Table 3.30 and graphically represented in P.3.F.4.

Table 3.30: Concentration of copper = 6×10^{-5} M $\quad$ 4×10^{-5} M

A $\quad$ B

Temp. = 20°C, $\quad$ pH = 5.3 ± 0.1, $\quad$ Ionic strength = 0.1

Total volume made up to = 25 ml

Ratio Cu : CHTS	Absorbance A	 B
1 : 0.4	0.089	0.055
1 : 0.8	0.191	0.125
1 : 1.2	0.306	0.204
1 : 1.6	0.439	0.291
1 : 2.0	0.540	0.360
1 : 2.5	0.580	0.390
1 : 3.0	0.609	0.405
1 : 3.5	0.625	0.424
1 : 4.0	0.644	0.436
1 : 5.0	0.676	0.454
1 : 6.0	0.709	0.475

The results show a break at a ratio of one mole of the metal to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of variable component was varied from 1 to 10 ml, in presence of excess concentration of the other. The absorbance of the solutions was noted using water as blank, at three wavelengths - 360 nm, 365 nm and 380 nm. The results of the studies at 360 nm only, have been recorded in Table 3.301 and represented in P.3.F.5.

Table 3.301:

Concentration of the constant component - 2.4×10^{-4}M

Concentration of the variable component, varies from

6×10^{-6}M to 6×10^{-5}M

pH = 5.3 ± 0.1; Temp. = 20 ± 0.1°C; Total volume = 25 ml

(P.3.F.5 - Curve 1, metal varying; Curve 2, ligand varying)

Volume of the variable component (ml)	Absorbance	
	1	2
1	0.185	0.021
2	0.231	0.049
3	0.276	0.067
4	0.328	0.084
5	0.373	0.115
6	0.414	0.136
7	0.465	0.170
8	0.516	0.185
9	0.556	0.209
10	0.606	0.231

The slope of the two straight lines, show that the Cu : CHQS is 1 : 2.

Determination of stability constant

The stability constant of the chelate has been determined by three different methods mentioned earlier. For the determination of the stability constant by the method of Dey et al and mole-ratio method, the concentration of the reactants are the same as shown in P.3.F.3 and P.3.F.4.

For the determination of stability constant by mole-ratio method, the values of Em, Es and α are given in Table 3.302.

Table 3.302:

Fig.	Curve	Concentration	Em	Es	α
P.3.F.4	A	6×10^{-5} M	0.57	0.54	0.0527
P.3.F.4	B	4×10^{-5} M	0.39	0.36	0.0769

Molecular extinction coefficient data (Table 3.303) have been used for calculating the stability constant by this method.

Table 3.303:

λ	D	C	ϵ	A	X	K	log K
365 nm	0.334	4×10^{-5} M	8350	0.315	3.772×10^{-5} M	7.956×10^{11}	11.900

The values of log K obtained by these methods have been given in Table 3.304.

Table 3.304:

pH = 5.3 ± 0.1; Ionic strength = 0.1; Temp. = 20°C

Method	Stability constant log K
(1) Mole-ratio method	11.58 ± .08
(2) Method of Dey et al	11.30 ± .08
(3) Molecular extinction coefficient method	11.90

Thermodynamic functions of the complex

The free energy change of complex formation has been calculated, using the equation $\Delta F = -RT \ln K$.

For the purpose of determination of the entropy and enthalpy changes during complex formation, the stability constants were determined at different temperatures (20 - 45°C). From the slope of the curve obtained by plotting log K against 1/T (T is the absolute temperature), the enthalpy change ΔH of the reaction has been calculated by temperature-coefficient method, using the formula $\Delta H = 2.303.R.(\log K_2 - \log K_1). 1/(1/T_1 - 1/T_2)$. Assuming this to be constant over the range of the temperatures employed, the entropy change ΔS of the reaction has been determined using the equation:

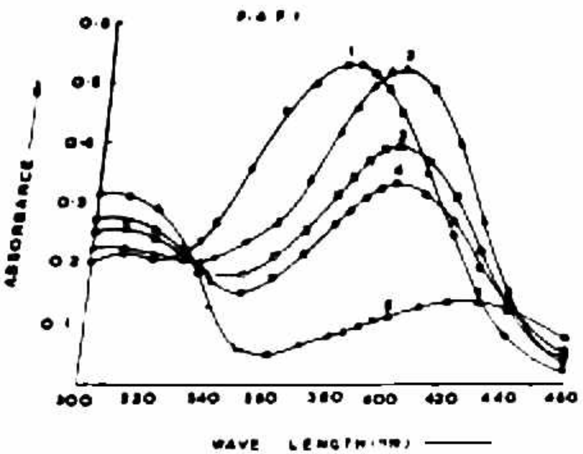
$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

The results obtained have been summarised in Table 3.305.

Table 3.305:

pH = 5.3 ± 0.1 Ionic strength = 0.1

Temperature	20°C	25°C	30°C	35°C	40°C	45°C
log K	11.90	11.77	11.59	11.43	11.27	11.12
ΔF(kcal/mole)	-15.95	-16.04	-16.06	-16.12	-16.14	-16.18
ΔH(kcal/mole)	-14.00	-14.00	-14.00	-14.00	-14.00	-14.00
ΔS(e.u.)	6.65	6.84	6.79	6.87	6.83	6.85


P.A.F.1
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0·2
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340
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380
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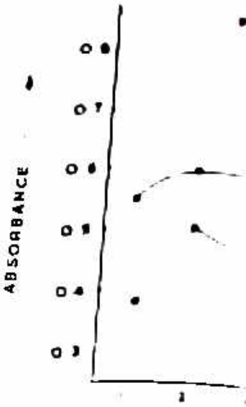
420
440
460
WAVE LENGTH(nm)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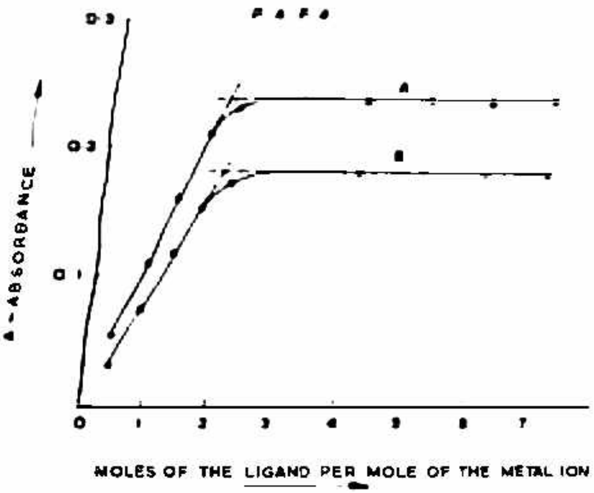
0·6
0·5
0·4
0·3
1


P.A.F.6
A - ABSORBANCE
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0·2
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A
B
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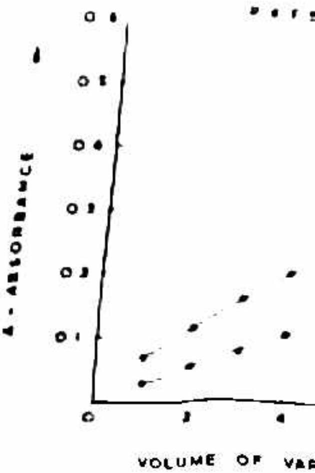
4
5
6
7
MOLES OF THE LIGAND PER MOLE OF THE METAL ION


A - ABSORBANCE
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2
4
VOLUME OF

IG. 2

FIG. 3

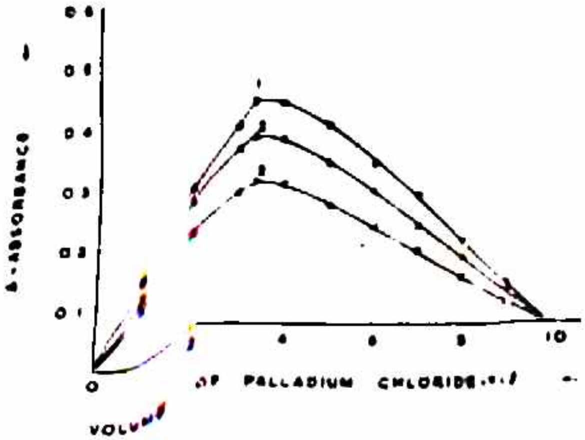
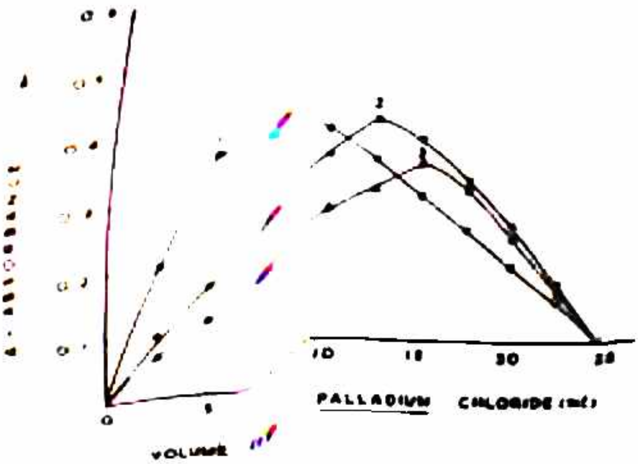


FIG. 4



PALLADIUM(II)- 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The complex formed between palladium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid has been investigated spectrophotometrically. The chelate is stable in the pH range 2 to 7. The composition of the chelate, in solution, has been determined by three different methods and it has been found that a stable complex is formed between one mole of palladium and two moles of 7-chloro-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by the mole-ratio method and the method using molecular extinction coefficient data. The free energy of formation of the complex has also been evaluated

EXPERIMENTAL

A standard solution of palladium was prepared by dissolving palladium chloride (Johnson Matthey & Co. London) in dilute hydrochloric acid, and the palladium content was estimated. A purified sample of 7-chloro-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand in double distilled water. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 30°C. The individual solutions and mixtures were kept in a thermostat maintaining a

temperature of 30 ± 0.1 °C, for one hour to attain equilibrium. Sodium perchlorate was used throughout to maintain a constant ionic strength of 0.1. The pH of the solution and the mixtures was adjusted with sodium acetate - acetic acid buffer.

Absorption spectra of the complex

To determine the nature of the complex formed, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of palladium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid (CHQS) were prepared. The concentrations employed in the studies are recorded in Table 3.31.

Table 3.31

Mixture	Conc. of palladium	Conc. of BHQS	Ratio
1	1.2×10^{-4}M	1.2×10^{-4}M	1:1
2	6.0×10^{-5}M	1.2×10^{-4}M	1:2
3	4.0×10^{-5}M	1.2×10^{-4}M	1:3
4	3.0×10^{-5}M	1.2×10^{-4}M	1:4
5	-	1.2×10^{-4}M	0:1

Absorbance of these mixtures at various wavelengths, from 280 nm to 500 nm was measured. The relevant section of the results has been graphically represented in P.4.F.1. The results show that only one complex is formed under the conditions of study (when the reagent is in excess, the shift due to complexation is suppressed), in the spectral region of 400 nm.

Effective pH range

Solutions containing 1.2×10^{-4}M of the reagent and $6.0 \times$ [illegible] of the metal ion were prepared at different pH and the ionic strength was maintained at 0.1 with $NaClO_4$. The Δ-absorbance of these solutions was noted. The complex showed λ_{max} at 400 nm in the pH range 2 to 7. pH 4.5 was, however, selected for subsequent studies. The results of the studies are graphically represented in P.4.F.2. Curve A shows variation of Δ - absorbance at 395 nm with pH, whereas curve B shows change of λ_{max} with pH.

Stoichiometry of the components

(1) Job's method

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions, has been adopted. The studies were performed at 385 nm and 400 nm, but only representative results of the studies at 385 nm have been graphically represented in P.4.F.3 and P.4.F.6. The concentrations employed and the specific conditions of study are as given in the Table 3.32.

Table 3.32:

pH = 4.5 ± 0.1, Ionic strength = 0.1, Temp. - 30°C, λ = [illegible] nm

Figure	Curve	Conc. of palladium(c)	Conc. of CHQS(c')	p=c'/c
P.4.F.3	1	2.0×10^{-4}M	2.0×10^{-4}M	1
P.4.F.3	2	1.6×10^{-4}M	1.6×10^{-4}M	1
P.4.F.3	3	1.2×10^{-4}M	1.2×10^{-4}M	1
P.4.F.6	1	3.2×10^{-4}M	1.6×10^{-4}M	0.5
P.4.F.6	2	1.2×10^{-4}M	2.4×10^{-4}M	2
P.4.F.6	3	8.0×10^{-5}M	2.4×10^{-4}M	3

The peaks are observed at metal : ligand ratio of 1 : 2.

(2) Mole-ratio method

A series of solutions was prepared from palladium and CHQS in such a way that the mole-ratio of palladium to CHQS varied from 1:0.4 to 1:7.0. The concentrations employed are given in Table 3.33

Table 3.33

Temp.=30°C; pH=4.5 ± 0.1; Ionic strength = 0.1;

Total volume made up to - 25 ml

Concentration of palladium (c)	4×10^{-5}M	3×10^{-5}M
P.4.F.4 Curve	A	B

The Δ - absorbance of these mixtures was measured at 385 nm and 400 nm. But only representative results, obtained from the studies at 385 nm, have been graphically represented in P.4.F.4.

The results show a break at a ratio of one mole of the metal ion to two moles of the reagent, indicating that a 1 : 2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 3.34.

Table 3.34:

pH – 4.5 ± 0.1, Temp. – $30 \pm 0.1^{\circ}$C, Total volume = 25 ml

λ = 385 nm

Concentration of the constant component = 2.4×10^{-4}M

Concentration of the variable component varies from 6×10^{-6}M to 6×10^{-5}M

Figure	Line	Remarks
P.4.F.5	1	Metal varying
P.4.F.5	2	ligand varying

The slope of the two straight lines, provides the Pd:CHQS ratio as 1:2.

Determination of stability constant

The stability constant of palladium (II) - 7-chloro-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by different methods, detailed earlier. For the determination of stability constant by the mole-ratio method, the concentration of the reactants are same as shown in Table 3.33 (graphically represented by F.4.F.4), the values of Em, Es and α are given in Table 3.35.

Table 3.35.

Figure	Curve	Concentration	Em	Es	α
F.4.F.4	A	4×10^{-5} M	0.237	0.230	0.0295
F.4.F.4	B	3×10^{-5} M	0.180	0.172	0.0400

Molecular extinction coefficient data (Table 3.36) have been used for calculating the stability constant by this method.

Table 3.36:

λ	D	C	ϵ	A	x	K	log K
385 nm	0.261	4×10^{-5}M	6525	0.247	3.7854×10^{-5}	9.521×10^{11}	11.9787

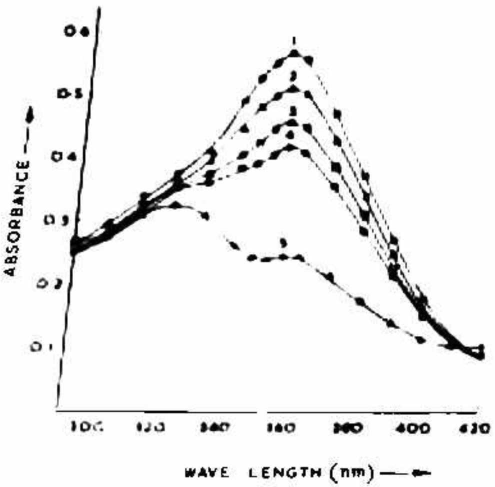
The values of log K obtained by these methods have been given in Table 3.37.

Table 3.37

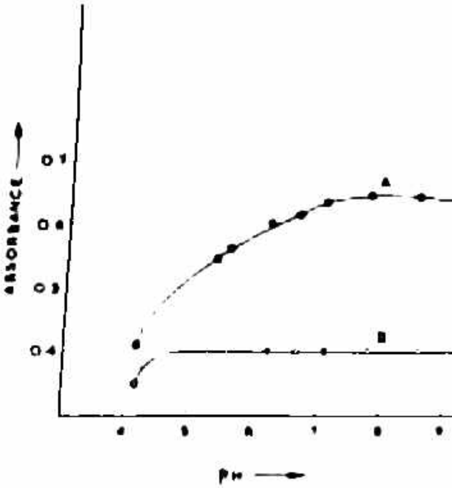
Method	Stability constant log K log K
(1) Mole-ratio method	12.695 ± 0.075
(2) Molecular extinction coefficient method	11.979

Mean: log K = 1[illegible] ± 0.[illegible]; ΔF = -16.665 ± [illegible] Kcals/mole

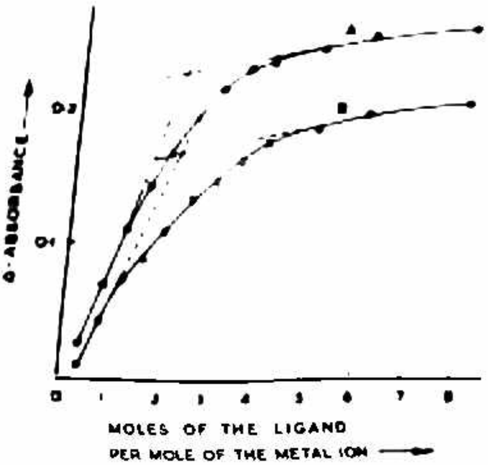
PSF 1



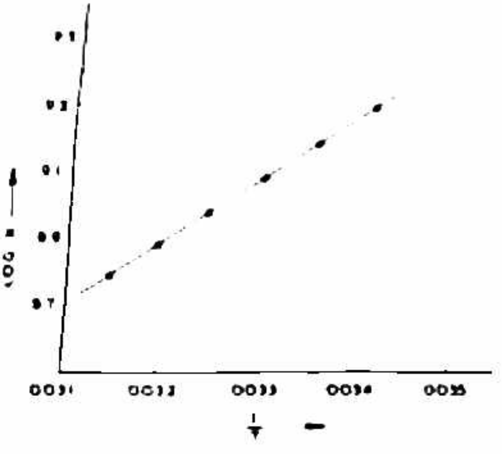
PSF 2

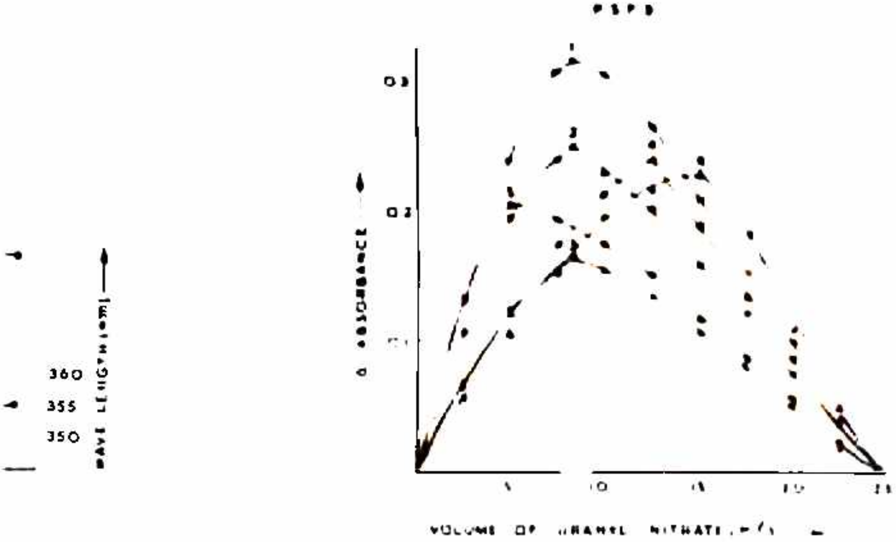


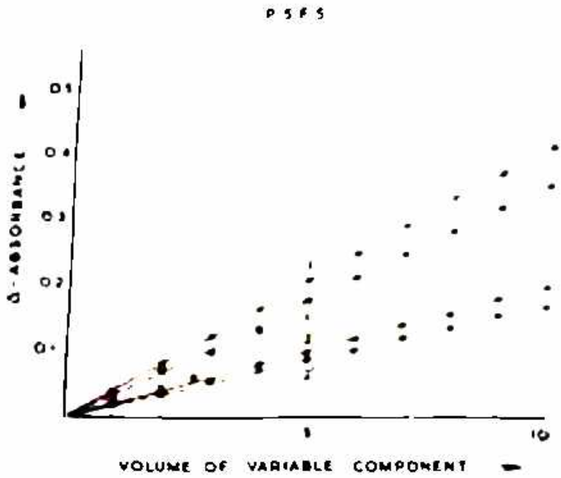
PSF 4



PSF 6




PSFS
0.3
0.2
0.1
Δ-ABSORBANCE
5
10
15
20
25
VOLUME OF URANYL NITRATE (ml)
360
355
350
WAVE LENGTH (mμ)


PSFS
0.5
0.4
0.3
0.2
0.1
Δ-ABSORBANCE
5
10
VOLUME OF VARIABLE COMPONENT

URANYL-7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of the orange red complex between uranium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid has been studied in the aqueous medium. The chelate is stable in the pH range 5.4 to 9.3. The composition of the chelate, in solution, has been determined by three different methods and it has been found that a stable complex is formed between one mole of uranium and two moles of 7-chloro-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by the method of Banerji and Dey, mole-ratio method and the method using molecular extinction coefficient. The effect of temperature on the stability and the thermodynamic functions such as free energy of formation, enthalpy change and entropy change during the chelate formation have also been investigated.

Experimental

A standard solution of uranium was prepared by dissolving Uranyl nitrate (B.D.H.) in double distilled water. A purified sample of 7-chloro-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand solution in double distilled water. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 30°C. The individual solutions and mixtures were kept in a thermostat maintaining a

temperature of 30 ± 0.1°C, for one hour to attain equilibrium. The pH of the solutions and mixtures was adjusted by the addition of ammonium acetate buffer.

Absorption spectra of the complex in solution

To determine the nature of the complex in solution, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of uranium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid (CHQS) were prepared. The concentrations employe and the conditions of studies are recorded in Table 3.41.

Table 3.41:

μ = 0.1; Temp. = 30°C; pH = 6.6 ± 0.1

Mixture	Conc. of uranium	Conc. of CHQS	Ratio
1	1.2×10^{-4}M	1.2×10^{-4}M	1:1
2	6×10^{-5}M	1.2×10^{-4}M	1:2
3	4×10^{-5}M	1.2×10^{-4}M	1:3
4	3×10^{-5}M	1.2×10^{-4}M	1:4
5	-	1.2×10^{-4}M	0:1

Absorbance of these mixtures at various wavelengths, from 290 nm to 500 nm, was measured. Some of the representative results have been graphically represented in P.5.F.1. The results show that only one complex is formed under the conditions of study, in the spectral region of 355 nm.

Effective pH range

Solutions containing the same concentration (1.2×10^{-4} M) of the reagent and uranyl nitrate were prepared at different pH with the help of dilute HCl and NaOH and the ionic strength at 0.1 with $NaClO_4$. The absorbance of these solutions was noted. The complex showed λ_{max} at 355 nm in the pH range 5.4 - 9.3.

pH 6.6 was selected for these studies. The results of the studies are as graphically represented in P.5.F.2. Curve A shows variation of absorbance, at 355 nm, with pH and the Curve B represents the change in λ_{max} with change in pH.

Stoichiometry of the components

Three methods were adopted for the determination of the empirical formula of the complex in solution.

(1) Job's method

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions, has been adopted.

The concentrations employed and the specific conditions of study are given in Table 3.42.

Table 3.42: pH = 6.6±0.1; Ionic strength = 0.1, Temp.=30°C, λ=355 nm

Figure	Curve	Concentration of uranium (c)	Conc. of CHQS(c')	p = c'/c
P.5.F.3	1	2.0×10^{-4}M	2.0×10^{-4}M	1.0
P.5.F3	2	1.6×10^{-4}M	1.6×10^{-4}M	1.0
P.5.F.3	3	1.2×10^{-4}M	1.2×10^{-4}M	1.0
P.5.F.3	4	1.0×10^{-4}M	2.0×10^{-4}M	2.0
P.5.F.3	5	8.0×10^{-5}M	2.4×10^{-4}M	3.0
P.5.F.3	6	2.4×10^{-4}M	1.2×10^{-4}M	0.5

The results of these studies have been graphically represented in P.5.F.3. The peaks are observed at metal-ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from uranium and CHQS in such a way that the mole-ratio of uranium to CHQS varied from 1:0.4 to 1:8. The concentrations employed are given in Table 3.43.

Table 3.43

Temp. = 30°C; pH = 6.6 ± 0.1, Ionic strength = 0.1; λ = 355 nm

Total volume made up to = 25 ml

Concentration of uranium (c)	=	4×10^{-5}M	3×10^{-5}M
P.5.F.4	Curves	A	B

The absorbance of these mixtures was measured using the reagent as blank. The results obtained have been graphically represented in P.5.F.4. The results show a break at a ratio of one mole of the metal to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are as given in Table 3.44.

Table 3.44:

pH = 6.6 ± 0.1, Temp. = 30 ± 0.1°C, Total volume = 25 ml

Concentration of the constant component = 2.4×10^{-4} M

Concentration of the variable component varies from = 4×10^{-6} M to 4×10^{-5} M

Figure	Line	Remarks
P.5.F.5	1,1'	Metal varies
P.5.F.5	2,2'	Ligand varies
P.5.F.5	1,2	λ used = 355 nm
P.5.F.5	1',2'	λ used = 370 nm

The Δ - absorbance of the solutions was noted at 355 nm and 370 nm. The results have been graphically represented in P.5.F.5. The slope of each set of the straight lines, provides UO_2^{2+} : CHQS ratio as 1:2.

Determination of stability constant

The stability constant of Uranyl -7-chloro-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by the three different methods, mentioned earlier. For the determination of the stability constant by the method of Dey et al and mole-ratio method, the concentrations of the reactants are the same as shown in P.5.F.3 and P.5.F.4. For the determination of stability constant by mole-ratio method, the values of Em, Es and α are given in Table 3.45.

Table 3.45:

Figure	Curve	Concentration	Em	Es	α
P.5.F.4	A	4×10^{-5}M	0.225	0.165	0.2666
P.5.F.4	B	3×10^{-5}M	0.165	0.110	0.3333

To determine the stability constant of the chelate by the third method, molecular extinction coefficient is given in Table 3.46.

Table 3.46

λ	D	c	ϵ	A	X	K	log K
355	0.263	4×10^{-5}M	6575	0.152	2.311×10^{-5}	1.199×10^{9}	9.079

The values of log K obtained by these methods have been given in Table 3.47.

Table 3.47:

pH = 6.6 ± 0.1, Ionic strength = 0.1; Temp. = 30°C

Method	Stability constant log K
(1) Mole-ratio method	9.74 ± 0.04
(2) Method of Dey et al	9.69 ± 0.04
(3) Molecular extinction coefficient method	9.079

Thermodynamic functions of the complex

The free energy of complex formation has been calculated, using the equation $\Delta F = -RT\ln K$.

For the purpose of determination of the enthalpy and entropy changes during complex formation, the stability constants were obtained by plotting log K against 1/T (T is the absolute temperature), the enthalpy change ΔH of the reaction has been calculated by temperature coefficient method, using the formula

$$\Delta H = 2.303.R.(\log K_2 - \log K_1).1/(1/T_1 - 1/T_2)$$

Assuming this to be constant over the range of temperatures employed, the entropy change ΔS of the reaction has been calculated, using the equation $\Delta S = \frac{\Delta H - \Delta F}{T}$

The results obtained, have been summarised in Table 3.48.

Table 3.48

pH = 6.6 ± 0.1;   Ionic strength = 0.1

Temperature °C	20	25	30	35	50	45
log K	9.293	9.183	9.079	8.979	8.882	8.789
ΔF(kcal/mole)	-12.46	-12.52	-12.59	-12.66	-12.72	-12.78
ΔH(kcal/mole)	- 8.696	-8.696	- 8.696	-8.696	-8.696	-8.696
Δ S(e.u.)	12.84	12.83	12.85	12.86	12.85	12.84

FIG. 1

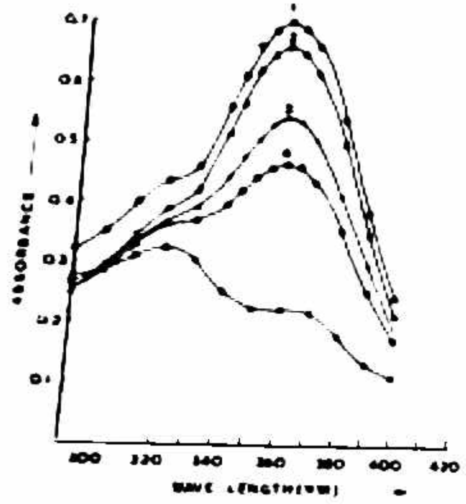


FIG. 2

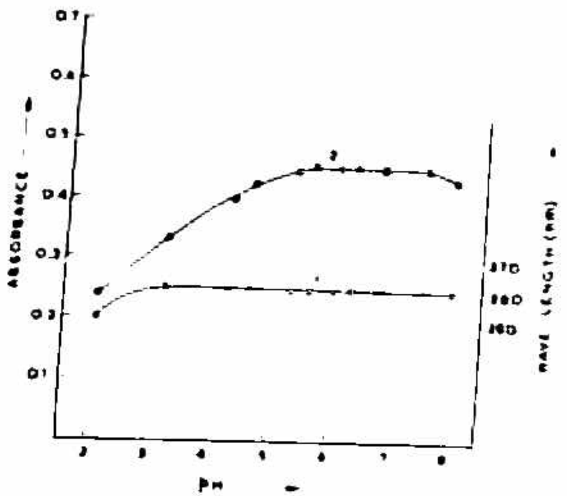


FIG. 3

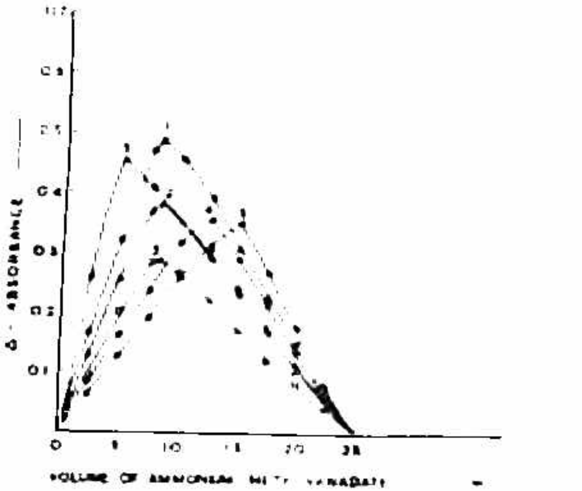


FIG. 4

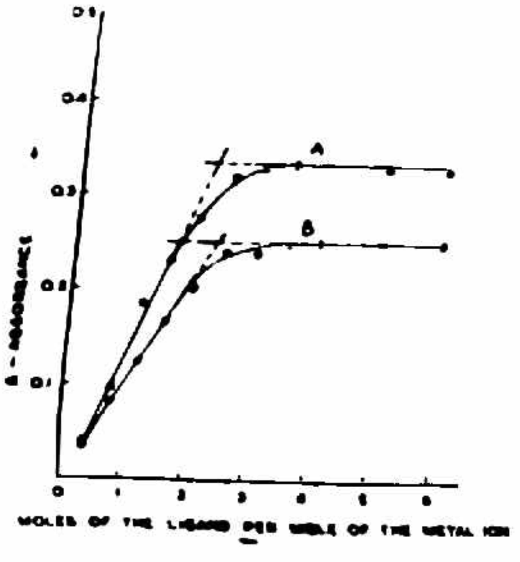


FIG. 5

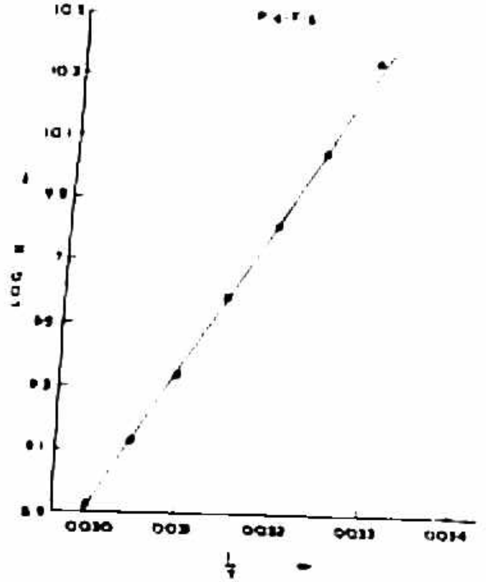
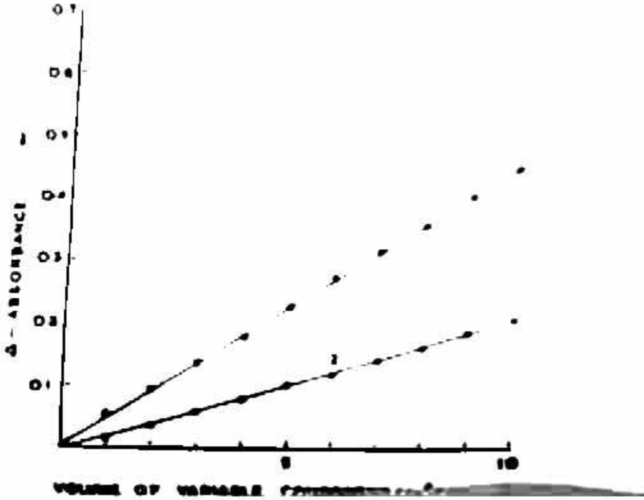


FIG. 6



PART-VI- 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of the complex between vanadium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid has been studied in the aqueous medium. The chelate is stable in the pH range 3.2 - 8.0. The composition of the chelate in solution has been determined by three different methods and it has been found that a stable complex is formed between one mole of vanadium and two moles of 7-chloro-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by the method of Banerji and Dey, mole-ratio and the method using molecular extinction coefficient. The effect of temperature on the stability and the thermodynamic functions such as free energy of formation, enthalpy change and entropy change during the chelate formation have also been investigated.

EXPERIMENTAL

A standard solution of vanadium was prepared by dissolving ammonium meta vanadate (Reanal A.R.) in hot water. A purified sample of 7-chloro-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand solution in aqueous medium. All other reagents were of analytical grade and were used without further purification.

Condition of study

All experiments were performed at 30°C. The individual solutions and mixtures were kept in a thermostat maintaining a temperature 30 ± 0.1°C, for one hour, to attain equilibrium. The pH of the solutions and mixtures was adjusted by the addition of ammonium acetate buffer.

Absorption spectra of the complex in solution

To determine the nature of the complex, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of vanadium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid (CHQS) were prepared. The concentrations employed are recorded in Table 3.51.

Table 3.51:

Mixture	Concentration of vanadium	Concentration of CHQS	Ratio
1	-	1.2×10^{-4}M	0:1
2	1.2×10^{-4} M	1.2×10^{-4}M	1:1
3	6.0×10^{-5}M	1.2×10^{-4}M	1:2
4	4.0×10^{-5}M	1.2×10^{-4}M	1:3
5	3.0×10^{-5}M	1.2×10^{-4}M	1:4

Absorbance of these mixtures was measured at various wavelengths from 290 to 400 nm. The results have been recorded in Table 3.52 and graphically represented in P.6.F.1. From the results, it can be concluded that only one complex is formed in the spectral region of 360 nm, under the condition of study.

Table 3.52: (P.6.F.1 Curves 1,2,3,4,5)

Wavelength nm	Absorbance 1	2	3	4	5
290	0.320	0.250	0.254	0.266	0.275
300	0.349	0.289	0.284	0.285	0.285
310	0.399	0.344	0.335	0.331	0.311
320	0.435	0.390	0.370	0.364	0.325
330	0.461	0.419	0.389	0.370	0.305
340	0.559	0.514	0.443	0.396	0.253
345	0.609	0.565	0.476	0.419	-
350	0.659	0.619	0.506	0.442	0.225
355	0.686	0.645	0.531	0.457	-
360	0.700	0.659	0.541	0.466	0.226
365	0.691	0.647	0.536	0.459	-
370	0.661	0.616	0.506	0.434	0.220
380	0.541	0.500	0.411	0.354	0.180
390	0.385	0.349	0.294	0.252	0.135
400	0.245	0.214	0.191	0.176	0.115

Effective pH range

Solutions containing the same concentration (8×10^{-5}M) of the reagent and ammonium meta vanadate were prepared at different pH and the ionic strength was maintained at 0.1 with $NaClO_4$. The absorbance of these solutions was noted. The complex showed λ_{max} at 360 nm in the pH range 3.2 - 8.0; and an almost constant absorbance was observed in the pH range 5.6 - 7.6.

To maintain uniform conditions of study, pH 6.6 was selected for subsequent studies as the complex shows maximum extinction at this pH. The results of the studies are recorded in Table 3.53 and graphically represented in P.6.F.2.Curve 1, shows the variation of λ_{max} with pH; whereas the Curve 2 shows the variation of absorbance at 360 nm with pH.

Table 3.53:

(F.[illegible].F.2 Curves 1,2)

Wavelength (nm)	pH												
	2.10	3.20	4.25	4.60	5.30	5.60	6.00	6.30	6.70	6.80	7.10	7.50	[illegible]
340	0.241	0.259	0.310	0.336	0.351	0.359	0.355	0.361	0.354	0.355	0.351	0.364	0.350
350	0.254	0.306	0.370	0.399	0.419	0.425	0.424	0.426	0.420	0.424	0.419	0.429	0.412
355	0.250	0.324	0.387	0.421	0.440	0.449	0.449	0.456	0.445	0.447	0.439	0.446	0.423
360	0.240	0.333	0.400	0.427	0.450	0.458	0.456	0.458	0.454	0.455	0.450	0.456	0.435
365	0.225	0.329	0.399	0.424	0.445	0.449	0.450	0.452	0.425	0.449	0.440	0.450	0.435
370	0.204	0.321	0.386	0.406	0.426	0.434	0.430	0.429	0.426	0.425	0.424	0.427	0.400
380	0.155	0.279	0.318	0.336	0.346	0.350	0.346	0.347	0.344	0.344	0.341	0.344	0.309

Stoichiometry of the components

Three methods were adopted for the determination of the empirical formula of the complex in solution.

(1) Job's method

Job's method of continuous variation, using both, equimolecular and non-equimolecular solutions, has been adopted. The results of the studies at 360 nm have been presented in Table 3.54 through 3.59 and graphically represented in P.6.F.3.

Table 3.54:

Concentration of ammonium metavanadate (c) = 2.0×10^{-4}M

Concentration of the ligand CHQS (c') = 2.0×10^{-4}M

pH = 6.6 ±0.1, $p = c'/c = 1$, $\lambda = 360$ nm; $\mu = 0.1$ $NaClO_4$

(P.6.F.3 Curve 1)

Volume of CHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of		Difference (a-b)
		Mixture (a)	CHQS (b)	
25.00	0.00	0.383	0.383	0.000
22.50	2.50	0.495	0.328	0.166
20.00	5.00	0.611	0.292	0.319
17.50	7.50	0.729	0.259	0.470
16.66	8.33	0.730	0.245	0.485
15.00	10.00	0.672	0.216	0.456
12.50	12.50	0.569	0.180	0.389
10.00	15.00	0.458	0.153	0.305
7.50	17.50	0.334	0.109	0.225
5.00	20.00	0.225	0.075	0.150
2.50	22.50	0.111	0.041	0.070
0.00	25.00	0.000	0.000	0.000

Table 3.55:

Concentration of ammonium metavanadate (c) = 1.6×10^{-4} M

Concentration of the ligand CHQS (c') = 1.6×10^{-4} M

pH = 6.6 ± 0.1, r = c'/c =1, λ = 360 nm; μ = 0.1 $NaClO_4$

(P.6.F.3 Curve 2)

Volume of CHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of Mixture (a)	Absorbance of CHQS (b)	Difference (a-b)
25.00	0.00	0.295	0.295	0.000
22.50	2.50	0.389	0.260	0.129
20.00	5.00	0.489	0.234	0.255
17.50	7.50	0.580	0.210	0.370
16.66	8.33	0.580	0.199	0.380
15.00	10.00	0.536	0.186	0.350
12.50	12.50	0.452	0.148	0.304
10.00	15.00	0.356	0.119	0.237
7.50	17.50	0.264	0.039	0.175
5.00	20.00	0.178	0.064	0.114
2.50	22.50	0.085	0.028	0.057
0.00	25.00	0.000	0.000	0.000

Table 3.56

Concentration of ammonium metavanadate (c) = 1.2×10^{-4} M

Concentration of the ligand CHQS (c') = 1.2×10^{-4} M

pH = 6.6 ± 0.1, p = c'/c = 1, λ = 360 nm; μ = 0.1 $NaClO_4$

(P.6.F.3 Curve 3)

25.00	0.00	0.227	0.227	0.000
22.50	2.50	0.290	0.195	0.095
20.00	5.00	0.364	0.164	0.200
17.50	7.50	0.430	0.148	0.282
16.66	8.33	0.426	0.140	0.286
15.00	10.00	0.390	0.125	0.265
12.50	12.50	0.334	0.114	0.220
10.00	15.00	0.260	0.089	0.171
7.50	17.50	0.195	0.075	0.120
5.00	20.00	0.127	0.045	0.082
2.50	22.50	0.065	0.023	0.042
0.00	25.00	0.000	0.000	0.000

Table 3.57:

Concentration of ammonium metavanadate (c) = 1.0×10^{-4}M

Concentration of the ligand CHQS (c') = 2.0×10^{-4}M

pH = 6.6 ± 0.1; p = c'/c = 2; λ = 360 nm; μ = 0.1 $NaClO_4$

(P.6.F.3 Curve 4)

Volume of CHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of		Difference (a-b)
		Mixture (a)	CHQS (b)	
25.00	0.00	0.383	0.383	0.000
22.50	2.50	0.411	0.328	0.083
20.00	5.00	0.454	0.292	0.162
17.50	7.50	0.494	0.259	0.235
15.00	10.00	0.533	0.216	0.317
12.50	12.50	0.534	0.180	0.354
10.00	15.00	0.440	0.153	0.287
7.50	17.50	0.323	0.108	0.215
5.00	20.00	0.211	0.075	0.136
2.50	22.50	0.101	0.041	0.060
0.00	25.00	0.000	0.000	0.000

Table 3.58:

Concentration of ammonium metavanadate (c) = 3.2×10^{-4}M

Concentration of the ligand CHQS (c') = 1.6×10^{-4}M

pH = 6.6 ± 0.1; p = c'/c = 1/2; λ = 360 nm; μ = 0.1 $NaClO_4$

(P.6.F.3 Curve 5)

25.00	0.00	0.292	0.292	0.000
22.50	2.50	0.518	0.260	0.258
20.00	5.00	0.689	0.234	0.455
17.50	7.50	0.617	0.209	0.408
15.00	10.00	0.534	0.186	0.348
12.50	12.50	0.440	0.148	0.292
10.00	15.00	0.348	0.119	0.229
7.50	17.50	0.260	0.090	0.170
5.00	20.00	0.169	0.064	0.105
2.50	22.50	0.083	0.028	0.055
0.00	25.00	0.000	0.000	0.000

Table 3.59:

Concentration of ammonium metavanadate (c) = 8×10^{-5}M

Concentration of the ligand CHQS (c') = 2.4×10^{-4}M

pH = 6.6 ± 0.1; p = c'/c = 3; λ = 360 nm; μ = 0.1 $NaClO_4$

(F.6.F.3 Curve 6)

Volume of CHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of Mixture (a)	Absorbance of CHQS (b)	Difference (a-b)
25.00	0.00	0.435	0.435	0.000
22.50	2.50	0.458	0.395	0.063
20.00	5.00	0.481	0.354	0.127
17.50	7.50	0.500	0.310	0.190
15.00	10.00	0.520	0.260	0.260
12.50	12.50	0.540	0.227	0.313
10.00	15.00	0.515	0.164	0.351
7.50	17.50	0.392	0.125	0.267
5.00	20.00	0.264	0.089	0.175
2.50	22.50	0.125	0.045	0.080
0.00	25.00	0.000	0.000	0.000

The peaks are observed at the metal : ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from vanadium and CHQS in such a way that the mole-ratio of vanadium to CHQS varied from 1:0.4 to 1:1.6. The results of the studies made at 360 nm have been presented in Table 3.60 and graphically represented in F.6.F.4.

Table 3.60:

Final concentration of the ligand CHQS (c') = 4.0×10^{-5}M, 3.0×10^{-5}M
A B

Temp. = 30°C, pH = 6.6 ± 0.1, Ionic strength = 0.1 $NaClO_4$

Total volume made up to = 25 ml.

(P.6.F.4 Curves A,B)

Ratio V : CHQS	Absorbance A	Absorbance B
1 : 0.4	0.039	0.035
1 : 0.8	0.097	0.082
1 : 1.2	0.185	0.124
1 : 1.6	0.231	0.167
1 : 2.0	0.275	0.202
1 : 2.5	0.319	0.239
1 : 3.0	0.331	0.238
1 : 3.5	0.334	0.249
1 : 4.0	0.333	0.250
1 : 5.0	0.330	0.251
1 : 6.0	0.328	0.250

The results show a break at a ratio of one mole of the metal to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The Δ - absorbance of the solutions was noted at 360 nm. The results of the studies have been recorded in Table 3.601 and graphically represented in P.6.F.5.

Table 3.601:

Final concentration of the constant component = 1.6×10^{-4}M

Final concentration of the variable component

varies from = 4.0×10^{-6}M to 4.0×10^{-5}M

pH = 4. ± 0.1, Temp. = 30 ± 0.1°C, Total volume = 25 ml

(P.6.F.5 Curves 1,2)

Volume of variable component (ml)	Absorbance: Metal varying 1	Absorbance: Ligand varying 2
1.0	0.053	0.015
2.0	0.095	0.037
3.0	0.140	0.060
4.0	0.131	0.079
5.0	0.230	0.105
6.0	0.277	0.122
7.0	0.323	0.145
8.0	0.366	0.164
9.0	0.410	0.191
10.0	0.457	0.211

The slope of the two straight lines, provides the VO^{3+}: CHQS ratio as 1:2.

Determination of stability constant

The stability constant of pervanadyl - 7-chloro-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by the three different methods mentioned earlier.

For the determination of stability constant by the method of Dey et al and mole-ratio method, the concentrations of the reactants are the same as shown in P.6.F.3 and P.6.F.4.

For the determination of stability constant by mole-ratio method, the values of Em, Es and α are given in Table 3.602.

Table 3.602:

Figure	Curve	Concentration	Em	Es	α
P.6.F.4	A	4×10^{-5}M	0.335	0.275	0.1791
P.6.F.4	B	3×10^{-5}M	0.250	0.202	0.1920

To determine the stability constant of the chelate by the third method, molecular extinction coefficient data is given in Table 3.603.

Table 3.603:

λ	D	C	ϵ	A	x	K	log K
360	0.335	4×10^{-5}M	8375	0.275	3.2835×10^{-5}	2.23×10^{10}	10.3483

The values of log K obtained by these methods have been given in Table 3.604.

Table 3.604:

pH = 6.6 ± 0.1, Ionic strength = 0.1, Temp. = 30°C

Method	Stability constant log K
(1) Mole-ratio method	10.425 ± 0.076
(2) Method of Dey et al	10.440 ± 0.002
(3) Molecular extinction coefficient method	10.350

Thermodynamic functions of the complex

The free energy of complex formation has been calculated, using the equation $\Delta F = -RT\ln K$.

For the purpose of determination of the enthalpy and entropy changes during complex formation, the stability constants were obtained by plotting log K against 1/T (T is the absolute temperature), the enthalpy change ΔH of the reaction has been calculated by temperature coefficient method, using the formula

$$\Delta H = 2.303.R.(\log K_2 - \log K_1).1/(1/T_1 - 1/T_2).$$

Assuming this to be constant over the range of temperatures employed, the entropy change ΔS of the reaction has been determined using the equation $\Delta S = \frac{\Delta H - \Delta F}{T}$.

The results obtained, have been summarised in Table 3.605.

Table 3.605:

pH = 6.6 ± 0.1 Ionic strength = 0.1

Temperature °C	30	35	40	45	50	55	60
log K	10.35	10.05	9.82	9.58	9.34	9.13	8.93
ΔF(kcal/mole)	-14.34	-14.17	-14.06	-13.95	-13.80	-13.71	-13.60
ΔH(kcal/mole)	-21.97	-21.97	-21.97	-21.97	-21.97	-21.97	-21.97
ΔS(e.u.)	-25.19	-25.32	-25.27	-25.23	-25.29	-25.19	-25.14

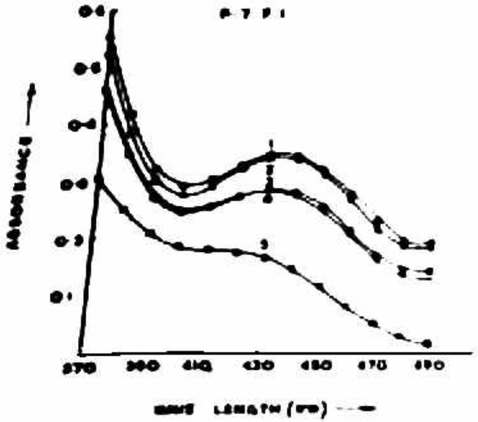


FIG 1

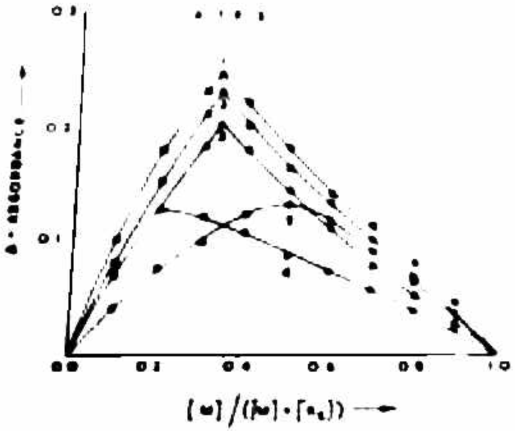


FIG 3

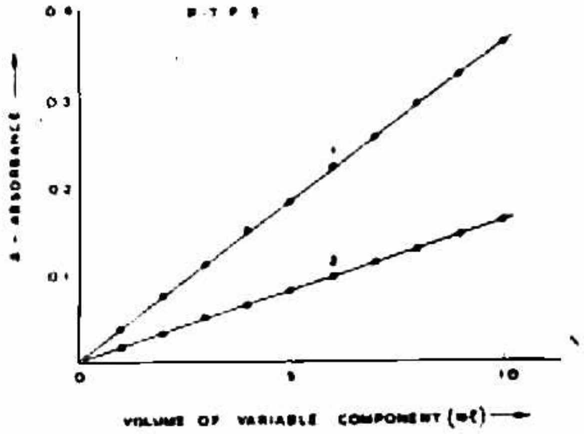


FIG 5

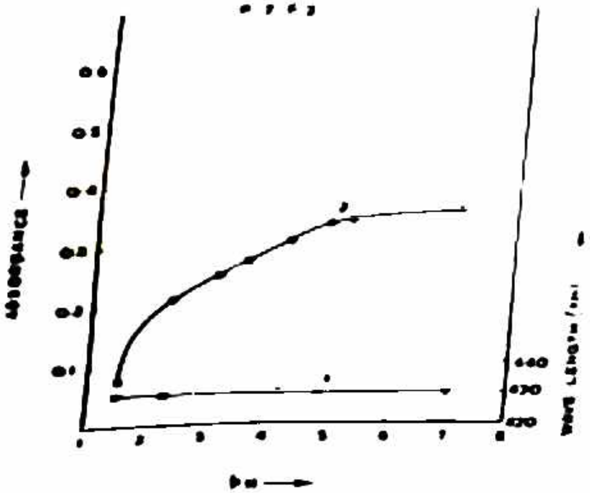


FIG 2

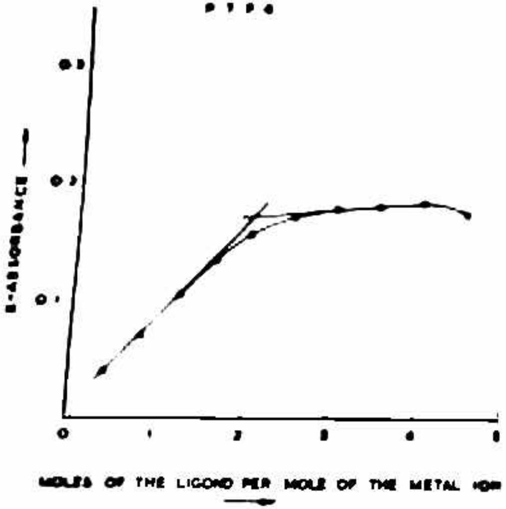


FIG 4

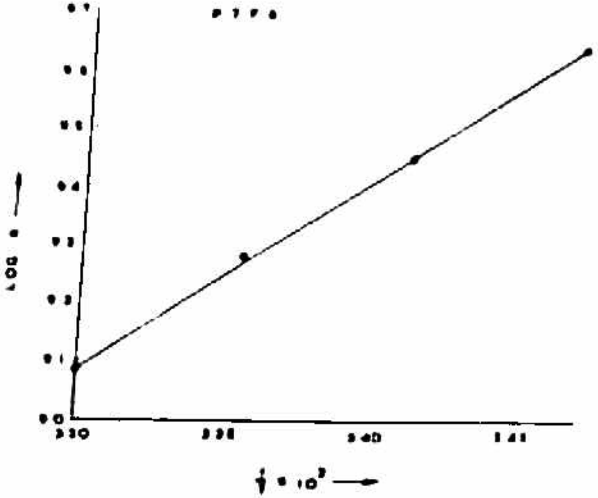


FIG 6

IRON (III)- 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of a green chelate between trivalent iron and 7-chloro-8-hydroxyquinoline-5-sulphonic acid ([illegible]) has been studied in aqueous medium spectrophotometrically. The composition of the complex in solution has been determined by the three different methods mentioned earlier and it has been found that a stable chelate is formed between one mole of iron and two moles of the ligand. The stability constant of the chelate has been determined by the method of Banerji and Dey, mole-ratio method and the method using molecular extinction coefficient. The effect of temperature on the stability and the thermodynamic functions such as free energy of formation, enthalpy change and entropy change during the chelate formation have also been investigated.

EXPERIMENTAL

A standard solution of iron was prepared by dissolving ferric chloride (BDH) in dilute hydrochloric acid and the iron content was estimated. The reagent solution was prepared from the recrystallised sample of 7-chloro-8-hydroxyquinoline-5-sulphoni acid in double distilled water. Suitable standard solutions were prepared from these stock solutions.

Conditions of study

All experiments were performed at 20°C. The individual solutions and the mixtures were kept in a Townson and Mercer precision thermostat, maintained at 20 ± 0.1 °C. The mixtures were allowed to stand for an hour in the thermostat to attain equilibrium. The ph of all the mixtures was adjusted by the addition of suitable amount of pthalate buffer.

Absorption spectra of the complex

To determine the nature of the complex formed, the method of Vosburgh and Cooper was adopted. Mixtures containing varying [illegible] of iron and 7-chloro-8-hydroxyquinoline-5-sulphonic [illegible] ([illegible]) were prepared. The concentrations employed in the studies are recorded in Table 3.61.

Table 3.61:

Mixture	Concentration of iron	Concentration of [illegible]	Ratio
1	3.6×10^{-4}M	3.6×10^{-4}M	1:1
2	1.8×10^{-4}M	3.6×10^{-4}M	1:2
3	1.2×10^{-4}M	3.6×10^{-4}M	1:3
4	9.0×10^{-5}M	3.6×10^{-4}M	1:4
5	-	3.6×10^{-4}M	0:1

The absorbance of these mixtures at various wavelengths, from 370 nm to 490 nm was measured and the results have been graphically represented in P.7.F.1. The results show that only one complex is formed under the conditions of study, in the spectral region of 430 nm.

Effective pH range

Solutions containing the same concentration (2.4×10^{-4} M) of metal and the ligand were prepared at different pH. The absorbance of these solutions was noted. The complex showed λ_{max} at 430 nm in the pH range 1.5 to 7.0. pH 3 was, however, selected for subsequent studies. The results of the studies are graphically represented in P.7.F.2. Curve 1 shows the variation of λ_{max} with pH; whereas Curve 2 shows variation of absorbance with pH.

Stoichiometry of the components

(1) Job's method

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions has been adopted. The studies were performed at 430 nm and 410 nm, but only representative results, obtained from the studies at 430 nm have been graphically represented in P.7.F.3. The concentrations employed and the specific conditions of study are as given in Table 3.62.

Table 3.62: pH = 3.0 ± 0.1, Temp. = 20°C, λ = 430 nm.

Figure	Curve	Conc. of CHQS	Conc. of iron	$p = c'/c$
P.7.F.3	1	8.4×10^{-4} M	8.4×10^{-4} M	1
P.7.F.3	2	7.2×10^{-4} M	7.2×10^{-4} M	1
P.7.F.3	3	6.0×10^{-4} M	6.0×10^{-4} M	1
P.7.F.3	4	3.6×10^{-4} M	7.2×10^{-4} M	0.5
P.7.F.3	5	6.0×10^{-4} M	3.0×10^{-4} M	2

The peaks are observed at metal:ligand ratio of 1:1.

(2) Mole-ratio method

A series of solutions was prepared from iron and CHQS in such a way that the mole-ratio of iron and CHQS varied from 1: .4 to 1:4.5. The concentrations employed are given in Table 3.63.

Table 3.63:

Temp. = 20°C; pH = 3.0 ± 0.1;

Total volume made up to - [illegible] ml.

Concentration of iron (c) = 1.8 x 10^{-4}.

P.7.F.4	Curve	A

The Δ - absorbance of these mixtures was measured at 410 nm and 430 nm. But only representative results, obtained from the studies at 430 nm, have been graphically represented in P.7.F.4.

The results show a break at a ratio of one mole of the metal ion to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 3.64.

Table 3.65:

2.0 ± 0.1, Temp. = 20°C, Total volume = 25 ml, λ = 430 nm

Concentration of the constant component = 7.2×10^{-4}.

Concentration of the variable component varies from 1.8×10^{-5} M to 1.8×10^{-4}.

[illegible]	Line	[illegible]
P.7.F.[illegible]	1	Metal varying
P.7.F.[illegible]	2	Ligand varying

The results have been graphically represented in P.7.F.[illegible]. The slope of the two straight lines, provides the Fe : CHQS ratio as 1:[illegible].

Determination of stability constant

The stability of iron (III)- 7-chloro-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by three different methods, mentioned earlier. For the determination of stability constant by the method of Dey et al and mole-ratio method, the concentrations of the reactants are the same as shown in P.7.F.3 (Curves 1-3) and P.7.F.4 respectively. For the determination of stability constant by mole-ratio method, the values of Em, Es and α are given in Table 3.65.

Table 3.65

Figure	Concentration	Em	Es	α
P.7.F.4	1.8×10^{-4}M	0.182	0.155	0.1483

The values of log obtained by these methods have been given in Table 3.66.

Table 3.66

pH = [illegible] ± 0.1, Temp. = 20°C., Ionic strength = 0.1

Method	Stability constant log K
(1) Method of Dey et al	8.972 ± 0.062
(2) Mole-ratio method	9.3036
(3) Molecular extinction coefficient method	9.4475

Thermodynamic functions of the complex

The free energy of complex formation has been calculated, using the equation:

$$\Delta F = -RT \ln K$$

For the purpose of determination of the enthalpy and entropy changes during the complex formation, the stability constants were obtained by plotting log K against 1/T (F.[illegible].6) (where T is the absolute temperature), the enthalpy change ΔH of the reaction has been calculated by temperature coefficient method, using the formula:

$$\Delta H = 2.303.R.(\log K_2 - \log K_1) . 1 (1/T_1 - 1/T_2)$$

Assuming this to be constant over the range of temperature employed, the entropy change, ΔS, of the reaction has been calculate

Using the equation:

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

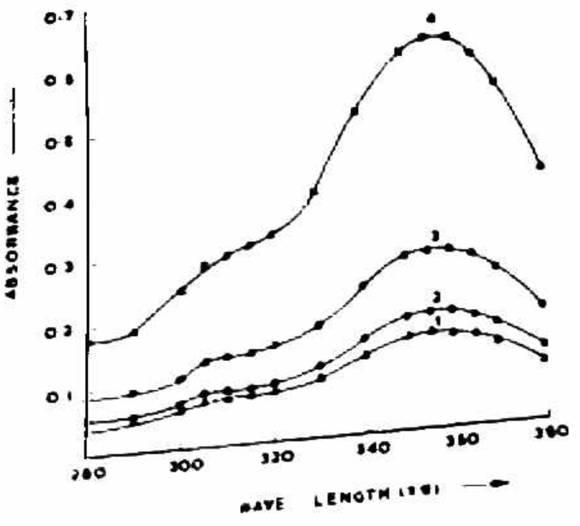
The results obtained have been summarised in Table 3.67.

Table 3.67:

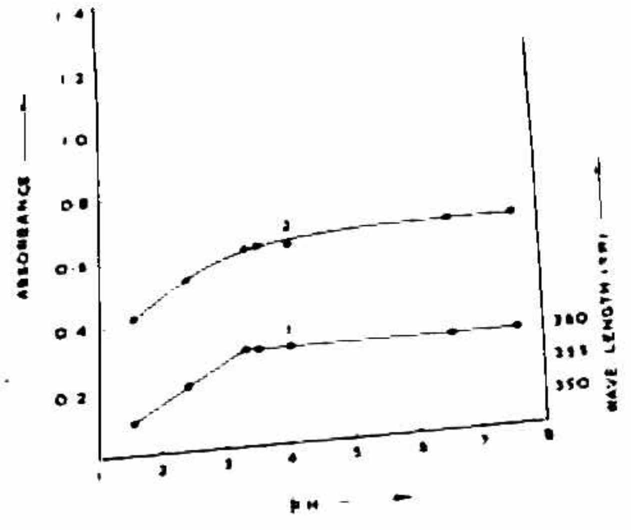
pH = 3.[illegible] ± 0.1 ; Ionic strength = 0.1

Temperature °C	15	20	25	30
log K	9.6376	9.4475	9.2650	9.0854
ΔF(kcals/mole)	-12.70	-12.67	-12.63	-12.60
ΔH(kcals/mole)	-14.64	-14.64	-14.64	-14.64
ΔS(e.u.)	-6.736	-6.723	-6.745	-6.733

P.B.F.1



P.B.F.2



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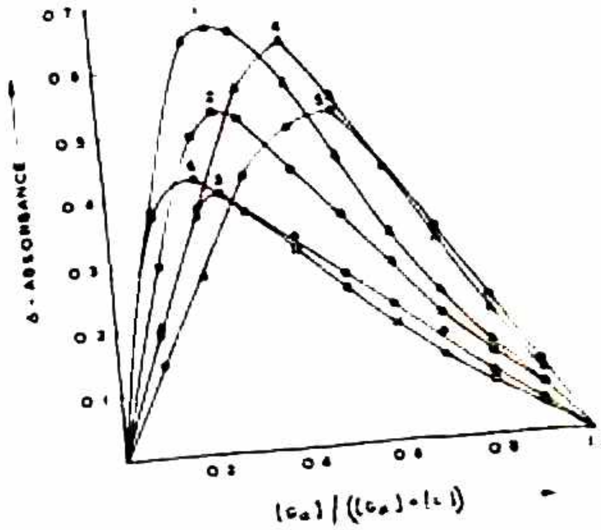
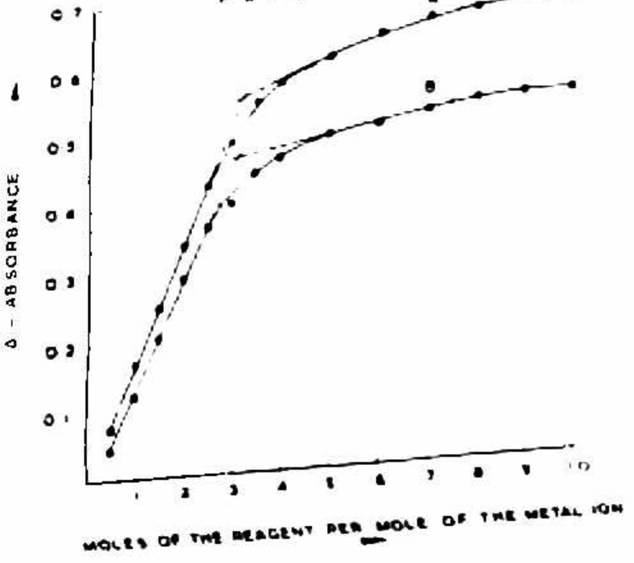


P.B.F.4



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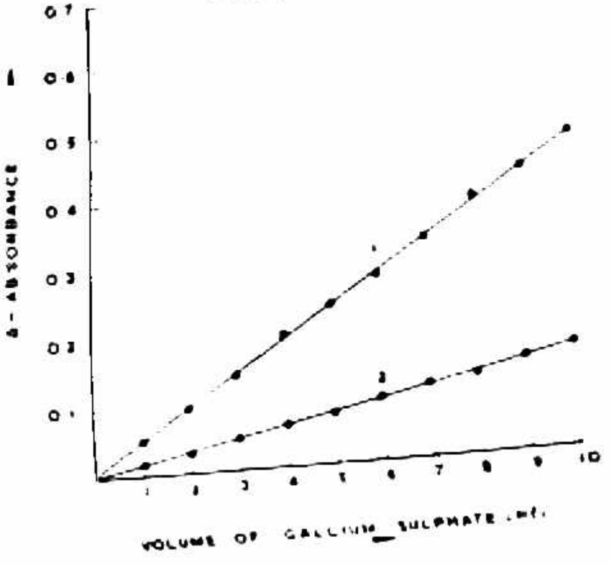
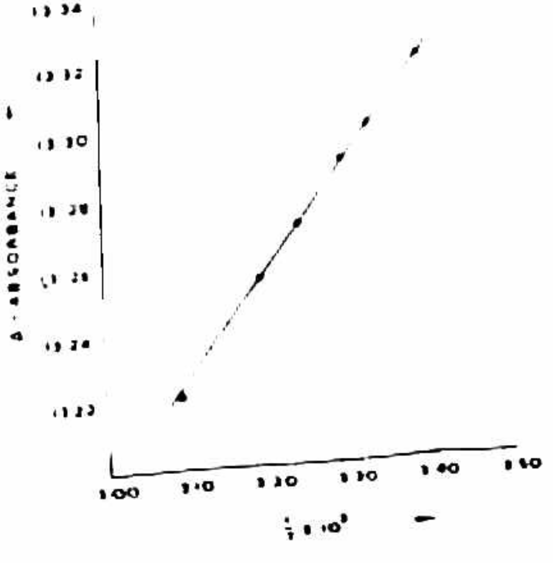


P.B.F.6



IUM (III)- 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The complex formed between gallium and 7-chloro- -hydroxyquinoline-5-sulphonic acid has been investigated spectrophotometrically. The chelate is stable in the ph range 3.3 to 7.6. The composition of the chelate, in solution, has been determined by two different methods and it has been found that a stable complex is formed between one mole of gallium and three moles of 7-chloro- -hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by mole-ratio method and the method using molecular extinction coefficient data. The effect of temperature on the stability and the thermodynamic functions such as free energy of formation, enthalpy change and entropy change during the chelate formation have also been investigated.

EXPERIMENTAL

A standard solution of gallium was prepared by dissolving gallium sulphate (α - Inorganics, U.S.A.) in dilute sulphuric acid. A purified sample of 7-chloro-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand in double distilled water. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 20°C. The individual solutions and mixtures were thermostated at 20 ± 0.1°C, for one hour to attain equilibrium. The pH of the solutions and the mixtures was adjusted with sodium acetate - acetic acid buffer.

Absorption spectra of the complex

To determine the nature of the complex formed, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of gallium and 7-chloro-8-hydroxyquinoline-5-sulphonic acid (CHQS) were prepared. The concentrations employed in the studies are recorded in Table 3.71.

Table 3.71:

Mixtures	Conc. of CHQS	Conc. of gallium	Ratio
1	$1.8 \times 10^{-4}M$	$1.8 \times 10^{-4}M$	1:1
2	$9.0 \times 10^{-5}M$	$1.8 \times 10^{-4}M$	1:2
3	$6.0 \times 10^{-5}M$	$1.8 \times 10^{-4}M$	1:3
4	$4.5 \times 10^{-5}M$	$1.8 \times 10^{-4}M$	1:4

The absorbance of these mixtures at various wavelengths, from 280 nm to 380 nm, was measured. The results have been graphically represented in P.8.F.1. The results show that only one complex is formed under the conditions of study in the spectral region of 355 nm.

Effective pH range

Solutions containing ($2.4 \times 10^{-4}M$) of the reagent and ($1.2 \times 10^{-4}M$) of the metal ion were prepared at different pH.

The absorbance of these solutions was noted. The complex showed a λ_{max} at 360 nm in the pH range 3.3 to 7.6 (in absence of the buffer). pH 4, was, however, selected for subsequent studies. The results of the studies are graphically represented in F. . . . . . Curve 1 shows the variation of λ_{max} with pH, whereas curve 2 shows the variation of absorbance with pH.

Stoichiometry of the components

(1) Job's method of continuous variation, using both equimolecular and non-equimolecular solutions has been adopted to determine the composition. The studies were performed at 345 nm and 355 nm, but only representative results, of the studies at 355 nm have been graphically represented in P.8.F.3. The concentrations employed are given in Table 3.72.

Table 3.72

pH = 4.0 ± 0.1, Temp. = 20°C, λ = 355 nm $\mu = 0.2$

Figure	Curve	Concentration of gallium (c)	Conc. of CHQS(c')	p=c'/c
P.8.F.3	1	3.0×10^{-4}M	3.0×10^{-4}M	1
P.8.F.3	2	2.4×10^{-4}M	2.4×10^{-4}M	1
P.8.F.3	3	1.8×10^{-4}M	1.8×10^{-4}M	1
P.8.F.3	4	1.2×10^{-4}M	3.6×10^{-4}M	3
P.8.F.3	5	1.8×10^{-4}M	3.6×10^{-4}M	2
P.8.F.3	6	3.6×10^{-4}M	1.8×10^{-4}M	0.5

The peaks are observed at metal : ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from gallium and CHQS in such a way that the mole ratio of gallium and CHQS varied from 1:0.5 to 1:10.0. The concentrations employed are given in Table 3.73.

Table 3.73

Temp. = 20°C, pH = 4.0 ± 0.1, μ = 0.2,
Total volume made up to - 25 ml

Concentration of gallium (c) =	6.0×10^{-5}M	4.8×10^{-5}M
P.8.F.4. Curves	A	B

The Δ - absorbance of these mixtures was measured at 345 nm and 355 nm. But only representative results, obtained from the studies at 355 nm, have been graphically represented in P.8.F.4.

The results show a break at a ratio of one mole of the metal ion to three moles of the reagent, indicating that a 1:3 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 3.74.

[illegible]

[illegible] = 20 ± 0.1°C, Total volume = 25 ml,

[illegible]

Concentration of the constant component = 4.8×10^{-4} M

[illegible]ncentration of the variable component varies from 6×10^{-6} M

to [illegible]

Figure	Line	Remarks
[illegible]	[illegible]	Metal varying
[illegible]	[illegible]	Ligand varying

The results have been graphically represented in P.8.F.5. The slope of the two straight lines, provides the Ga : CHQS ratio [illegible] 1 : [illegible].

Determination of stability constant

The stability constant of gallium (III) - 7-chloro-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by two different methods detailed earlier. For the determination of stability constant by the mole-ratio method, the concentrations of the reactants are same as shown in Table 3.73 (graphically represented by P.8.F.4); the values of Em, Es and α are given in Table 3.75.

Table [illegible]:

Figure	Curve	Concentration	Es	Es	α
[illegible]	A	6.0×10^{-5} M	0.679	0.490	0.2784
P.8.F.4	B	4.8×10^{-5} M	0.540	0.400	0.2592

To determine the stability constant of the chelate by the third method, molecular extinction coefficient data is given in Table 3.76.

Table 3.76

λ	D	C	ϵ	A	α	log K
355 nm	0.678	6x10^{-5}M	11300	0.490	4.[illegible] x 10^{-5} M	13.3211

The values of log K obtained by these methods have been given in Table 3.77.

Table 3.77

pH = 4.0 ± 0.1, Ionic strength = 0.2; Temp. = 20°C

Method	Stability constant log K
(1) Mole-ratio method	13.527 ± 0.213
(2) Molecular extinction coefficient method	13.3211

Thermodynamic functions of the complex

The free energy of complex formation has been calculated, using the equation

$$\Delta F = -RT \ln K$$

For the purpose of determination of the enthalpy and entropy changes during the complex formation, the stability constants were obtained by plotting log K against 1/T (P.8.[illegible].6) (T is the absolute temperature), the enthalpy change ΔH, of the reaction has been calculated by temperature coefficient method, using the formula

$$\Delta H = 2.303.R.(\log K_2 - \log K_1) . 1/(1/T_1 - 1/T_2).$$

Assuming this to be constant over the range of temperatures employed, the entropy change, ΔS, of the reaction has been calculated, using the equation:

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

The results obtained have been summarised in Table 3.78.

Table 3.78:

pH = 4.0 ± 0.1 Ionic strength = 0.2

Temperature °C	20	25	30	35	40	50
log K	13.3211	13.3008	13.2903	13.2715	13.2559	13.2216
ΔF (Kcal/mole)	-17.860	-18.130	-18.430	-18.710	-18.980	-19.540
ΔH (Kcal/mole)	1.442	1.442	1.442	1.442	1.442	1.442
ΔS (e.u.)	65.38	65.66	65.58	65.42	65.24	64.95

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CHAPTER IV

THERMODYNAMIC IONIZATION CONSTANTS AND METAL CHELATES OF 7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

Introduction

The ability of 8-quinolinol and its analogues, to form stable metal chelates, is due to the peri position of the phenolic hydroxyl group forming the grouping N-C-C-O which can give rise to the formation of a five membered chelate ring.

The principal bromo substituted 8-quinolinols, investigated by various workers are : 5-7-dibromo-8-quinolinol, 5-bromo-8-quinolinol, 7-bromo-8-quinolinol, 5-bromo-8-quinolinol-7-sulphonic acid and 7-bromo-8-quinolinol-5-sulphonic acid. Earlier work on bromo-substituted 8-quinolinols concentrated around the composition, stability and molecular structure of their metal chelates. Currently attention is being given to their utility in detection and estimation of trace amounts of metal ions. This is mainly due to the possibility of extracting these chelates from aqueous medium, into an organic phase by solvent extraction processes.

Considerable interest has also centred around the studies of the effect of substituents, on the ionization constants, chelate stability constants and thermodynamic functions of the halo substituted 8-quinolinols and its sulphonates. In continuation of these studies, we have taken up the studies on 7-bromo-8-hydroxyquinoline-5-sulphonic acid, which forms water soluble chelates, regarding (a) its ionization constants (b) composition, stability, molecular structure of its metal chelates and

(c) some thermodynamic functions, associated with their formation. Very scanty work on 7- bromo-8-hydroxyquinoline-5-sulphonic acid is on record, as compared to the work that has been done on 7-iodo-8-hydroxyquinoline-5-sulphonic acid and 8-hydroxyquinoline-5-sulphonic acid.

It was observed by Richard Berg (1), in course of his studies of the influence of substituents on the stability and insolubility of the metal complexes of 8-quinolinol derivatives, that 7-bromo-8-hydroxyquinoline-5-sulphonic acid in a acetone-water solution containing a mineral acid gave a greenish yellow precipitate with copper and a greenish black precipitate with ferric salts. The sensitivity of this reagent for copper and iron is (1:500,000 and 1:100,000 respectively). Jacob Molland (2) formulated the possibility of colorimetric determination of iron with 7-bromo-8-hydroxyquinoline-5-sulphonic acid and with some other 8-quinolinol derivatives. The reagent produced a dark green colour with ferric chloride. The use of pthalate and borate buffers was suggested by him, as a result of his observation that these buffers did not influence the colouration. On the basis of calculations of acid and basic dissociation constants, indicator properties of 7-bromo-8-quinolinol-5-sulphonic acid and its derivatives were reported by Harry B.Feldman and Arnet L. Powell (3). Methods of synthesizing the halogenated derivatives of 8-quinolinol and 8-quinolinol-5-sulphonic acid were improved by Antonio Luis,Palomo Coll and Gabriel Palomo Coll (4) and the melting point of the 7-bromo-8-quinolinol-5-sulphonic acid was reported as 280°C.

Tiao-Hsu Chang and coworkers (6) prepared some of the derivatives of 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulphonic acid. Dissociation constants of 7-bromo-8-quinolinol-5-sulphonic acid and the chelate stability constants of its chelates with Cd(II), Pb(II), Zn(II), Co(II) and Ni(II) were reported along with similar studies on certain other derivatives of 8-hydroxyquinoline.

Hans Berge (7) carried out polarographic studies of complex equilibrium in dioxane-water mixtures and determined the stability constants via exchange equilibriums.

As ~~already~~ mentioned earlier, although a lot of work has been reported on ferron and 8-hydroxyquinoline-5-sulphonic acid, yet, not much work has been reported on 7-bromo-8-hydroxyquinoline-5-sulphonic acid.

It was therefore thought proper to investigate in detail the chelates of copper, palladium, uranium, vanadium, iron and gallium.

As in the earlier chapter, to reduce the bulk of the thesis, complete data on only one dipositive and one tripositive metal chelate have been presented, along with the graphical representation. The data obtained in the detailed investigation of the other chelates have, however, been represented graphically.

Preparation of 7-bromo-8-hydroxyquinoline-5-sulphonic acid

The compound has been prepared by the method used by Tiao-Hsu Chang et al (6): 5 gm of 8-hydroxyquinoline-5-sulphonic acid (method of preparation, described earlier, in Chapter III) was dissolved in 200 ml of 10% potassium carbonate solution. Concentrated hydrochloric acid was slowly added to the solution till precipitation. A small amount of 10% potassium carbonate solution was added in amounts just sufficient to redissolve the precipitate. At this point, the pH value of the solution was about 6.6. Then 20 ml of the saturated bromine water was poured into the solution from a separating funnel. The reaction mixture was stirred for 2 hours and then acidified. The precipitate obtained was separated out, filtered and recrystallized from distilled water. The yield was about 60%.

Colour reactions of 7-bromo-8-hydroxyquinoline-5-sulphonic acid

The colour reactions of the reagent, so obtained were observed, with a number of cations. Table 4.01 records the observations.

Table 4.01

Reagent Light yellow in colour

Sl. No.	Metal	Colouration	Remarks
1	Hg^{2+}	A slight intensification in colour	Not very sensitive with dilute solutions
2	Cu^{2+}	Slight bluish coloured tinge developed	Sensitive with dilute solutions
3	Ni^{2+}	Greenish yellow	Sensitive with dilute solutions
4	UO_2^{2+}	Orange-red	Very sensitive with dilute solutions
5	Fe^{3+}	Green	Most sensitive with dilute solutions
6	Cr^{3+}	Yellow colour intensified	Sensitive with dilute solutions
7	Ce^{4+}	Pink colour	Fades very soon, leaving a yellow tinge behind
8	Ti^{4+}	Colour intensified	Sensitive with dilute solutions
9	V^{5+}	Deep yellow	Sensitive with dilute solutions
10	Mo^{6+}	Yellow colour intensified	Sensitive with dilute solutions

THERMODYNAMIC IONIZATION CONSTANTS OF 7-BROMO-8-HYDROXYQUINOLINE-5- SULPHONIC ACID

The thermodynamic ionization constants of 7-bromo-8-hydroxyquinoline-5-sulphonic acid have been determined in the aqueous medium at 25°C, using spectrophotometric method .

The sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid was recrystallised twice from double distilled water before use. Other chemicals used were of A.R. quality. The spectra of solutions were taken against a blank consisting of the aqueous buffer, acid or alkali used as solvent for the reagent.

All solutions were kept in a thermostat having a temperature of 25 ± 0.1°C for about thirty minutes to attain equilibrium. The pH of the solutions were adjusted using chloro-acetic acid - KOH buffer, succinic acid - KOH buffer and KH_2PO_4-Na_2HPO_4 buffer.

Spectral studies

The absorption spectra of, fully protonated form in 0.1 N HCl, partially protonated form in a buffer of pH 5.5 and completely unprotonated form in 0.1 N NaOH, of 7-bromo-8-hydroxyquinoline-5-sulphonic acid (abbreviated as BHQS) were taken in the range of 220 nm to 380 nm. The results have been presented in Table 4.11 and represented graphically in P.9.F.1.

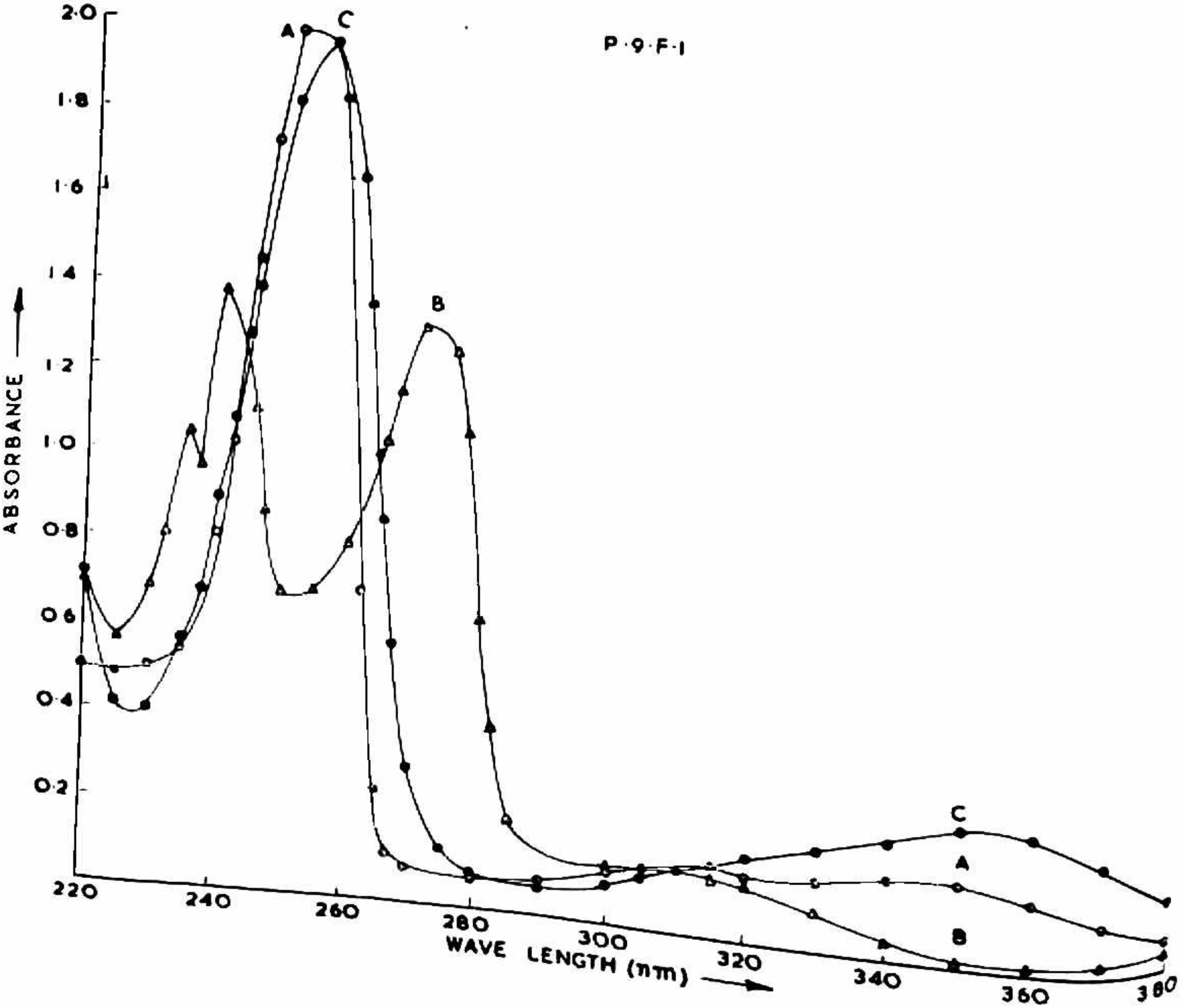

P·9·F·1
ABSORBANCE
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
A
C
B
C
A
B
220
240
260
280
300
320
340
360
380
WAVE LENGTH (nm)

Table 4.11

Concentration of BHQS = 6 x 10^{-5}M;   Temp. = 25 ± 0.1°C

P.q.F.1   Curve A = BHQS in 0.1 N HCl

Curve B = BHQS in a buffer of pH 5.5

Curve C = BHQS in 0.1 N NaOH

Wavelength (nm)	Absorbance		
	A	B	C
220	0.470	0.626	0.375
225	0.551	0.790	0.327
230	0.506	1.165	0.447
235	0.525	1.605	0.715
237	0.630	1.700	0.864
239	0.805	1.677	1.030
240	0.919	1.617	1.124
242	1.176	1.315	1.295
244	1.458	0.890	1.466
245	1.570	0.690	1.545
248	1.795	0.395	1.716
250	1.820	0.330	1.774
252	1.765	0.295	1.765
254	1.534	0.272	1.646
255	1.313	0.255	1.560
256	1.061	0.241	1.450
257	0.810	0.228	1.315
258	0.564	0.212	1.170
259	0.391	0.209	1.025
260	0.241	0.204	0.880
262	0.095	0.199	0.615
264	0.035	0.205	0.415
265	0.025	0.205	0.340
267	0.016	0.215	0.230
270	0.014	0.205	0.141
280	0.030	0.150	0.059
285	-	-	
290	0.055	0.201	0.056
300	0.089	0.240	0.075
305	0.094	0.239	0.104
310	0.102	0.230	0.125
315	0.106	0.211	0.145
320	0.085	0.180	0.177
330	0.110	0.099	0.225
340	0.136	0.034	0.270
350	0.145	0.014	0.298
360	0.131	0.011	0.275
370	0.098	0.009	0.206
380	0.056	0.006	0.121

The results obtained indicate the presence of different ionic species of BHQS which correspond to the neutralization reactions:

$$H_2A \rightleftharpoons HA^- + H^+ \; ; \quad K_1 = [H^+][HA^-]/[H_2A]$$

$$HA^- \rightleftharpoons H^+ + A^{-2} \; ; \quad K_2 = [H^+][A^{-2}]/[HA^-]$$

Thermodynamic ionization constants

The ionization constants of BHQS have been obtained, since there is a significant difference in the absorbance between the different ionic species. By measuring the absorbance of the compound in a buffer of known pH, the ionization constant of the compound can be obtained from the following equation (8):

$$pK_c = pH + \log \frac{b-x}{x-a}$$

where pH is that of the buffer and x is the absorbance of the compound in that buffer and a and b are the absorbances of the same concentration of the compound in acidic and basic solutions.

Further the thermodynamic ionization constant can be obtained by the expression:

$$pK_a = pK_c + \frac{I^{1/2}}{1 + I^{1/2}}$$

where I is the ionic strength of the medium in which the absorbance of the compound is measured. The value of 'x' has been determined, using different buffers and wavelengths and the

pK_{a1} and pK_{a2}, obtained for 7-bromo-8-hydroxyquinoline-5-sulphonic acid have been represented in tables 3.12 to 3.15.

Table 4.12:

Concentration of BHQS = 6 x 10^{-5}M λ = 248 nm

a = 1.795;   b = 0.395;   Temp. = 25°C

Buffer	pH	x	pK_{c1}	pK_{a1}
Chloro-acetic acid - KOH buffer	2.8	1.660	3.5786	3.6695
Succinic acid - KOH buffer	3.6	1.056	3.5516	3.6425
Succinic acid - KOH buffer	3.9	0.804	3.5156	3.6065
Succinic acid - KOH buffer	4.3	0.619	3.5798	3.6707

Table 4.13:

Concentration of BHQS = 6 x 10^{-5}M; λ = 250 nm

a = 1.820;   b = 0.330;   Temp. = 25°C

Buffer	pH	x	pK_{c1}	pK_{a1}
Succinic acid - KOH buffer	3.6	1.070	3.5941	3.6850
Succinic acid - KOH buffer	3.9	0.780	3.5362	3.6271
Succinic acid - KOH buffer	4.3	0.575	3.5940	3.6849

Table 4.14:

Concentration of BHQS = 6 x 10^{-5}M; λ = 255 nm

a = 1.313; b = 0.255; Temp. = 25°C

Buffer	pH	x	pK_{c_1}	pK_{a_1}
Succinic acid - KOH buffer	4.3	0.425	3.5820	3.6729

Table 4.15:

Concentration of BHQS = 6 x 10^{-5}M; λ = 264 nm

a = 0.205; b = 0.415; Temp. = 25°C

KH_2PO_4 - Na_2HPO_4	7.4	0.290	7.5675	7.6584
KH_2PO_4 - Na_2HPO_4	7.6	0.320	7.5170	7.6079

FIG. 1

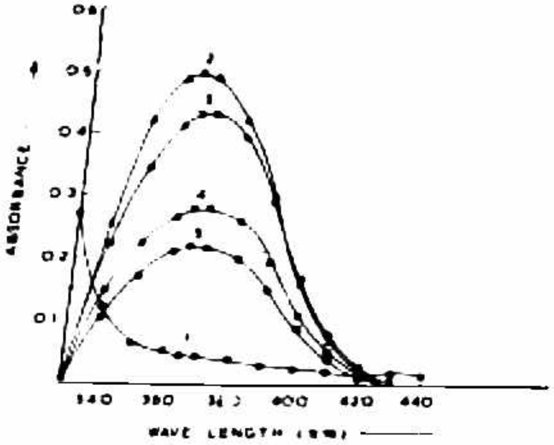


FIG. 2

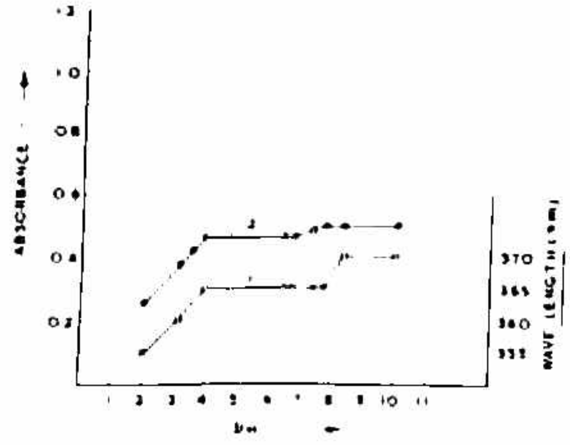


FIG. 6

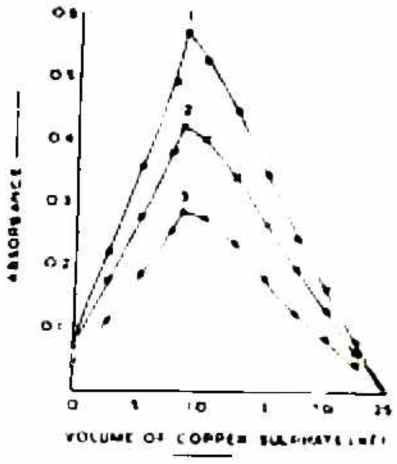


FIG. 4

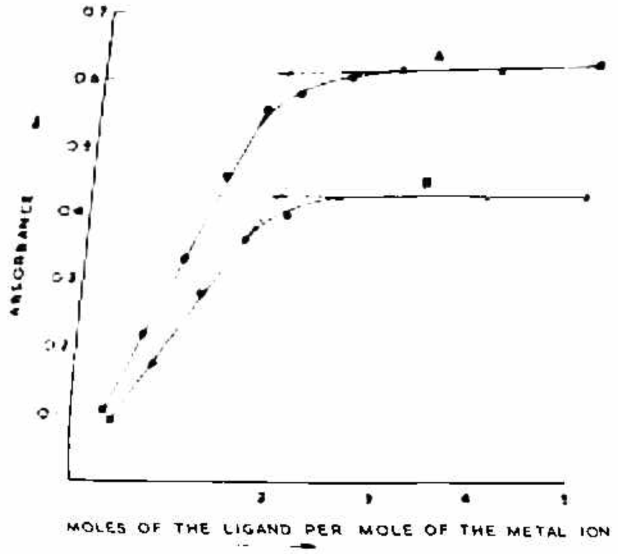


FIG. 5

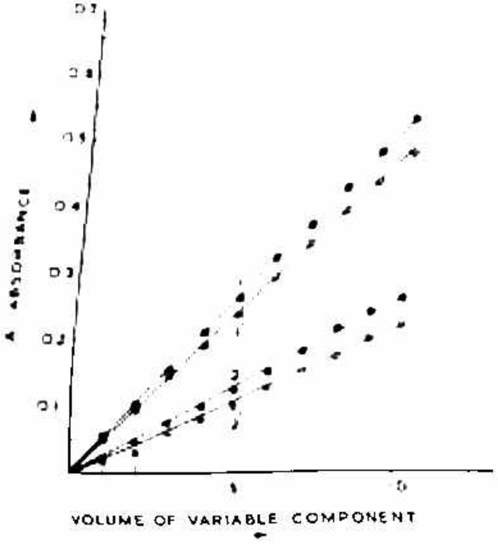
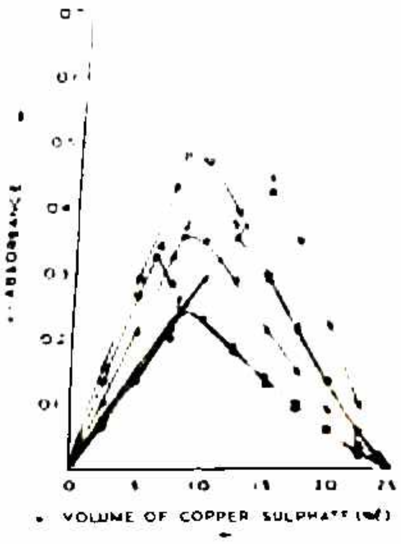


FIG. 7



COPPER(II) - 7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of the complex between copper(II) and 7-bromo-8-hydroxyquinoline-5-sulphonic acid has been investigated in the aqueous medium. The empirical formula of the complex in solution, was found to be Cu $(BHQS)_2$ (where BHQS stands for the ligand). The stability constant of the complex and the free energy of formation, during the complex formation have been evaluated.

Experimental

A standard solution of copper was prepared from a sample of G.R. $CuSO_4 \cdot 5H_2O$ (E.Merck) and the copper content was estimated. A purified sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand solution in aqueous medium. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All the solutions and mixtures were kept in a thermostat for about one hour to attain equilibrium. The pH and ionic strength of the solutions was kept constant ~~value~~ throughout, so that uniform conditions may be maintained for these studies.

Absorption spectra of the complex

To determine the nature of the complex formed in solution, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of copper and 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BHQS) were prepared. The concentrations employed are recorded in Table 4.21.

Table 4.21:

Mixture	Concentration of copper	Concentration of BHQS	Ratio
1	-	9.6×10^{-5}M	0:1
2	9.6×10^{-5}M	9.6×10^{-5}M	1:1
3	4.8×10^{-5}M	9.6×10^{-5}M	1:2
4	3.2×10^{-5}M	9.6×10^{-5}M	1:3
5	2.4×10^{-5}M	9.6×10^{-5}M	1:4

Absorbance of these mixtures was measured at various wavelengths from 330 to 440 nm. The relevant section of the results, which have been graphically represented in P.10.F.1, indicate that the λ max of all the mixtures are in the spectral region of 365 nm. It is evident therefrom that only one complex is formed under the conditions of study. The results have been recorded in Table 4.22.

Table 4.22

Wavelength (nm)	Absorbance 1	2	3	4	5
[illegible]	0.271	0.008	0.001	0.006	0.009
[illegible]	0.123	0.256	0.222	0.148	0.106
350	0.065	0.419	0.344	0.226	0.169
360	0.055	0.486	0.410	0.266	0.210
365	0.046	0.495	0.431	0.280	0.218
370	0.046	0.488	0.430	0.281	0.215
380	0.039	0.419	0.393	0.260	0.201
390	0.030	0.299	0.289	0.194	0.151
400	0.025	0.160	0.168	0.111	0;089
410	0.021	0.069	0.079	0.051	0.041
420	0.017	0.017	0.029	0.019	0.016
430	0.021	0.000	0.006	0.006	0.006
440	0.016	0.000	0.000	0.001	0.001

Effective pH range

Solutions containing the same concentration (8 x 10^{-5}M) of the reagent and copper sulphate were prepared at different pH and the ionic strength was maintained at 0.1 with $NaClO_4$. The absorbance of these solutions was noted. The complex showed λ_{max} at 365 nm in the pH range 3.9 - 7.7 and an almost constant absorbance was shown by the complex in the pH range 3.9 - 6.7. To maintain uniform conditions of study, pH 5.3 was selected for subsequent studies, as the complex shows maximum extinction at this pH. The results of the studies are recorded in Table 4.23 and graphically represented in P.10.F.2, where curve 1 shows variation of λ_{max} with pH, and curve 2 shows the variation of absorbance at 365 nm with pH.

Table 4.23

Wavelength (nm)	pH										
	2.0	3.1	3.5	3.9	4.7	6.4	6.7	[illegible]	[illegible]	[illegible]	11.1
350	0.286	0.350	0.371	0.396	0.405	0.409	[illegible]	[illegible]	[illegible]	0.421	[illegible]
355	0.294	0.369	0.388	0.430	0.435	0.441	0.430	0.440	0.459	0.455	0.444
360	0.274	0.380	0.422	0.446	0.455	0.450	0.456	0.474	0.479	0.444	0.456
365	0.254	0.376	0.422	0.459	0.461	0.460	0.455	0.485	0.496	0.471	0.469
370	0.220	0.373	0.404	0.444	0.453	0.450	0.445	0.476	0.488	[illegible]	0.456
375	0.191	0.325	0.374	0.405	0.414	0.414	0.428	[illegible]	0.446	0.473	0.439

Stoichiometry of the components

(1) Job's method

The composition of the complex was determined at 365 nm by Job's method of continuous variation, using both equimolecular and non-equimolecular solutions. The absorbance was measured using ligand solution as blank. The results of the studies have been presented in Tables 4.24 and 4.25 and graphically represented in P.10.F.3.

Table 4.24:

Concentration of Cu(c) = 1.6x10^{-4}M, 1.2x10^{-4}M, 8.0x10^{-5}M

Concentration of BHQS (c') = 1.6x10^{-4}M, 1.2x10^{-4}M, 8.0x10^{-5}M

(P.10.F.3) (curves) 1 2 3

pH = 5.3 ± 0.1, Temp. = 30°C, Ionic strength = 0.1,

p = c'/c = 1, λ = 365 nm.

Volume of BHQS (ml)	Volume of Cu (ml)	Δ - Absorbance 1	2	3
25.00	0.00	0.000	0.000	0.000
22.50	2.50	0.155	0.102	0.065
20.00	5.00	0.291	0.210	0.136
17.50	7.50	0.430	0.324	0.200
16.67	8.33	0.481	0.355	0.239
15.00	10.00	0.469	0.350	0.229
12.50	12.50	0.395	0.291	0.186
10.00	15.00	0.294	0.215	0.131
7.50	17.50	0.209	0.149	0.094
5.00	20.00	0.135	0.089	0.060
2.50	22.50	0.056	0.038	0.019
0.00	25.00	0.000	0.000	0.000

[illegible]:

Concentration of Cu (c) = 1.6×10^{-4}M, 8.0×10^{-5}M, 8.0×10^{-5}M

Concentration of BHCS(c') = 8.0×10^{-5}M, 1.6×10^{-4}M, 2.4×10^{-4}M

[illegible] 1,4 2 3

[illegible] (curve) 4 5 6

[illegible] = [illegible].1, Temp. = 30°C, Ionic strength = 0.1, λ = 365 nm

Volume of BHCS (ml)	Volume of Cu (ml)	Δ - Absorbance		
		4	5	6
25.00	0.00	0.000	0.000	0.000
22.50	2.50	0.136	0.069	0.075
20.00	5.00	0.265	0.149	0.146
18.75	6.25	0.324	-	-
17.50	7.50	0.286	0.225	0.214
15.00	10.00	0.229	0.289	0.290
12.50	12.50	0.180	0.355	0.355
10.00	15.00	0.139	0.290	0.424
7.50	17.50	0.100	0.220	0.350
5.00	20.00	0.059	0.136	0.220
2.50	22.50	0.025	0.056	0.100
0.00	25.00	0.000	0.000	0.000

The peaks are observed at the metal:ligand ratio of 1:2.

(2) Mole-ratio method

In the mole-ratio method, the metal to ligand ratio was varied from 1:0.33 to 1:6 when the concentration of the metal ion was kept constant at 6 x 10^{-5}M. In another series the metal to ligand ratio was varied from 1:0.4 to 1:6, when the concentration of the metal ion was kept at 4 x 10^{-5}M. Although the studies were made at 365 nm and 380 nm; only the representative results obtained in case of studies performed at 365 nm have been presented in Table 4.26 and represented graphically in P.10.F.4.

Table 4.26:

Concentration of Cu (c) = 6.0×10^{-5}M, 4.0×10^{-5}M

P.10.F.4 Curves A B

Temp. = 30°C; pH = 5.3 ± 0.1; Ionic strength = 0.1

Total volume made up to = 25 ml.

Curve A		Curve B	
Ratio Cu : BHQS	Absorbance	Ratio Cu : BHQS	Absorbance
1 : 0.33	0.106	1 : 0.40	0.880
1 : 0.66	0.217	1 : 0.80	0.176
1 : 1.00	0.326	1 : 1.20	0.281
1 : 1.33	0.455	1 : 1.60	0.360
1 : 1.66	0.555	1 : 2.00	0.395
1 : 2.00	0.581	1 : 2.50	0.423
1 : 2.50	0.605	1 : 3.00	0.425
1 : 3.00	0.615	1 : 4.00	0.425
1 : 4.00	0.615	1 : 5.00	0.425
1 : 5.00	0.624	1 : 6.00	0.425
1 : 6.00	0.630		

The results obtained, show a break at a ratio of one mole of the metal to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of excess concentration of the other. The Δ-absorbance of the solutions was noted at two wavelengths - 365 nm and 380 nm. The results have been recorded in Table 4.27 and represented in P.10.F.5.

Table 4.27:

Concentration of the constant component = 2.4×10^{-4}M

Concentration of the variable component varies from 6.0×10^{-6}M to 6.0×10^{-5}M

pH = 5.3 ± 0.1, Temp. = 30 ± 0.1°C; Total volume = 25 ml

P.10.F.5 Curves 1,2 (365 nm) 1', 2' (380 nm)

Vol. of variable component (ml)	Δ - Absorbance			
	Metal varying		Ligand varying	
	1	1'	2	2'
1	0.055	0.051	0.022	0.015
2	0.102	0.094	0.047	0.030
3	0.155	0.144	0.074	0.059
4	0.210	0.190	0.100	0.080
5	0.259	0.236	0.125	0.100
6	0.320	0.290	0.150	0.125
7	0.370	0.339	0.180	0.149
8	0.426	0.389	0.214	0.170
9	0.480	0.435	0.241	0.199
10	0.531	0.480	0.260	0.220

The slope of each set of the straight lines, provides a Cu : BHQS ratio as 1:2.

Determination of stability constant

The stability constant of copper(II) - 7-bromo-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by two different methods detailed earlier. For the determination of the stability constant by the method of Dey et al and mole-ratio method, the concentrations of the reactants are the same as shown in P.10.F.3 (keeping ligand as blank) and P.10.F.6(keeping water as blank), and P.10.F.4.

For the determination of stability constant by mole-ratio, the values of Em, Es and α are given in Table 4.28.

Table 4.28:

Figure	Curve	Concentration	Em	Es	α
P.10.F.4	A	6×10^{-5}M	0.610	0.580	0.0492
P.10.F.4	B	4×10^{-5}M	0.425	0.400	0.0589

The values of log K obtained by these methods have been given in Table 4.29.

Table 4.29

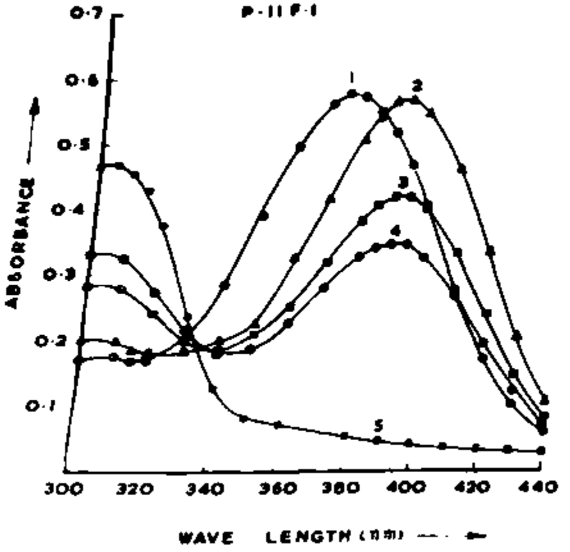
pH = 5.3 ± 0.1; Ionic strength = 0.1; Temp. = 30 °C

Method	Stability constant log K
(1) Mole-ratio method	11.80 ± 0.06
(2) Method of Dey et al	11.70 ± 0.74

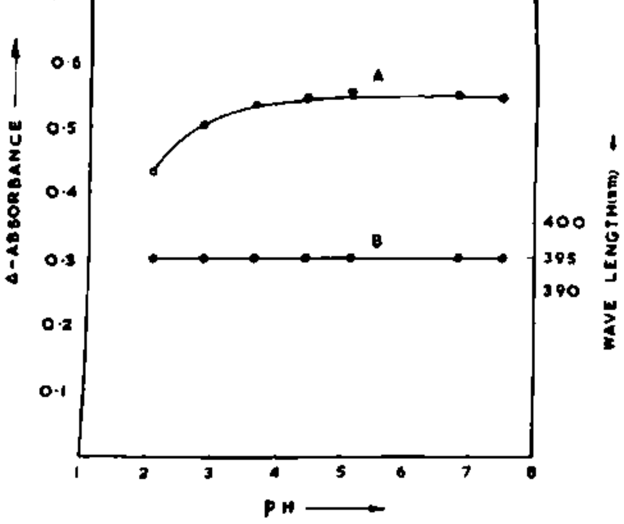
Computational values of: log K = 11.635 ± 0.165

ΔF =-16.135 ± 0.225 kcal/mole

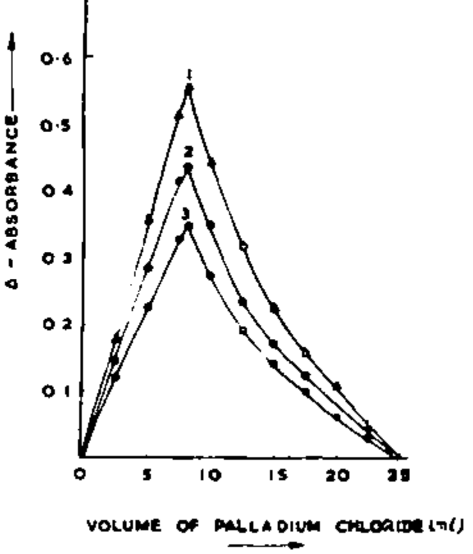
P-II F-1



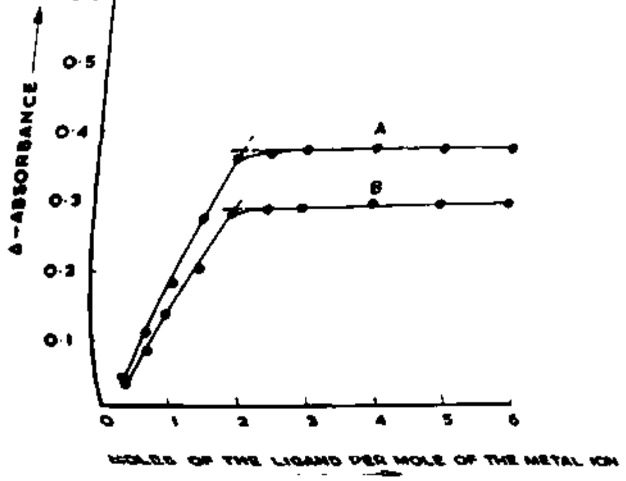
P-II F-2



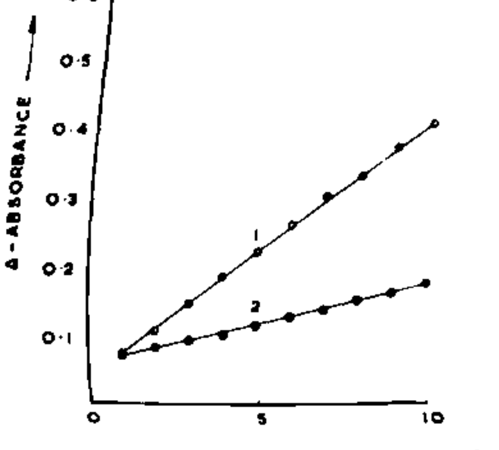
P-II F-3



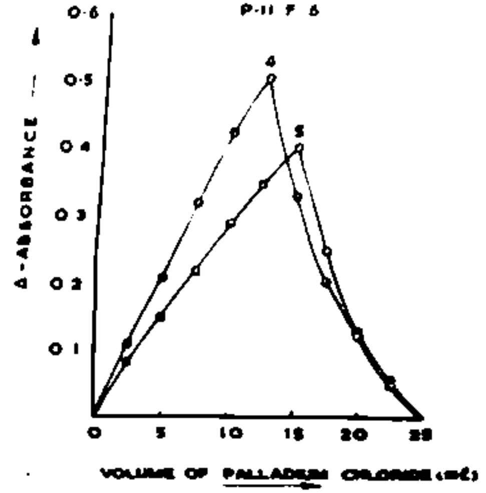
P-II F-4



P-II F-5



P-II F 6



PALLADIUM (II)-7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The complex formed between palladium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid has been investigated spectrophotometrically. The chelate is stable in the pH range 2 to 7.5. The composition of the chelate in solution has been determined by three different methods and it has been found that a stable complex is formed between one mole of palladium and two moles of 7-bromo-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by mole-ratio method and the method using molecular extinction coefficient data. The free energy of formation of the complex has also been evaluated.

EXPERIMENTAL

A standard solution of palladium was prepared by dissolving palladium chloride (Johnson Matthey & Co. London) in dilute HCl, and the palladium content was estimated. A purified sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand in double distilled water. All other reagents used were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 30°C. The individual solutions and mixtures were kept in a thermostat maintaining a

$\pm$ 0.1°C, for one hour to attain equilibrium. Sodium perchlorate was used throughout to maintain a constant ionic strength of 0.1. The pH of the solutions and the mixtures were adjusted with sodium acetate-acetic acid buffer.

Absorption spectra of the complex

To determine the nature of the complex formed, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of palladium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BHQS) were prepared. The concentrations employed in the studies are recorded in Table 4.31.

Table 4.31:

Mixture	Concentration of palladium	Concentration of BHQS	Ratio
1	1.2×10^{-4}M	1.2×10^{-4}M	1:1
2	6.0×10^{-5}M	1.2×10^{-4}M	1:2
3	4.0×10^{-5}M	1.2×10^{-4}M	1:3
4	3.0×10^{-5}M	1.2×10^{-4}M	1:4
5	-	1.2×10^{-4}M	0:1

Absorbance of these mixtures at various wavelengths, from 280 nm to 500 nm, was measured. Some representative results have been graphically represented in P.11.F.1. The results show that only one complex is formed under the condition of study (when the reagent is in excess, shift due to complexation is partially suppressed), in the spectral region of 395 nm.

Effective pH range

Solutions containing 1.[illegible] x 10^{-4}M of the reagent and 6.0 x 10^{-5}M of the metal ion were prepared at different pH and the ionic strength was maintained at 0.1 with $NaClO_4$. The absorbance of these solutions was noted. The complex showed λ_{max} at 395 nm in the pH range 2 to 7.5. pH 4.5 was, however, selected for subsequent studies. The results of the studies are graphically represented in P.11.F.2. Curve A shows variation of Δ-absorbance at 395 nm with pH, whereas Curve B shows change of λ_{max} with pH.

Stoichiometry of the components

1. Job's method

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions, has been adopted. The studies were performed at 380, 395 and 410 nm, but only representative results of the studies at 395 nm have been graphically represented in P.11.F.3 and P.11.F.6. The concentrations employed and the specific conditions of study are as given in Table 4.32.

Table 4.32:

pH = 4.5 ± 0.1, Ionic strength = 0.1, Temp. = 30°C, λ = 395 nm

Figure	Curve	Conc. of palladium(c)	Conc. of [illegible] (c')	p=c'/c
P.11.F.3	1	2.0 x 10^{-4}M	2.0 x 10^{-4}M	1
P.11.F.3	2	1.6 x 10^{-4}M	1.6 x 10^{-4}M	1
P.11.F.3	3	1.2 x 10^{-4}M	1.2 x 10^{-4}M	1
P.11.F.6	1	1.2 x 10^{-4}M	2.4 x 10^{-4}M	2
P.11.F.6	2	[illegible] x 10^{-5}M	2.4 x 10^{-4}M	[illegible]

The peaks are observed at metal:ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from palladium and BHQS in such a way that the mole-ratio of palladium to BHQS varied from 1:0.4 to 1:6.0. The concentrations employed are given in Table 4.33.

Table 4.33:

Temp. = 30 °C, pH = 4.5 ± 0.1, Ionic strength = 0.1,

Total volume made up to - 25 ml.

Final concentration of palladium (c) =	4.0×10^{-5} M	[illegible].0 x 10^{-5}
P.11.F.4 Curves	A	B

The Δ - absorbance of these mixtures was measured at [illegible] nm, and 410 nm. But only representative results, obtained from the studies at 385 nm, have been graphically represented in P.11.F.4.

The results show a break at a ratio of one mole of the metal ion to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 4.34.

Table 4.34

[illegible] Temp. = 30 ± 0.1°C, Total volume = 25 ml

λ = [illegible] nm

Concentration of the constant component = 2.4 x 10^{-4}M

Concentration of the variable component varies from
4 x 10^{-6}M to 4 x 10^{-5}M

Fig.	Line	Remarks
P.11.F.5	1	Metal varying
P.11.F.5	2	Ligand varying

The results have been graphically represented in P.11.F.5.

The slope of the two straight lines, provides the Pd:BHQS ratio as 1:2.

Determination of stability constant

The stability constant of palladium (II) -7-bromo-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by two different methods detailed earlier. For the determination of stability constant by the mole-ratio method, the concentrations of the reactants are same as shown in Table 4.32 (graphically represented by P.11.F.4.); the values of Em, Es and α are given in Table 4.35.

Table 4.35

Figure	Curve	Concentration	Em	Es	α
P.11.F.4	A	4.0 x 10^{-5}M	0.375	0.363	0.0320
P.11.F.4	B	[illegible].0 x 10^{-4}M	0.29[illegible]	0.285	0.0339

Molecular extinction coefficient data (Table 4.36) have been used for calculating the stability constant by this method.

[illegible]

λ	D		ε	A	[illegible]	[illegible]	[illegible]
[illegible] nm	[illegible]	4x10$^{-[illegible]}$	[illegible]	[illegible]	3.78x10^{-5}M	9.661x10^{-11}	11.[illegible]

The values of log K obtained by these methods have been given in Table 4.37.

Table 4.37:

pH = 4.5 ± 0.1, Ionic strength = 0.1, Temp. = 30°C

Method	Stability constant log K
(1) Mole-ratio method	12.751 ± 0.087
(2) Molecular extinction coefficient method	11.985

Computational values of: log K = 12.41 ± 0.43;

ΔF = -17.21 ± 0.60 Kcals/mole

FIG. 2

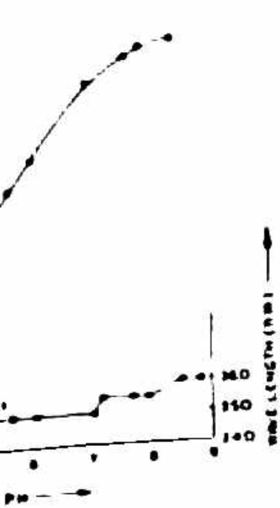


FIG. 1

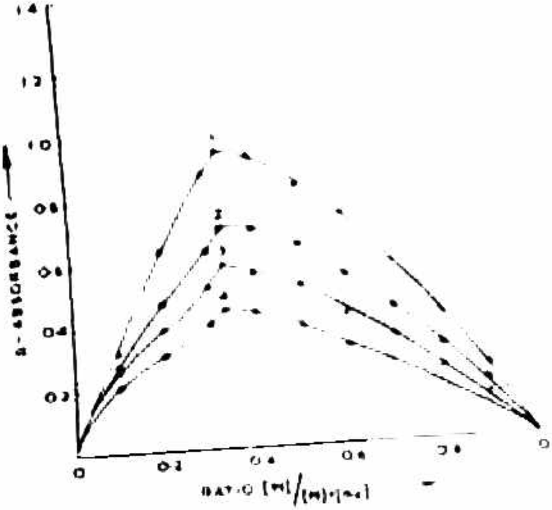


FIG. 5

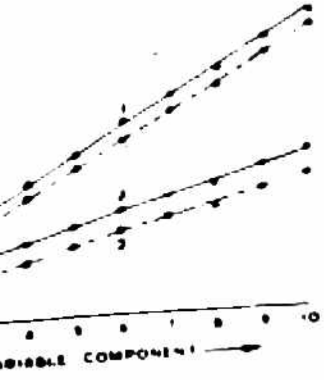
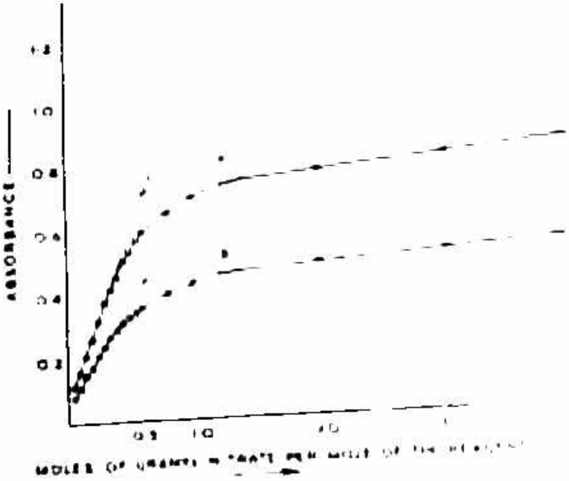
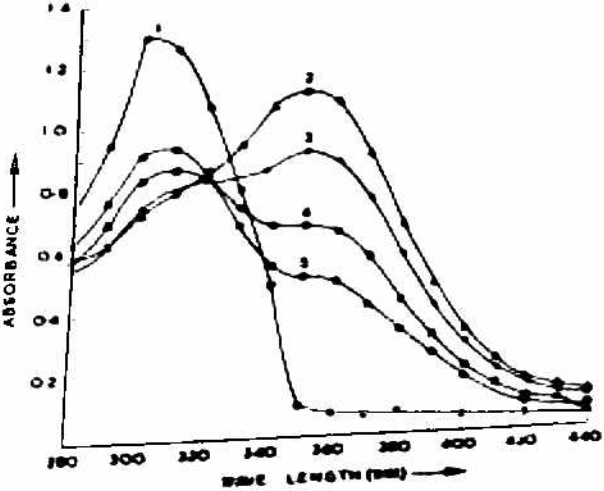
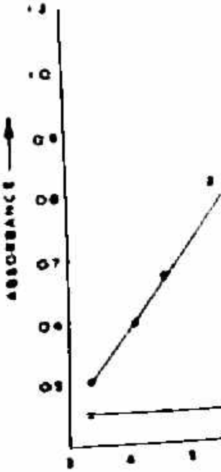


FIG. 4

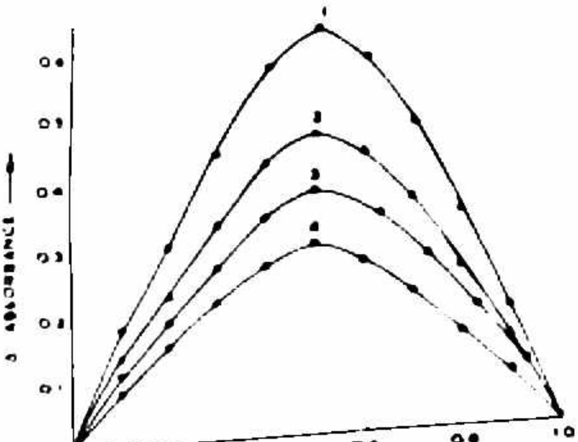


P12P1


1
2
3
4
5
1.4
1.2
1.0
0.8
0.6
0.4
0.2
ABSORBANCE
280
300
320
340
360
380
400
420
440
WAVE LENGTH (nm)


1.1
1.0
0.9
0.8
0.7
0.6
0.5
ABSORBANCE
2
3
4
5

P12-P6


1
2
3
4
0.6
0.5
0.4
0.3
0.2
0.1
ABSORBANCE
0
0.2
0.4
0.6
0.8
1.0
RATIO [M]/[M]+[R]


0.4
0.3
0.2
0.1
ABSORBANCE
0
1
2
3
VOLUME OF

URANYL- 7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of an orange red complex between uranium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid has been studied in aqueous medium. The chelate is stable in the pH range 3.4 - 7.0. The composition of the chelate in solution has been determined by two different methods and it has been found that a stable complex is formed between one mole of uranium and two moles of 7-bromo-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by the method of Banerji and Dey, and mole-ratio method. The free energy of formation of the complex has also been evaluated.

Experimental

A standard solution of uranium was prepared by dissolving uranyl nitrate (B.D.H.) in double distilled water. A purified sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand solution in double distilled water. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 30°C. The individual solutions and mixtures were kept in a thermostat maintaining a temperature of 30 ± 0.1°C, for one hour to attain equilibrium. The pH of the solutions and mixtures was adjusted with NaOH and HCl.

Absorption spectra of the complex in solution

To determine the nature of the complex in solution, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of uranium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BHQS) were prepared. The concentrations employed in the studies are as recorded in Table 4.41.

Table 4.41

Mixtures	Concentration of uranium	Concentration of BHQS	Ratio
1	-	$2.0 \times 10^{-4}M$	0:1
2	$2.0 \times 10^{-4}M$	$2.0 \times 10^{-4}M$	1:1
3	$1.0 \times 10^{-4}M$	$2.0 \times 10^{-4}M$	1:2
4	$6.66 \times 10^{-5}M$	$2.0 \times 10^{-4}M$	1:3
5	$5.00 \times 10^{-5}M$	$2.0 \times 10^{-4}M$	1:4

Absorbance of these mixtures at various wavelengths, from 270 nm to 600 nm, was measured. The relevant section of the results obtained has been graphically represented in P.12.F.1. The results show that only one complex is formed under the conditions of study, in the spectral region of 350 nm.

Effective pH range

Solutions containing the same concentration ($2.0 \times 10^{-4}M$) of the reagent and uranyl nitrate were prepared at different pH and the ionic strength was maintained at 0.1 with $NaClO_4$. The absorbance of these solutions was noted. The complex showed

λ_{max} at 350 nm in the pH range 3.4 - 7.0. To maintain uniform conditions of study and to avoid hydrolysis by going to the basic range, pH 6.6 was selected for subsequent studies. The results of the studies are as graphically represented in P.12.F.2 where Curve 1 shows change of λ_{max} with change of pH, whereas Curve 2 shows variation of absorbance, at 350 nm, with pH.

Stoichiometry of the components

Three methods were adopted for the determination of the empirical formula of the complex in solution.

(1) Job's method

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions, has been adopted. The studies were performed at 340 nm and 360 nm, but only representative results of the studies at 350 nm have been graphically represented in P.12.F.3 and P.12.F.6. The concentrations employed and the specific conditions of study are as given in Table 4.42.

Table 4.42

pH = 6.6 ± 0.1, Ionic strength = 0.1, Temp. = 30°C, λ = 350 nm

Figure	Curve	Concentration of uranium(c)	Concentration of BHQS(c')	$n = c'/c$
P.12.F.3	1	3.2×10^{-4}M	3.2×10^{-4}M	1
P.12.F.3	2	2.4×10^{-4}M	2.4×10^{-4}M	1
P.12.F.3	3	2.0×10^{-4}M	2.0×10^{-4}M	1
P.12.F.3	4	1.6×10^{-4}M	1.6×10^{-4}M	1
P.12.F.6	1	1.6×10^{-4}M	3.2×10^{-4}M	2
P.12.F.6	2	1.2×10^{-4}M	2.4×10^{-4}M	2
P.12.F.6	3	1.0×10^{-4}M	2.0×10^{-4}M	2
P.12.F.6	4	0.8×10^{-4}M	1.6×10^{-4}M	2

The peaks are observed at metal:ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from uranium and BHQS in such a way that the mole-ratio of BHQS to uranium varied from 1:0.05 to 1:8.00. The concentrations employed are given in Table 4.43.

Table 4.43:

Temp. = 30°C, pH = 6.6 ± 0.1, Ionic strength = 0.1

Total volume made up to = 25 ml

Final concentration of BHQS (c') = 1.2×10^{-4}M 8.0×10^{-5}M

A B

P.12.F.5 Curves

The absorbance of these mixtures was measured, at 350 nm and 360 nm. But only a section of the representative results, obtained from the studies at 350 nm, have been graphically represented in P.12.F.4.

The results show a break at a ratio of one mole of the metal ion to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 4.44.

Table 4.44:

pH = 6.6 ± 0.1, Temp. = 30 ± 0.1°C; Total volume = 25 ml

Concentration of the constant component = 1.2×10^{-4}M

Concentration of the variable component varies from 2.4×10^{-6}M to 2.4×10^{-5}M

Figure	Line	Remarks
P.12.F.5	1,1'	metal varies
P.12.F.5	2,2'	ligand varies
P.12.F.5	1,2	λ used = 350 nm
P.12.F.5	1',2'	λ used = 360 nm

The absorbance of the solutions was noted at 350 nm and 360 nm. The results have been graphically represented in P.12.F.5.

The slope of each set of the straight lines, provides UO_2^{++} : BHQS ratio as 1:2.

Determination of stability constant

The stability constant of uranyl - 7-bromo-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by two different methods mentioned earlier. For the determination of the stability constant by the method of Dey et al and mole-ratio method, the concentrations of the reactants are the same as shown in [illegible] and P.12.F.4. For the determination of stability constant by mole-ratio method, the values of Em, Es and α are given in Table 4.45.

Table 4.45:

Figure	Curve	Concentration	Em	Es	α
P.12.F.5	A	6.0 x 10^{-5}M	0.690	0.535	0.2246
P.12.F.5	B	4.0 x 10^{-5}M	0.430	0.329	0.2348

The values of log K obtained by these methods have been given in Table 4.46.

Table 4.46:

pH = 6.6 ± 0.1, Ionic strength = 0.1, Temp. = 30°C.

Method	Stability constant log K
(1) Mole-ratio method	9.832 ± 0.122
(2) Method of Dey et al	9.228 ± 0.281

Computational values of: log K = 9.455 ± 0.509

Δ F = -13.105 ± 0.705 kcal/mole

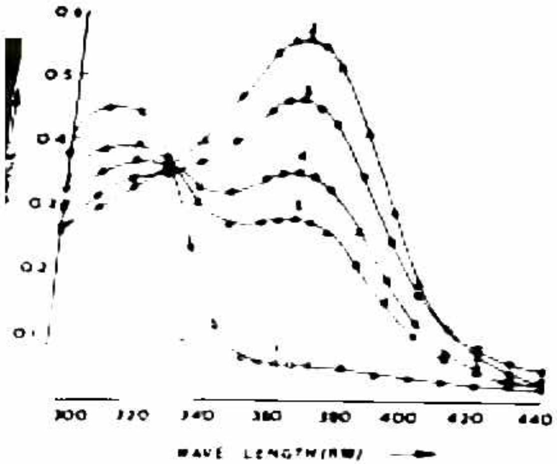


FIG. 1

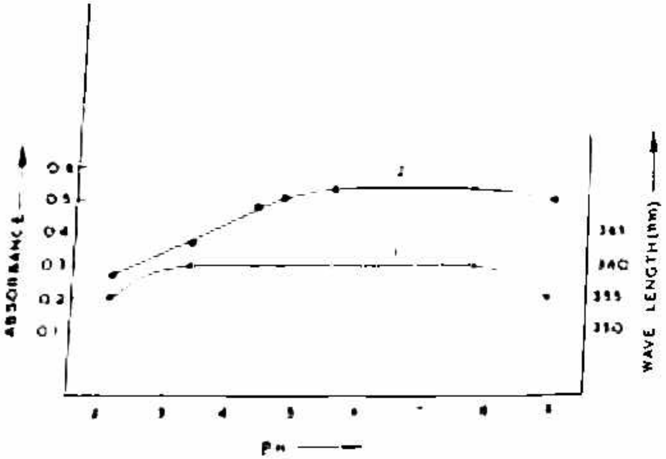


FIG. 2

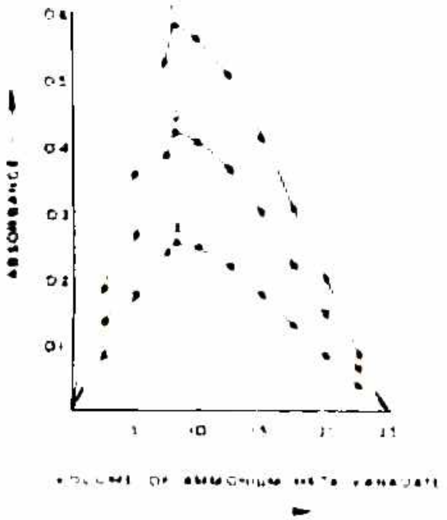


FIG. 3

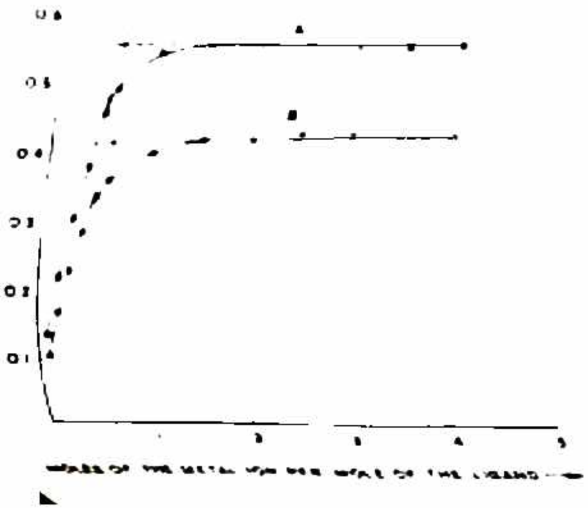


FIG. 4

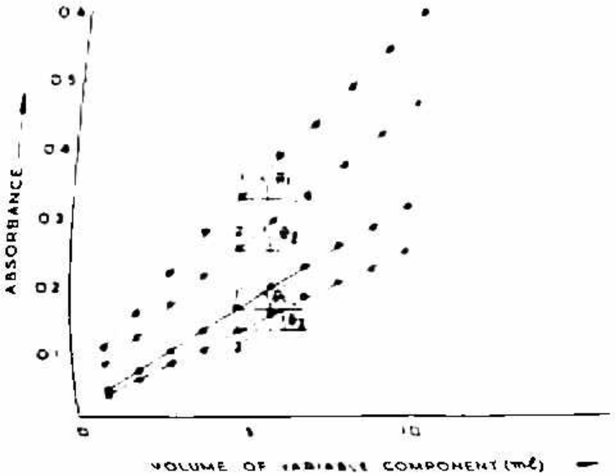


FIG. 5

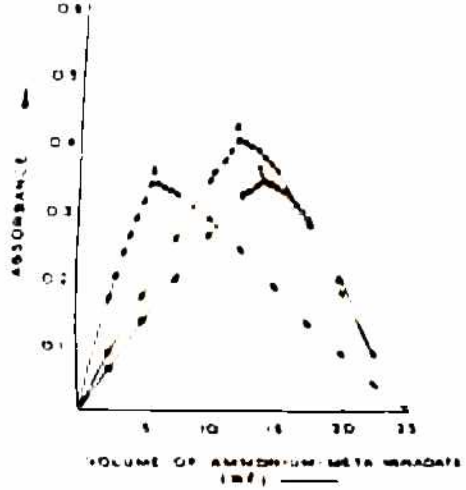


FIG. 6

PERVANADYL- 7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The formation of the complex between vanadium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid has been studied in the aqueous medium. The chelate is stable in the pH range 4.3 - 7.8. The composition of the chelate in solution has been determined by three different methods and it has been found that a stable complex is formed between one mole of vanadium and two moles of 7-bromo-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by the method of Banerji and Dey, mole-ratio method and Job's method. The free energy of formation of the complex has also been evaluated.

Experimental

A standard solution of vanadium was prepared by dissolving ammonium meta vanadate (Reanal A.R.) in hot water. A purified sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand solution in aqueous medium. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 30°C. The individual solutions and mixtures were kept in a thermostat maintaining a temperature 30 ± 0.1°C, for one hour, to attain equilibrium. The pH of the solutions and mixtures was adjusted by the addition of suitable amount of ammonium acetate buffer.

Absorption spectra of the complex in solution

To determine the nature of the complex in solution, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of vanadium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BHQS) were prepared. The concentrations employed are given in Table 4.51.

Table 4.51:

Mixture	Concentration of vanadium	Concentration of BHQS	Ratio Metal:Ligand
1	-	8.0×10^{-5}M	0:1
2	8.0×10^{-5}M	8.0×10^{-5}M	1:1
3	4.0×10^{-5}M	8.0×10^{-5}M	1:2
4	2.66×10^{-5}M	8.0×10^{-5}M	1:3
5	2.00×10^{-5} M	8.0×10^{-5}M	1:4

The absorbance of these mixtures was measured at various wavelengths, from 290 to 500 nm. The results have been recorded in Table 4.52 and a section of the results has been graphically represented in P.13.F.1. From the results, it can be concluded that only one complex is formed, in the spectral region of 360 nm, under the conditions of study.

Table 4.52: (P.13.F.1 Curves 1,2,3,4,5)

Wavelength (nm)	Absorbance 1	2	3	4	5
290	0.379	0.261	0.266	0.296	0.324
300	0.451	0.296	0.315	0.349	0.384
310	0.444	0.328	0.341	0.370	0.394
320	0.372	0.360	0.351	0.358	0.368
330	0.234	0.400	0.367	0.328	0.306
340	0.114	0.471	0.399	0.319	0.269
350	0.066	0.537	0.448	0.341	0.275
355	0.060	0.558	0.463	0.350	0.280
360	0.057	0.560	0.464	0.353	0.278
365	0.056	0.547	0.450	0.344	0.274
370	0.055	0.516	0.428	0.324	0.259
380	0.049	0.413	0.347	0.261	0.211
390	0.040	0.291	0.244	0.186	0.152
400	0.035	0.178	0.165	0.120	0.101
410	0.029	0.109	0.110	0.076	0.068
420	0.026	0.068	0.083	0.052	0.049
430	0.024	0.045	0.059	0.036	0.036
440	0.022	0.029	0.048	0.029	0.030
450	0.019	0.021	0.044	0.020	0.022
460	0.016	0.015	0.039	0.014	0.018
480	0.011	0.010	0.026	0.010	0.015
500	0.008	0.009	0.024	0.008	0.011

Effective pH range

Solutions containing the same concentration (8×10^{-5} M) of the reagent and ammonium meta vanadate were prepared at different pH, and the ionic strength was maintained at 0.1 with $NaClO_4$. The absorbance of these solutions was noted. The complex showed λ_{max} at 360 nm in the pH range 3.3 - 7.7. To maintain uniform conditions of study, pH 6.6 was selected for subsequent studies, as the complex shows maximum extinction at this pH. The results of the studies are recorded in Table 4.53 and graphically represented in P.13.F.2. Curve 1 shows the variation of λ_{max} with pH;

Table 4.53 ([illegible].2 Curves 1,2)

Wavelength (nm)	pH										
	2.1	2.3	4.3	4.7	5.5	6.0	[illegible]	[illegible]	[illegible]	7.7	[illegible]
340	0.271	0.318	0.401	0.428	0.449	0.453	0.447	0.474	0.474	[illegible]	[illegible]
345	0.280	0.337	0.431	0.461	0.485	.488	[illegible]	0.466	[illegible]	[illegible]	[illegible]
350	0.281	0.354	0.456	0.487	0.509	0.515	0.511	0.519	[illegible]	[illegible]	[illegible]
355	0.284	0.364	0.474	0.508	0.533	0.533	0.531	0.536	0.527	[illegible]	[illegible]
360	0.272	0.365	0.479	0.510	0.535	0.538	0.535	0.540	0.539	0.533	0.504
365	-	0.359	0.466	0.497	0.522	0.525	0.519	0.528	0.526	0.518	0.482
370	0.216	0.339	0.443	0.466	0.493	0.494	0.493	0.497	0.496	0.486	0.424

whereas the curve 2 shows the variation of Δ - absorbance at 360 nm with pH.

Stoichiometry of the components

Three methods were adopted for the determination of the empirical formula of the complex in solution.

(1) Job's method

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions, has been adopted. The results of the studies at 360 nm have been presented in Tables 4.54 through 4.59 and graphically represented in P.13.F.3 and P.13.F.6.

Table 4.54:

Concentration of ammonium metavanadate (c) = 1.6×10^{-4}M

Concentration of the ligand BHQS (c') = 1.6×10^{-4} M

pH = 6.6 ± 0.1, p = c'/c = 1, λ = 360 nm, μ = 0.1 $NaClO_4$

(P.13.F.3 Curve 1)

Volume of BHQS (ml)	Volume of Ammonium metavanadate (ml)	Absorbance of		Difference (a-b)
		Mixture (a)	BHQS (b)	
25.00	0.00	0.065	0.065	0.000
22.50	2.50	0.240	0.055	0.185
20.00	5.00	0.411	0.054	0.357
17.50	7.50	0.579	0.054	0.525
16.67	8.33	0.631	0.050	0.581
15.00	10.00	0.610	0.050	0.560
12.50	12.50	0.550	0.045	0.505
10.00	15.00	0.443	0.034	0.409
7.50	17.50	0.329	0.025	0.304
5.00	20.00	0.216	0.015	0.201
2.50	22.50	0.105	0.015	0.090
0.00	25.00	0.000	0.000	0.000

Table 4.55:

Concentration of ammonium metavanadate (c) = 1.2 x 10^{-4}M

Concentration of the ligand BHQS (c') = 1.2 x 10^{-4}M

pH = 6.6 ± 0.1, p = c'/c = 1, λ = 360 nm, μ = 0.1 $NaClO_4$

(P.13.F.3 Curve 2)

Volume of BHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of Mixture (a)	Absorbance of BHQS (b)	Difference (a-b)
25.00	0.00	0.051	0.051	0.000
22.50	2.50	0.185	0.050	0.135
20.00	5.00	0.310	0.045	0.265
17.50	7.50	0.419	0.035	0.384
16.67	8.33	0.454	0.035	0.419
15.00	10.00	0.440	0.035	0.405
12.50	12.50	0.400	0.035	0.365
10.00	15.00	0.323	0.025	0.298
7.50	17.50	0.245	0.025	0.220
5.00	20.00	0.162	0.015	0.147
2.50	22.50	0.075	0.010	0.065
0.00	25.00	0.000	0.000	0.000

Table 4.56:

Concentration of ammonium metavanadate (c) = 8.0 x 10^{-5}M

Concentration of the ligand BHQS (c') = 8.0 x 10^{-5}M

pH = 6.6 ± 0.1, p = c'/c = 1, λ = 360 nm; μ = 0.1 $NaClO_4$

(P.13.F.3 Curve 3)

25.00	0.00	0.035	0.035	0.000
22.50	2.50	0.115	0.030	0.085
20.00	5.00	0.205	0.030	0.175
17.50	7.50	0.270	0.030	0.240
16.67	8.33	0.286	0.030	0.256
15.00	10.00	0.278	0.030	0.248
12.50	12.50	0.248	0.027	0.221
10.00	15.00	0.199	0.024	0.175
7.50	17.50	0.145	0.015	0.130
5.00	20.00	0.099	0.015	0.084
2.50	22.50	0.049	0.010	0.039
0.00	25.00	0.000	0.000	0.000

Table 4.57

Concentration of ammonium metavanadate (c) = 8.0 x 10^{-5} M

Concentration of the ligand BHQS (c') = 1.6 x 10^{-4} M

pH = 6.6 ± 0.1, $p = c'/c = 2$, λ = 360 nm , μ = 0.1 $NaClO_4$

(P.13.F.6 Curve 1)

Volume of BHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of Mixture (a)	Absorbance of BHQS (b)	Difference (a-b)
25.00	0.00	0.065	0.065	0.000
22.50	2.50	0.155	0.063	0.092
20.00	5.00	0.235	0.060	0.175
17.50	7.50	0.315	0.055	0.260
15.00	10.00	0.393	0.048	0.345
14.50	10.50	0.405	0.046	0.359
14.00	11.00	0.420	0.045	0.375
13.50	11.50	0.435	0.045	0.390
13.00	12.00	0.447	0.043	0.404
12.50	12.50	0.444	0.042	0.402
18.00	13.00	0.438	0.042	0.396
11.50	13.50	0.431	0.040	0.391
11.00	14.00	0.420	0.040	0.380
10.50	14.50	0.410	0.040	0.370
10.00	15.00	0.400	0.039	0.361
7.50	17.50	0.315	0.035	0.280
5.00	20.00	0.205	0.025	0.180
2.50	22.50	0.099	0.015	0.084
0.00	25.00	0.000	0.000	0.000

Table 4.58:

Concentration of ammonium metavanadate (c) = 6.0×10^{-5}M

Concentration of the ligand BHQS (c') = 1.8×10^{-4}M

pH = 6.6 ± 0.1, p = c'/c = 3, λ = 360 nm; μ = 0.1 $NaClO_4$

(P.13.F.6 Curve 2)

Volume of BHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of Mixture (a)	Absorbance of BHQS (b)	Difference (a-b)
25.00	0.00	0.068	0.068	0.000
22.50	2.50	0.126	0.061	0.065
20.00	5.00	0.192	0.055	0.137
17.50	7.50	0.249	0.048	0.201
15.00	10.00	0.310	0.045	0.265
14.50	10.50	0.370	0.045	0.325
14.00	11.00	0.375	0.045	0.330
13.50	11.50	0.385	0.045	0.340
13.00	12.00	0.390	0.045	0.345
12.50	12.50	0.385	0.045	0.340
12.00	13.00	0.375	0.040	0.335
11.50	13.50	0.370	0.040	0.330
11.00	14.00	0.360	0.040	0.320
10.50	14.50	0.350	0.040	0.310
10.00	15.00	0.335	0.035	0.300
7.50	17.50	0.320	0.030	0.290
5.00	20.00	0.225	0.025	0.200
2.50	22.50	0.106	0.015	0.091
0.00	25.00	0.000	0.000	0.000

Table 4.59:

Concentration of ammonium metavanadate (c) = 1.6×10^{-4} M

Concentration of the ligand BHQS (c') = 8.0×10^{-5} M

pH = 6.6 ± 0.1, p = c'/c = 0.5 λ = 360 nm, μ = 0.1 $NaClO_4$

(P.13.F.6 Curve 3)

Volume of BHQS (ml)	Volume of ammonium metavanadate (ml)	Absorbance of Mixture (a)	Absorbance of BHQS (b)	Difference (a-b)
25.00	0.00	0.035	0.035	0.000
22.50	2.50	0.200	0.030	0.170
20.00	5.00	0.236	0.030	0.206
17.50	7.50	0.270	0.030	0.240
15.00	10.00	0.294	0.030	0.264
14.50	10.50	0.320	0.030	0.290
14.00	11.00	0.346	0.030	0.316
13.50	11.50	0.368	0.025	0.343
13.00	12.00	0.365	0.025	0.340
12.50	12.50	0.360	0.025	0.335
12.00	13.00	0.356	0.025	0.331
11.50	13.50	0.350	0.025	0.325
11.00	14.00	0.319	0.025	0.290
10.50	14.50	0.270	0.025	0.245
10.00	15.00	0.214	0.024	0.190
7.50	17.50	0.159	0.024	0.135
5.00	20.00	0.109	0.020	0.089
2.50	22.50	0.054	0.016	0.038
0.00	25.00	0.000	0.000	0.000

The peaks are observed at the metal:ligand ratio of 1:2.

(2) Mole-ratio method

A series of solutions was prepared from vanadium and BHQS in such a way that the mole-ratio of BHQS to vanadium varied from 1:0.1 to 1:4. The absorbance of these mixtures was measured using water as blank. Although the studies were made at 360 nm and 380 nm; only the representative results, obtained in case of studies performed at 360 nm have been presented in Table 4.60 and graphically represented in P.13.F.4.

Table 4.60:

Final concentration of the ligand BHQS (c')=3.0x10^{-5}M, 6.0x10^{-5}M
A , B

Temp. = 30°C, pH = 6.6 ± 0.1, Ionic strength = 0.1

Total volume made up to = 25 ml (P.13.F.4 Curves A,B)

Ratio BHQS : V	Absorbance A	Absorbance B
1 : 0.1	0.136	0.105
1 : 0.2	0.221	0.169
1 : 0.3	0.305	0.230
1 : 0.4	0.380	0.285
1 : 0.5	0.454	0.335
1 : 0.6	0.491	0.361
1 : 1.0	0.544	0.401
1 : 1.5	0.558	0.419
1 : 2.0	0.554	0.419
1 : 2.5	0.559	0.430
1 : 3.0	0.560	0.428
1 : 3.5	0.560	0.429
1 : 4.0	0.563	0.431

The results show a break at a ratio of one mole of the metal to two moles of the reagent, indicating that a 1:2 complex is formed.

Slope-ratio method

The volume of variable component was varied from 1 to 10 ml, in presence of excess concentration of the other. The absorbance of the solutions was noted using water as blank at 360 nm and 380 nm. The results of the studies have been recorded in Table 4.601 and graphically represented in P.13.F.5.

Table 4.601:

Final concentration of the constant component = 1×10^{-4}M

Final concentration of the variable component varies from = 5×10^{-6}M to 5×10^{-5} M

pH = 6.6 ± 0.1, Temp. = 30 ± 0.1°C , Total volume = 25 ml

(P.13.F.5. Curves 1,2(360 nm),1',2'(380 nm)

Volume of variable component (ml)	Absorbance			
	Metal varying		Ligand varying	
	1	2	1'	2'
1	0.110	0.084	0.044	0.036
2	0.159	0.125	0.075	0.061
3	0.221	0.175	0.104	0.085
4	0.280	0.221	0.136	0.105
5	0.330	0.255	0.170	0.136
6	0.390	0.294	0.200	0.159
7	0.436	0.329	0.231	0.185
8	0.490	0.375	0.259	0.205
9	0.545	0.421	0.285	0.226
10	0.600	0.465	0.315	0.250

The slope of the two straight lines, provides the VO^{3+}:BHQS ratio as 1:2.

Determination of stability constant

The stability constant of pervanadyl- 7-bromo-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by three different methods mentioned earlier. For the determination of the stability constant by the method of Dey et al, Job's method, and mole-ratio method, the concentrations of the reactants are the same as shown in P.13.F.[illegible], P.13.F.6 and P.13.F.4.

For the determination of stability constant by mole-ratio method, the values of Em, Es and α are given in Table 4.602.

Table 4.602:

Figure	Curve	Concentration	Em	Es	α
P.13.F.4	A	8.0 x 10^{-5}M	0.555	0.455	0.180
P.13.F.4	B	4.0 x 10^{-5}M.	0.410	0.335	0.183

The values of log K obtained by these methods have been given in Table 4.603.

Table 4.603

pH = 6.6 ± 0.1, Ionic strength = 0.1, Temp. = 30°C

Method	Stability constant log K
(1) Mole-ratio method	10.454 ± 0.115
(2) Method of Dey et al	10.610 ± 0.300
(3) Job's method	10.663 ± 0.165

Computational values of: log K = 11.610 ± 0.300

ΔF = -14.710 ± 0.410 kcal/mole

(III) - 7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE:

The formation of a green chelate between trivalent iron and 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BHQS) has been determined by the three different methods mentioned earlier and it has been found that a stable chelate is formed between one mole of iron and two moles of the ligand. The stability constant and the free energy of formation of the complex have been evaluated.

EXPERIMENTAL

A standard solution of iron was prepared by dissolving ferric chloride (BDH) in dilute hydrochloric acid and the iron content was estimated. The reagent solution was prepared from the recrystallised sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid in double distilled water. Suitable standard solutions were prepared from these stock solutions.

Conditions of study

All experiments were performed at 20°C. The individual solutions and the mixtures were kept in a Townson and Mercer precision thermostat maintained at 20±0.1°C. The mixtures were allowed to stand for an hour in the thermostat to attain equilibrium. The pH of all the mixtures was adjusted by the addition of suitable amount of phthalate buffer.

Absorption spectra of the complex

To determine the nature of the complex formed, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of iron and 7-bromo- -hydroxyquinoline-5-sulphonic acid (BHQS) were prepared. The concentrations employed in the studies are recorded in Table 4.41.

Table 4.41:

Mixture	Concentration of iron	Concentration of BHQS	Ratio
1	-	3.2×10^{-4}M	0:1
2	3.2×10^{-4}M	3.2×10^{-4}M	1:1
3	1.6×10^{-4}M	3.2×10^{-4}M	1:2
4	1.06×10^{-4}M	3.2×10^{-4}M	1:3
5	8.0×10^{-5}M	3.2×10^{-4}M	1:4

Absorbance of these mixtures at various wavelengths, from 390 to 480 nm was measured and the results have been graphically represented in P.14.F.1. The results show that only one complex is formed under the conditions of study in the spectral region of 430 nm.

Effective pH range

Solutions containing the same concentration (2.0×10^{-4}M) of metal and ligand were prepared at different pH. The absorbance of these solutions was noted. The complex showed a λ_{max} at 430 nm in the pH range 1.9 to 8.6. pH 3 was, however, selected for subsequent studies. The results of the studies are graphically represented in P.14.F.2 Curve 1 shows variation of λ_{max} with pH; whereas curve 2 shows variation of absorbance with pH.

[illegible]toichiometry of the components

[illegible]

Job's method of continuous variation, using both equimolecular and non-equimolecular solutions has been adopted. The [illegible] were performed at 430 nm and 450 nm, but only representative re[illegible] o[illegible] studies at 430 nm have been graphically [illegible] P.14.F.3 and P.14.F.6. The concentrations employed [illegible] the [illegible]ic conditions of study are as given in Table 4.62.

[illegible]:

pH = [illegible], Temp. = 20°C, λ = 430 nm

[illegible]	[illegible]	Conc. of [illegible]	Conc. of iron	[illegible]
[illegible]	1	[illegible].1 x 10^{-4} [illegible]	[illegible] x 10^{-4}	1
P.14.F.[illegible]	[illegible]	[illegible] 10^{-4} [illegible]	[illegible] x 10^{-4}	1
[illegible]	3	[illegible] x 10^{-4} M	[illegible] x 10^{-4}	1
[illegible]	1	6.4 x 10^{-4} [illegible]	[illegible] x 10^{-4}	2
[illegible]	2	5.6 x 10^{-4} [illegible]	[illegible] x 10^{-4}	2
P.14.[illegible]	[illegible]	4.[illegible] x 10^{-4} [illegible]	[illegible].4 x 10^{-4}	2

The peaks are observed at metal:ligand ratio of 1:2.

(2) [illegible]-ratio method

A series of solutions was prepared from iron and BHQS in such [illegible] way that the mole-ratio of iron and BHQS varied from 1:0.1 to 1:4.0. The concentrations employed are given in Table 4.63.

Table 4.63:

Temp. = 20°C, pH = 3.0 ± 0.1, Total volume made up to - 25 ml.

Concentration of iron (c) =	$1.2 \times 10^{-[illegible]}$ M	$8.0 \times 10^{-[illegible]}$ M
P.14.F.4 Curves	A	B

The Δ - absorbance of these mixtures was measured at 430 nm and 450 nm. But only representative results, obtained from the studies at 430 nm, have been graphically represented in P.14.F.4.

The results show a break at a ratio of one mole of the metal ion to two moles of the reagent, indicating that a 1:2 complex is formed.

(3) Slope-ratio method:

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 4.64.

Table 4.64:

pH = 3.0 ± 0.1, Temp. = 20°C, Total volume = 25 ml

Concentration of the constant component = 4.8×10^{-4} M

Concentration of the variable component varies from

1.2×10^{-5} M to 1.2×10^{-4} M

Figure	Line	Remarks
P.14.F.5	1,1'	Metal varying
P.14.F.5	2,2'	Ligand varying
P.14.F.5	1,2	λ used = 430 nm
P.14.F.5	1',2'	λ used = 450 nm

The results have been graphically represented in P.14.F.5. The slope of the two straight lines, provides the Fe:BHQS ratio as 1: .

Determination of stability constant

The stability constant of iron(III)- 7-bromo-8-hydroxyquinoline-5-sulphonic acid chelate has been determined by two different methods, mentioned earlier. For the determination of stability constant by the mole-ratio method, the concentrations of the reactants are the same as shown in Table 4.64 (graphically represented by P.14.F.4); the values of Em, Es and α are given in Table 4.65.

Table 4.65:

Figure	Curve	Concentration	Em	Es	α
P.14.F.4	A	1.2×10^{-4} M	0.325	0.270	0.1692
P.14.F.4	B	[illegible] x 10^[illegible] M	0.205	0.160	0.2195

For the determination of stability constant by the method of Dey et al, the concentration of the reactants are the same as shown in P.14.F.3 and recorded in Table 4.62.

The values of log K obtained by these methods have been given in Table 4.66.

Table 4.66

pH = 3.0 ± 0.1, Temp. = 20°C. Ionic strength = 0.1

Method	Stability constant log K
(1) Method of Dey et al	9.366 ± 0.104
(2) Mole-ratio method	9.467 ± 0.007

Computational values of: log K = 9.368 ± 0.106

ΔF = -12.570 ± 0.140 Kcals/mole

GALLIUM(III)- 7-BROMO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID CHELATE

The complex formed between gallium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid, in solution, has been investigated spectrophotometrically. The chelate is stable in the pH range [illegible] 5. . The composition of the chelate in solution has been determined by three different methods and it has been found that a stable complex is formed between one mole of gallium and three moles of 7-bromo-8-hydroxyquinoline-5-sulphonic acid. The stability constant of the chelate has been determined by mole-ratio method and the method using molecular extinction coefficient data. The free energy of formation of the complex has also been evaluated.

EXPERIMENTAL

A standard solution of gallium was prepared by dissolving gallium sulphate (α - Inorganics, U.S.A.) in dilute sulphuric acid. A purified sample of 7-bromo-8-hydroxyquinoline-5-sulphonic acid was used for the preparation of the ligand in double distilled water. All other reagents were of analytical grade and were used without further purification.

Conditions of study

All experiments were performed at 20°C. The individual solutions and mixtures were kept in a thermostat maintaining a temperature 20 ± 0.1°C, for one hour to attain equilibrium. The pH of the solutions and the mixtures was adjusted with sodium acetate-acetic acid buffer.

Absorption spectra of the complex

To determine the nature of the complex formed, the method of Vosburgh and Cooper was adopted. Mixtures containing varying proportions of gallium and 7-bromo-8-hydroxyquinoline-5-sulphonic acid (BHQS) were prepared. The concentrations employed in the studies are recorded in Table 4.71.

Table 4.71:

Mixture	Concentration of BHQS	Concentration of gallium	Ratio
1	1.6×10^{-4}M	1.6×10^{-4}M	1:1
2	8.0×10^{-5}M	1.6×10^{-4}M	1:2
3	5.33×10^{-5}M	1.6×10^{-4}M	1:3
4	4.0×10^{-5}M	1.6×10^{-4}M	1:4

Absorbance of these mixtures at various wavelengths, from 280 nm to 3[illegible] nm, was measured. The results have been graphically represented in P.15.F.1. The results show that only one complex is formed under the conditions of study in the spectral region of 355 nm.

Effective pH range

Solutions containing (1.6×10^{-4}M) of the reagent and (8×10^{-5}M) of the metal ion were prepared at different pH. The absorbance of these solutions was noted. The complex showed λ_{max} at 355 nm in the pH range 2.9 to 5.9. pH 4 was, however, selected for subsequent studies. The results of the studies are graphically represented in P.15.F.2. Curve 1 shows variation of λ_{max} with pH; whereas curve 2 shows variation of absorbance with pH.

Stoichiometry of the components

(1) Job's method

The method of continuous variation, using both equimolecular and non-equimolecular solutions has been adopted. The studies were performed at 340 nm, 355 nm, and 370 nm, but only representative results, of the studies at 355 nm have been graphically represented in P.15.F.3 and P.15.F.6. The concentrations employed and the specific conditions of study are as given in Table 4.72.

Table 4.72

pH = 4.0 ± 0.1, Ionic strength = 0.2, Temp. = 20°C, λ = 355 nm

Figure	Curve	Conc. of gallium (c)	Conc. of BHQS (c')	n = c'/c
P.15.F.3	1	2.0×10^{-4}M	2.0×10^{-4}M	1
P.15.F.3	2	1.6×10^{-4}M	1.6×10^{-4}M	1
P.15.F.3	3	1.2×10^{-4}M	1.2×10^{-4}M	1
F.15.F.6	4	1.2×10^{-4}M	2.4×10^{-4}M	2
F.15.F.6	5	8.0×10^{-5}M	2.4×10^{-4}M	3
F.15.F.6	6	2.4×10^{-4}M	1.2×10^{-4}M	0.5

The peaks are observed at metal:ligand ratio of 1:3.

(2) Mole-ratio method

A series of solutions was prepared from gallium and BHCS in such a way that the mole-ratio of gallium and BHCS varied from 1:0.5 to 1:9.0. The concentrations employed are given in Table 4.73.

Table 4.73:

Temp. = 20°C ; pH = 4.0 ± 0.1,

Total volume made up to = [illegible] ml.

Concentration of gallium (c) =	4×10^{-5}M	3.2×10^{-5}M
	A	B
P.15.F.4		

The Δ - absorbance of these mixtures was measured at 340 nm, 355 nm and 370 nm. But only representative results, obtained from the studies at 355 nm, have been graphically re-presented in P.15.F.4.

The results show a break at a ratio of one mole of the metal ion to three moles of the reagent, indicating that a 1:3 complex is formed.

(3) Slope-ratio method

The volume of the variable component was varied from 1 to 10 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 4.74.

Table .74:

[illegible] ± 0.1, Temp. = 20 ± 0.1°C, Total volume = 25 ml

λ = 355 nm, $\mu = 0.$

Concentration of the constant component = 3.2 x 10^{-4} M

Concentration of the variable component varies from

4 x 10^{-5} M to 4 x 10^{-5} M

Figure	Line	Remarks
P.15.F.5	1	Metal varying
P.15.F.5	2	Ligand varying

The results have been graphically represented in P.15.F.5. The slope of the two straight lines, provides the Ga:BHQS ratio as 1:3.

Determination of stability constant

The stability constant of gallium (III)- 7-bromo-8-hydroxy-quinoline-5-sulphonic acid chelate has been determined by two different methods detailed earlier. For the determination of the stability constant by the mole-ratio method, the concentrations of the reactants are same as shown in Table 4.73 (graphically represented by P.15.F.4.); the values of Em, Es and α are given in Table 4.75.

Table 4.75:

Figure	Curve	Concentration	Em	Es	α
F.15.[illegible].4	A	4×10^{-5} M	0.5600	0.3675	0.3437
F.15.[illegible].4	B	3.2×10^{-5} M	0.4200	0.2840	0.3238

Molecular extinction coefficient data (Table 4.76) have been used for calculating the stability constant by this method.

Table 4.76:

λ	D	C	ϵ	A	x	K	log K
355 nm	0.588	4×10^{-5}	14700	0.383	2.6054×10^{-5} M	2.547×10^{13}	13.406

The values of log K obtained by these methods have been given in Table 4.77.

Table 4.77:

pH = 4.0 ± 0.1, Temp. = 20°C, Ionic strength = 0.2

Method	Stability constant log K
(1) Mole-ratio method	13.638 ± 0.204
(2) Molecular extinction coefficient method	13.406

Computational values of: log K = 13.654 ± 0.21[illegible];

Δ[illegible] = -18.275 ± 0.29[illegible] kcals/mole

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CHAPTER V

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM AND IRON WITH 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

[illegible] the past two decades, there has been a universal [illegible] the need for highly sensitive and accurate analytical methods for the determination of micro amounts of uranium [illegible] of sample materials, and such, efforts have also been made towards the development of analytical chemistry of uranium. Among the large variety of methods studied, chemical procedures, based on chelate formation have also been devised in [illegible] to estimate small amounts of uranium.

The present study was undertaken to explore the possibility of developing a sensitive and selective spectrophotometric reagent for uranium which will be water soluble e.g. dibenzoylmethane, has been found to be one of the most sensitive reagent for the determination of uranium, but it suffers from the disadvantage of being insoluble in water. 7-chloro-8-hydroxyquinoline-5-sulphonic acid forms complexes with various metal ions, but it gives distinct colour with only a few of them (namely uranium and iron). With uranium, it reacts sensitively to form an orange red colour. The present study deals with the use of this reagent for the spectrophotometric determination of very small quantities of uranium.

EXPERIMENTAL METHODS

Spectrophotometric measurements were made with a Hilger-Uvispek Spectrophotometer (model H 700 - 380) using 1 cm light [illegible]. The cell compartment was fitted with a jacket for maintaining a constant temperature. Measurements of pH were made at 30°C, $\mu = 0.1$ M and at pH 6.6. The total volume in all cases was kept at 25 ml.

Standard procedure for the determination

An aliquot of the standard solution (33 ppm) was introduced into a 25 ml flask. A 5.0 ml sample of a pH [illegible] buffer, [illegible] ml of [illegible] $NaClO_4$ and [illegible] ml of 2 x 10^{-3} M reagent solution were added, [illegible] 25 ml by the addition of distilled water and was [illegible] for [illegible] to attain equilibrium. The absorbance of the solution was measured against the reagent blank at 355 nm. The concentration of the unknown solution was calculated by comparing the absorbance values with the calibration curve obtained by plotting values of absorbance observed in case of a number of aliquots, against the metal ion concentration in ppm, in each case.

RESULTS AND DISCUSSION

The standard procedure was formulated, in light of the study of the optimum conditions established, as reported below:

Absorption curves

The nature of the complex formed was studied by the method of Vosburgh and Cooper, and it was found that only one complex is formed under the conditions of study, with λ_{max} at 355 nm. The λ_{max} of the reagent at this pH is at [illegible] nm (Fig.[illegible].1).

Effect of pH

The effective pH range for the stable existence of the [illegible] was found to be between 5.4 and 9.3 (P.5.F.2). However, [illegible] ± 0.1, was selected for subsequent studies.

[illegible] time and temperature

The colour of the uranium complex, develops instantaneously and remains constant for at least 24 hours at room temperature. With an increase in temperature, a decrease in the value of absorbance of the complex was observed. However, in presence of an excess of the reagent, the temperature has little effect on the absorbance of the complex.

[illegible] of reagent concentration

A study of effect of reagent concentration at a pH 6.6±0.1 and 355 nm indicated that there should be at least six fold molar excess of the reagent over uranium concentration, for maximum colour formation of the complex. The results obtained have been graphically represented in Fig. P.5.F.4.

Order of addition of the reagents

Varying the order in which the reagents were added, had no significant effect on the results.

Composition of the chelate

The composition of the chelate was confirmed by Job's method [illegible], mol -ratio method (P.[illegible]) and slope ratio method ([illegible].5) to be 1:2.

Calibration curve, sensitivity and precision

The complex obeys Beer's law over a wide range of uranium [illegible]. F.16.F.1 shows the calibration curve for determination of uranium obtained as a result of experiments carried out with 1-3[illegible] ppm of the metal. The optimum concentration range for the determination of uranium by the Ringbom method was found to be [illegible].7 - 28.5 ppm (F.16.F.2). The molar absorptivity comes out to be 6575 at 355 nm. Spectrophotometric sensitivity (Sandell [illegible]) [illegible] from Beer's law curve and was found to be [illegible].036 µ-g of [illegible]/cm^2. The reproducibility and precision of the method was studied by applying the standard procedure to a number of solutions of known concentration of uranium and comparing the results, so obtained with the calibration curve. The deviation was found to be within a range of 1%.

Effect of diverse ions

The effect of diverse ions on the determination of uranium was examined under the conditions of standard procedure. In every case 19 ppm of uranium solution was used. The tolerance limit was taken as the amount that caused absorbance error - not exceeding 2%. It was observed that even 4 ppm concentration of the ions like magnesium, lead, cadmium, zinc, copper, nickel, cobalt, palladium, beryllium, ferric, aluminium, gallium, indium, thallic, lanthanum, thorium, cerous, vanadium, chromium, molybdenum, order for causing interference was observed further.

Mercury and phosphate (8); nitrate (12); strontium, thallous, sulphate, and oxalate (40); fluoride (50); citrate (80); [illegible] (140); tartarate (200); iodide, nitrite, and barium (280). Chloride and bromide ions did not interfere even in presence of 280 ppm of these ions. These interfering ions must be removed or masked in the usual ways (1,2,3) before proceeding for the determination.

Comparison with the other methods of determination of uranium

Several sensitive organic reagents have been used for the determination of uranium. The proposed method is simple, rapid and sensitive, but not selective. An idea of sensitivity of complexation reactions of uranium with various other reagents, with regard to molar absorptivities of the uranium complexes formed, can be had from the comparative account given in Table 5.1

Table 5.1:

Comparison with other reagents

Reagent	Wavelength (nm)	Molar absorptivity
Arsenazo (4)	[illegible]	22900
Azide ([illegible])	420	1650
[illegible]ylmethane ([illegible])	395	20000
[illegible] (7)	510	10625
[illegible] ([illegible])	375	3850
1-(pyridyl-2-azo)-2-naphthol(10)	560	23000
7-chloro-8-hydroxyquinoline-5-sulphonic acid (11)	[illegible]	[illegible]

From the results obtained, it will be clear, that the method compares favourably with the other methods available and commonly used for the determination of uranium, with regard to their sensitivity.

SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH 7-CHLORO-8-HYDROXYQUINOLINE-5-SULPHONIC ACID

Apart from aluminium, iron is the most abundant metal in nature. The most important use for iron is in the manufacture of various steels. Manganese, Nickel, Chromium, Cobalt, Tungsten, Molybdenum, Tantalum, Vanadium and zirconium, in small amounts, is invariably mixed with iron, to impart a particular, desired property to steels.

The importance of determination of iron needs no comments. Numerous methods are available for its colorimetric determination. These have been well described and summarized in various reviews and standard texts (1-3, 12-22). Among the large number of reagents for its determination, the most widely used are thiocyanate (23-27), 1,10-phenanthroline (26,28-33), 2,2'-bipyridine (3,34-38), bathophenanthroline (39), ferron (40,41), 8-hydroxyquinoline (42-45), [illegible] (27,46,47), salicylic acid (36, 48-51) and sulpho-salicylic acid (52-54), salicylaldoxime (55), disodium-1,2-dihydroxybenzene 3,5-disulphonate (56) and nitroso-R salt (57,58).

In order to avoid interference due to the foreign ions, and to have a stable colour, solvent extraction methods are frequently used; and after the extraction of iron into suitable organic solvents, it can subsequently be determined spectrophotometrically with 1,10-phenanthroline (59,60), dibenzoylmethane (61), thiocyanate (62-65), or 2-mercaptopyridine-1-oxide (thione)

(66). Several reviews and texts have been published which deal with the extraction of iron (67, 68-76). Compounds like β-diketones have been employed for the extraction as well as for the photometric determination of iron. A comprehensive study of acetyl acetone and its use in chelating and extracting iron has been made (71,77,78).

7-Chloro-8-hydroxyquinoline-5-sulphonic acid forms a very stable green coloured chelate with iron (III) in aqueous medium. The present investigation was undertaken to evaluate 7-chloro-8-hydroxyquinoline-5-sulphonic acid as a spectrophotometric reagent for the determination of iron (III).

EXPERIMENTAL METHODS

The instruments used for pH and absorbance measurements are the same as described earlier. The studies were made at 20°C and at pH 3.0. The total volume in all cases was kept at 25 ml.

The recommended procedure for the determination

An aliquot of the standard solution (17.88 ppm) was introduced into a 25 ml flask. A 5.0 ml sample of a pH 3.0 buffer (chloro-acetic acid-KOH) and a four-fold excess of the reagent solution were added, and the volume was adjusted to 25 ml by the addition of distilled water and was allowed to stand for 30 minutes to attain equilibrium. The absorbance of the solution was measured against the reagent blank at 355 nm. The concentration of the unknown solution was obtained by comparing the absorbance values with the calibration curve obtained by plotting values of absorbance observed in case of a number of aliquots, against the [illegible]l iron concentration in ppm, in each case.

RESULTS AND DISCUSSION

The standard procedure was formulated, in light of the study of the optimum conditions established, as reported below.

Absorption curves

The nature of the complex formed was studied by the method of Vosburgh and Cooper, and it was found that only one complex is formed under the conditions of study, with λ_{max} at 430 nm. (F.7.F.1).

Effect of pH

The effective pH range for the stable existence of the complex was found to be between 1.5 to 7.0. pH 3 was, however, selected for subsequent studies. (F.7.F.2).

Effect of time and temperature

The colour of the iron complex, develops instantaneously and remains constant for at least 24 hours at room temperature. With an increase in temperature, a slight decrease in the value of absorbance of the complex was observed. However, in presence of an excess of the reagent, the temperature has little effect on the absorbance of the complex.

Effect of reagent concentration

A study of effect of reagent concentration at a pH 3.0±0.1 and 430 nm, indicated that there should be a four-fold molar excess of the reagent over iron concentration, for maximum colour formation of the complex. (P.7.F.4)

Order of addition of the reagents

Varying the order, in which the reagents were added, had no significant effect on the results.

Composition of the chelate

The composition of the chelate was confirmed by Job's method (P.7.F.3), mole-ratio method (P.7.F.4) and slope-ratio method (P.7.F.5) to be 1:2.

Calibration curve, sensitivity and precision

The complex obeys Beer's law over a wide range of iron concentration. P.17.F.1 shows the calibration curve for determination of iron obtained as a result of experiments carried out with 2.235 - 13.410 ppm of the metal. The optimum concentration for the determination of iron by the Ringbom method was found to be 4.47 - 13.41 ppm (P.17.F.2). The molar absorptivity at 430 nm comes out to be 1869. Spectrophotometric sensitivity (Sandell) was calculated from Beer's law curve and was found to be 0.0298 µg of iron/cm^2. The reproducibility and precision of the method was studied by applying the standard procedure to a number of solutions of known concentration of iron and comparing the results, so obtained with the calibration curve. The deviation was found to be within range of 1%.

Effect of diverse ions

[illegible] iverse ions, on the determination of iron was examined under the conditions of standard procedure. In [illegible], 0.94 ppm of iron solution was taken. The tolerance [illegible] taken as the amount of diverse ion that caused absor- [illegible] error - not [illegible] 2%. It was observed that even 2 ppm concentration of the ions like, copper, nickel, palladium, [illegible], cerium, vanadium, tungsten, molybdenum, ruthenium and platinum could not be tolerated, no interferences were observed. The following concentration order (in ppm) for causing interferences was observed further: beryllium, cobalt, aluminium and nitrite (5); oxalate and borate (8); lead, cadmium and zinc (10); chlorate, nitrate, thorium and lanthanum (15); fluoride (20); tartarate (25); and phosphate (100). Chloride ions did not interfere, even in presence of 100 ppm of this ion, whereas, a large excess, of the order of 200 ppm, of magnesium and uranium could be tolerated. These interfering ions must be removed or masked by the usual methods (1,2,3) before proceeding for the determination.

Comparison with the other methods of determination of iron

Several sensitive organic reagents have been used for the determination of iron. The proposed method is simple and rapid, but not very selective and sensitive. The sensitivities of other widely used methods for iron along with that of the present one are summarized in Table 5.2.

Table 5.2:

Comparison with other reagents

Reagent	Sensitivity (Sandell) µg/cm^2
Thiocyanate + acetone	0.004/480 nm
1,10 phenanthroline	0.005/508 nm
2,2'- Bipyridine	0.007/522 nm
Ferron	0.015/610 nm
Methophenanthroline/cyclohexane	0.0021/533 nm
Sulfosalicylic acid	0.01/430 nm
Mercaptoacetate	0.014/540 nm
[illegible]	0.173/435 nm
[illegible] -sulphonic acid [illegible] (present method)	0.0298/430 nm

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CHAPTER VI

POTENTIOMETRIC STUDIES ON THE METAL CHELATES OF ALUMINON

ALUMINON

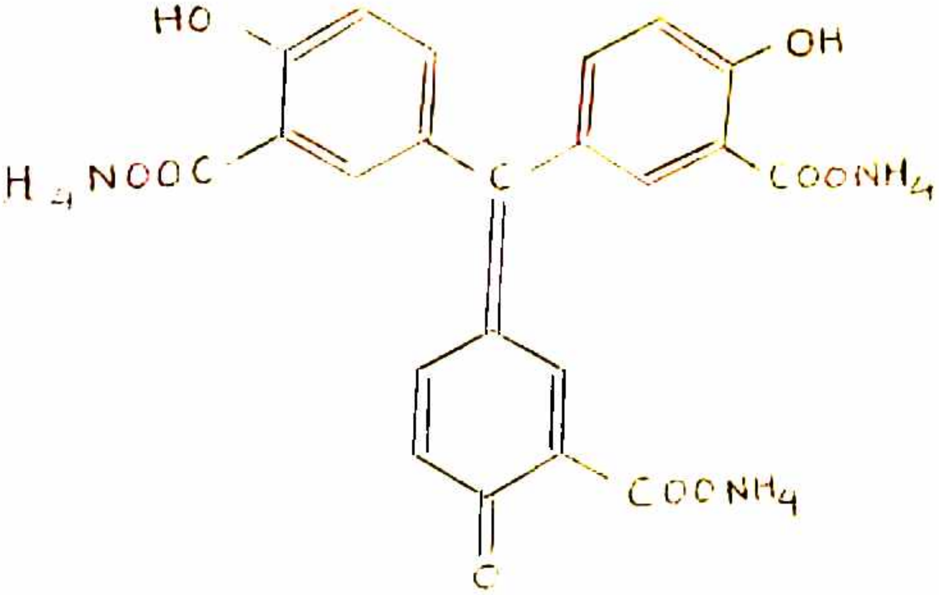
Introduction

Dyes of the hydroxytriphenylmethane group are well known for their interesting property of forming coloured products with inorganic ions, and this property has been profitably used in the field of inorganic analysis. The chromogenic reaction between a metal ion and the dye is essentially due to the formation of coloured metal chelate or lake which may be soluble or insoluble, depending upon the concentration, as well as on the nature of the metal ion. The colour reaction is often sensitive enough to permit micro detection and determination of ions.

Considerable work has been done on the use of the hydroxyanthraquinone group of dyes and their use as spot reagents and as colorimetric reagents for the detection and determination of various inorganic ions at micro level concentrations.

The chief among the hydroxytriphenylmethane dyes are Aluminon, Chrome Azurol S, Eriochrome Cyanine RC, Xylenol Orange and Pyrogallol Red.

Their structures have been represented overleaf.



Aluminon

urintricarboxylic acid (Triammonium salt)

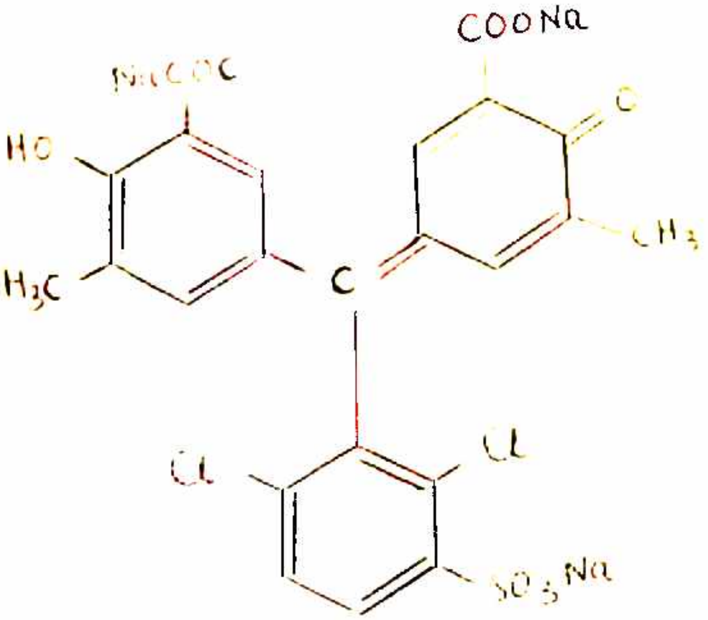
Ammonium Aurintricarboxylate

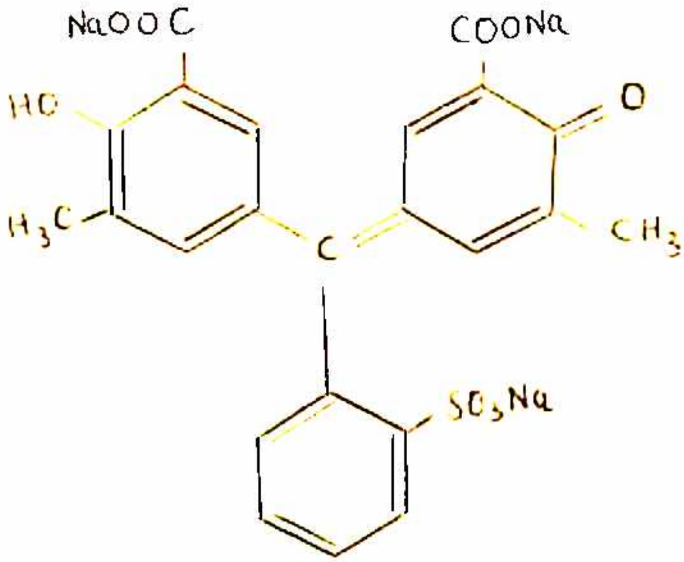
Salicylic acid (Triammonium salt)

5,5'- (3-carboxy-4-oxo-2,5-cyclohexadien-1-ylidene)
methylene di -

Triammonium salt (1,4-cyclohexadiene-1-carboxylic acid,
3- bis(carboxy-4-hydroxyphenyl)
methylene) -6-oxo.

(Abbreviated as AAC)





Chrome Azurol S

3"-sulpho-2",

6"-dichloro-3,

3' -dimethyl-4-hydroxyfuchsone-5,

5'-dicarboxylic acid

(Trisodium salt)

(Abbreviated as CAS)

Eriochrome Cyanine RC

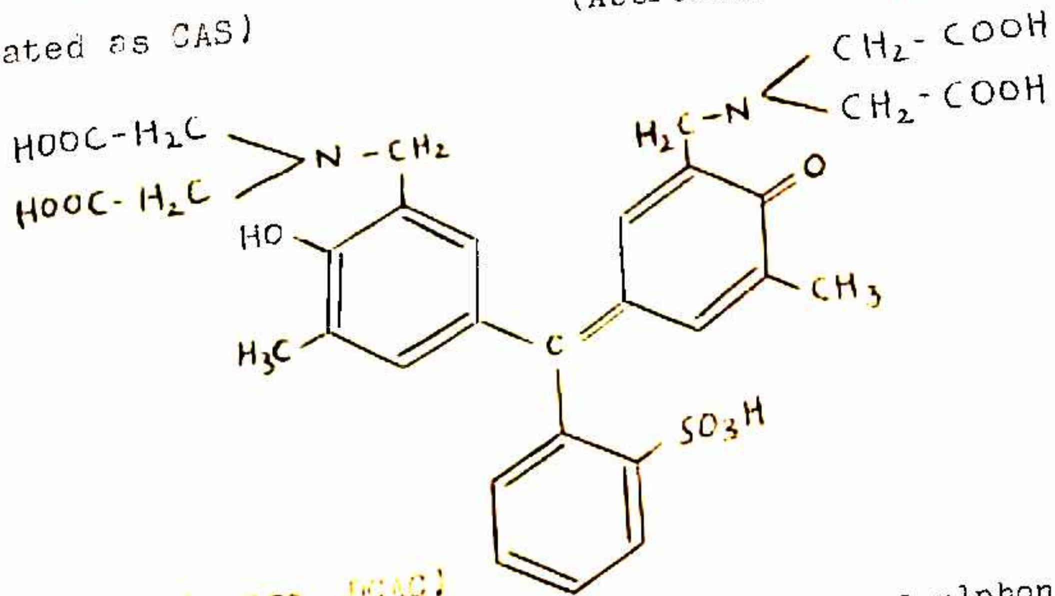
2"-sulpho-3,3'-dimethyl-

4-hydroxyfuchsone-5,5'-

dicarboxylic acid

(Tri sodium salt)

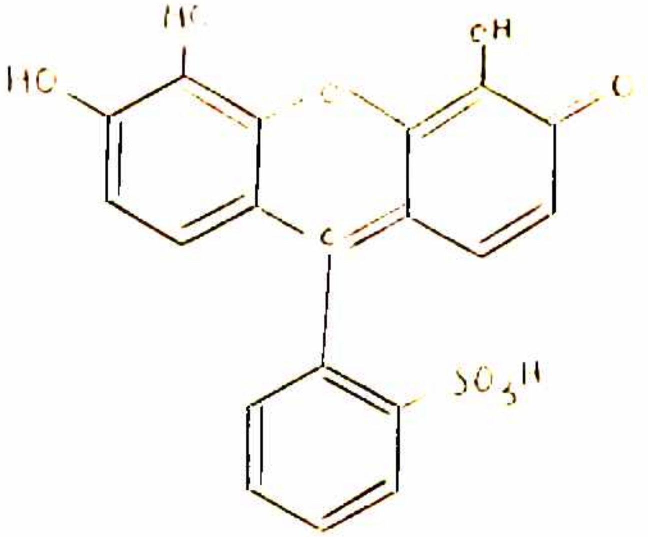
(Abbreviated as ECRC)



(Xylenol Orange, DCAC)

3, 3'-Bis[N,N-di(carboxymethyl)-aminomethyl]-o-cresolsulphonphthalein

(Abbreviated as DCAC)



Pyrogallol Red

[illegible] hydroxy-3-oxo-9(phenyl-o-sulphonic acid) xanthene

(Abbreviated as PGR)

Ammonium aurintricarboxylate was first reported to form a red coloured lake with aluminium by Hammet and Sottery (1) in 1925, who suggested the use of the reagent for the detection of aluminium. The reagent, thus thought to be specific for aluminium, came to be known as Aluminon (Abbreviated as AAC or AN). Subsequently a large amount of work has been done on the detection and estimation of aluminium using this reagent.

It was realised that the method of preparation of the reagent is of importance. The earlier methods of preparation (2,3,4,5) yielded unsatisfactory products. Smith and coworkers (6,7) emphasized the quality of the reagent and they discussed the spectral characteristics of Aluminon. They recommended that, in the preparation of the reagent, the methylene salicylic acid employed should have an average molecular weight of 300 and a melting point-247°C. They also found that in order to obtain a stable colour, the addition of alkali should be avoided. Monomer sample of aluminon has been found most suitable for colorimetric analysis. Recently a method for improving the quality of the aluminon reagent for the use in metal, steel and alloy analysis has been reported by Fedrov et al (8).

Mukherji and Dey (9), found from electrical conductance measurements that the reagent behaved as a collidal electrolyte, and they suggested that physico-chemical measurements should preferably be carried out in extremely dilute solutions, when the solution of the reagent behaves as a true solution (10). In cases where the concentrations employed are high, the composition of the chelates are often found to be non-stoichiometric, more so with a metal having a tendency to form polymerized aggregates.

Aluminon has been extensively employed in specialised cases (11,12,13,14,15,16,17,18,19,20) for the detection and estimation of aluminium, in water, blood and animal material, in plants, non-ferrous alloys, in zinc, in steel, in titanium alloys, in ores, in zirconium and titanium powders, in ores and concentrates respectively.

Considerable work has been reported on the favourable conditions under which Aluminon can be used for the determination of aluminium (21,22,23,24,25,26,27). The interference of various foreign ions on the sensitivity of the reagent in colorimetric analysis of aluminium has also attracted wide attention (28,29,30,31,32,33,34,35). Van Nieuwenburg and Uitenbrock (36) modified the well known reaction of aluminium with Aluminon in such a way as to make it specific for the element. This has been accomplished by adding sulphurous acid beforehand and ethanol and hydrochloric acid afterwards. Sulphurous acid prevents the interference of chromium, indium, gallium and titanium whereas the ethanol and hydrochloric acid prevents those of beryllium, scandium, zirconium and small amounts of ferric iron.

Extensive work has been reported on the determination of aluminium with Aluminon (37,38,39,40,41,42,43,44,45,46), describing various modifications in order to increase the sensitivity and the selectivity of the chromogenic reaction.

Attempts were also made to use the reagent for other elements also. Middleton (47) studied the reaction of Aluminon with hydroxides of beryllium, rare-earths, zirconium and thorium. Corey and Rogers (48) studied colour formation with scandium, gallium, indium and germanium, while Mukherji and Dey (49) noted the colour reactions of various metals with Aluminon and reported that the reagent forms coloured chelates with various metal ions. Dey and coworkers (50,51,52,53,54,55,56,57,58,59,60) have investigated a large number of metal chelates with Aluminon, regarding their composition, stability, structure and colorimetric deter-

[illegible]. These studies comprise of metal chelates of aluminon, with Be(II), Cu(II), Pd(II), Fe(III), Sc(III), Lanthanides(III), Th(IV) and U(VI).

Aluminon has also been used for the heterometric determination [illegible] (61) and chelometric determination of aluminium, iron, calcium and magnesium (62).

Kosel and Neuman (63) have reported the determination of Be(II) with aluminon. Using aluminon, determination of traces of Beryllium, in a mixture of calcium, strontium and Barium has been reported (64). Separation of beryllium from Aluminium in hydrofluoric acid solutions on Ar-17 anion-exchanger in the fluoride form, with the help of Aluminon, have been recently reported (64a). Reaction of Be(II) with Aluminon has been studie in detail by Serdyuk and Fedorova (65).

Colorimetric determinations of Iron(III)(50), Mg(II) (66,67), In(III), (68), [illegible] (69) and Ca(II) (70) have been reported, employing aluminon. Determination of Ytterbium(III) (71) has been done, on the basis of the difference in the pH of complex formation and reagent ionization and the rate of change of absorbance with pH. Complex compounds of Zr(IV) have been synthesized with the help of Aluminon (72). Studies of some metal chelates of some lanthanides with AAC have been reported by Serdyuk and Fedrova (73). Spectrophotometric determination of Th(IV) (74), V(IV) (75), In(III) (76) and U(VI) (77,78) have also been carried out. A comparative study of indicators for

Photometric determination of aluminium has been made by Borova (79). The use of aluminon has been recommended by them in refractory materials.

Cherkesov and Kozakov (80) have studied the properties and structure of some complexes of aluminium with the reagents of the triphenylmethane series and have suggested that for the synthesis of more efficient reagents of the triphenylmethane series, group $CH_2N(CH_2CO_2H)_2$ or other analogous groups may be introduced in the ortho position to the carbonyl group of the quinoid ring and the introduction of electron-donor substituents should be made only in 1 of the 2 benzene rings.

Dey and coworkers have recently reported the stepwise formation of metal chelates of Uranium(VI), Thorium (IV) (81), ~~and~~ Zirconium(IV) and Hafnium(IV) (82). In course of these studies the stepwise protonation constants of AAC and formation constants of its chelate with bi-, tri and tetravalent metals, using Bjerrum-Calvin technique, as described by Irving and Rossotti (83) have been described.

EXPERIMENTAL

Apparatus and reagents

A Beckman pH meter, model H2, was used for pH measurements. BDH AnalaR grade cobalt sulphate, nickel sulphate, aluminium sulphate and lead nitrate, AR Fluka gallium chloride and beryllium chloride; G.R. E. Merck ceric sulphate and B.D.H. reagent grade lanthanum nitrate and vanadyl sulphate were used in these studies. Aluminium used [illegible] studies was also B.D.H. reagent grade. Vanadium and gallium were standardized by usual gravimetric methods [illegible]. Sodium chloride B.D.H. A.R. and AnalaR hydrochloric acid were used in some studies. [illegible] perchloric acid and sodium perchlorate were used in these studies.

All the solutions were prepared, using double-distilled, CO_2-free water. Sodium hydroxide was dissolved in double distilled water free from CO_2 and was kept overnight over lime. The [illegible] standardised against a standard oxalic acid solution.

All the studies were carried out at 25 ± 1°C. The ionic strength was adjusted with $NaClO_4$.

As already mentioned in Chapter II, Calvin-Bjerrum titration technique was employed for these studies. Three titrations were performed pH - metrically; using N/10 sodium hydroxide as titrant against the following solutions (Total volume 100 ml).

<u>Acid titration (Curve A)</u>

<u>For studies at ionic strength 0.02</u>

W * Perchloric acid (M/10-10 ml) + sodium perchlorate (M/10-10 ml) + water (80 ml)

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* Instead of perchloric acid and sodium perchlorate, hydrochloric acid and sodium chloride were used in case of copper only.

For studies at ionic strength 0.05:

Perchloric acid (M/10-10 ml) + sodium perchlorate (M/10-10 ml) + water (50 ml).

For [illegible] .1

Perchloric acid (M/10-10 ml) + sodium perchlorate (M - 9 ml) + water ([illegible]1 ml).

ci [illegible] curve B)

For [illegible] th 0.02

Perch[illegible] + sodium perchlorate (M/10-10 ml [illegible] ml) + water (55 ml).

For studies at ionic strength 0.05

[illegible]hloric acid [illegible] + sodium perchlorate [illegible] [illegible]-25 ml) + water (25 ml).

For [illegible] ionic strength 0.1

Perch[illegible] acid [illegible] + sodium perchlorate (M - 9 ml) + [illegible] ml) + water (56 ml).

[illegible] tion (curve [illegible])

For [illegible] ionic strength 0.02

[illegible]cid [illegible] 10 ml) + sodium perchlorate (M/10-10 ml) + aluminon [illegible]0-25 ml) + metal ion (M/100 - 5 ml) + water ([illegible] ml).

For studies at ionic strength 0.02

Perchloric acid (M/10-10 ml) + sodium perchlorate (M/10 - 40 ml) + aluminon (M/100 - 25 ml) + metal ion (M/100 - 5 ml) + water (20 ml).

For studies at ionic strength 0.1

Perchloric acid (M/10 - 10 ml) + sodium perchlorate (M - 9 ml) + aluminon (M/100 - 25 ml) + Metal ion (M/100 - 5 ml) + water (51 ml).

RESULTS

Studies at ionic strength 0.02

Table 6.1 presents the record of the observations made during the three titrations represented by curves A, B and C. Some of the representative results have also been graphically represented.

Table 6.2 records the values of v', v'' and v''' (obtained in case of 8 elements) at various pH values. Table 6.3 embodies the variation of $\bar{n}_A$ (calculated with IBM computer (Model 1130)) with pH and these results are graphically represented in P.18.F.2. From this plot, a set of values of acid dissociation constants, log K_1^H, log K_2^H and [illegible] have been obtained by applying Bjerrum's half $\bar{n}_A$ method (85), (denoted by H), Irving and Rossotti's inter-polation at various $\bar{n}_A$ values (83) (denoted by V) and Bjerrum's mid point method (85) (denoted by M) and these are being presented in Table 6.4.

Tables 6.5 through 6.12 record the values of $\bar{n}$ and pLs, calculated by IBM Computer (Model 1130), at different pH values for the elements Be(II), Co(II), Ni(II), Pb(II), Al(III), Ga(III), [illegible](IV) and V(IV). Fig. 2 (curves H and V) in plate numbers 19-21; are the graphical representations of $\bar{n}$ values plotted against corresponding values of PLs - pL (H) and pL (V), for the above mentioned elements, serially. pL (H) and pL (V) are the values of pL obtained by using β_1^H and β_2^H values obtained by taking antilog of the $\log \beta_1^H$ and $\log \beta_2^H$ values obtained by applying Bjerrum's half $\bar{n}_A$ values method and interpolation at various $\bar{n}_A$ values method. pL ([illegible]) has not been plotted versus $\bar{n}$ in these figures, as the basic conditions for applying Bjerrum's mid point method for calculation of $\log \beta_1$ and $\log \beta_2$ are not fulfilled. From these plots (Fig. 2; plate numbers 19-21 and 23-27), two sets of values of $\log \beta_1$ and $\log \beta_2$ have been obtained by applying half $\bar{n}$ values method and various $\bar{n}$ values method for each element and these are being recorded in Table 6.13.

Table 6.1: Temperature = 25°C; Ionic strength (μ) = 0.02; y = 2; $T_L = 2.5 \times 10^{-3}$M;

$T_M = 0.5 \times 10^{-3}$M; N = 0.1 M; E = 0.01 M; V_o = 100 ml

Sl. No.	Volume of NaOH added (ml)	A	B	Observed pH in Titration C for							
				Be(II)	Co(II)	Ni(II)	Pb(II)	Al(III)	Ga(III)	Ce(III)	V(IV)
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
1	0.10	-	-	2.60	2.60	2.60	2.50	2.50	2.60	2.60	2.60
2	0.50	-	-	2.65	2.65	2.65	2.55	2.50	2.65	2.65	2.65
3	1.00	2.20	2.60	2.70	2.70	2.70	2.60	2.55	2.70	2.70	2.70
4	1.50	-	-	2.75	2.75	2.75	2.65	2.60	2.75	2.75	2.75
5	2.00	2.25	2.75	2.80	2.80	2.80	2.70	2.65	2.80	2.80	2.80
6	2.50	-	-	2.85	2.90	2.85	2.75	2.75	2.85	2.85	2.85
7	2.70	-	-	-	-	-	-	2.80	-	-	-
8	2.80	-	-	-	-	-	-	-	-	3.00	-
9	2.90	-	-	-	-	-	-	-	2.90	-	-
10	3.00	2.30	2.95	2.95	3.00	3.00	2.80	2.85	-	3.00	2.90
11	3.20	-	-	-	-	-	-	2.90	-	-	-
12	3.30	-	-	3.00	-	3.10	-	-	-	3.10	-
13	3.40	-	-	-	-	-	-	2.95	-	-	-

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.
14	3.50	-	-	3.05	3.10
15	3.60	-	-	-	-
16	3.70	-	-	3.10	-
17	3.80	-	-	3.13	-
18	3.85	-	-	3.15	-
19	3.90	-	-	3.18	-
20	4.00	2.35	3.25	3.20	3.20
21	4.20	-	-	3.25	3.25
22	4.40	-	-	3.30	3.30
23	4.50	-	-	-	-
24	4.60	-	-	3.35	3.35
25	4.70	-	-	-	-
26	4.80	-	-	3.40	3.40
27	4.90	-	-	-	-
28	5.00	2.42	3.55	3.45	3.50
29	5.10	-	-	-	-
30	5.20	-	-	3.50	-

7.	8.	9.	10.	11.	12.
3.15	2.90	-	3.00	3.15	3.00
-	-	2.98	-	-	-
-	-	-	-	-	-
3.20	-	3.00	-	3.20	-
-	-	-	-	-	-
-	-	-	-	-	-
3.25	3.00	3.05	-	-	3.10
3.30	3.05	3.10	3.10	3.25	-
3.35	3.10	3.15	-	-	-
-	-	-	-	3.30	3.20
3.40	3.15	3.18	-	-	-
3.45	-	-	-	-	-
3.50	3.20	3.22	-	3.35	-
3.55	-	-	-	-	-
3.60	3.25	3.25	3.20	3.40	3.30
3.63	-	-	-	-	3.33
3.66	3.30	-	-	-	3.36

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
31	5.30	-	-	-	-	3.69	3.35	3.30	3.30	3.52	3.38
32	5.40	-	-	3.55	-	3.72	3.40	-	-	-	3.42
33	5.50	-	-	-	3.60	3.75	3.45	3.35	-	3.60	3.45
34	5.60	-	-	3.60	-	3.78	3.50	3.40	3.40	3.63	3.48
35	5.70	-	-	-	-	3.81	3.55	3.45	-	3.65	3.51
36	5.80	-	-	3.65	-	3.84	3.60	3.50	-	3.68	3.54
37	5.90	-	-	-	-	3.87	3.65	3.55	3.50	3.70	3.57
38	6.00	2.52	3.85	3.70	3.70	3.90	3.70	3.60	-	3.70	3.60
39	6.10	-	-	-	-	-	3.74	-	3.60	3.80	3.64
40	6.20	-	-	3.75	-	-	3.78	3.65	-	3.90	3.68
41	6.30	-	-	-	-	-	3.82	3.68	3.70	3.90	3.70
42	6.40	--	-	3.80	-	-	3.86	3.71	-	3.95	3.72
43	6.50	-	-	-	3.80	3.95	3.90	3.75	-	3.98	3.75
44	6.60	-	-	3.85	-	-	3.94	3.80	3.80	4.00	3.78
45	6.70	-	-	-	-	-	3.98	3.84	-	4.02	3.81
46	6.80	-	-	3.90	-	-	4.02	3.88	-	4.05	3.84
47	6.90	-	-	-	-	-	4.06	3.91	3.90	4.07	3.87
48	7.00	2.68	4.00	3.95	3.90	4.00	4.10	3.95	-	4.10	3.90

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.
49	7.10	-	-	-	-
50	7.20	-	-	4.00	-
51	7.30	-	-	4.05	-
52	7.40	-	-	4.10	-
53	7.50	-	-	4.15	3.98
54	7.60	-	-	-	-
55	7.80	-	-	4.20	-
56	7.90	-	-	-	-
57	8.00	2.75	4.15	4.25	4.05
58	8.10	2.80	4.20	-	4.10
59	8.20	2.85	4.25	-	4.15
60	8.25	-	-	4.30	-
61	8.30	2.90	4.30	-	418
62	8.35	-	-	-	-
63	8.40	2.95	4.35	-	4.22
64	8.50	3.00	4.40	4.35	4.25
65	8.60	-	4.45	-	4.30
66	8.70	3.05	4.50	-	4.35

7.	8.	9.	10.	11.	12.
-	4.12	-	-	4.15	-
-	4.15	4.03	4.00	4.18	3.92
-	4.18	4.05	-	4.20	-
-	4.21	4.08	-	4.20	3.96
4.08	4.25	4.10	4.10	4.25	-
-	4.30	4.13	-	4.28	4.00
-	4.33	4.17	-	4.30	-
-	4.36	4.21	-	4.32	-
4.15	4.40	4.25	4.20	4.35	4.05
4.18	4.42	-	-	4.38	-
4.20	4.45	-	-	4.42	-
-	-	-	-	-	-
4.24	4.47	4.30	-	4.45	-
-	-	-	-	-	-
4.28	4.50	-	-	4.48	-
4.35	4.52	4.35	4.30	4.50	4.10
4.40	4.54	-	-	4.54	-
4.45	4.58	-	-	4.58	-

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
67	8.75	-	-	-	-	-	4.60	-	-	-	4.15
68	8.80	3.10	4.55	4.40	4.40	4.50	4.62	4.40	-	4.62	-
69	8.90	3.15	4.60	-	4.45	4.55	4.66	-	-	4.66	-
70	9.00	3.20	4.65	4.45	4.50	4.60	4.70	4.45	4.40	4.70	4.20
71	9.10	3.25	4.70	4.50	4.60	4.65	4.75	-	-	4.70	4.25
72	9.20	3.30	4.80	4.54	4.70	4.75	4.85	4.45	4.45	4.75	4.30
73	9.30	3.40	4.90	4.58	4.75	4.85	4.90	-	-	4.80	4.35
74	9.35	3.45	-	-	-	-	-	-	-	-	-
75	9.40	3.50	5.00	4.61	4.80	4.90	4.95	-	4.50	4.90	4.40
76	9.45	3.55	--	--	-	-	-	-	-	-	-
77	9.50	3.60	5.10	4.65	4.88	4.98	5.00	4.55	-	4.95	4.45
78	9.55	3.65	-	-	-	-	-	-	-	-	-
79	9.60	3.75	5.20	4.70	4.95	5.05	5.05	4.60	4.60	5.00	4.60
80	9.65	3.85	-	-	-	-	-	-	-	-	-
81	9.70	4.00	5.30	4.75	5.05	5.15	5.10	4.65	-	5.10	4.70
82	9.75	4.15	5.40	4.80	-	-	-	-	-	-	-
83	9.80	4.50	5.50	4.85	5.12	5.25	5.15	4.70	4.70	5.20	4.78

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
84	9.85	5.25	5.55	-	-	-	-	-	-	-	-
85	9.90	6.50	5.60	4.90	5.25	5.40	5.20	4.75	-	5.30	4.85
86	9.92	7.50	5.70	-	-	-	-	-	-	-	-
87	9.95	8.40	-	-	-	5.45	-	-	-	5.35	-
88	10.00	9.20	5.80	5.00	5.35	5.50	5.30	4.80	4.75	5.45	4.96
89	10.05	9.60	5.90	5.07	5.45	5.60	-	-	-	5.50	-
90	10.10	9.75	6.00	5.15	5.50	5.70	5.40	4.90	-	5.55	5.00
91	10.15	9.90	6.05	5.20	5.60	5.80	5.50	-	-	5.65	-
92	10.20	10.00	6.15	5.25	5.65	5.90	5.65	5.00	4.85	5.80	5.10
93	10.25	10.10	6.25	5.30	5.75	6.05	5.82	-	-	5.95	-
94	10.30	10.20	6.40	5.35	5.90	6.20	5.95	5.10	-	6.10	5.20
95	10.35	10.25	6.50	5.40	6.00	6.40	6.00	-	-	6.25	-
96	10.40	10.30	6.75	5.45	6.10	6.55	6.20	5.20	5.05	6.40	5.30
97	10.45	-	7.00	5.50	6.35	6.75	6.50	-	-	6.85	-
98	10.50	10.35	7.25	5.55	6.60	7.00	6.70	5.30	-	7.10	5.40
99	10.55	10.40	7.45	5.60	6.85	7.30	6.85	-	--	7.25	-
100	10.60	10.50	7.50	5.70	7.15	7.45	7.00	5.35	5.25	7.40	5.55

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
101	10.65	-	7.75	5.77	-	7.60	7.20	-	-	-	-
102	10.70	10.55	7.85	5.85	7.40	7.65	7.35	5.40	-	7.70	5.65
103	10.75	-	7.90	5.92	-	7.70	7.45	--	-	-	-
104	10.80	10.60	8.00	6.00	7.65	7.75	7.50	5.55	5.40	7.85	5.80
105	10.85	-	-	6.10	-	7.80	7.60	-	-	-	-
106	10.90	10.65	8.10	6.20	7.80	7.85	7.70	5.70	5.50	7.99	5.95
107	10.95	-	-	6.25	-	7.90	7.75	5.80	-	-	6.07
108	11.00	10.70	8.20	6.30	7.92	7.95	7.80	5.90	5.65	8.08	6.15
109	11.05	-	-	6.40	-	8.00	7.90	6.00	-	-	6.27
110	11.10	-	8.28	6.50	8.00	8.05	7.95	6.10	5.85	8.15	6.40
111	11.15	-	-	6.65	-	8.10	8.00	6.20	5.90	-	6.50
112	11.20	-	8.35	6.80	8.05	8.15	8.10	6.40	6.00	8.20	6.60
113	11.25	-	-	6.92	-	8.20	-	6.55	6.25	-	6.70
114	11.30	-	8.40	7.05	8.10	8.25	8.15	6.70	6.40	8.30	6.80
115	11.35	-	-	7.25	-	-	-	6.90	6.60	-	6.98
116	11.40	-	8.45	7.40	8.20	8.30	8.20	7.00	6.80	8.37	7.10
117	11.45	-	-	7.50	-	-	-	7.30	7.10	-	7.25

contd..

Table 6.1 (contd..):

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
118	11.50	-	8.50	7.60	8.25	8.35	8.25	7.45	7.50	8.45	7.40
119	11.55	-	-	7.70	-	-	-	7.60	-	-	7.55
120	11.60	-	-	7.80	8.30	8.40	8.30	7.70	7.60	8.50	7.70
121	11.65	-	-	7.87	-	-	-	7.77	7.70	-	7.77
122	11.70	-	-	7.95	8.35	8.45	8.40	7.85	-	8.55	7.85
123	11.75	-	-	8.02	-	-	-	7.92	7.80	-	7.90
124	11.80	-	-	8.10	8.40	8.50	8.45	8.00	7.94	8.60	8.00
125	11.85	-	-	-	-	-	-	8.05	-	-	8.05
126	11.90	-	-	8.20	8.45	8.55	8.50	8.10	8.00	8.65	8.10
127	11.95	-	-	-		-	-	8.15		-	8.15
128	12.00	10.95	8.75	8.25	8.50	8.60	8.60	8.20	8.20	8.70	8.20
129	12.50	-	-	8.55	8.75	8.80	8.75	8.45	-	-	8.45
130	13.00	11.10	9.10	8.75	9.00	9.00	8.90	8.70	8.70	9.00	8.70
131	13.50	-	-	8.95	-	9.12	9.05	8.85	-	-	8.85
132	14.00	11.20	9.40	9.10	9.25	9.25	9.20	9.00	9.00	9.25	9.00
133	14.50	-	-	9.25	-	9.37	9.35	9.15	-	-	9.15
134	15.00	-	-	9.40	9.50	9.50	9.50	9.30	9.30	9.50	9.30

Table 6.2: $y = 2.0$; $N = 0.1$; $E=0.01$; $V_o = 100$; $T_L = 0.0025$; $T_M = 0.0005$;

$$\begin{array}{cccc} & (H) & (V) & (M) \\ \beta_1^H = & 2.065 \times 10^9 & 3.614 \times 10^9 & 2.716 \times 10^9 \\ \beta_2^H = & 4.446 \times 10^{17} & 6.745 \times 10^{17} & 5.370 \times 10^{17} \end{array}$$

.	pH	v'	v"	v''' for							
				Be	Co	Ni	Pb	Al	Ga	Ce	V
1.	4.4	9.787	8.500	8.750	8.800	8.700	8.000	8.750	9.000	8.150	9.400
2	4.6	9.812	8.950	9.375	9.100	9.000	8.750	9.600	9.600	8.750	9.600
3	4.8	9.825	9.200	9.750	9.400	9.250	9.200	10.000	10.075	9.300	9.850
4	5.0	9.837	9.400	10.000	9.637	9.500	9.500	10.200	10.375	9.550	10.100
5	5.2	9.850	9.600	10.150	9.850	9.750	9.900	10.400	10.575	9.800	10.300
6	5.4	9.862	9.750	10.350	10.025	9.900	10.100	10.650	10.800	9.975	10.500
7	5.6	9.875	9.900	10.525	10.150	10.050	10.187	10.850	10.962	10.100	10.625
8	5.8	9.880	10.000	10.650	10.275	10.150	10.275	10.975	11.100	10.200	10.800
9	6.0	9.887	10.125	10.800	10.350	10.250	10.325	11.067	11.200	10.262	10.925
10	6.2	9.890	10.225	10.937	10.425	10.300	10.400	11.137	11.250	10.325	11.025
11	6.4	9.900	10.300	11.050	10.475	10.350	10.425	11.200	11.300	10.375	11.100
12	6.6	9.900	10.350	11.125	10.500	10.412	10.475	11.275	11.350	10.412	11.225
13	6.8	9.910	10.400	11.200	10.525	10.462	10.525	11.325	11.400	10.450	11.300

contd..

Table 6.2 (contd..)

Sl. No.	pH	v'	v''	v''' for							
				Be	Co	Ni	Pb	Al	Ga	Ce	V
14	7.0	9.915	10.450	11.287	10.575	10.500	10.600	11.375	11.430	10.487	11.375
15	7.2	9.920	10.500	11.350	10.625	10.537	10.650	11.437	11.475	10.537	11.437
16	7.4	9.925	10.525	11.425	10.700	10.587	10.725	11.500	11.525	10.575	11.500
17	7.6	9.925	10.590	11.500	10.775	10.650	10.850	11.550	11.600	10.650	11.550
18	7.8	9.925	10.680	11.600	10.900	10.800	11.000	11.650	11.725	10.750	11.650
19	8.0	9.930	10.800	11.725	11.100	11.000	11.150	11.800	11.900	10.900	11.800
20	8.2	9.940	11.000	11.800	11.400	11.250	11.400	12.000	12.100	11.125	12.000
21	8.4	9.950	11.300	12.200	11.750	11.625	11.625	12.300	12.375	11.400	12.300
22	8.6	9.960	11.700	12.265	12.200	12.000	12.000	12.750	12.775	11.850	12.750
23	8.8	9.970	12.250	13.125	12.600	12.600	12.625	13.350	13.300	12.337	13.350
24	9.0	9.980	12.800	13.600	13.000	13.000	13.450	14.000	14.000	13.000	14.000
25	9.2	10.000	13.400	14.325	13.600	13.825	14.000	-	-	13.600	-
26	9.4	10.012	14.000	15.000	14.450	14.625	14.625	-	-	14.575	-

Some of the relevant observed *p*H values recorded in Table 6.1 have also been represented graphically. The details are given below:

Titration	Graphical representation
A	P.18-21;23-27.F.1. Curve A
B	P.18-21;23-27.F.1. Curve B
C for Be(II)	P.19.F.1 Curve C
C for Co(II)	P.20.F.1 Curve C
C for Ni(II)	P.21.F.1 Curve C
C for Pb(II)	P.23.F.1 Curve C
C for Al(III)	P.24.F.1 Curve C
C for Ga(III)	P.25.F.1 Curve C
C for Ce(III)	P.26.F.1 Curve C
C for V(IV)	P.27.F.1 Curve C

Table 6.3: Ionic strength 0.02;
Elements Al, Be, V, Ga, Pb, Ni, Co, Ce

S.No.	v'	v"	v'-v"	Vo+v'	pH	$\bar{n}_A$
1	9.787	8.500	1.28699	109.787	4.40	2.51579
2	9.812	8.950	0.86200	109.812	4.60	2.34539
3	9.825	9.200	0.62500	109.825	4.80	2.25039
4	9.837	9.400	0.43699	109.837	5.00	2.17505
5	9.850	9.600	0.25000	109.850	5.20	2.10013
6	9.862	9.750	0.11199	109.862	5.40	2.04485
7	9.875	9.900	-0.02499	109.875	5.60	1.98998
8	9.880	10.000	-0.12000	109.880	5.80	1.95194
9	9.887	10.125	-0.23800	109.887	6.00	1.90470
10	9.890	10.225	-0.33500	109.890	6.20	1.86586
11	9.900	10.300	-0.39999	109.900	6.40	1.83985
12	9.900	10.350	-0.44999	109.900	6.60	1.81983
13	9.910	10.400	-0.49000	109.910	6.80	1.80383
14	9.915	10.450	-0.53499	109.915	7.00	1.78583
15.	9.920	10.500	-0.58000	109.920	7.20	1.76783
16	9.925	10.525	-0.60000	109.925	7.40	1.75983
17	9.925	10.590	-0.66499	109.925	7.60	1.73381
18	9.925	10.675	-0.75000	109.925	7.80	1.69979
19	9.930	10.800	-0.86999	109.930	8.00	1.65177
20	9.940	11.000	-1.06000	109.940	8.20	1.57576
21	9.950	11.300	-1.35000	109.950	8.40	1.45975
22	9.960	11.700	-1.74000	109.960	8.60	1.30374
23	9.970	12.250	-2.28000	109.970	8.80	1.08775
24	9.980	12.800	-2.82000	109.980	9.00	0.87179
25	10.000	13.400	-3.40000	110.000	9.20	0.64000
26	10.012	14.000	-3.98800	110.012	9.40	0.40497

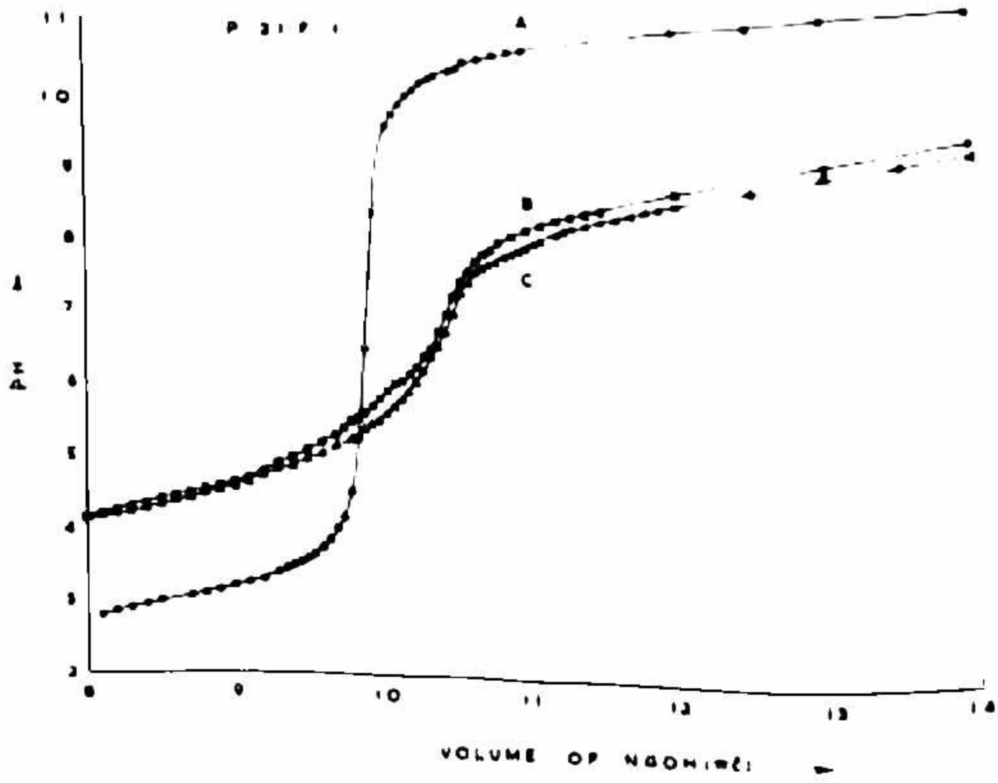
Table 6.4: Ionic strength = 0.02

$\log K_1^H = \log \beta_1^H$			$\log K_2^H$			$\log \beta_2^H$		
(H)	(V)	(M)	(H)	(V)	(M)	(H)	(V)	(M)
9.315	9.558	9.434	8.333	8.271	8.296	17.648	17.829	17.730

Table 6.5: Ionic strength 0.02; Element Be (II)

S.No.	v"'-v"	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1.	0.2500	0.1991	4.40	11.50414	11.68516	11.58614
2	0.4250	0.3630	4.60	11.12179	11.30282	11.20381
3	0.5500	0.4896	4.80	10.73537	10.91640	10.81739
4	0.6000	0.5525	5.00	10.34247	10.52352	10.42449
5	0.5999	0.5876	5.40	9.54758	9.72867	9.62963
6	0.6299	0.6289	5.60	9.15273	9.33386	9.23480
7	0.6499	0.6667	5.80	8.75746	8.93866	8.83957
8	0.6700	0.7095	6.00	8.36304	8.54436	8.44522
9	0.7099	0.7640	6.20	7.97037	8.15187	8.05266
10	0.7500	0.8160	6.40	7.57794	7.75972	7.66039
11	0.7800	0.8525	6.60	7.18504	7.36726	7.26774
12	0.7999	0.8877	6.80	6.79362	6.97652	6.87672
13	0.8400	0.9381	7.00	6.40644	6.59040	6.49015
14	0.8499	0.9623	7.20	6.02046	6.20602	6.10510
15	0.8999	1.0240	7.40	5.64446	5.83239	5.73048
16	0.9100	1.0510	7.60	5.27350	5.46480	5.36149
17	0.9200	1.0890	7.80	4.91604	5.11191	5.00671

contd..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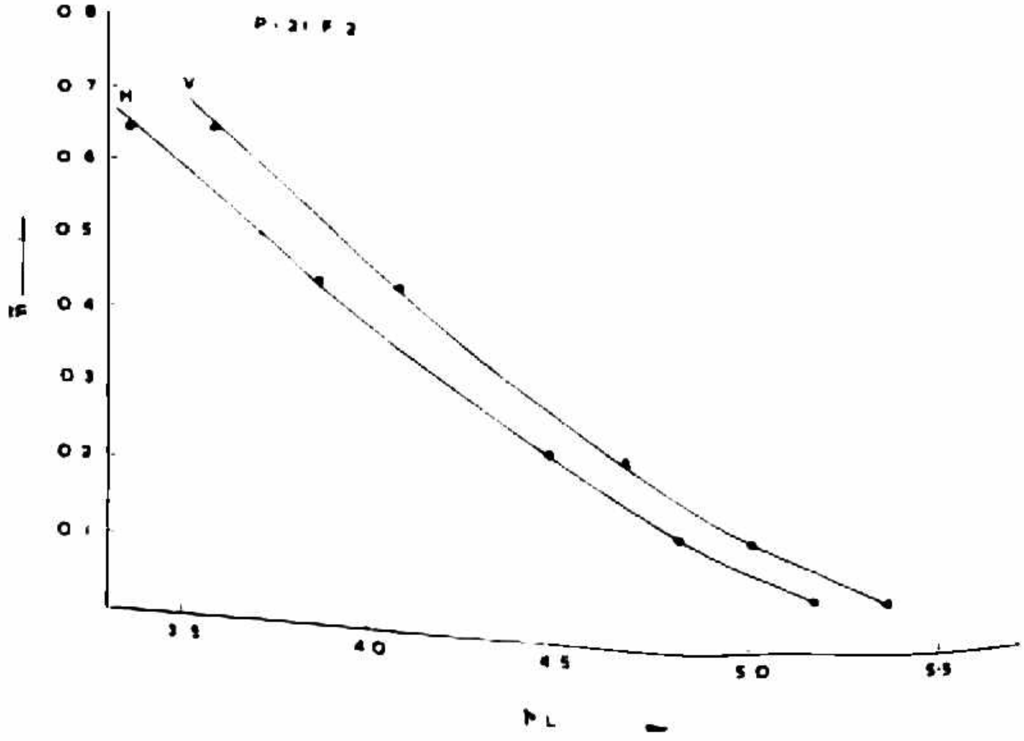
A
B
C
pH
11
10
9
8
7
6
5
4
3
2
8
9
10
11
12
13
14
VOLUME OF NaOH(ml)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H
V
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3.5
4.0
4.5
5.0
5.5
pL

Table 6.5 (contd.)

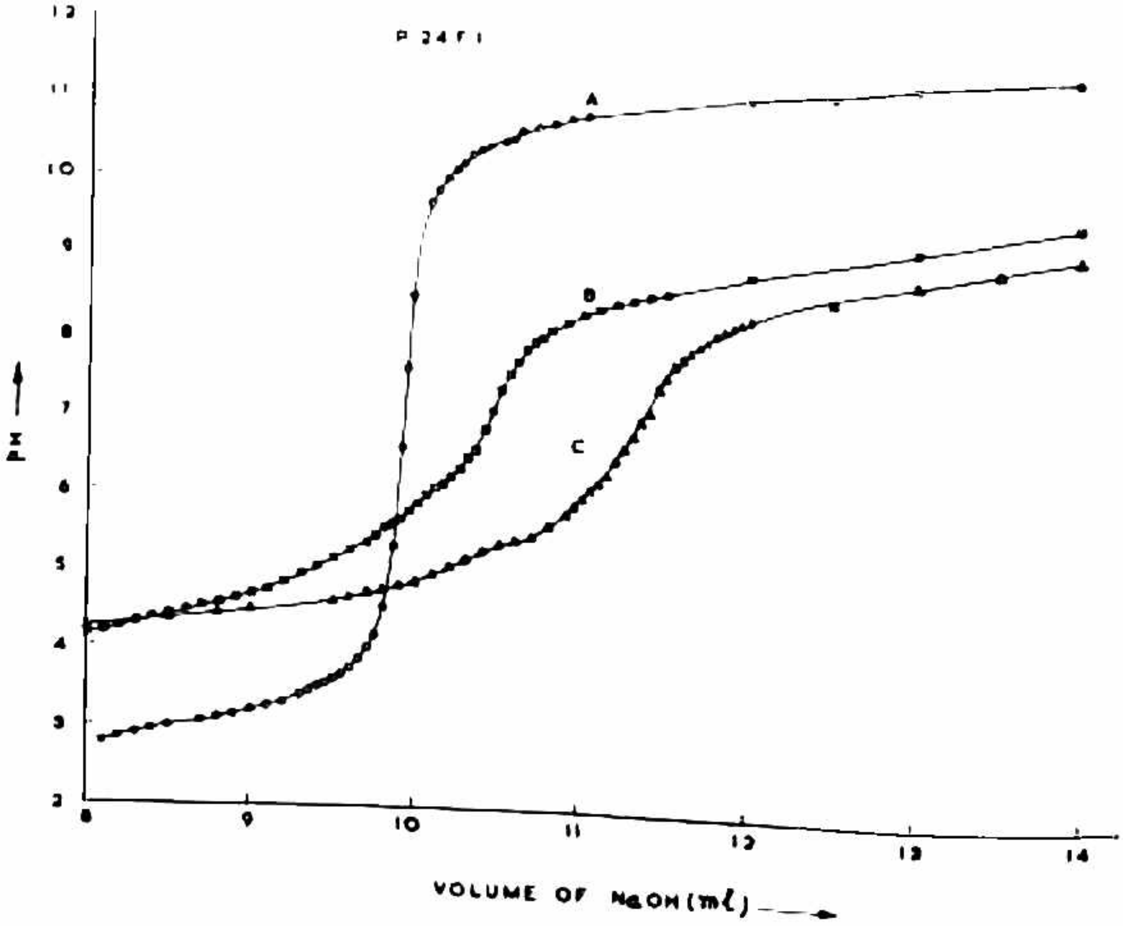
S.No.	v"'-v"	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
18	0.9300	1.1210	8.00	4.57412	4.77579	4.66821
19	0.8999	1.2340	8.40	3.95889	4.17441	4.06121
20	0.9300	1.4200	8.60	3.70149	3.92377	3.80787
21	0.8799	1.6090	8.80	3.46674	3.69484	3.57663
22	0.7999	1.8360	9.00	3.25577	3.48847	3.6845

Table 6.6: Ionic strength 0.02; Element Co(II)

1.	0.1299	0.1387	6.80	6.71832	6.90123	6.80143
2	0.1300	0.1401	7.00	6.32576	6.50972	6.40948
3	0.1299	0.1415	7.20	5.93727	6.12283	6.02191
4	0.1900	0.2135	7.60	5.18716	5.37846	5.27515
5	0.2200	0.2649	7.80	4.83027	5.02614	4.92094
6	0.2999	0.3635	8.00	4.49420	4.69587	4.58828
7	0.3999	0.5080	8.20	4.18307	4.39148	4.28115
8	0.5000	0.7673	8.60	3.62710	3.84938	3.73347

Table 6.7: Ionic strength 0.02; Element Ni(II)

1	0.0600	0.0692	7.60	5.17375	5.36505	5.26174
2	0.1200	0.1472	7.80	4.81921	5.01508	4.90988
3	0.2000	0.2423	8.00	4.48260	4.68427	4.57668
4	0.3299	0.4455	8.40	3.87412	4.08964	3.97644
5	0.3499	0.6437	8.80	3.35591	3.58401	3.46580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B
C
PH
12
11
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6
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8
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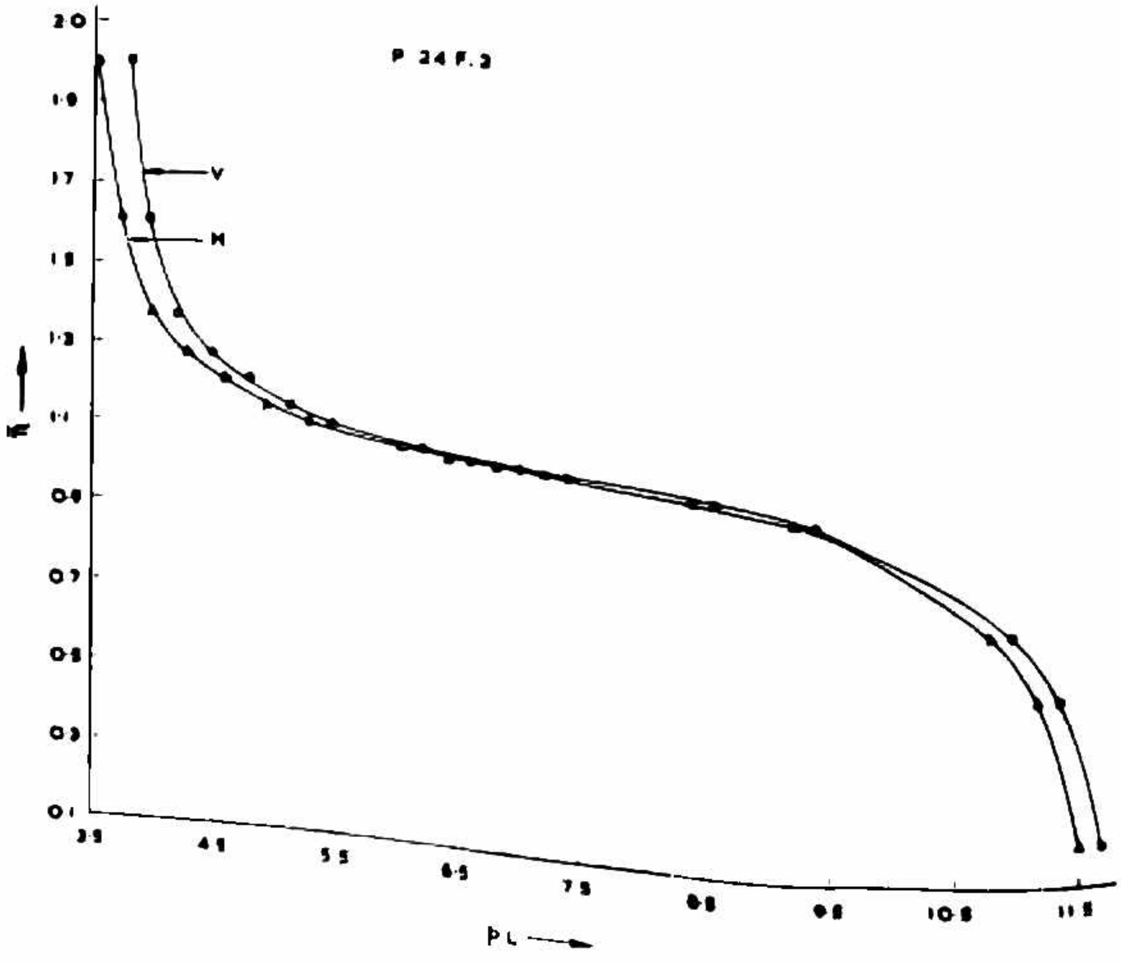
10
11
12
13
14
VOLUME OF NaOH (ml)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V
M
n̄
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1·9
1·7
1·5
1·3
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0·3
0·1
3·5
4·5
5·5
6·5
7·5
8·5
9·5
10·5
11·5
pL

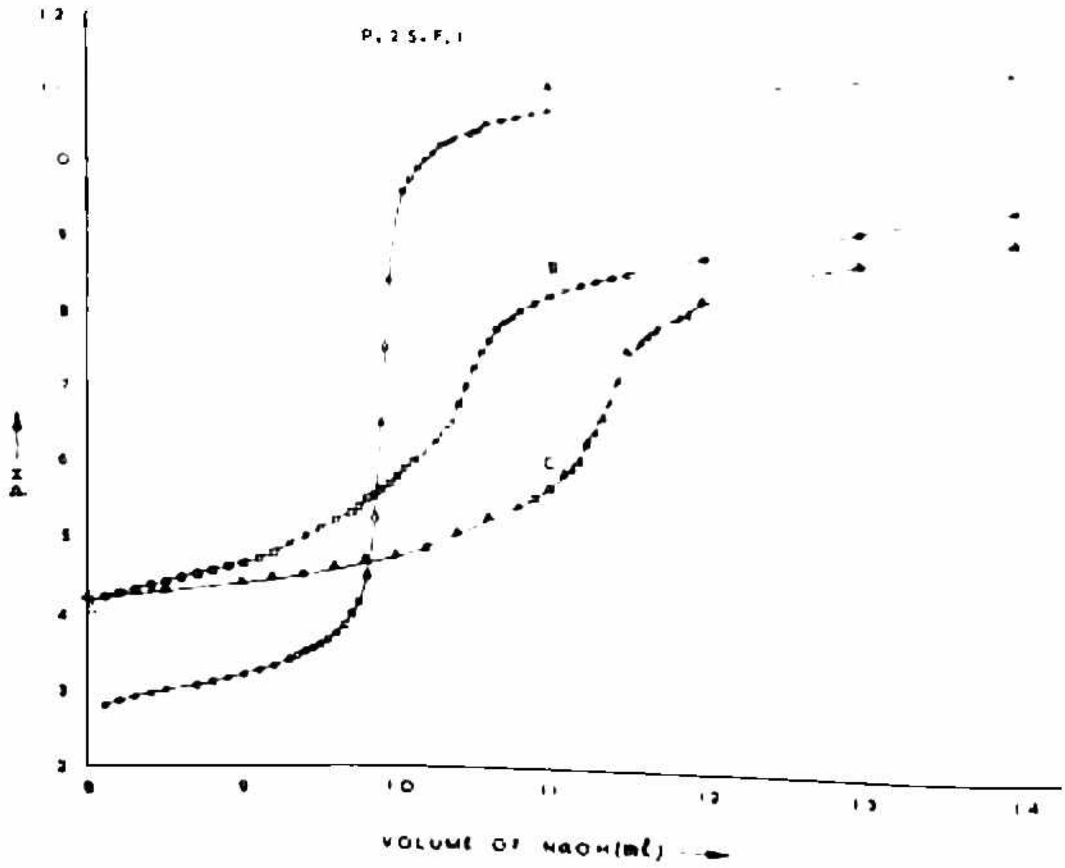
Table 6.8: Ionic strength 0.02; Element Pb(II)

S.No.	v"'-v"	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.1299	0.1360	6.40	7.51011	7.69189	7.59256
2	0.1300	0.1375	6.60	7.11341	7.29564	7.19612
3	0.1299	0.1387	6.80	6.71832	6.90123	6.80143
4	0.1499	0.1698	7.20	5.93988	6.12545	6.02453
5	0.2000	0.2274	7.40	5.56241	5.75034	5.64844
6	0.2600	0.3001	7.60	5.19536	5.38666	5.28335
7	0.3200	0.3827	7.80	4.84160	5.03747	4.93227
8	0.3500	0.4241	8.00	4.50011	4.70178	4.59419
9	0.3299	0.4455	8.40	3.87412	4.08964	3.97644
10	0.3000	0.4604	8.60	3.59592	3.81820	3.70230
11	0.3799	0.6897	8.80	3.36063	3.58873	3.47052
12	0.5000	1.0004	8.90	3.27520	3.50180	-

Table 6.9: Ionic strength 0.02; Element Al(III)

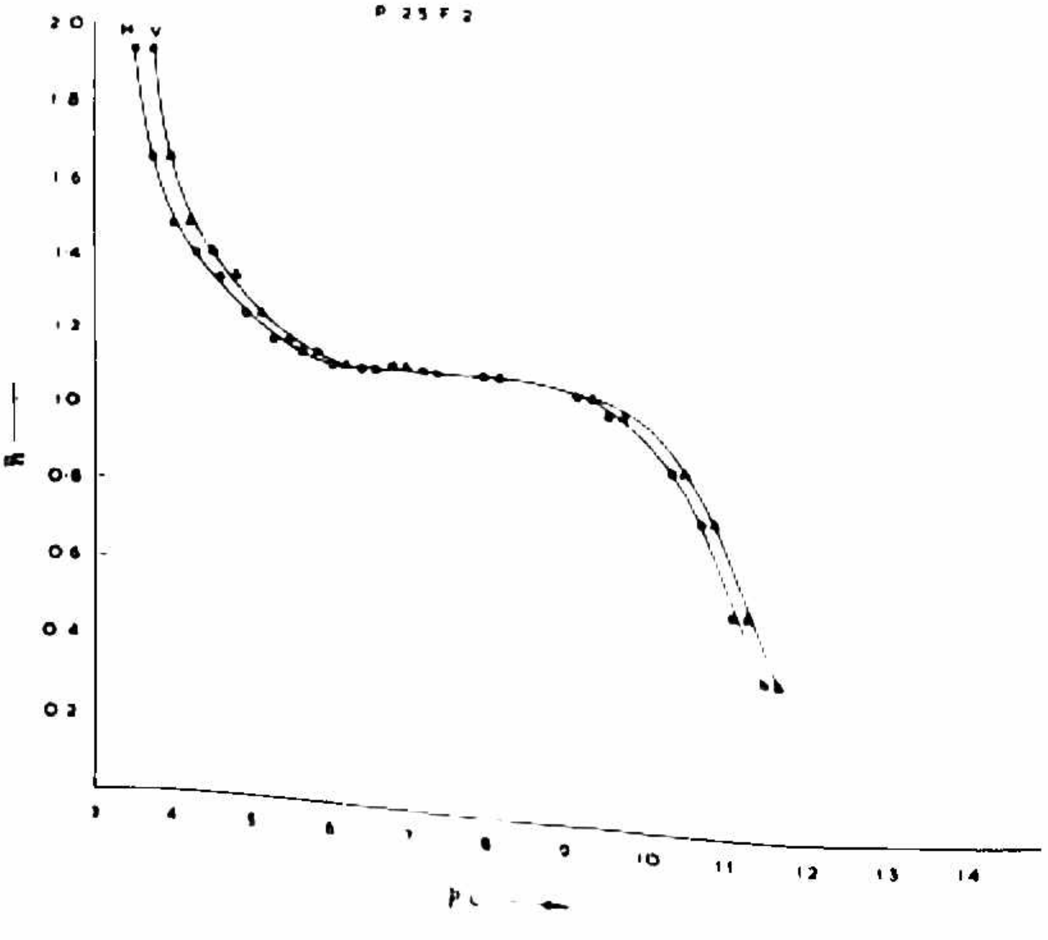
1	0.2500	0.1991	4.40	11.50415	11.68517	11.58616
2	0.6499	0.5552	4.60	11.14107	11.32210	11.22308
3	0.8000	0.7121	4.80	10.75833	10.93636	10.84034
4	0.9499	0.9559	5.60	9.18775	9.36889	9.26983
5	0.9419	0.9901	6.00	8.39348	8.57480	8.47566
6	0.9250	1.0180	6.60	7.20331	7.38553	7.28601
7	0.9249	1.0270	6.80	6.80909	6.99200	6.89219
8	0.9250	1.0370	7.00	6.41749	6.60146	6.50121
9	0.9369	1.0610	7.20	6.03155	6.21712	6.11620
10	0.9600	1.1000	7.60	5.27690	5.46820	5.36489

contd..



P. 25. F. 1

12
11
10
9
8
7
6
5
4
3
2
pH
A
B
C
8
9
10
11
12
13
14
VOLUME OF NaOH(ml)



P. 25 F. 2

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
M
V
3
4
5
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7
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11
12
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14
pc

Table 6.9 (contd.)

S.No.	$v''' - v''$	$\bar{n}$	ph	pL(H)	pL(V)	pL(M)
11	0.9750	1.148	7.30	4.92284	5.11871	5.01351
12	1.0000	1.212	8.00	4.58516	4.78683	4.67925
13	1.0000	1.270	8.20	4.26613	4.47454	4.36421
14	1.0000	1.371	8.40	3.97537	4.19089	4.07769
15	1.0500	1.611	8.60	3.72577	3.94805	3.83214
16	1.0999	2.023	8.80	3.52413	3.75223	3.63402

Table 6.10: Ionic strength 0.02; Element Ga (III)

1	0.5000	0.3982	4.40	11.52353	11.70455	11.60554
2	0.6499	0.5552	4.60	11.14107	11.32210	11.22308
3	0.8099	0.7788	4.80	10.76518	10.94621	10.84719
4	0.9799	0.8978	5.00	10.37907	10.56011	10.46109
5	1.0499	1.0280	5.40	9.59502	9.77611	9.67707
6	1.0599	1.0690	5.60	9.20050	9.38163	9.28257
7	1.0200	1.1000	6.20	8.00747	8.18897	8.08976
8	1.0000	1.1000	6.60	7.21262	7.39484	7.29532
9	1.0000	1.1100	6.80	6.81853	7.00144	6.90163
10	0.9799	1.0980	7.00	6.42443	6.60839	6.50814
11	0.9799	1.1040	7.20	6.03648	6.22204	6.12112
12	1.0000	1.1370	7.40	5.65737	5.84530	5.74339
13	1.0100	1.1660	7.60	5.28673	5.47803	5.37472
14	1.0500	1.2360	7.80	4.93318	5.12906	5.02386
15	1.1000	1.3330	8.00	4.59919	4.80086	4.69328
16	1.0999	1.3970	8.20	4.28156	4.48998	4.37964

contd..

Table 6.10(contd.)

S.No.	v'''-v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
17	1.0800	1.4740	8.40	3.98818	4.20371	4.09051
18	1.0800	1.6500	8.60	3.73091	3.95319	3.83729
19	1.0499	1.9310	8.80	3.51072	3.73882	3.62061

Table 6.11: Ionic strength 0.02; Element Ce(IV)

1	0.300	0.0414	7.00	6.31664	6.50060	6.40035
2	0.0399	0.0418	7.20	5.92809	6.11366	6.01274
3	0.0500	0.0568	7.40	5.54657	5.73450	5.63259
4	0.0600	0.0692	7.60	5.17375	5.36505	5.26174
5	0.0700	0.0883	7.80	4.81378	5.00965	4.90445
6	0.1000	0.1211	8.00	4.47128	4.67295	4.56537
7	0.1299	0.1587	8.20	4.14949	4.35790	4.24757
8	0.1499	0.2301	8.60	3.57385	3.79613	3.68023
9	0.2000	0.4589	9.00	3.09655	3.32925	3.20923
10	0.1999	0.6245	9.20	2.88565	3.12174	3.00039

Table 6.12: Ionic strength 0.02; Element V(IV)

1	0.64999	0.5552	4.6	11.14107	11.32210	11.22308
2	0.64999	0.5786	4.8	10.74442	10.92545	10.82644
3	0.69999	0.6446	5.0	10.35195	10.53300	10.43398
4	0.70000	0.6675	5.2	9.95521	10.13627	10.03724
5	0.75000	0.7345	5.4	9.56288	9.74397	9.64493

contd..

Table 6.12 (contd.)

S.No.	v''' -v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
6	0.79999	0.8206	5.8	8.77375	8.95496	8.85587
7	0.79999	0.8409	6.0	8.37706	8.55838	8.45924
8	0.87500	0.9625	6.6	7.19710	7.37932	7.27981
9	0.89999	0.9987	6.8	6.80589	6.98880	6.88899
10	0.92500	1.0370	7.0	6.41749	6.60146	6.50121
11	0.93699	1.0610	7.2	6.03155	6.21712	6.11620
12	0.97500	1.1090	7.4	5.65412	5.84204	5.74014
13	0.96000	1.1080	7.6	5.23304	5.42434	5.32103
14	0.97500	1.1480	7.8	4.92284	5.11871	5.01351
15	1.00000	1.2120	8.0	4.58470	4.78637	4.67879
16	1.00000	1.2700	8.2	4.26613	4.47454	4.36421
17	1.00000	1.3710	8.4	3.97537	4.19089	4.07769
18	1.05000	1.6110	8.6	3.72577	3.94805	3.83214
19	1.09999	2.0230	8.8	3.52413	3.75223	3.63402

Table 6.13: Stability constants of metal chelates of Aluminon
Ionic strength = 0.02

Metal	$\log K_1 = \log \beta_1$		$\log K_2$		$\log \beta_2 = \log K_1 + \log K_2$	
	(H)	(V)	(H)	(V)	(H)	(V)
Be(II)	10.616	10.541	3.586	3.832	14.202	14.373
Co(II)	4.192	4.414	-	-	-	-
Ni(II)	3.728	3.943	-	-	-	-
Pb(II)	3.520	3.740	-	-	-	-
Al(III)	11.215	11.348	3.820	4.090	15.035	15.438
Ga(III)	11.300	11.487	3.970	4.289	15.270	15.776
Ce(IV)	3.067	3.284	-	-	-	-
V(IV)	11.490	11.670	3.833	4.079	15.323	15.749

The results indicate that generally there is an agreement in the values obtained by the two methods.

Potentiometric studies on the chelate formation of bivalent copper with Aluminon, were made, using sodium chloride and hydrochloric acid in the acid titration, in stead of sodium perchlorate and perchloric acid, which were used throughout these studies with the other elements.

As usual, three titrations were performed; change of pH in these titrations was plotted against the volume of alkali added (in ml) (P.22.F.1). At various pH values, v', v" and v"' were noted and $\bar{n}_A$ values were calculated. Some of the representative results are recorded in Table 6.14 and variation of $\bar{n}_A$ with pH is graphically represented in P.22.F.2. From this plot, 3 set of values of acid dissociation constants, log K_1^H, log K_2^H and log β_2^H have been obtained by applying Bjerrum's half $\bar{n}_A$ method (denoted by H), Irving and Rossotti's interpolation at various $\bar{n}_A$ values method (denoted by V) and Bjerrum's mid point method (denoted by M) and these are also being recorded in Table 6.14.

Table 6.14:

y = 2; N = 0.098 M; μ = 0.02; E = 0.01 M; Temp. = 25°C;

V_o = 100 ml; T_L = 2.5 x 10^{-3}M

S.No.	pH	v'	v"	V_o+v'	v'-v"	$\bar{n}_A$
1	6.5	10.19	10.15	110.19	0.04	2.015
2	6.8	10.20	10.23	110.20	-0.03	1.990
3	7.0	10.20	10.28	110.20	-0.08	1.970
4	7.3	10.20	10.36	110.20	-0.16	1.940
5	7.5	10.20	10.42	110.20	-0.22	1.910
6	7.8	10.20	10.52	110.20	-0.32	1.875
7	8.0	10.20	10.60	110.20	-0.40	1.840
8	8.3	10.22	10.76	110.22	-0.54	1.790
9	8.4	10.22	10.83	110.22	-0.61	1.760
10	8.5	10.23	10.91	110.23	-0.68	1.730
11	8.8	10.24	11.30	110.24	-1.06	1.585
12	9.0	10.26	11.68	110.26	-1.42	1.440
13	9.2	10.28	12.18	110.28	-1.90	1.255
14	9.3	10.30	12.50	110.30	-2.20	1.140
15	9.4	10.31	12.90	110.31	-2.59	0.985
16	9.5	10.33	13.26	110.33	-2.93	0.850
17	9.9	10.40	14.64	110.40	-4.24	0.340

	(H)	(V)	(M)
log K_1^H =	9.76	9.76	9.925
log K_2^H =	8.93	9.23	8.855
log β_2^H =	18.69	18.99	18.780

Table 6.15 records the values of $\bar{n}$ and pLs, calculated at different pH values and these values of pL pL(H) and pL(V) are plotted against the corresponding $\bar{n}$ values in P.22.F.3. (curves H and V) pL(H) and pL(V) are the values of pL obtained by using β_1^H and β_2^H values obtained by taking antilog of the log β_1^H and log β_2^H values obtained by applying Bjerrum's half $\bar{n}_A$ values method and interpolation at various $\bar{n}_A$ values method. pL(M) has not been plotted versus $\bar{n}$ in this figure, as the basic conditions for applying this method (Bjerrum's mid point method) for calculation of log β_1 and log β_2 are not fulfilled. From this plot (P.22.F.3), two set of values of log β_1 and log β_2 have been obtained by applying Bjerrum's half $\bar{n}$ values method and Irving and Rossitti's interpolation at various $\bar{n}$ values method and these values are also being recorded in Table 6.15.

Table 6.15: $y=2$; $N=0.098$ M; $\mu = 0.02$; $E=0.01$M; Temp.$=25^{\circ}$C; $V_o=100$ ml; $T_L=2.5\times10^{-3}$M; $T_M=5\times10^{-4}$M

S.No.	pH	v'''	v''	V_o+v''	$v'''-v''$	$\bar{n}$	pL(H)	pL(V)	pL(M)
1	6.5	10.74	10.15	110.15	0.59	0.574	8.356	8.646	8.437
2	6.8	10.86	10.23	110.23	0.63	0.620	7.763	8.051	7.844
3	7.0	10.95	10.28	110.28	0.67	0.666	7.368	7.657	7.450
4	7.3	11.09	10.36	110.36	0.73	0.737	6.781	7.061	6.863
5	7.8	11.34	10.52	110.52	0.82	0.857	5.814	6.090	5.901
6	8.0	11.45	10.60	110.60	0.85	0.905	5.436	5.704	5.525
7	8.3	11.66	10.76	110.76	0.90	0.985	4.888	5.135	4.984
8	8.4	11.74	10.83	110.83	0.91	1.013	4.711	4.950	4.811
9	8.5	11.84	10.91	110.91	0.93	1.053	4.540	4.769	4.644
10	8.8	12.28	11.30	111.30	0.98	1.211	4.061	4.250	4.177
11	9.0	12.78	11.68	111.68	1.10	1.496	3.791	3.947	3.916
12	9.2	13.34	12.18	112.18	1.16	1.810	3.552	3.673	3.684

		(H)	(V)
$\log \beta_1 = \log K_1$	=	9.33	9.730
$\log K_2$	=	9.76	3.948
$\log \beta_2 = \log K_1 + \log K_2$	=	13.09	13.678

Studies at ionic strength 0.05

Table 6.16 records the observations made during the three titrations, represented by curves A, B and C, detailed already. Some representative results have also been graphically represented.

Table 6.17 records the values of v', v" and v"' (obtained in case of elements Beryllium, aluminium and vanadium) at various pH values. Table 6.18 embodies the variation of $\bar{n}_A$ (calculated by IBM - 1130 Computer) with pH and these results are graphically represented in P.28.F.2. From this plot, 3 set of values of acid dissociation constants, log K_1^H, log K_2^H and log β_2^H have been obtained by applying Bjerrum's half $\bar{n}_A$ method (denoted by H), Irving and Rossotti's interpolation at various $\bar{n}_A$ values (denoted by V) and Bjerrum's mid point method (denoted by M) and these are being presented in Table 6.19.

Table 6.20 through 6.22 serially record the values of $\bar{n}$ and pLs, calculated by IBM - 1130 Computer, at different pH values; for the elements Be(II), Al(III) and V(IV). Fig.2(Curves H and V) in plate numers 29,30,31 are graphical representations of $\bar{n}$ values plotted against corresponding values of pLs - pL(H) and pL(V) for the above mentioned elements, serially. From these plots (P.29-30-31. F.2), two sets of values of log β_1 and log β_2 have been obtained by applying half $\bar{n}$ values method and interpolation at various $\bar{n}$ values method for each element and these are being recorded in Table 6.23.

Table 6.16:

Temp. = 25°C; Ionic strength = 0.05; y = 2;

$T_L = 2.5 \times 10^{-3}$M; $T_M = 0.5 \times 10^{-3}$M; N = 0.1M; E = 0.1M;

V_o = 100 ml

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for		
				Be(II)	Al(III)	V(IV)
1	1.00	2.20	2.40	2.60	-	2.50
2	2.00	2.25	2.50	-	-	-
3	3.00	2.30	2.70	-	-	-
4	4.00	2.40	3.20	-	-	-
5	5.00	2.50	3.50	3.40	3.30	3.30
6	6.00	2.60	3.70	-	3.70	3.60
7	7.00	2.70	3.80	-	3.90	3.85
8	8.00	2.90	4.00	4.00	4.10	4.00
9	8.10	-	4.03	-	-	-
10	8.20	-	4.07	4.05	-	-
11	8.30	-	4.10	4.05	-	-
12	8.40	-	4.15	-	-	-
13	8.50	3.05	4.20	4.10	4.20	4.07
14	8.60	-	4.25	4.15	4.20	-
15	8.70	-	4.30	4.20	4.22	-
16	8.80	-	4.35	4.25	4.25	-
17	8.90	-	4.40	-	-	-
18	9.00	3.30	4.45	4.30	4.28	4.20
19	9.10	3.35	4.60	4.35	4.30	4.22
20	9.20	3.40	4.75	-	4.35	4.25

contd..

Table 6.16 (contd.)

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for		
				Be(II)	Al(III)	V(IV)
21	9.30	3.45	4.80	-	4.40	4.30
22	9.40	3.55	4.90	-	4.45	4.35
23	9.50	3.65	5.00	4.50	4.50	4.40
24	9.60	3.80	5.10	4.60	4.55	4.45
25	9.65	3.90	-	-	-	-
26	9.70	4.00	5.20	4.70	4.60	4.50
27	9.75	4.20	-	-	-	-
28	9.80	4.80	5.30	4.80	4.65	4.55
29	9.85	5.60	-	-	-	-
30	9.90	6.40	5.40	4.90	4.70	4.60
31	9.92	6.80	-	-	-	-
32	9.95	7.40	-	-	-	-
33	10.00	8.40	5.50	5.00	4.75	4.70
34	10.05	9.20	5.60	-	-	4.75
35	10.10	9.70	5.70	5.10	4.80	4.85
36	10.15	9.85	5.80	-	-	4.90
37	10.20	10.00	5.90	5.20	4.90	4.95
38	10.25	-	6.00	-	-	5.00
39	10.30	10.20	6.10	5.30	4.95	5.05
40	10.35	10.30	6.25	-	-	5.10
41	10.40	10.35	6.40	5.40	5.00	5.15
42	10.45	10.40	6.65	-	-	-

contd..

Table 6.16(contd.)

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for		
				Be(II)	Al(III)	V(IV)
43	10.50	10.45	6.90	5.50	5.05	5.20
44	10.55	10.50	7.20	-	-	5.25
45	10.60	10.55	7.40	5.65	5.15	5.30
46	10.65	10.65	7.55	-	-	5.40
47	10.70	10.70	7.70	5.78	5.30	5.45
48	10.75	10.72	7.80	-	-	5.52
49	10.80	10.75	7.90	5.90	5.40	5.60
50	10.85	-	8.00	6.00	-	-
51	10.90	10.78	8.15	6.10	5.55	5.70
52	11.00	10.80	8.20	6.30	5.70	5.90
53	11.10	-	8.25	6.60	5.95	6.10
54	11.15	-	-	6.80	-	6.22
55	11.20	-	8.30	7.00	6.20	6.35
56	11.25	-	-	7.20	6.40	6.50
57	11.30	-	8.35	7.40	6.60	6.65
58	11.35	-	-	7.55	6.80	6.80
59	11.40	-	8.40	7.70	7.10	7.00
60	11.45	-	-	7.75	7.30	7.15
61	11.50	-	8.45	7.80	7.50	7.25
62	11.60	-	-	8.00	7.70	7.60
63	11.70	-	-	8.10	7.80	7.75
64	11.80	-	-	8.20	7.94	7.90
65	11.90	-	-	8.30	8.05	8.00

contd..

Table 6.16 (contd..)

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for		
				Be(II)	Al(III)	V(IV)
66	12.00	10.90	8.70	8.35	8.20	8.10
67	12.50	-	8.85	8.60	-	8.50
68	13.00	10.95	9.00	8.75	8.70	8.65
69	13.50	-	-	8.90	-	8.80
70	14.00	11.00	9.30	9.05	9.00	8.95

Some of the relevant observed pH values recorded in Table 6.16 have also been represented graphically. The details are given below:

Titration	Graphical Representation
A	P.28-31.F.1. Curve A
B	P.28-31F.1. Curve B
C for Be(II)	P.29.F.1. Curve C
C for Al(III)	P.30.F.1. Curve C
C for V(IV)	P.31.F.1. Curve C

Table 6.17:

y = 2; N = 0.1; E = 0.01; $T_L = 2.5\times10^{-3}$; $T_M = 0.5\times10^{-3}$

$V_o = 100$

		(H)	(V)	(M)
β_1^H	=	1.679×10^9	3.141×10^9	2.486×10^9
β_2^H	=	3.614×10^{17}	5.358×10^{17}	4.721×10^{17}

S.No.	pH	v'	v"	v'"		
				Be (II)	Al (III)	V (IV)
1	4.2	9.750	8.500	8.700	8.600	9.000
2	4.4	9.775	8.875	9.300	9.300	9.500
3	4.6	9.800	9.125	9.600	9.700	9.862
4	4.8	9.810	9.300	9.800	10.062	10.062
5	5.0	9.820	9.500	10.000	10.362	10.262
6	5.2	9.825	9.700	10.200	10.600	10.500
7	5.4	9.837	9.900	10.400	10.800	10.650
8	5.6	9.850	10.050	10.550	10.937	10.800
9	5.8	9.862	10.150	10.700	11.050	10.950
10	6.0	9.875	10.250	10.825	11.130	11.050
11	6.2	9.890	10.325	10.950	11.200	11.150
12	6.4	9.900	10.400	11.025	11.250	11.212
13	6.6	9.910	10.450	11.100	11.300	11.275
14	6.8	9.920	10.475	11.150	11.325	11.325
15	7.0	9.930	10.512	11.200	11.400	11.412
16	7.2	9.937	10.562	11.250	11.437	11.475
17	7.4	9.950	10.600	11.300	11.475	11.550
18	7.6	9.962	10.675	11.375	11.550	11.625

contd..

Table 6.17 (contd.):

S.No.	pH	v'	v"	v'''		
				Be (II)	Al (III)	V (IV)
19	7.8	9.975	10.750	11.500	11.675	11.725
20	8.0	9.980	10.850	11.625	11.837	11.900
21	8.2	9.987	11.000	11.800	12.025	12.100
22	8.4	10.000	11.400	12.075	12.250	12.325
23	8.6	10.012	11.800	12.500	12.600	12.750
24	8.8	10.020	12.400	13.125	13.300	13.500
25	9.0	10.025	13.000	13.825	14.000	14.250
26	9.2	10.050	13.700	-	-	-

Table 6.18:

Ionic strength 0.05; Elements Be, Al, V

S.No.	v'	v"	v'-v"	V_o+v'	pH	$\bar{n}_A$
1	9.750	8.500	1.25000	109.75000	4.20	2.50113
2	9.775	8.875	0.89999	109.77500	4.40	2.36073
3	9.800	9.125	0.67499	109.80000	4.60	2.27049
4	9.810	9.300	0.50999	109.81000	4.80	2.20435
5	9.820	9.500	0.31999	109.82000	5.00	2.12820
6	9.825	9.700	0.12500	109.82500	5.20	2.05007
7	9.837	9.900	-0.06300	109.83700	5.40	1.97476
8	9.850	10.050	-0.20000	109.85000	5.60	1.91989
9	9.862	10.150	-0.28800	109.86200	5.80	1.88465
10	9.875	10.250	-0.37500	109.87500	6.00	1.84982

contd...

Table 6.18

S.No.	v'	v"	v'-v"	V_o+v'	pH	$\bar{n}_A$
11	9.890	10.325	-0.43500	109.89000	6.20	1.82582
12	9.900	10.400	-0.50000	109.90000	6.40	1.79981
13	9.910	10.450	-0.53999	109.91000	6.60	1.78382
14	9.920	10.475	-0.55500	109.92000	6.80	1.77783
15	9.930	10.512	-0.58199	109.93000	7.00	1.76705
16	9.937	10.562	-0.62500	109.93700	7.20	1.74985
17	9.950	10.600	-0.64999	109.95000	7.40	1.73988
18	9.962	10.675	-0.71299	109.96200	7.60	1.71470
19	9.975	10.750	-0.77500	109.97500	7.80	1.68992
20	9.980	10.850	-0.86999	109.98000	8.00	1.65193
21	9.987	11.000	-1.01300	109.98700	8.20	1.59475
22	10.000	11.400	-1.40000	110.00000	8.40	1.44000
23	10.012	11.800	-1.68800	110.01200	8.60	1.28487
24	10.020	12.400	-2.38000	110.02000	8.80	1.04817
25	10.025	13.000	-2.97500	110.02500	9.00	0.81027
26	10.050	13.700	-3.65000	110.05000	9.20	0.54066

Table 6.19: Ionic strength = 0.05

log K_1^H = log β_1^H			log K_2^H			log β_2^H		
(H)	(V)	(M)	(H)	(V)	(M)	(H)	(V)	(M)
9.225	9.497	9.3956	8.333	8.232	8.2784	17.558	17.729	17.674

Table 6.20: Ionic strength 0.05; Element Be(II)

S.No.	v''' - v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.4249	0.3607	4.40	11.43122	11.60224	11.54727
2	0.4749	0.4191	4.60	11.03799	11.20803	11.15405
3	0.5000	0.4544	4.80	10.64221	10.81326	10.75827
4	0.5000	0.4706	5.00	10.24457	10.41563	10.36064
5	0.5000	0.4885	5.20	9.84725	10.01835	9.96334
6	0.5000	0.5071	5.40	9.44995	9.62109	9.56606
7	0.5000	0.5215	5.60	9.05228	9.22351	9.16843
8	0.5499	0.5843	5.80	8.65949	8.83084	8.77571
9	0.5800	0.6223	6.00	8.26444	8.43598	8.38075
10	0.6199	0.6853	6.20	7.87243	8.04428	7.98890
11	0.6299	0.6951	6.40	7.47551	7.64784	7.59223
12	0.6499	0.7293	6.60	7.08223	7.25530	7.19932
13	0.6700	0.7599	6.80	6.69015	6.86439	6.80784
14	0.6900	0.7791	7.00	6.29944	6.47547	6.41805
15	0.6900	0.7868	7.20	5.91161	6.09036	6.03162
16	0.7500	0.8878	7.80	4.80391	4.99996	4.93290
17	0.7800	0.9384	8.00	4.46381	4.66948	4.59786
18	0.7999	1.0030	8.20	4.14540	4.36214	4.28535
19	0.7000	1.0890	8.60	3.57268	3.81186	3.72480
20	0.7299	1.3830	8.80	3.34882	3.59728	3.50606
21	0.8300	2.0360	9.00	3.19512	3.45087	3.35642

Table 6.21: Ionic strength 0.05; Element Al(III)

S.No.	v''' -v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.4249	0.3607	4.40	11.43122	11.60224	11.54727
2	0.5749	0.5074	4.60	11.04684	11.21788	11.16290
3	0.7600	0.6925	4.80	10.66660	10.83765	10.78267
4	0.8599	0.8114	5.00	10.27996	10.45103	10.39603
5	0.8999	0.8794	5.20	9.88819	10.05928	10.00428
6	0.8999	0.9128	5.40	9.49262	9.66377	9.60873
7	0.8899	0.9252	5.60	9.09484	9.26606	9.21099
8	0.8999	0.9562	5.80	8.69907	8.87042	8.81529
9	0.8699	0.9594	6.20	7.90192	8.07376	8.01839
10	0.8799	1.0010	7.20	5.93501	6.11376	6.05502
11	0.8800	1.0060	7.40	5.55272	5.73546	5.67478
12	0.8700	1.0210	7.60	5.18045	5.36886	5.30545
13	0.9299	1.0950	7.80	4.82706	5.02312	4.95605
14	0.9899	1.1950	8.00	4.49297	4.69863	4.62702
15	1.0299	1.2860	8.20	4.17818	4.39492	4.31813
16	0.8999	1.7170	8.30	3.39155	3.64001	3.54879

Table 6.22: Ionic strength 0.05; Element V(IV)

S.No.	v‴ -v″	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.5000	0.4007	4.20	11.83384	12.00486	11.94989
2	0.6250	0.5305	4.40	11.44820	11.61923	11.56426
3	0.7369	0.6503	4.60	11.06152	11.23256	11.17758
4	0.7599	0.7172	5.00	10.26991	10.44097	10.38598
5	0.7500	0.7607	5.40	9.47616	9.64731	9.59227
6	0.7500	0.7823	5.60	9.07932	9.25054	9.19547
7	0.7999	0.8659	6.00	8.29016	8.46170	8.40648
8	0.8099	0.9031	6.40	7.49772	7.67005	7.61444
9	0.8300	0.9257	6.60	7.10338	7.27645	7.22047
10	0.8400	0.9569	6.80	6.71148	6.88572	6.82917
11	0.9200	1.0440	7.20	5.93987	6.11861	6.05987
12	0.9500	1.1080	7.60	5.19036	5.37877	5.31536
13	0.9799	1.1540	7.80	4.83387	5.02992	4.96286
14	0.9300	1.2850	8.40	3.87539	4.10370	4.02158
15	0.9500	1.4790	8.60	3.61926	3.85844	3.77139
16	1.1000	2.0990	8.80	3.44604	3.69450	3.60328

Table 6.23: Ionic strength = 0.05

Element	$\log K_1 = \log \beta_1$		$\log K_2$		$\log \beta_2 = \log K_1 + \log K_2$	
	(H)	(V)	(H)	(V)	(H)	(V)
Be(II)	9.670	9.900	3.300	3.552	12.970	13.452
Al(III)	11.120	11.202	3.730	3.976	14.850	15.178
V(IV)	11.540	11.712	3.600	3.862	15.140	15.574

The results indicate that generally there is an agreement in the values obtained by the two methods.

Studies at ionic strength 0.1

Table 6.24 records the observations made during the three titrations, represented by Curves A, B and C, detailed already. Some representative results have also been graphically represented.

Table 6.25 embodies the values of v', v" and v''' (obtained in case of elements Beryllium, Aluminium and Vanadium) at various pH values. Table 6.26 records the variation of $\bar{n}_A$ (calculated with IBM - 1130 Computer) with pH and these results are graphically represented in P.32.F.2. From this plot, 3 set of values of acid dissociation constants, log K_1^H, log K_2^H and log β_2^H have been obtained by applying Bjerrum's half $\bar{n}_A$ method (denoted by H), Irving and Rossotti's interpolation at various $\bar{n}_A$ values (denoted by V) and Bjerrum's mid point method (denoted by M) and these are being presented in Table 6.27.

Tables 6.28 through 6.30 serially record the values of $\bar{n}$ and pLs, calculated by IBM - 1130 Computer, at different pH values; for the elements Be(II), Al(III) and V(IV). Fig. 2 (Curves H and V) in plate numbers 33-34-35 are graphical representations of $\bar{n}$ values plotted against corresponding values of pLs - pL(H) and pL(V) for the above mentioned elements, serially. From these plots (P.33-34-35.F.2), two sets of values of log β_1 and log β_2 have been obtained by applying half $\bar{n}$ values method and interpolation at various $\bar{n}$ values method, for each element and these are being recorded in Table 6.31.

Table 6.24:

Temp. = 25°C; Ionic strength (μ) = 0.10; y = 2

T_L = 2.5 x 10^{-3}M; T_M = 0.5 x 10^{-3}M; N = 0.1 M; E = 0.10 M

V_o = 100 ml

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for Be(II)	C for Al(III)	C for V(IV)
1	1.00	2.20	2.60	2.50	-	-
2	2.00	2.25	2.85	-	-	-
3	3.00	2.30	2.95	-	-	-
4	4.00	2.40	3.30	-	-	-
5	5.00	2.50	3.60	3.35	3.25	3.35
6	6.00	2.60	3.80	-	3.50	3.60
7	7.00	2.70	4.00	-	3.75	3.85
8	8.00	2.90	4.10	4.00	4.00	4.00
9	8.10	-	-	-	-	-
10	8.20	-	-	-	-	-
11	8.30	2.95	-	-	-	-
12	8.40	--	-	-	-	-
13	8.50	3.00	4.30	4.10	4.10	4.10
14	8.60	3.05	4.35	-	-	-
15	8.70	3.10	4.40	-	-	-
16	8.80	3.15	4.45	-	-	-
17	8.90	-	4.50	-	-	-
18	9.00	3.20	4.55	4.20	4.20	4.20
19	9.10	3.25	4.65	4.25	-	-
20	9.20	3.30	4.75	4.30	-	-

contd..

Table 6.24 (contd.)

S.No.	Volume of NaOH added (ml)	Observed pH in titration A	B	C for Be(II)	Al(III)	V(IV)
21	9.30	3.40	4.82	4.35	-	-
22	9.40	3.50	4.90	4.40	-	-
23	9.50	3.60	4.98	4.45	4.30	4.35
24	9.60	3.75	5.08	4.50	4.35	4.40
25	9.65	-	-	-	-	-
26	9.70	3.95	5.15	4.55	4.40	4.45
27	9.75	-	-	-	-	-
28	9.80	4.40	5.25	4.60	4.45	4.50
29	9.85	5.00	-	-	-	-
30	9.90	5.85	5.30	4.70	4.50	4.55
31	9.92	-	-	-	-	-
32	9.95	7.00	-	-	-	-
33	10.00	8.30	5.50	4.80	4.55	4.65
34	10.05	8.90	5.58	-	-	-
35	10.10	9.40	5.65	4.90	4.60	4.75
36	10.15	9.70	5.72	-	-	-
37	10.20	9.85	5.80	5.00	4.65	4.85
38	10.25	9.92	5.92	-	-	-
39	10.30	10.00	6.05	5.10	4.75	4.95
40	10.35	-	6.18	-	-	-
41	10.40	10.15	6.30	5.20	4.80	5.05
42	10.45	10.20	6.55	-	-	-
43	10.50	10.25	6.75	5.30	4.90	5.15

contd..

Table 6.24 (contd.)

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for		
				Be(II)	Al(III)	V(IV)
44	10.55	10.30	7.10	-	-	-
45	10.60	10.35	7.35	5.45	5.00	5.25
46	10.65	10.40	7.55	-	-	5.30
47	10.70	10.45	7.70	5.60	5.12	5.35
48	10.75	-	7.80	-	-	-
49	10.80	10.50	7.90	5.75	5.25	5.50
50	10.85	-	8.00	-	-	-
51	10.90	10.55	8.10	5.90	5.40	5.65
52	11.00	10.60	8.20	6.10	5.55	5.85
53	11.10	-	8.25	6.30	5.75	6.05
54	11.15	-	-	6.45	5.87	6.17
55	11.20	-	8.30	6.65	6.00	6.30
56	11.25	-	-	6.85	6.15	6.45
57	11.30	-	8.35	7.00	6.30	6.60
58	11.35	-	-	7.15	6.55	6.75
59	11.40	-	8.40	7.35	6.80	6.90
60	11.45	-	-	7.50	7.00	7.10
61	11.50	-	8.45	7.65	7.15	7.30
62	11.60	-	-	7.85	7.50	7.50
63	11.70	-	-	8.00	7.70	7.75
64	11.80	-	-	8.10	7.90	7.90
65	11.90	-	-	8.20	8.00	8.00
66	12.00	10.90	8.70	8.30	8.10	8.10

contd.

Table 6.24 (contd.):

S.No.	Volume of NaOH added (ml)	Observed pH in titration				
		A	B	C for		
				Be(II)	Al(III)	V(IV)
67	12.50	10.95	8.85	8.55	-	8.40
68	13.00	11.00	9.00	8.30	8.70	8.65
69	13.50	11.05	-	-	-	8.85
70	14.00	11.10	9.30	9.10	9.00	9.00

Some of the relevant observed pH values recorded in Table 6.24 have also been represented graphically. The details are given below:

Titration	Graphical representation
A	P.32-35.F.1. Curve A
B	P.32-35.F.1. Curve B
C for Be(II)	P.33.F.1. Curve C
C for Al(III)	P.34.F.1. Curve C
C for V(IV)	P.35.F.1 Curve C

Table 6.25:

y=2; N=0.1M; E=0.01M; $T_L=2.5\times10^{-3}M$; $T_M=0.5\times10^{-3}M$; $V_o=100$ ml

		(H)	(V)	(M)
β_1^H	=	1.778×10^{9}	3.266×10^{9}	2.523×10^{9}
β_2^H	=	3.828×10^{17}	5.636×10^{17}	5.012×10^{17}

S.No.	pH	v'	v"	v‴		
				Be	Al	V
1	3.6	9.500	5.000	6.150	6.400	6.000
2	3.8	9.625	6.000	7.125	7.150	6.875
3	4.0	9.710	7.000	8.000	8.000	8.000
4	4.2	9.760	8.250	9.000	9.150	9.000
5	4.4	9.800	8.700	9.400	9.700	9.625
6	4.6	9.825	9.025	9.750	10.100	9.925
7	4.8	9.837	9.300	10.000	10.400	10.150
8	5.0	9.850	9.500	10.200	10.625	10.350
9	5.2	9.862	9.750	10.400	10.775	10.525
10	5.4	9.875	9.925	10.575	10.900	10.700
11	5.6	9.880	10.075	10.750	11.025	10.850
12	5.8	9.887	10.200	10.850	11.125	10.975
13	6.0	9.895	10.287	10.950	11.200	11.062
14	6.2	9.900	10.362	11.050	11.275	11.150
15	6.4	9.905	10.420	11.125	11.325	11.237
16	6.6	9.912	10.462	11.187	11.375	11.300
17	6.8	9.920	10.500	11.237	11.400	11.375
18	7.0	9.925	10.530	11.300	11.462	11.425

contd..

Table 6.25 (contd.):

S.No.	pH	v'	v"	v'''		
				Be	Al	V
19	7.2	9.930	10.562	11.350	11.512	11.487
20	7.4	9.937	10.612	11.425	11.562	11.550
21	7.6	9.945	10.650	11.487	11.637	11.637
22	7.8	9.955	10.750	11.575	11.750	11.750
23	8.0	9.970	10.850	11.700	11.900	11.900
24	8.2	9.987	11.025	11.900	12.100	12.100
25	8.4	10.000	11.375	12.200	12.500	12.500
26	8.6	10.020	11.800	12.600	12.850	12.850
27	8.8	10.037	12.300	13.025	13.300	13.300
28	9.0	10.050	13.000	13.650	14.000	14.000
29	9.2	10.075	13.650	-	-	-

Table 6.26: Ionic strength 0.10; Elements Be, Al, V

S.No.	v'	v"	v'-v"	V_o+v'	pH	$\bar{n}_A$
1	9.800	8.700	1.10000	109.80000	4.40	2.44080
2	9.825	9.025	0.79999	109.82500	4.60	2.32050
3	9.837	9.300	0.53700	109.83700	4.80	2.21511
4	9.850	9.500	0.34999	109.85000	5.00	2.14019
5	9.862	9.750	0.11199	109.86200	5.20	2.04485
6	9.875	9.925	-0.04999	109.87500	5.40	1.97997
7	9.880	10.075	-0.19500	109.88000	5.60	1.92191
8	9.887	10.200	-0.31300	109.88700	5.80	1.87467

contd..

Table 6.26 (contd..)

S.No.	v'	v"	v'-v"	V_o+v'	pH	$\bar{n}_A$
9	9.895	10.287	-0.39199	109.89500	6.00	1.84305
10	9.900	10.362	-0.46199	109.90000	6.20	1.81503
11	9.905	10.420	-0.51500	109.90500	6.40	1.79382
12	9.912	10.462	-0.55000	109.91200	6.60	1.77982
13	9.920	10.500	-0.58000	109.92000	6.80	1.76783
14	9.925	10.530	-0.60499	109.92500	7.00	1.75783
15	9.930	10.562	-0.63199	109.93000	7.20	1.74703
16	9.937	10.612	-0.67499	109.93700	7.40	1.72984
17	9.945	10.650	-0.70500	109.94500	7.60	1.71785
18	9.955	10.750	-0.79500	109.95500	7.80	1.68186
19	9.970	10.850	-0.87999	109.97000	8.00	1.64790
20	9.987	11.025	-1.03800	109.98700	8.20	1.58475
21	10.000	11.375	-1.37500	110.00000	8.40	1.45000.
22	10.020	11.800	-1.78000	110.02000	8.60	1.28812
23	10.037	12.300	-2.26300	110.03700	8.80	1.09510
24	10.050	13.000	-2.95000	110.05000	9.00	0.82053
25	10.075	13.650	-3.57500	110.07500	9.20	0.57097

Table 6.27: Ionic strength = 0.1

$\log K_1^H = \log \beta_1^H$			$\log K_2^H$			$\log \beta_2^H = \log K_1^H + \log K_2^H$		
(H)	(V)	(M)	(H)	(V)	(M)	(H)	(V)	(M)
9.250	9.514	9.402	8.333	8.237	8.298	17.583	17.751	17.700

Table 6.28: Ionic strength 0.1; Element Be(II)

S.No.	v''' -v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.7000	0.5746	4.40	11.47710	11.64511	11.59414
2	0.7250	0.6258	4.60	11.08362	11.25164	11.20067
3	0.7000	0.6329	4.80	10.68538	10.85341	10.80243
4	0.6999	0.6550	5.00	10.28839	10.45644	10.40545
5	0.6499	0.6365	5.20	9.88751	10.05559	10.00458
6	0.6550	0.6573	5.40	9.49040	9.65853	9.60749
7	0.6499	0.6941	5.80	8.69600	8.86431	8.81314
8	0.6599	0.7201	6.00	8.29970	8.46820	8.41691
9	0.6900	0.7588	6.20	7.90527	8.07406	8.02257
10	0.7100	0.7867	6.40	7.51023	7.67947	7.62769
11	0.7299	0.8153	6.60	7.11639	7.28634	7.23409
12	0.7399	0.8343	6.80	6.72317	6.89422	6.84125
13	0.7700	0.8766	7.00	6.33495	6.50770	6.45361
14	0.7899	0.9026	7.20	5.94908	6.12439	6.06861
15	0.8199	0.9300	7.40	5.56931	5.74841	5.69014
16	0.8400	0.9749	7.60	5.20018	5.38464	5.32286
17	0.8300	0.9814	7.80	4.83918	5.03089	4.96439
18	0.8500	1.0320	8.00	4.49916	4.69999	4.62759
19	0.8700	1.1040	8.20	4.18184	4.39320	4.31044
20	0.8199	1.1380	8.40	3.88296	4.10533	4.01917
21	0.7299	1.3240	8.80	3.36631	3.60798	3.50967
22	0.6499	1.5840	9.00	3.15769	3.40623	3.30369

Table 6.29: Ionic strength 0.1 ; Element Al(III)

S.No.	v''' -v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.8999	0.6924	4.20	11.88788	12.05588	12.00492
2	1.0000	0.8208	4.40	11.50315	11.67116	11.62019
3	1.0749	0.9280	4.60	11.11610	11.28412	11.23314
4	1.1000	0.9946	4.80	10.72451	10.89254	10.84156
5	1.0199	1.0040	5.20	9.92717	10.09525	10.04424
6	0.9750	0.9859	5.40	9.52583	9.69396	9.64291
7	0.9499	0.9896	5.60	9.12709	9.29529	9.24420
8	0.9300	0.9878	5.80	8.72778	8.89609	8.84492
9	0.9099	0.9916	6.00	8.32914	8.49764	8.44635
10	0.9200	1.0070	6.20	7.93236	8.10114	8.04966
11	0.9100	1.0100	6.40	7.53466	7.70389	7.65212
12	0.9200	1.0270	6.60	7.13968	7.30963	7.25738
13	0.9300	1.0610	7.00	6.35545	6.52819	6.47410
14	0.9499	1.0880	7.20	5.96982	6.14513	6.08934
15	0.9899	1.1500	7.60	5.22008	5.40454	5.34276
16	1.0000	1.1900	7.80	4.86299	5.05470	4.98820
17	1.0500	1.2750	8.00	4.52738	4.72822	4.65581
18	1.0699	1.3570	8.20	4.21177	4.42313	4.34397
19	1.0499	1.6300	8.60	3.66360	3.89633	3.80364
20	1.0000	1.8260	8.80	3.43112	3.67270	3.57448

Table 6.30: Ionic strength 0.1 ; Element V(IV)

S.No.	v''' -v''	$\bar{n}$	pH	pL(H)	pL(V)	pL(M)
1	0.8750	0.5082	3.80	12.66053	12.82853	12.77756
2	1.0000	0.6496	4.00	12.27891	12.44692	12.39595
3	0.7799	0.7589	5.20	9.90038	10.06846	10.01744
4	0.7749	0.7837	5.40	9.50370	9.67183	9.62079
5	0.7699	0.8073	5.60	9.10708	9.27528	9.22419
6	0.7800	0.8276	5.80	8.71019	8.87850	8.82733
7	0.7700	0.8418	6.00	8.31266	8.48116	8.42987
8	0.7900	0.8690	6.20	7.91709	8.08588	8.03440
9	0.8200	0.9116	6.40	7.52373	7.69296	7.64119
10	0.8400	0.9424	6.60	7.13022	7.30017	7.24792
11	0.8799	0.9906	6.80	6.74033	6.91138	6.85840
12	0.8999	1.0190	7.00	6.35072	6.52347	6.46938
13	0.9300	1.0600	7.20	5.96664	6.14195	6.08617
14	0.9400	1.0750	7.40	5.58554	5.76463	5.70636
15	0.9899	1.1500	7.60	5.22008	5.40454	5.34276
16	1.0000	1.1900	7.80	4.86299	5.05470	4.98820
17	1.0500	1.2750	8.00	4.52722	4.72822	4.65581
18	1.0699	1.3570	8.20	4.21177	4.42313	4.34397
19	1.0499	1.6300	8.60	3.66360	3.89633	3.80364
20	1.0000	1.8260	8.80	3.43112	3.67270	3.57448

Table 6.31: Ionic strength = 0.1

Elements	$\log K_1 = \log \beta_1$		$\log K_2$		$\log \beta_2 = \log K_1 + \log K_2$	
	(H)	(V)	(H)	(V)	(H)	(V)
Be(II)	11.600	11.843	3.193	3.453	14.793	15.296
Al(III)	12.368	12.505	3.868	4.108	16.236	16.613
V(IV)	12.680	12.827	3.868	4.121	16.548	16.948

The entire calculations in the potentiometric studies have been done on IBM Computer (Model 1130). Suitable programming has been made for the various calculations. Some representative results (along with the programming) have been given in the Appendices (No. 1-9).

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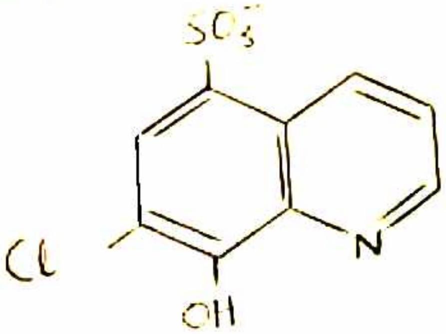
DISCUSSION

DISCUSSION

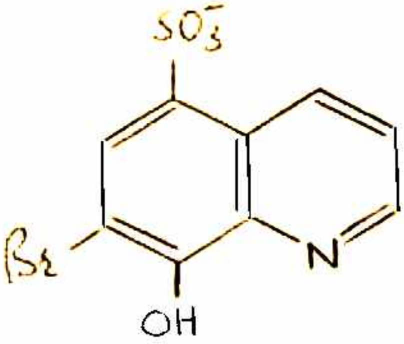
PART : Spectrophotometric investigations

In course of these investigations, a detailed study has been made of twelve metal chelates, involving chelating agents [illegible] structures:



7-chloro-8-hydroxyquinoline-5-sulphonic acid

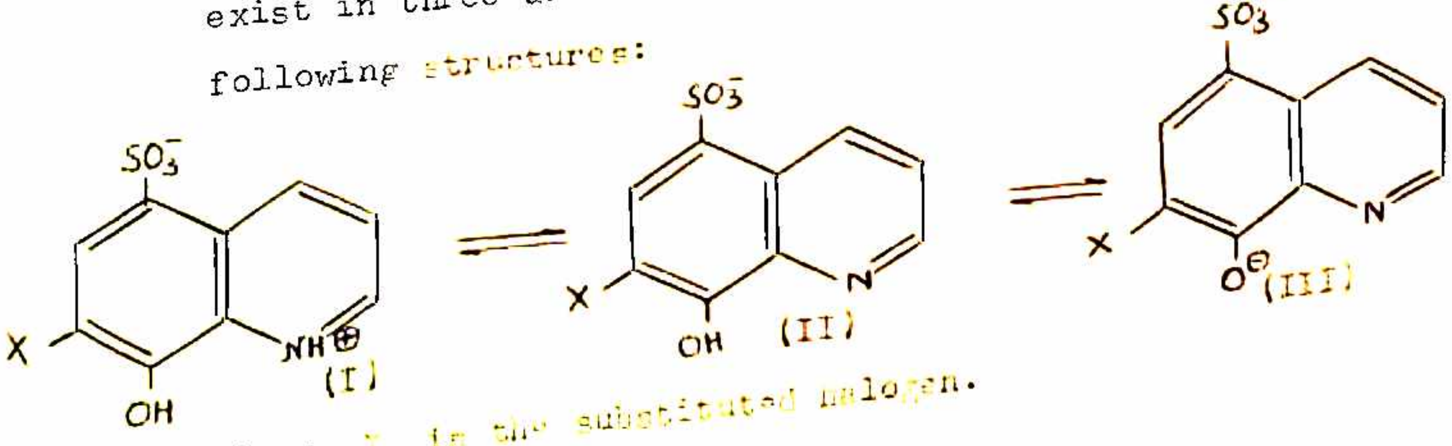
(Abbreviated as CHQS)



7-bromo-8-hydroxyquinoline-5-sulphonic acid

(Abbreviated as BHQS)

The analysis of absorption spectra of these ligands (P.2.F.1 & P.9.F.1) reveals that there is shift in λ_{max} with change in hydrogen ion concentration. It will be apparent from these graphs that there are three distinct regions of maximum absorption and it may be reasonably concluded that the ligands exist in three different forms, which can be represented by the following structures:



where X is the substituted halogen.

These ligands are weakly acidic in solution, therefore, with an increase in the acid concentration, the ionization of -NH group is suppressed and the acid form of the ligand develops the structure (I), in the pH range below 3.0. Structure (II) represents the half neutralized state, which predominates in the pH range 4 to 7. In moderately alkaline medium, above pH 8.0, the hydroxyl group ionizes and the structure of the chelating agents can be represented as (III).

The thermodynamic ionization constants of these ligands have been determined spectrophotometrically, by the method of Phillips (1) and the relevant pH values obtained at 25°C have been presented in Table 1.

Table 1: Thermodynamic ionization constants of the ligands in aqueous medium.

Ligands	pK_{a_1}	pK_{a_2}
8-hydroxyquinoline	5.02	9.81
8-hydroxyquinoline-5-sulphonic acid (HQS)	3.84	8.35
UHQS	3.65	7.63
CHQS	3.19	7.29

A comparison of the thermodynamic ionization constants of 8-hydroxyquinoline-5-sulphonic acid, with that of the parent compound, 8-hydroxyquinoline (2,3) reveals that the substituent group decreases the pK values, i.e., increases the ionization of the ligand. The sulphonic acid group is known to be a σ and π electron acceptor. The lower values of the sulphonate derivative may be considered as a result of electronic interaction of the sulphonate group with the aromatic ring. Although the sulphonic acid group itself is negative, the nature of the interaction is such that the negative charge is withdrawn from the ring.

The halo substituted derivatives are more acidic than 8-hydroxyquinoline-5-sulphonic acid. The ionization of the halo substituted acids is more owing to the inductive electron withdrawing effect of halogen. Our observations reveal that the halogen substitution affects the ionization only to a small extent, due to the fact that -I and +T effects of halogen oppose each other and as the -I effect predominates over +T effect, there is a small increase in the ionization. The order of the effect is

$$Cl > Br$$

Having made these preliminary observations on the characteristics of these 8-hydroxyquinoline-5-sulphonic acid derivatives, the chelate formation of copper (II), palladium (II), uranium (II), vanadium (III), iron(III) and gallium(III) may now be looked into. Out of the twelve metal chelates investigated, the two of gallium have a composition 1:3, the rest of them have a metal to ligand ratio of 1:2. For these studies, normally, wavelengths corresponding to λ_{max} have been selected.

The λ_{max} of the chelates, the pH at which the chelate has been investigated and the stoichiometry of the components in these chelates have been reported in Table II.

Table II: Characteristics of the metal chelates of 8-hydroxyquinoline-5-sulphonic acid derivatives.

[illegible]	pH	λ_{max} (mμ)	Composition M:L
[illegible]	5.3	365	1:2
Pd- [illegible]	4.5	400	1:2
[illegible]	6.6	355	1:2
VC -CH'S	6.6	360	1:2
[illegible]	3.0	430	1:2
[illegible]	4.0	355	1:3
[illegible]	5.3	365	1:2
Pd- [illegible]	4.5	395	1:2
UC_2- [illegible]	6.6	350	1:2
VC- [illegible]	6.6	360	1:2
Fe- [illegible]	3.0	430	1:2
[illegible]	4.0	355	1:3

The stability constants of the complexes were calculated by the methods suggested earlier. Temperature studies were carried out in case of metal chelates of 7-chloro-8-hydroxyquinoline-5-sulphonic acid and the values of enthalpy and entropy changes have been reported in Table III.

Table III: Stability constants and thermodynamic parameters of metal chelates of 7-chloro-8-hydroxyquinoline-5-sulphonic acid.

Chelate	Temp. °C	log K	-ΔF (kcal/mole)	* ΔH (kcal/mole)	* ΔS (e.u.)
Cu- CHQS	20	11.560±0.340	15.950	-14.00	6.65
Pd- CHQS	30	12.374±0.395	16.620	-	-
UO_2-CHQS	30	9.430±0.350	12.590	-8.696	12.85
VO- CHQS	30	10.426±0.076	14.340	-21.970	-25.19
Fe- CHQS	20	9.179±0.269	12.670	-14.640	-67.23
Ga- CHQS	20	13.527±0.213	17.860	1.442	65.88

(*values, obtained by applying molecular extinction coefficient method only).

Table IV records the stability constants and free energies of formation of the metal chelates of 7-bromo-8-hydroxyquinoline-5-sulphonic acid.

Table IV: Stability constants and free energies of formation of the metal chelates of 7-bromo-8-hydroxyquinoline-5-sulphonic acid

Chelate	Temp. °C	log K	-ΔF (Kcal/mole)
Cu- BHQS	20	11.635 ± 0.165	16.135 ± 0.225
Pd- BHQS	30	12.410 ± 0.430	17.210 ± 0.600
UO_2-BHQS	30	9.455 ± 0.509	13.105 ± 0.705
VO- BHQS	30	10.610 ± 0.300	14.710 ± 0.410
Fe- BHQS	20	9.368 ± 0.106	12.570 ± 0.140
Ga- BHQS	20	13.654 ± 0.218	18.275 ± 0.295

roughly linear relationship was observed between pK_a no values in course of the studies on the correlationship between ionization of the ligands and their chelate stability. [illegible] observed that 7-bromo-8-hydroxyquinoline-5-sulphonic [illegible] which has a pK_a value greater than that of 7-chloro- [illegible]oline-5-sulphonic acid (CHQS), also forms more stable [illegible] with metal ions, as compared to 7-chloro-8-hydroxyquinoline-5-sulphonic acid. It seems to be quite reasonable in view of the fact that the inductive effect of halogens decreases in the order Cl > Br > I. A similar relationship is also obtained in free energy of formation of their complexes.

Further, in case of both the ligands, the order of stability constant of the chelates is as follows:

Cu > Th > Co > V > U > Fe

This order can be explained on the basis of the values of ionization potential and electronegativity of these elements, which are recorded in Table V and also keeping in view some other considerations.

Table [illegible]:

Elements	Ionization Potential (ev)			Electronegativity Pauling's values
	I	II	I+II	
Gallium	6.000	20.510	26.510	1.81
Palladium	8.330	19.420	27.750	2.20
Copper	7.724	20.290	28.014	1.90
Vanadium	6.740	14.650	21.390	1.63
Uranium	4.000	-	-	1.70
Iron	7.900	16.180	24.080	1.83
Nitrogen	14.540	29.605	44.145	3.04
Oxygen	13.614	35.146	48.760	3.44

The number of ligands combining per metal atom, in case of gallium is the higher in the series (three, as compared to two, for the rest of the elements in the series). That is the main reason for its greater stability. Further, from Table V, it is clear that gallium has the highest ionization potential(II) value which contributes to greater stability of its chelates. Moreover, closer proximity of its electronegativity value to that of nitrogen and oxygen, as compared to those of vanadium, uranium, etc., is also responsible for its greater stability.

Besides gallium, copper and palladium also form very stable complexes; because of a number of reasons. Palladium and copper are capable of forming strong dsp^2 (square-planer) bonds. The greater stability of their chelates can also be ascribed to their [illegible], a result of which they acquire greater [illegible] form homopolar bonds, resulting in the formation of [illegible]. Besides, in case of copper and palladium, [illegible] $3d^{10}$ electron configuration, which is lacking in case of many other bivalent metals like Zn, Fe. Co and Ni, etc., which [illegible] their ability to form more stable complexes (4). Apart from this, copper and palladium, both have very high values of ionization potential (Copper having comparatively highest $\Delta V_1 + \Delta V_2$ value) as compared to those of other metals of this series. Further, the value of electronegativity of palladium [illegible] is again highest in the series; which results in closer proximity to the electronegativity values of nitrogen and oxygen. This renders them more capable for covalent bond formation, which subsequently leads to greater stability of their metal chelates.

The results obtained in course of these investigations, also indicate that palladium forms, more stable complexes than even copper. This can be ascribed to the fact that as one passes from the first to the second transition series, the stability of the metal chelates increases. Moreover, palladium exists in aqueous solution, in the form of covalent compounds (i.e. complexes and chelates) (5); as a result of which, it can more easily form covalent bonds with electron donors. It is further clear from Table V, that the value of electronegativity of palladium is more closer to nitrogen and oxygen, than that of copper.

From the point of view of greater ionization potential and greater value of electronegativity (closer to those of N and O), iron should have greater value of stability constant than those for vanadium and uranium; but it forms least soluble complexes. Obviously in this case, factors like hydrolysis, play a more dominant role.

As regards comparison of stability constant of uranium and vanadium, it has been observed that vanadium forms far more stable complexes than uranium. It is obvious from the considerations of the ionization potential and from the point of view of greater number of 3d electrons(two against one in case of uranium) in the configuration of vanadium; that the experimental results obtained follow the desired trend.

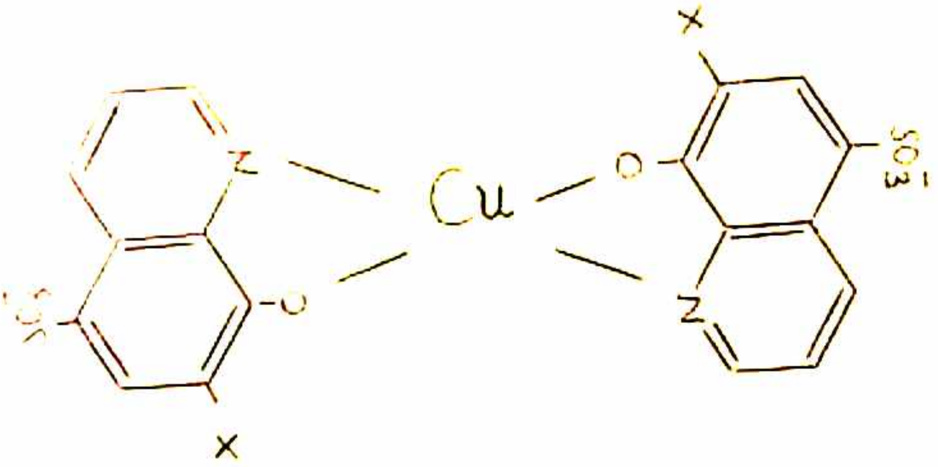
Temperature studies, in case of metal chelates of 7-chloro-8-hydroxyquinoline-5-sulphonic acid reveal that with an increase in temperature, log K values decrease, in all the cases. It clearly indicates that the complex formation between metal ions and 7-chloro-8-hydroxyquinoline, constitute exothermic reactions and hence result in negative (or very small) enthalpy changes. The entropy change relates to the amount of order in the products compared, to that in the reactants. When ΔS is positive, it contributes to a more negative free energy change, which accounts for the greater stability of the complexes, e.g., results show that the gallium chelate is very stable, rather the more stable in the series, which is also evident from the values of the stability constant obtained.

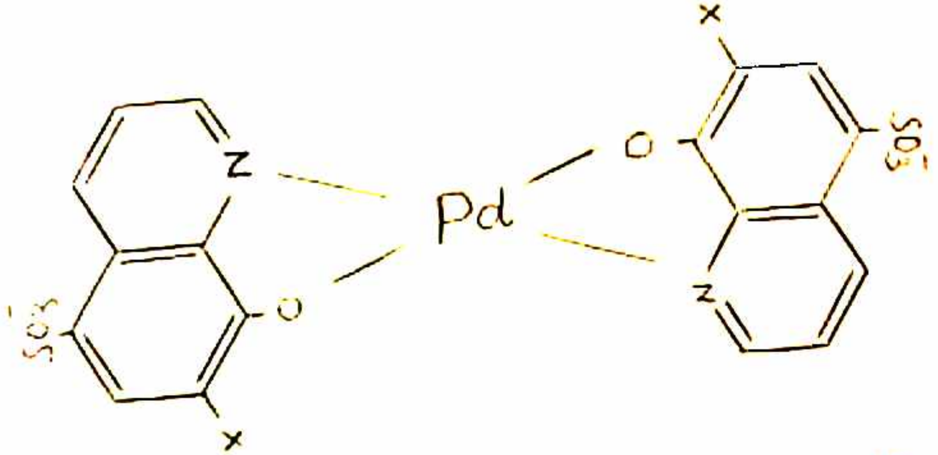
In the spectrophotometric determination of uranium, using

7-chloro-8-hydroxyquinoline-5-sulphonic acid, the results obtained indicate a satisfactory agreement with those obtained by other methods, as regards sensitivity in terms of molecular extinction coefficient, as can be seen in Table 5.1. Some of the additional advantages of the method are its applicability in the ultraviolet [illegible], less consumption of time and water solubility of the reagent. Spectrophotometric determination of iron with this reagent (Table 5.2) does not, however, provide greater sensitivity, than the other conventional methods.

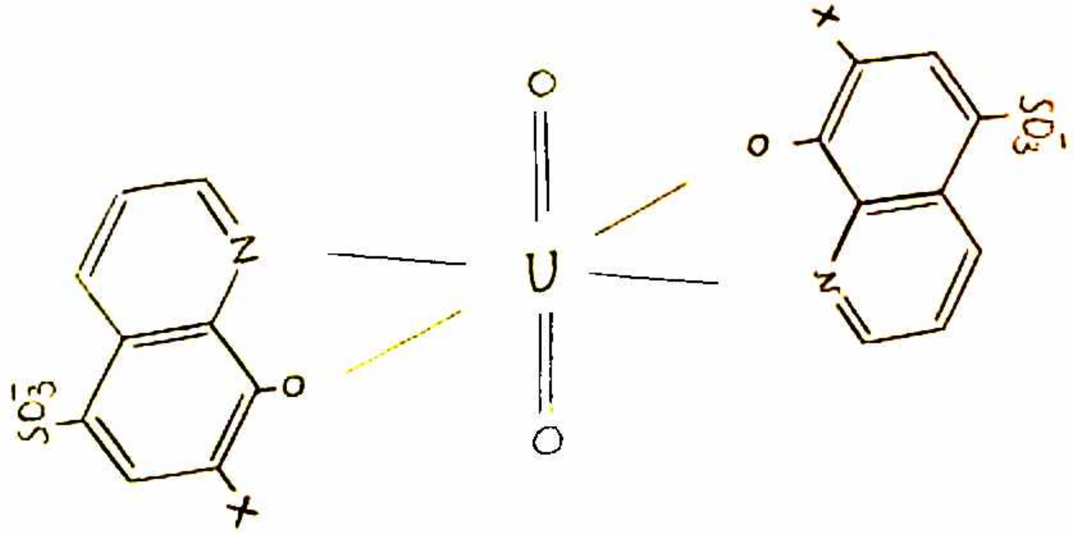
Some remarks on the possible structures of the chelates may be made here, though the suggestions advanced are purely tentative and can only be established by further investigations, which are outside the purview of the present work.

Copper and palladium are tetracoordinated bivalent ions and 8-hydroxyquinoline-5-sulphonic acid derivatives, like the parent compound, 8-hydroxyquinoline, act as strong chelating agents. During chelation, the hydroxyl group may be replaced by metal ion (6,7) and the coordination link may then be formed between the metal atom and the adjacent nitrogen atom, resulting in the formation of a five-membered chelate ring. On the basis of this, a tentative structure of the 1:2 complex of copper and palladium may be represented as overleaf:

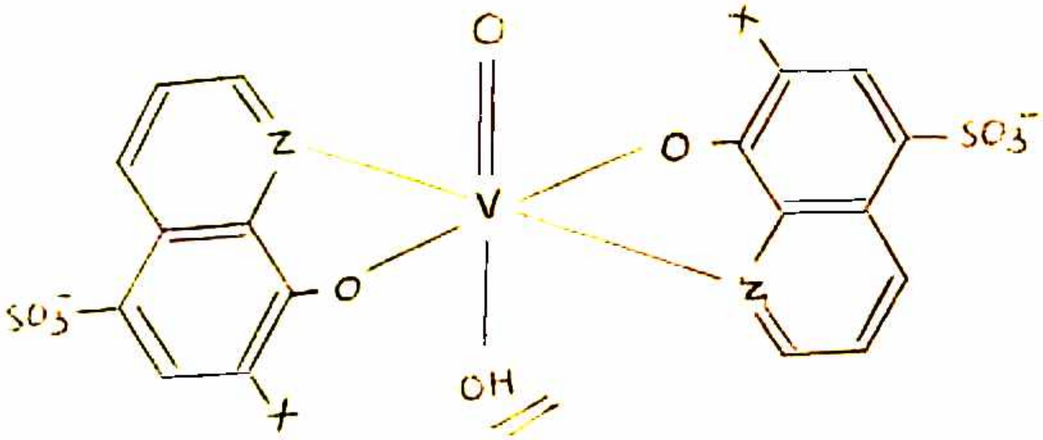




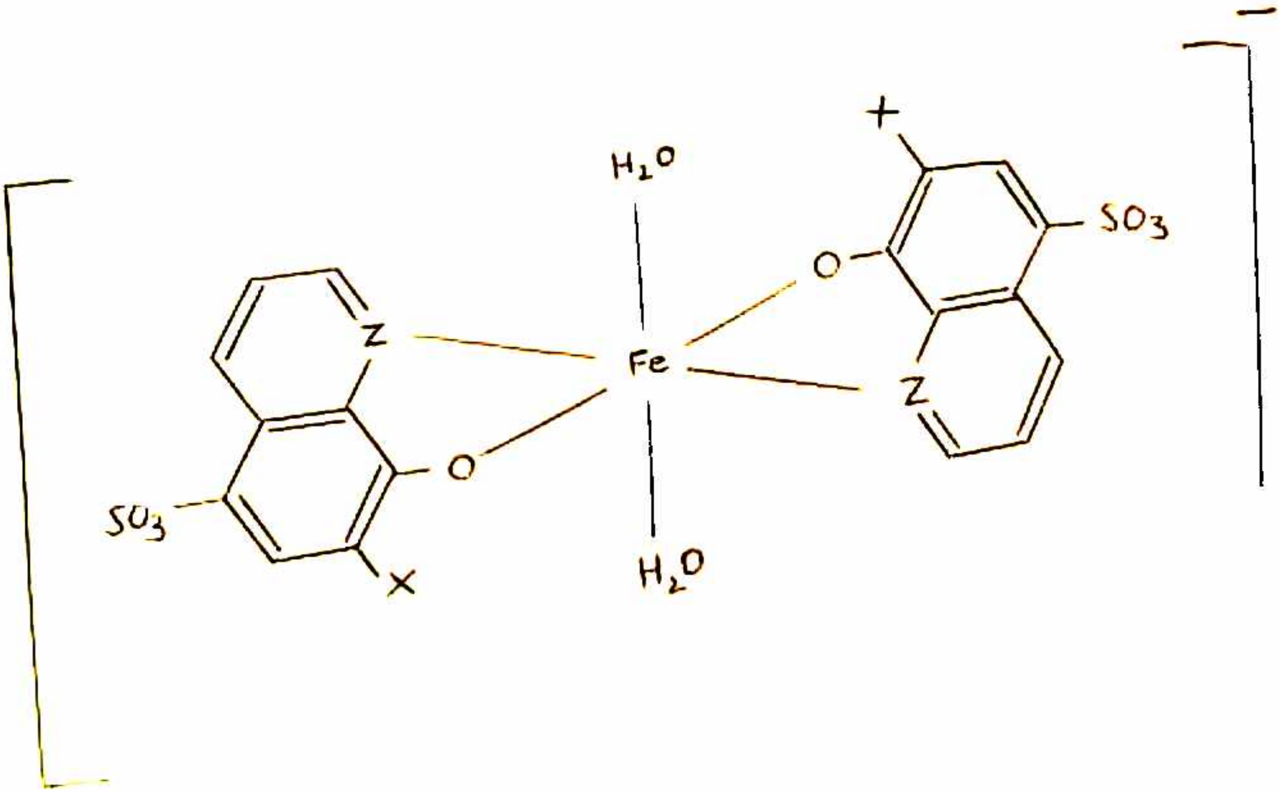
Uranium ion, in solution exists as UO_2^{++} and consequently, the following structure may be postulated for the uranium chelates of these reagents:



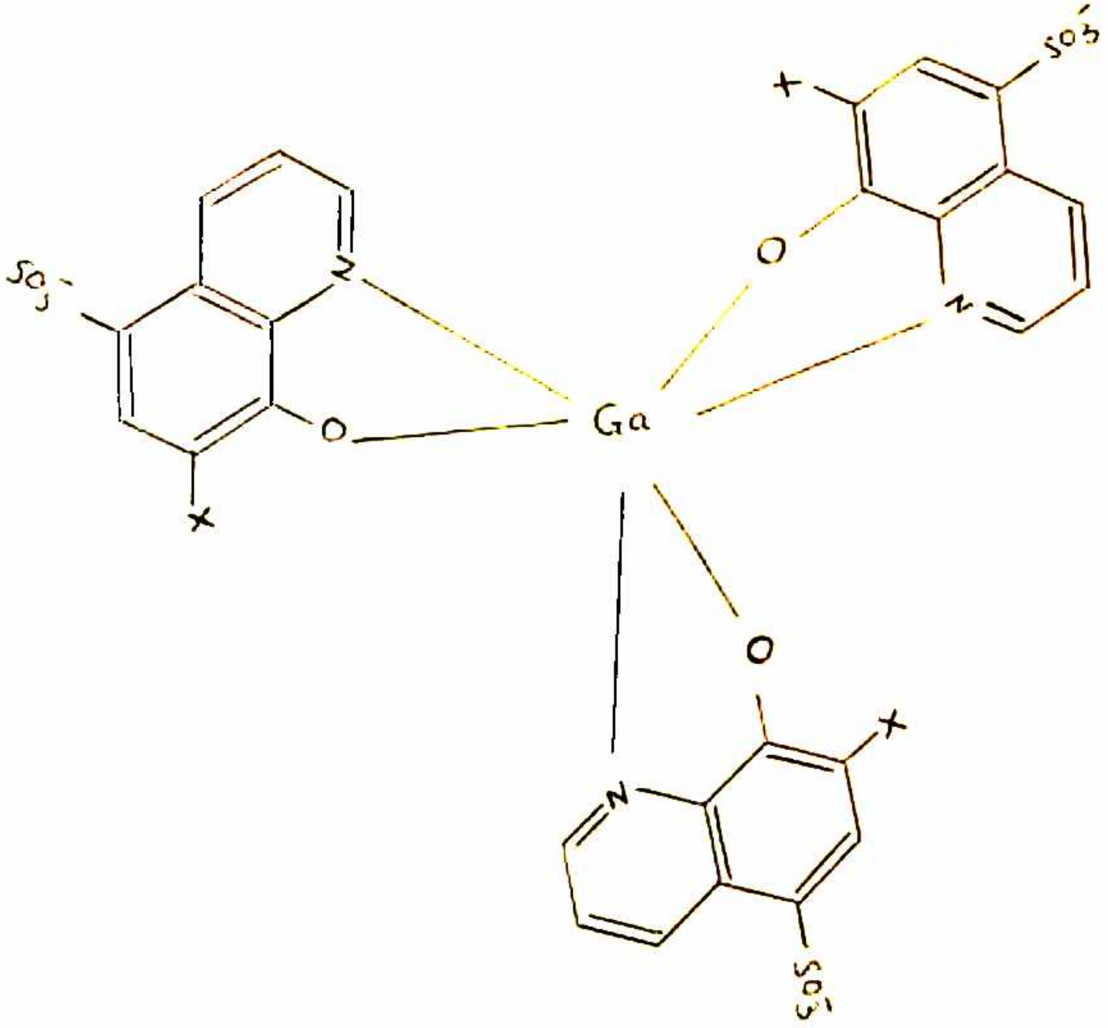
The tentative structure, proposed for the vanadium chelates of these reagents, based on the studies of [illegible]J. Blair et al (6) is as given below:



In accordance with the suggestions of Dey et al (8) and (9) [illegible]kman et al, following structure for the iron chelates of these reagents can be proposed:

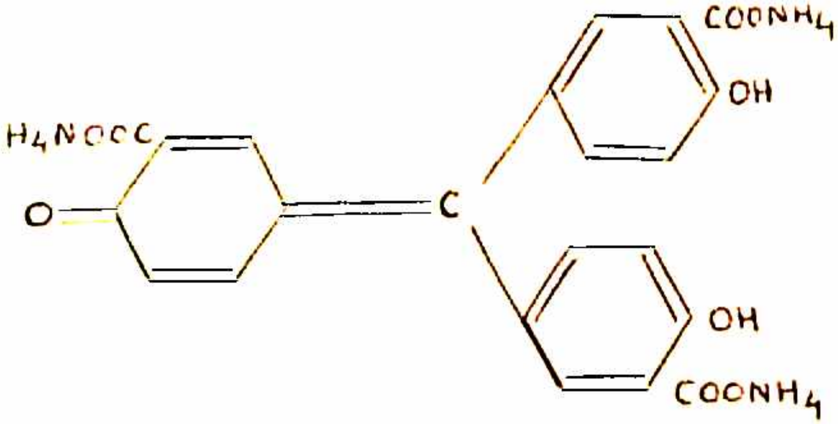


On the basis of these and similar other reasoning, the following structure for gallium chelates of these reagents can also be proposed:



PART B: Potentiometric studies

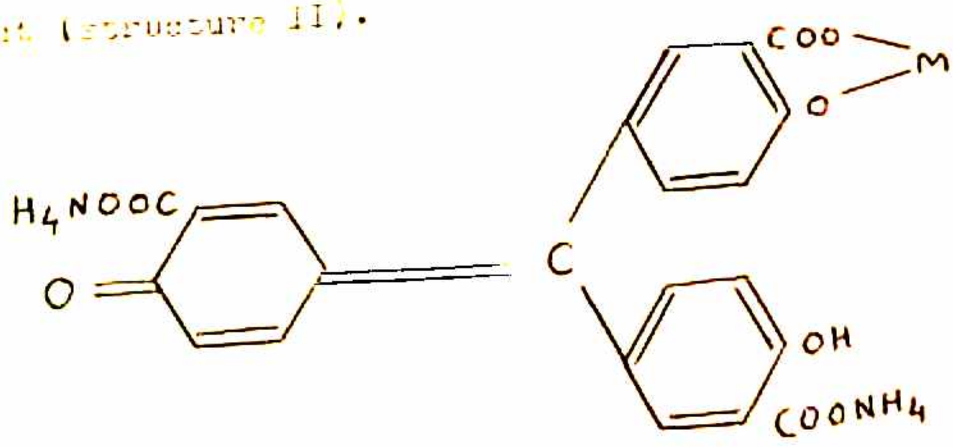
Ammonium aurintricarboxylate is represented by the following structure:



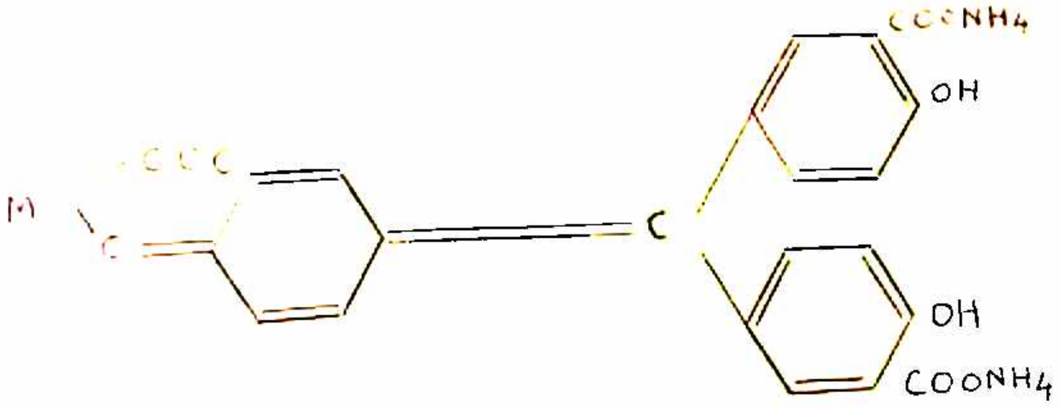
Coordination in ammonium aurintricarboxylate is possible in two ways:

(i) The coordination may be by the donation of a pair of electrons from the CCO^- group and by the replacement of hydrogen from the CH group (structure I)

(ii) Alternatively, a metal may be coordinated between the carboxylic oxygen and the quinoid oxygen of the chelating agent (structure II).



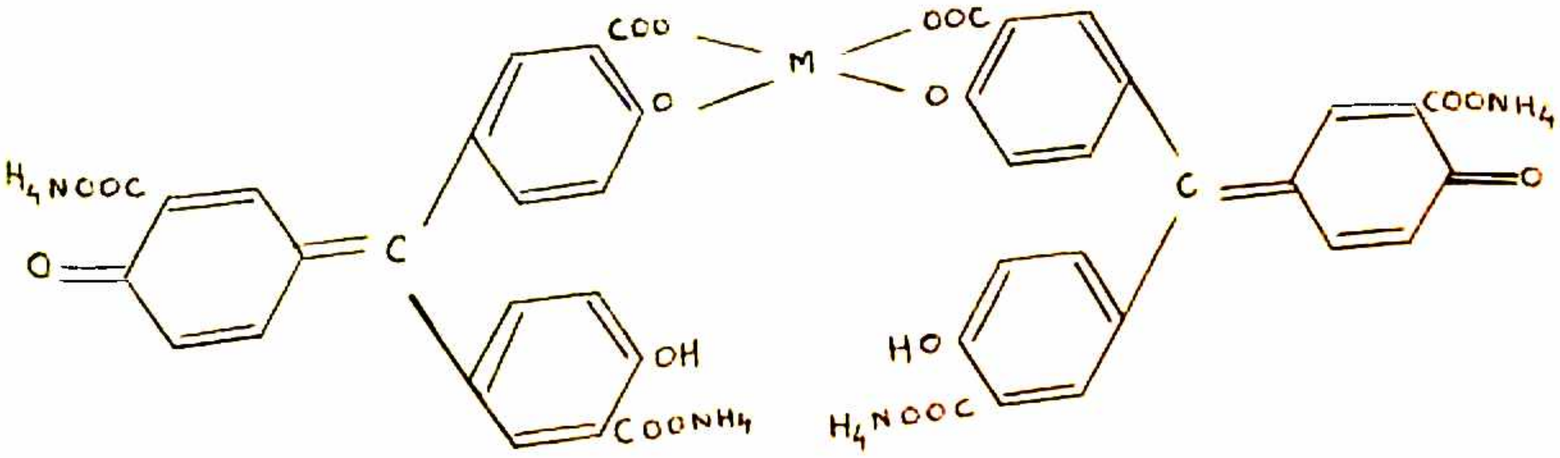
(I)



(II)

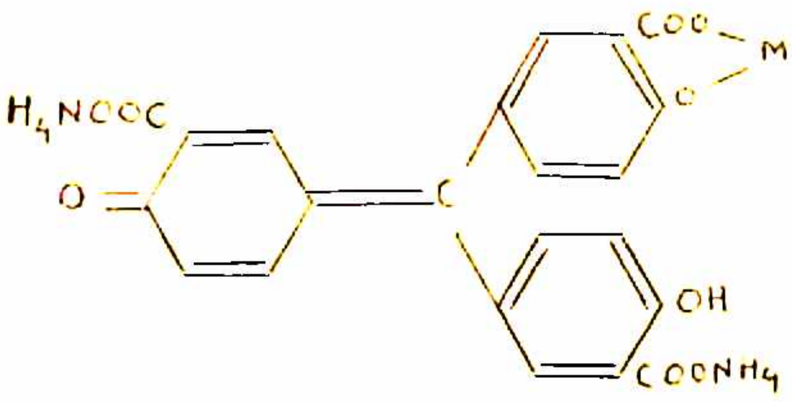
If the coordination takes place as according to (I),there would be an increase in the hydrogen ion concentration of the system, due to the liberation of H^+ by the chelation process. On the other hand, if chelation takes place as in (II), the pH of the mixture would remain unaltered. It has, however, been found, in course of our potentiometric studies, that there is always an increase in acidity, following chelation with various bivalent, trivalent and tetravalent metal ions. Thus the chelates appear to have structures of the type I.

It may, therefore, be concluded that the structure of the 1:1 (as is the case with Ni, Co, Pb, or Ce) and 1:2 (as is the case with Be, Al, V, Cu or Ga) complexes can at best be represented by structure (III) and (IV) respectively.



(Where M = Cu,Be,Al,Ga or V)

(III)



(where M = Co, Ni, Pb or Ce)

(IV)

In course of these investigations, stepwise protonation constants of Aluminon and formation constants of its chelates with some of the di, tri and tetrapositive metals, have been determined potentiometrically using Bjerrum-Calvin technique as detailed in Chapter II and Chapter VI. The results have been recorded in Tables VI and VII respectively.

These studies reveal that Co(II), Ni(II), Pb(II) and Ce(IV) form 1:1 (1:1) complexes. The order of log β_1 observed in case of these chelates is given below:

Co > Ni > Pb > Ce

Taking into consideration, the values of ionization potential and electronegativity of these elements, which are recorded in Table VIII, the order can be explained.

Table VI: Stepwise protonation constants of Aluminon

Ionic Strength	log K_1^H = log β_1^H			log K_2^H			log β_2 = log K_1^H + log K_2^H		
	(H)	(V)	(M)	(H)	(V)	(M)	(H)	(V)	(M)
0.02	9.315	9.558	9.434	8.333	8.291	8.296	17.413	17.[illegible]	17.73[illegible]
	*9.760	9.760	9.2[illegible]	9.930	9.230	[illegible]	1[illegible].490	1[illegible].99[illegible]	1[illegible].7[illegible]
0.05	9.225	9.497	9.396	8.333	8.232	[illegible].27[illegible]	17.55[illegible]	17.[illegible]	1[illegible].67[illegible]
0.10	9.250	9.514	9.402	8.333	8.237	[illegible].290	17.5[illegible]	17.751	17.700

(* Studies carried out in somewhat different conditions)

Table VII: Stepwise formation constants of metal chelates of Aluminon.

Metal	Ionic strength	$\log K_1 = \log \beta_1$		$\log K_2$		$\log \beta_2 = \log K_1 \log K_2$	
		(H)	(V)	(H)	(V)	(H)	(V)
Be(II)	0.02	10.616	10.541	3.586	3.832	14.202	14.373
Co(II)	0.02	4.192	4.414	-	-	-	-
Ni(II)	0.02	3.728	3.943	-	-	-	-
Cu(II)	0.02	9.330	9.730	3.760	3.948	13.090	13.678
Pb(II)	0.02	3.520	3.740	-	-	-	-
Al(III)	0.02	11.215	11.348	3.820	4.090	15.035	15.438
Ga(III)	0.02	11.300	11.487	3.970	4.289	15.270	15.776
Ce(IV)	0.02	3.067	3.284	-	-	-	-
V(IV)	0.02	11.490	11.670	3.833	4.079	15.323	15.749
Be(II)	0.05	9.670	9.900	3.300	3.552	12.970	13.452
Al(III)	0.05	11.120	11.202	3.730	3.976	14.850	15.178
V(IV)	0.05	11.540	11.712	3.600	3.862	15.140	15.374
Be(II)	0.10	11.600	11.843	3.193	3.453	14.793	15.296
Al(III)	0.10	12.368	12.505	3.868	4.108	16.236	16.613
V(IV)	0.10	12.680	12.827	3.868	4.121	16.548	16.948

(* Studies carried out in somewhat different conditions)

Table III:

Elements	(I) Ionization Potential(ev)	Electronegativity Allred-Rochow formula values
Cobalt	7.860	1.70
Nickel	7.633	1.75
Lead	7.415	1.55
Cerium	6.910	1.06
Oxygen	13.614	3.50

Studies of the characteristics of the chelates and the ionization potentials of the metal atoms show that cobalt, having the maximum value of ionization potential, forms more stable complexes than the others. The results obtained further, indicate that the stability constant of the complexes increases linearly with the increase in the ionization potential of the metal atoms.

The electronegativity of an atom is a measure of the relative tendency of an atom, in bonding to go to a negative condition, i.e., to attract a shared electron pair (11). The knowledge of the electronegativity of the elements is useful in predicting the nature of the bond. Since the electronegativity indicates the relative attraction for electron pairs, two elements with very different electronegativity are expected to form ionic bonds. The less the difference in electronegativity, the more covalent is likely to be the nature of the bond, and the more stable is the metal chelate formed. The difference between the electronegativity of cobalt and nickel, and oxygen is lesser than in the case of lead and cerium, and oxygen. So cobalt and nickel form more stable complexes than do lead and cerium. On the same basis, stability constant of cerium, should be less than that of lead, which is also the case in the results obtained.

Again, the sequence of stability constants, observed in case of metals forming 1: 2 complexes, is:

V(IV) > Ga(III) > Al(III) > Be(II)

Taking into consideration, again, the values of ionization potential and electronegativity of these elements which are presented in Table IX, this sequence can also be explained.

Table IX.

Elements	(I) Ionization Potential (ev)	Electronegativity Allred-Rocnow formula values
Vanadium	6.740	1.45
Gallium	6.000	1.82
Aluminium	5.984	1.47
Beryllium	9.320	1.47
Oxygen	13.614	3.50

Studies of the stability constants of the chelates and the ionization potential of the metal atoms suggest an order of stability constant:

V > Ga > Al

[illegible], stability-electronegativity considerations suggest an order:

Ca > Al & Be

Experimental results obtained are in agreement with these [illegible].

Higher values of stability constant of V(IV) can also be [illegible], as compared to trivalent gallium and aluminium and bivalent beryllium. Similarly, higher values [illegible] stability constants of gallium(III) and aluminium(III), compared to beryllium(II) can also be attributed to the same factor.

Between Gallium(III) and aluminium(III), the higher order of stability constant in case of gallium, can also be attributed to small ionic size of gallium (1.22) as compared to aluminium (1.43).

It has also been observed, in course of these studies, that the values of protonation constants $\log \beta_1^H$ and $\log \beta_2^H$ of Aluminon, obtained by various computational methods observe a sequence:

(V) > (M) > (H).

The formation constants values of various metal chelates, also follow the same sequence:

(n) denotes, values of stepwise protonation constants and formation constants, calculated by applying the Bjerrum's half $\bar{n}$ values (11);

(v) denotes, the values, obtained by applying Irving and Rossotti's interpolation at various n values method (12) and

.. denotes the values obtained by Bjerrum's mid point method (11).

In course of our studies, at various ionic strengths, it has been observed that the values of stepwise-protonation constants of aluminon, follow the sequence 0.02 > 0.10 > 0.05. The values of formation constants of the aluminon chelates, with various metal ions, follow the order 0.10 > 0.02 > 0.05. This may be explained on the basis that the activity coefficients of the ions may be passing through a minima (at say $\mu = 0.05$), as the ionic strength is increased.

The results obtained, in course of these investigations, under the conditions of study, bear a close correlation with those expected on theoretical grounds.

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SUMMARY

SUMMARY

STUDIES IN METAL CHELATE COMPOUNDS

(Metal Chelates of 8-Hydroxyquinoline-5-sulphonic Acid Derivatives and Aluminon)

This thesis concerns itself with discerning chelate formation in solution, by spectrophotometric as well as potentiometric methods. In course of these studies, metal chelates of some 8-hydroxyquinoline-5-sulphonic acid derivatives have been investigated spectrophotometrically whereas potentiometric studies have been carried out on the metal chelates of aluminon.

PART A: Spectrophotometric investigation

This part of the thesis concerns itself with the study of metal chelates involving some halo-derivatives of 8-hydroxyquinoline-5-sulphonic acid as chelating agents. A detailed study has been made of, both coloured as well as colourless chelates. The primary aim of the present work has been to investigate systematically, the composition, stability and the thermodynamic functions such as free energy of formation, entropy and enthalpy changes, associated with the formation of metal chelates in solution. Incidentally, an attempt has also been made to find out the thermodynamic ionization constants of these ligands and the application of the reagent for the micro determination of metal ions, and some of the representative results have been reported in this thesis.

PART I: Potentiometric studies

This part of the thesis deals with the study of chelate formation of Ammonium Aurintricarboxylate (AAC) with a number of bipositive, tripositive and tetrapositive metals. Stepwise protonation constants of AAC and stepwise formation constants of its chelates with these metal ions have been reported.

The work has been presented in six chapters. The first chapter gives a brief introduction of coordination chemistry, with particular reference to the chemistry of metal chelates.

In chapter II, the methods of discerning chelate formation in solution are outlined, both spectrophotometric as well as potentiometric, with which the present work is concerned. For the determination of composition of metal chelates in solution, using absorbance measurements, the following methods have been employed:

(1) The method of continuous variation
(2) The mole-ratio method
and (3) The slope-ratio method.

The present studies have shown that the results obtained by these different methods are in good agreement and show the utility of these methods for such studies.

The stability constant and other thermodynamic functions are useful for understanding the characteristics of a chelate (or a complex) in solution. Several methods based on absorp-

[illegible] measurements have been described for the determination of stability constants. They are

(i) Method of Banerji and Dey
(ii) Mole-ratio method
(iii) [illegible] method, using non-equimolar solutions
(iv) Method using molecular extinction coefficient data

For the determination of stability constants at different temperatures, the method based on molecular extinction coefficient data, has been mainly employed. The enthalpy and entropy changes have been calculated using Van't Hoff isotherm and Gibb's helmholtz equation respectively.

The method of J. Philip has been adopted for the determination of thermodynamic ionization constants of the ligands employing spectrophotometric investigations.

The stepwise protonation constants of AAC and the stepwise formation constants of its metal chelates have been determined using Bjerrum-Calvin technique, as described by Irving and Rossotti. The computational methods mainly employed for determination of protonation constants of AAC and formation constants of its metal chelates are

(1) Bjerrum's half $\bar{n}$ method
(2) Bjerrum's mid point method
and (3) Irving and Rossotti's interpolation at various $\bar{n}$ values method.

Chapters three, four, five and six describe the experimental results.

A detailed investigation of metal chelates of Copper(II), Palladium(II), Uranyl ion(II), Per-Vanadyl ion(III), Iron(III) and Gallium(III) with 7-chloro-8-hydroxyquinoline-5-sulphonic acid has been described in chapter III. It also records the thermodynamic ionization constants of the ligand. Some significant results of the studies are recorded in Table I.

Chapter IV describes the work done on the studies of Copper(II), Palladium(II), Uranyl ion(II), Per-Vanadyl ion(III), Iron(III) and Gallaium(III) with 7-bromo-8-hydroxyquinoline-5-sulphonic acid. This chapter too, records the thermodynamic ionization constants of the ligand. The significant results of the studies are presented in Table II.

Next chapter is a short one and it presents an attempt to find out the utility of the reagent for the spectrophotometric determination of iron and uranium. A comparison has also been made of these methods with others available for colorimetric determination. The results obtained indicate a satisfactory agreement with those obtained by earlier methods.

The potentiometric studies on the metal chelates of Aluminon with Be(II), Pb(II), Co(II), Ni(II), Cu(II), Al(III), Ga(III), Ce(IV) and V(IV), form chapter VI of this thesis. It also records protonation constant of the ligand and the effect of ionic strength on stepwise protonation constant of AAC and stepwise formation constants of some of its metal chelates. Tables III and IV record the results so obtained.

At the end, a discussion and summary of the results obtained have been presented. The present work has been able to throw light on the chelating properties of some halo-derivatives -hydroxyquinoline-5-sulphonic acid, which had not received sufficient attention earlier. Similarly, stepwise formation constants of a number of metal chelates of AAC and its stepwise protonation constants have also been determined, potentiometrically.

Table I: Thermodynamic ionization constants of 7-chloro- -hydroxyquinoline-5-sulphonic acid

Temperature	pK_{a_1}	pK_{a_2}
25°C	3.198	7.[illegible]

Characteristics of 7-chloro-8-hydroxyquinoline-5-sulphonic acid chelates

Chelate	pH	λ_{max}	Composition M:L	Temp.	log K	$-^*\Delta F$ (Kcal/mole.	$^*\Delta H$ (K cal/mole)	$^*\Delta S$ (e.u.)
Cu- CHQS	5.3	365	1:1	20°C	11.560±0.[illegible]	15.95	-14.[illegible]	[illegible].55
Pd- CHQS	4.5	400	1:2	30°C	12.374±0.196	14.42	-	-
UO2-CHQS	4.6	3[illegible]5	1:2	30°C	9.430±0.250	1[illegible].55	- [illegible].404	12.85
VO- CHQS	4.6	360	1:2	30°C	10.426±0.[illegible]76	14.34	-[illegible]1.9[illegible]	-2[illegible].19
Fe- CHQS	3.0	430	1:2	20°C	9.179±0.269	12.67	-1[illegible].540	-47.23
Ga- CHQS	4.0	3[illegible]	1:3	20°C	13.427±0.213	17.[illegible]	1.442	6[illegible].86

* (Values, obtained by applying molecular extinction coefficient method).

Table II: Thermodynamic ionization constants of 7-bromo-8-hydroxyquinoline-5-sulphonic acid

Temperature	pK_1	pK_2
25°C	3.657	7.6[illegible]

Characteristics of 7-bromo-8-hydroxyquinoline-5-sulphonic acid chelates

Chelate	pH	λ max	Composition M:L	Temp.	log K	$-\Delta F$ (K cal/mole)
Cu- BHQS	5.3	365	1:2	30°C	11.635 ± 0.165	16.135 ± 0.228
Pd- BHQS	4.5	395	1:2	30°C	12.410 ± 0.430	17.210 ± 0.600
UO_2-BHQS	6.6	350	1:2	30°C	9.455 ± 0.509	13.105 ± 0.705
VO- BHQS	6.6	360	1:2	30°C	10.610 ± 0.300	14.710 ± 0.416
Fe- BHQS	3.0	430	1:2	20°C	9.368 ± 0.106	[illegible]
Ga- BHQS	4.0	355	1:3	20°C	13.664 ± 0.214	18.274 ± 0.295

Table III: Stepwise protonation constants of AAC.

μ	log K_1^H = log β_1^H			log K_2^H			log β_2^H = log K_1^H + log K_2^H		
	(H)	(V)	(I)	(H)	(V)	(I)	(H)	(V)	(I)
0.02	9.315	9.558	9.434	8.333	8.271	8.296	17.648	17.829	17.730
	→ *9.760	9.760	9.925	8.930	9.230	8.855	18.690	18.990	18.780
0.05	9.225	9.497	9.396	8.333	8.232	8.278	17.558	17.729	17.674
0.10	9.250	9.514	9.402	8.333	8.237	8.298	17.583	17.751	17.700

(* studies carried out in somewhat different conditions)

[illegible]	[illegible]	[illegible] log β_1		log K_2		log β_2=log K_1+log K_2	
		(H)	([illegible])	(H)	([illegible])	(H)	([illegible])
[illegible]	[illegible]	[illegible]	10.541	3.586	3.832	14.202	14.373
[illegible]	0.02	[illegible]	4.414	-	-	-	-
[illegible]	0.02	[illegible]	3.943	-	-	-	-
[illegible]	[illegible]	9.330	9.730	3.760	3.948	13.090	13.678
[illegible]	0.02	3.520	3.740	-	-	-	-
Al(III)	0.02	[illegible]	11.348	3.820	4.090	15.035	15.438
[illegible]	[illegible]	[illegible]	11.487	3.970	4.289	15.270	15.776
[illegible]	0.02	[illegible]	3.284	-	-	-	-
V(IV)	0.02	11.490	11.670	3.833	4.079	15.323	15.749
Be(II)	0.02	9.670	9.900	3.300	3.552	12.970	13.452
Al(III)	0.05	11.120	11.202	3.730	3.976	14.850	15.178
V(IV)	0.05	11.540	11.512	3.600	3.862	15.140	15.374
Be(II)	0.10	11.600	11.843	3.193	3.453	14.793	15.296
Al(III)	0.10	12.368	12.405	3.868	4.108	16.236	16.613
V(IV)	0.10	12.620	12.827	3.868	4.121	16.546	16.948

(* Studies carried out in somewhat different conditions)

APPENDICES

(1)

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PAGE    1       02505

// JOB T                                                   02505

LOG DRIVE   CART SPEC   CART AVAIL   PHY DRIVE
  0000        0004        0004         0000

V2 M07   ACTUAL 16K  CONFIG 16K

// FOR
*IOCS(2501 READER,1403PRINTER)
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*EXTENDED PRECISION
C
C BALRAJ K. AVINASHI  PH.D.  THESIS  '1971
C CHEMISTRY DEPARTMENT, B.I.T.S.  PILANI(RAJ.)
C
C POTENTIOMETRIC  CALCULATIONS ON DIGITAL COMPUTER IBM 1130
      REAL NA,NO,II
      DIMENSION V1(30),V11(30)
      READ(8,2)Y,NO,VO,EO,TL
      WRITE(5,6) Y,NO,VO,EO,TL
      READ(8,3)(V1(I),I=1,30),(V11(J),J=1,30)
      WRITE(5,4)
      II=4.2
      I=0
      DO 10 J=1,26
      II=II+0.200001
      I=I+1
      X=V1(I)-V11(J)
      XX=VO+V1(I)
      XXX=(NO+EO)/TL
      NA=Y+X*XXX/XX
      WRITE(5,9) J,V1(I),V11(J),X,XX,II,NA
   10 CONTINUE
    2 FORMAT(5F9.4)
    3 FORMAT(10F6.3)
    4 FORMAT(1H ,43X,'TABLE NO. 6.3  ',///,10X,'TABLE APPLICABLE TO ',
                                 ,AT IONIC STRENGTH 0.02              ',/,
     $'
     $11X,75('-'),/,13X,'S.NO.',4X,'V1',7X,'V11',6X,'V1-V11',9X,'VO+V1',
     $8X,'PH',7X,'NA BAR',/,11X,75('-'),/)
    6 FORMAT(1H1,24X,'Y=',F3.1,3X,'NO=',F3.1,3X,' VO=',F5.1,3X,'EO=',
     $F4.2,3X,'TL=',F6.4,/)
    9 FORMAT(13X,I3,3X,F6.3,4X,F6.3,F12.5,4X,F11.5,4X,F5.2,F12.5/)
      CALL EXIT
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 EXTENDED PRECISION
 IOCS

CORE REQUIREMENTS FOR
 COMMON       0  VARIABLES     214  PROGRAM     362

 END OF COMPILATION

// XEQ
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PAGE    1        02505

// JCB  T
                                                              025C5

LCG DRIVE    CART SPEC    CART AVAIL   PHY DRIVF
  CCOC          C004          C004         C000

V2 MC7    ACTUAL 16K  CONFIG 16K

// FCR
*IOCS(2501 READER,1403PRINTER)
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
*EXTENDED PRECISION
C
C BALRAJ K. AVINASHI  PH.D.  THESIS  '1971
C CHEMISTRY DEPARTMENT, B.I.T.S.  PILANI(RAJ.)
C
C POTENTIOMETRIC  CALCULATIONS CN DIGITAL COMPUTER IBM 1130
      REAL N,NO
      DIMENSION V11(3C),V111(30),BNA(30)
      READ(8,2)Y,NO,VC,EO,TL,TM
    2 FORMAT(6F9.4)
      WRITE(5,6) Y,NC,VO,EO,TL,TM
    6 FORMAT(1H1,' Y=',F3.1,3X,'NO=',F3.1,3X,'VO=',F5.1,3X,'EO=',F4.2,
     $3X,'TL=',F6.4,'TM=',F6.4,//)
      DC 1C  LL=1,2
      READ(8,3)(V11(I),I=1,30),(BNA(K),K=1,30)
    3 FCRMAT(10F8.5)
      DC 1C KK=1,3
      READ(8,5)(V111(J),J=1,30)
    5 FCRMAT(10F8.5)
      WRITE(5,4)
    4 FORMAT(111('-'),/,11X,'S.NO.',6X,'PH',6X,'NA BAR',7X,'V11',6X,
     $'V111',5X,'V111-V11',5X,'VO+V11',6X,'N BAR',/,11X,100('-'),/)
      RK=3.4
      I=0
      K=0
      DC  10  J=1,30
      RK=RK+0.200C01
      I=I+1
      K=K+1
      X=V111(J)-V11(I)
      XX=VC+V11(I)
      XXX=(NO+EO+(Y-BNA(K))*TL)/(BNA(K)*TM)
      N=X*XXX/XX
      WRITE(5,9)J,RK,BNA(K),V11(I),V111(J),X,XX,N
    9 FORMAT(13X,I3,4X,F4.1,4X,F8.5,2(4X,F6.3),3(4X,F8.4),/)
   10 CONTINUE
      CALL EXIT
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 EXTENDED PRECISION
 IOCS

CORE REQUIREMENTS FOR
 COMMCN        C  VARIABLES     318  PROGRAM    4C4

END OF COMPILATICN

// XEQ
```

```
Y- .          .      VC=  0.0    E0=0.00    TL=0.0000TM=0.0000
                                                              (3

// FOR
*IOCS(2501 READER,1403PRINTER)
*LIST SOURCE PROGRAM
*ONE WORD INTEGERS
C
C BALRAJ K. AVINASHI  PH.D.  THESIS  '1971
C CHEMISTRY DEPARTMENT, B.I.T.S.  PILANI(RAJ.)
C
C POTENTIOMETRIC  CALCULATIONS ON DIGITAL COMPUTER IBM 1130
      DIMENSION BH1(4),BH2(4),BN(40),H(40),V111(40),PL(4,40),Z(40)
      DIMENSION V11(40)
      READ(8,1)TM,VC,(H(J),J=1,26)
      XXX=ALOG(10.0)
      DO 101 IK = 1,3
      READ(8,1) (BH1(I),I=1,3),(BH2(II),II=1,3),TL
      READ(8,1)(V11(LL),LL=1,28)
      READ(8,1) (BN(KK),KK=1,28),(V111(M),M=1,28)
      PH=4.2
      DO 10 L=1,3
      DO 10 K=1,24
      X=(BH1(L)+BH2(L)*H(K))*H(K)
      YY=VC+V111(K)
      YYY=(TL-BN(K)*TM)*VC
      Y=X*YY/YYY
      XX=ALOG(Y)
      PL(L,K)=XX/XXX
      Z(K)=V111(K)-V11(K)
   10 CONTINUE
      WRITE(5,8)
      DO 101 N=1,24
      PH=PH+0.200001
      WRITE(5,9)N,Z(N),BN(N),PH,(PL(KL,N),KL=1,3)
  101 CONTINUE
    1 FORMAT(7E11.4)
    8 FORMAT(1H1,43X,'TABLE NO.        ',///,22X,'TABLE APPLICABLE TO ',
     $'BERYLLIUM, AT IONIC STRENGTH                                      ',/,
     $11X,75('-'),/,13X,'S.NO.',3X,'V111-V11',4X,'N BAR',7X,'PH',7X,
     $'PL(H)',7X,'PL(V)',7X,'PL(M)',/,11X,75('-'),/)
    9 FORMAT(14X,I3,2(3X,F8.4),4X,F5.2,3(3X,F9.5),/)
      CALL EXIT
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CORE REQUIREMENTS FOR
 COMMON        0  VARIABLES      772  PROGRAM     486

 END OF COMPILATION

// XEQ
```

Y=2.0 NO=0.1 VC=100.0 EO=0.01 TL=0.0025 (A)

TABLE NO. 6.3

TABLE [illegible] Be,Co,Ni,Pb,Al,Ga,Ce & V ,AT IONIC STRENGTH 0.02

S.NO.	V1	VII	V1-VII	VO+V1	PH	NA BAR
1	9.787	8.500	1.28699	109.78700	4.40	2.51579
2	9.812	8.950	0.86200	109.81200	4.60	2.34539
3	9.825	9.200	0.62500	109.82500	4.80	2.25039
4	9.837	9.400	0.43699	109.83700	5.00	2.17505
5	9.850	9.600	0.25000	109.85000	5.20	2.10013
6	9.862	9.750	0.11199	109.86200	5.40	2.04485
7	9.875	9.900	-0.02499	109.87500	5.60	1.98998
8	9.880	10.000	-0.12000	109.88000	5.80	1.95194
9	9.887	10.125	-0.23800	109.88700	6.00	1.90470
10	9.890	10.225	-0.33500	109.89000	6.20	1.86586
11	9.900	10.300	-0.39999	109.90000	6.40	1.83985
12	9.900	10.350	-0.44999	109.90000	6.60	1.81983
13	9.910	10.400	-0.49000	109.91000	6.80	1.80383
14	9.915	10.450	-0.53499	109.91500	7.00	1.78583
15	9.920	10.500	-0.58000	109.92000	7.20	1.76783
16	9.925	10.525	-0.60000	109.92500	7.40	1.75983
17	9.925	10.590	-0.66499	109.92500	7.60	1.73381
18	9.925	10.675	-0.75000	109.92500	7.80	1.69979
19	9.930	10.800	-0.86999	109.93000	8.00	1.65177
20	9.940	11.000	-1.06000	109.94000	8.20	1.57576
21	9.950	11.300	-1.35000	109.95000	8.40	1.45975
22	9.960	11.700	-1.74000	109.96000	8.60	1.30374
23	9.970	12.250	-2.28000	109.97000	8.80	1.08775
24	9.980	12.800	-2.82000	109.98000	9.00	0.87179
25	10.000	13.400	-3.40000	110.00000	9.20	0.64000
26	10.012	14.000	-3.98800	110.01200	9.40	0.40497

Y=2.0 NC=0.1 V0=100.0 E0=0.01 TL=0.0025

TABLE NO. 6.18

TYPE APPLICABLE TO Be,Al & V. AT IONIC STRENGTH 0.05

S.NO.	V1	V11	V1-V11	V0+V1	PH	NA BAR
1	9.750	8.500	1.25000	109.75000	4.20	2.50113
2	9.775	8.875	0.89999	109.77500	4.40	2.36073
3	9.800	9.125	0.67499	109.80000	4.60	2.27049
4	9.810	9.300	0.50999	109.81000	4.80	2.20435
5	9.820	9.500	0.31999	109.82000	5.00	2.12820
6	9.825	9.700	0.12500	109.82500	5.20	2.05007
7	9.837	9.900	-0.06300	109.83700	5.40	1.97476
8	9.850	10.050	-0.20000	109.85000	5.60	1.91989
9	9.862	10.150	-0.28800	109.86200	5.80	1.88465
10	9.875	10.250	-0.37500	109.87500	6.00	1.84982
11	9.890	10.325	-0.43500	109.89000	6.20	1.82582
12	9.900	10.400	-0.50000	109.90000	6.40	1.79981
13	9.910	10.450	-0.53999	109.91000	6.60	1.78382
14	9.920	10.475	-0.55500	109.92000	6.80	1.77783
15	9.930	10.512	-0.58199	109.93000	7.00	1.76705
16	9.937	10.562	-0.62500	109.93700	7.20	1.74985
17	9.950	10.600	-0.64999	109.95000	7.40	1.73988
18	9.962	10.675	-0.71299	109.96200	7.60	1.71470
19	9.975	10.750	-0.77500	109.97500	7.80	1.68992
20	9.980	10.850	-0.86999	109.98000	8.00	1.65193
21	9.987	11.000	-1.01300	109.98700	8.20	1.59475
22	10.000	11.400	-1.39999	110.00000	8.40	1.44000
23	10.012	11.800	-1.78800	110.01200	8.60	1.28487
24	10.020	12.400	-2.38000	110.02000	8.80	1.04817
25	10.025	13.000	-2.97500	110.02500	9.00	0.81027
26	10.050	13.700	-3.65000	110.05000	9.20	0.54066

2.0 NC=0.1 VO=100.0 EO=0.01 TL=0.0025

TABLE NO. 6.26

APPLICABLE TO Be,Al & V.AI IONIC STRENGTH 0.10

S.NO.	V1	V11	V1-V11	VO+V1	PH	NA BAR
1	9.800	8.700	1.10000	109.80000	4.40	2.44080
2	9.825	9.025	0.79999	109.82500	4.60	2.32050
3	9.837	9.300	0.53700	109.83700	4.80	2.21511
4	9.850	9.500	0.34999	109.85000	5.00	2.14019
5	9.862	9.750	0.11199	109.86200	5.20	2.04485
6	9.875	9.925	-0.04999	109.87500	5.40	1.97997
7	9.880	10.075	-0.19500	109.88000	5.60	1.92191
8	9.887	10.200	-0.31300	109.88700	5.80	1.87467
9	9.895	10.287	-0.39199	109.89500	6.00	1.84305
10	9.900	10.362	-0.46199	109.90000	6.20	1.81503
11	9.905	10.420	-0.51500	109.90500	6.40	1.79382
12	9.912	10.462	-0.55000	109.91200	6.60	1.77982
13	9.920	10.500	-0.58000	109.92000	6.80	1.76783
14	9.925	10.530	-0.60499	109.92500	7.00	1.75783
15	9.930	10.562	-0.63199	109.93000	7.20	1.74703
16	9.937	10.612	-0.67499	109.93700	7.40	1.72984
17	9.945	10.650	-0.70500	109.94500	7.60	1.71785
18	9.955	10.750	-0.79500	109.95500	7.80	1.68186
19	9.970	10.850	-0.87999	109.97000	8.00	1.64790
20	9.987	11.025	-1.03800	109.98700	8.20	1.58475
21	10.000	11.375	-1.37500	110.00000	8.40	1.45000
22	10.020	11.800	-1.78000	110.02000	8.60	1.28812
23	10.037	12.300	-2.26300	110.03700	8.80	1.09510
24	10.050	13.000	-2.95000	110.05000	9.00	0.82053
25	10.075	13.650	-3.57500	110.07500	9.20	0.57097

TABLE NO. 6.5

TABLE APPLICABLE TO BERYLLIUM, AT IONIC STRENGTH 0.02

S.NO.	V111-V11	N BAR	PH	PL(H)	PL(V)	PL(M)
1	0.2500	0.1991	4.40	11.50414	11.68516	11.58614
2	0.4250	0.3630	4.60	11.12179	11.30282	11.20381
3	0.5500	0.4896	4.80	10.73537	10.91640	10.81739
4	0.6000	0.5525	5.00	10.34247	10.52352	10.42449
5	0.5500	0.5245	5.20	9.94052	10.12158	10.02255
6	0.5999	0.5876	5.40	9.54758	9.72867	9.62963
7	0.6299	0.6289	5.60	9.15273	9.33386	9.23480
8	0.6499	0.6667	5.80	8.75746	8.93866	8.83957
9	0.6700	0.7095	6.00	8.36304	8.54436	8.44522
10	0.7099	0.7640	6.20	7.97037	8.15187	8.05266
11	0.7500	0.8160	6.40	7.57794	7.75972	7.66039
12	0.7800	0.8525	6.60	7.18504	7.36726	7.26774
13	0.7999	0.8877	6.80	6.79362	6.97652	6.87672
14	0.8400	0.9381	7.00	6.40644	6.59040	6.49015
15	0.8499	0.9623	7.20	6.02046	6.20602	6.10510
16	0.8999	1.0240	7.40	5.64446	5.83239	5.73048
17	0.9100	1.0510	7.60	5.27350	5.46480	5.36149
18	0.9200	1.0890	7.80	4.91604	5.11191	5.00671
19	0.9300	1.1210	8.00	4.57412	4.77579	4.66821
20	0.7999	1.1430	8.20	4.25081	4.45923	4.34889
21	0.8999	1.2340	8.40	3.95889	4.17441	4.06121
22	0.9300	1.4200	8.60	3.70149	3.92377	3.80787
23	0.8799	1.6090	8.80	3.46674	3.69484	3.57663
24	0.7999	1.8360	9.00	3.25577	3.48847	3.36845

TABLE NO. 6.20

TABLE APPLICABLE TO BERYLLIUM, AT IONIC STRENGTH 0.05

S.NO.	[illegible]	N BAR	PH	PL(H)	PL(V)	PL(M)
1	[illegible]	0.3607	4.40	11.43122	11.60224	11.54727
2	[illegible]	0.4191	4.60	11.03799	11.20903	11.15405
3	0.5000	0.4544	4.80	10.64221	10.81326	10.75827
4	0.5000	0.4706	5.00	10.24457	10.41563	10.36064
5	0.5000	0.4885	5.20	9.84725	10.01835	9.96334
6	0.5000	0.5071	5.40	9.44995	9.62109	9.56606
7	0.5000	0.5215	5.60	9.05228	9.22351	9.16843
8	0.5699	0.5843	5.80	8.65949	8.83084	8.77571
9	0.5400	0.6223	6.00	8.26444	8.43598	8.38075
10	0.6199	0.6853	6.20	7.87243	8.04428	7.98890
11	0.6299	0.6951	6.40	7.47551	7.64784	7.59223
12	0.6499	0.7293	6.60	7.08223	7.25530	7.19932
13	0.6700	0.7599	6.80	6.69015	6.86439	6.80784
14	0.6900	0.7791	7.00	6.29944	6.47547	6.41805
15	0.6900	0.7868	7.20	5.91161	6.09036	6.03162
16	0.7000	0.8050	7.40	5.53070	5.71344	5.65276
17	0.7000	0.8167	7.60	5.15804	5.34645	5.28304
18	0.7500	0.8878	7.80	4.80391	4.99996	4.93290
19	0.7800	0.9384	8.00	4.46381	4.66948	4.59786
20	0.7999	1.0030	8.20	4.14540	4.36214	4.28535
21	0.6800	0.9374	8.40	3.83558	4.06388	3.98177
22	0.7000	1.0890	8.60	3.57268	3.81186	3.72480
23	0.7299	1.3830	8.80	3.34882	3.59728	3.50606
24	0.8300	2.0360	9.00	3.19512	3.45087	3.35642

TABLE NO- 6.28

TABLE APPLICABLE TO BERYLLIUM, AT IONIC STRENGTH 0.10

S.NO.	V111-V11	N BAR	PH	PL(H)	PL(V)	PL(M)
1	0.7000	0.5746	4.40	11.47710	11.64511	11.59414
2	0.7250	0.6258	4.60	11.08362	11.25164	11.20067
3	0.7000	0.6329	4.80	10.68538	10.85341	10.80243
4	0.6999	0.6550	5.00	10.28839	10.45644	10.40545
5	0.6499	0.6365	5.20	9.88751	10.05559	10.00458
6	0.6550	0.6573	5.40	9.49040	9.65853	9.60749
7	0.6700	0.7031	5.60	9.09603	9.26423	9.21313
8	0.6499	0.6941	5.80	8.69600	8.86431	8.81314
9	0.6599	0.7201	6.00	8.29970	8.46820	8.41691
10	0.6900	0.7588	6.20	7.90527	8.07406	8.02257
11	0.7100	0.7867	6.40	7.51023	7.67947	7.62769
12	0.7299	0.8153	6.60	7.11639	7.28634	7.23409
13	.7399	0.8343	6.80	6.72317	6.89422	6.84125
14	0.7700	0.8766	7.00	6.33495	6.50770	6.45361
15	0.7899	0.9026	7.20	5.94906	6.12439	6.068
16	0.8199	0.9300	7.40	5.56931	5.74841	5.690
17	0.8400	0.9749	7.60	5.20018	5.38464	5.322
18	0.8300	0.9814	7.80	4.83918	5.03089	4.964
19	0.8500	1.0320	8.00	4.49916	4.69999	4.627
20	0.8700	1.1040	8.20	4.18184	4.39320	4.31404
21	0.8199	1.1380	8.40	3.88296	4.10533	4.01917
22	0.7999	1.2420	8.60	3.61531	3.84804	3.75535
23	0.7299	1.3240	8.80	3.36631	3.60789	3.50967
24	0.6499	1.5840	9.00	3.15769	3.40623	3.30369