STUDIES ON SOME BIVALENT METAL CHELATES

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in this thesis entitled "STUDIES ON SOME BIVALENT METAL CHELATES" is original and was carried out by Mr. Pradip Kumar Govil, under my guidance and supervision during the period of August, 1969 to July, 1972.

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CHAPTER I

INTRODUCTION

INTRODUCTION

The rapid pace of the advances and the varied character of the work being done in the realm of coordination chemistry, has largely been responsible for the renaissance of inorganic chemistry. Expansion of this area of scientific endeavour has been fostered by world-wide interest. The field of coordination chemistry has grown in a half-century from a well-defined and limited area into what is now the most active field of inorganic chemistry. In recent years, it has received not only a large amount of experimental investigation but also a rather extensive theoretical treatment. From earlier times to the present day, the hard core of advances and the fascinating results have changed drastically the picture of the coordination chemistry. Tremendous activities in this field make one believe that in future too, this dramatic scientific saga will continue to attract promising scientists. With the availability of physico-chemical methods and instruments for investigation, complex formation in the solution has been an active field for investigations for nearly three decades.

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 may be a neutral molecule or a charged species with two or more points of attachment. In ordinary complexes, as apart from a metal chelate, the ligand is monofunctional and no ring formation takes place. The ring formation is a special characteristic of chelate compounds and the term chelate (chela meaning Crab's claw) was introduced in coordination chemistry by Morgan and Drew (1) to designate such a cyclic structure .

The formation of inner complex compounds also involve a ring structure, which was noted by various investigators including Werner (2), Ley (3,4) and others, who found that these structures are exceptionally stable, insoluble in water and are often intensely coloured. The chemical and physical properties of 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 behavior, they can at best be regarded as belonging to a special type, under the general class of complexes. Thus, all chelates are complex compounds but all complex compounds are not necessarily chelates.

A chelating agent may be bidentate, tridentate, quadridentate, quinquidentate, sexadentate or more, depending upon the presence of two, three, four, five, six or more donor groups, placed suitably in the ligand molecule. Chelation is most favoured when donor groups occupy such a position as to form a ring of low strain, i.e., five membered or six membered ring. In the case of bidentate chelates the concerned linkages may either be (i) covalent bonds, (ii) one covalent and one coordinate bond, or (iii) both coordinate bonds. However, as in other cases, once the chelate is formed, there really is no way of distinguishing a coordinate covalent bond from any other covalent bond present. When saturated rings are formed, the five membered ring is the most stable; where chelate rings involving double bonds are formed, the formation of the six membered ring is favoured. Chelates with higher membered rings have also been described but are less common. With multidendate ligands, as the formation of chelate rings per ligand molecule increases, the stability of the complex also increases. It is found that chelation is invariably attended with an increase in stability. This is known as chelate effect.

Theories of Chelation

The structural theory of coordination compounds is about sixty years old, when Alfred Werner in 1913 found that chemical composition and properties of the complex inorganic substances could be explained by assuming that metal atoms often coordinate about themselves a number of atoms different from their valency, usually four atoms at the corners either of a tetrahedron or of a square coplanar with the central atom or six atoms at the corner of an octahedron.

According to the Werner's coordination theory, one of the atoms, usually a metal atom, in the molecule of any complex compound occupies a central position and neutral molecules or ions are arranged or coordinated around it forming an inner coordination sphere. The rest of the ions not present in the inner sphere constitute the outer coordination sphere. The total number of neutral molecules or ions linked to the central atom in the complex compound is called the coordination number and this was found to have values ranging from 2 to 8 (values 4 and 6 being more common). The coordination number mainly depends upon the size, charge and electronic configuration of the central atom as well as the experimental conditions under which the reaction is being studied.

After the discovery of the electron, many efforts were made to develop an electronic theory of the chemical bond. A great contribution was made in 1916 by G.N. Lewis, who proposed that the chemical bond consists of a pair of electrons held jointly by the two atoms that are bonded together. The earliest electronic interpretation of coordination was given by Sidgwick who introduced the concept of the coordinate or semi-polar bond.

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 advanced by Heitler and London in 1927 and later extended by Pauling and Slater in 1931. It assumes that the association results from the overlap of an orbital of the ligand containing an unshared pair of electrons with hybridised orbitals of the metal ion. This may be thought of being formed either due to a sharing of the electron pair between the metal ion and the ligand or due to 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 and (ii) the formation of hybridised bonds by mixing of atomic orbitals that are capable of forming stable bonds. The valence bond theory provides the chemist with a pictorial representation of complexes but it has been found to be highly inadequate in explaining the magnetic properties of some complexes and is incapable of explaining their spectra (5).

The crystal field theory, first proposed by Bethe (6) was applied to explain the magnetic properties of the transition metal ions by Schlapp and Penny (7), Van Vleck (8) and many others (9, 10). This theory deals with the electrostatic interaction of the ligand ions with the central metal ion and the consequent effect of the field on the energy of metal d orbitals. In particular, the theory is concerned with the effect of various possible electrostatic fields, which arise from the differing geometries and strengths of various ligands on the five d orbitals of a transition metal. If a ligand that possesses an electrostatic field, approaches a metal ion or atom, the energies of degenerate d orbitals (in ligand field free state) become differentiated. The orbitals lying in the direction of the ligands are raised in energy to a greater extent, in comparison to those which lie between the ligands. The strength of the electrostatic field of the ligand is influenced mainly by two factors viz. the charge density of the central metal ion and the nature of the ligand itself. This theory is most successful in the prediction of properties of ionic complexes. Orgel (11-13) was the first to call attention to the consequences of the theory on the stability of coordination compounds of the transition metals. This theory gives adequate explanation for the observed magnetic properties and spectra of these complexes.

The molecular orbital theory assumes the formation of molecular orbital rather than the simple overlap of the orbitals of the reactants. The electronic configuration of the molecule is then obtained by introducing electrons to the lowest molecular orbital. 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 non-bonding electrons. The energy separation between the non-bonding 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 considers only coulombic interactions between the metal ion and ligands. This is far removed from the reality of the situation. The molecular orbital theory is, at the moment, unsuitable for quantitative calculations, but the underlying symmetry considerations and overlap criteria are essentially correct. The ligand field theory attempts to reconcile both these theories in so far as it incorporates the best aspects of both these theories; it has the quantitative rigour of the crystal field theory and the theoretical soundness and elegance of the molecular orbital theory. Thus it provides an adequate approach to the study of metal compounds.

Importance of Metal Chelates

Metal chelates are of tremendous practical importance in addition to the theoretical interest commonly 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.

Among their important uses cited, their utility both in qualitative and quantitative chemical analysis is a major one. A new use of chelating agent has been suggested by Schwarzenbach (14) for the direct determination of metals in solution. 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 for the identification of ions even on the micro scale and forms the basis of "spot methods" (15) for their identification.

Chelation also plays an important part in the field of physiological chemistry. Cyanocobaltamin, chlorophyll, blood pigment and cytochrome are chelates (16,17) which are important for life processes. These naturally occurring chelates have functions which are vital to the organism.

Chemotherpeutic studies of a number of drugs have shown that the activity of most of the drugs is due to their ability to chelate with the essential metallic ions. Chelation also plays an important role in the electro-deposition of metals and in leather industry.

The stability of these chelates are of considerable importance in evaluating their utility. Potentiometric measurements provide probably the most accurate and reliable method for the determination of stability constants. It can be used in aqueous as well as in non aqueous media.

The advent of excellent and relatively cheap spectrophotometer has given a great impetus to the methodology and technique of photometric determination. A ligand which shows high sensitivity and has an appreciable amount of selectivity and has reproducibility may be considered to be useful for photometric determination.

The formation of the metal chelates generally involve the replacement of hydrogen ions by the metal ions, from the acid form of a chelating agent (18). The conventional type of organic acids, particularly those containing the carboxylic group, however, have limited application in analytical chemistry. Of great 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. The most common acidic group in organic compounds is the hydroxyl (-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 (19). A number of typical non-metallic elements like nitrogen, phosphorous, sulphur and oxygen are known to behave as suitable electron donors in a chelate or complex formation.

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CHAPTER II

METHODS OF INVESTIGATION

METHODS OF INVESTIGATION

There are many physical and chemical properties which may, in principle, be used to detect the formation of complexes in solution. Any physical property may be used for this purpose, if variation in it can be attributed unambiguously to specific chemical interactions. 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 in the solution. Some of the techniques which have been used for such studies are absorption by ion exchange (1-3), 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, ultracentrifugation, dialysis and light scattering are useful in specialised situations (12).

pH Metric Measurements

The most widely used and probably the most accurate and reliable method for the determination of stability of metal complexes, is the potentiometric measurement of hydrogen ion concentration. The method may be used for any chelate which is soluble in water or in mixed aqueous solvents in which the hydrogen ion concentration may be determined potentiometrically. 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.

Determination of Stability Constants

The determination of stability constants is of primary importance in the study of chelate compounds, since it gives a comprehensive understanding of the chelates and the relationships which govern their formation and structure. It is also useful in the understanding of its behaviour in solution. Thus the conditions required for the maximal or complete formation of a complex may be predicted on the basis of its stability constants. Since the stability constant refers to a system in equilibrium, it may be used to calculate the free energy change and other thermodynamic functions. The quantitative measurements of the tendency towards formation of a complex species in aqueous solution is represented by the formation constant, the magnitude of which gives a quantitative measure of the relative stability of various complexes. The formation constant is generally taken as the equilibrium constant of reaction (at the given temperature) in which the complex is formed by the interaction of the central ion (M) and the ligand (L), usually an ion .

Many examples of the existence of the polynuclear complexes have been reported but it has been found that the complex/chelate exists in a mononuclear form in a large majority of cases particularly in dilute solutions. In a system, which contains only mononuclear species, the ion or the molecule M may be considered as the central group of the complex and L is usually referred to as the ligand. The maximum number of ligands that can combine with one central group is denoted by n i.e. the coordination number of the central atom.

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

$$M + L \rightleftharpoons ML \; ; \; T_{K_1} = \frac{\{ML\}}{\{M\}\,\{L\}} \qquad ..(2.1)$$

$$ML + L \rightleftharpoons ML_2 \; ; \; T_{K_2} = \frac{\{ML_2\}}{\{ML\}\,\{L\}} \qquad ..(2.2)$$

- -

$$ML_{n-1} + L \rightleftharpoons ML_n \quad ; \quad {}^{T}K_n = \frac{\{ML_n\}}{\{ML_{n-1}\}\{L\}} \qquad (2.3)$$

$$M + nL \rightleftharpoons ML_n \quad ; \quad {}^{T}\beta_n = \frac{\{ML_n\}}{\{M\}\{L\}^n} \qquad (2.4)$$

where M may be univalent or bivalent etc. and L may be molecular or ionic. The charges have been omitted for the sake of simplicity. The quantities $\{ML_n\}$, $\{M\}$ and $\{L\}$ represent the activity of the complex, metal ion and the ligand respectively, ${}^{T}K_1$ ......, ${}^{T}K_n$ 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. From the equations (2.3) and (2.4)

$$\{ML_n\} = {}^{T}\beta_n \{M\}\{L\}^n = {}^{T}K_n \{ML_{n-1}\}\{L\}$$

Thus $\quad {}^{T}\beta_o = {}^{T}K_o = 1 \quad$ and $\quad {}^{T}\beta_1 = {}^{T}K_1$

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

$${}^{T}\beta_n = {}^{T}K_1 \cdot {}^{T}K_2 \cdot {}^{T}K_3 \text{ ---- } {}^{T}K_{n-1} \cdot {}^{T}K_n = \prod_o^n {}^{T}K_n \qquad (2.5)$$

In the above discussion, 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 also 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. 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 is expressed as:

$$K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]} = \frac{\{ML_n\}}{\{ML_{n-1}\}\,\{L\}} \cdot \frac{\gamma_{ML_{n-1}}\,\gamma_L}{\gamma_{ML_n}}$$

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

or $$K_n = T_{K_n} \cdot \frac{\gamma_{ML_{n-1}} \cdot \gamma_L}{\gamma_{ML_n}} \qquad (2.6)$$

and similarly

$$\beta_n = \frac{[ML_n]}{[M]\,[L]^n} = T_{\beta_n}\,\frac{\gamma_M\,\gamma_L}{\gamma_{ML_n}} \qquad (2.7)$$

where the 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 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 the various methods available. In fact, the stoichiometric stability constants are also the thermodynamic stability constants which are valid for the particular ionic strength of the solution.

Thermodynamic Stability Constants

The thermodynamic stability constants (T_{β_n}, T_{K_n}, etc.) which are more important from the thermodynamic and structural point of view, can be calculated by substituting the appropriate values of the activity coefficients, which are seldom available in the equation (2.6) and (2.7).

Two principal procedures are mainly followed in evaluating the thermodynamic stability constants of the chelates. Lewis and Randall (13) first introduced the concept of ionic strength which later received theoretical justification from the Debye-Hückel theory. The classical approach for the evaluation of thermodynamic stability constants involves the experimental determination of the stability constants in media of different low ionic strengths followed by an extrapolation to zero ionic strength (infinite dilution). For water soluble chelates, it appears to be the best approach. Some workers (14) have used the value of a single determination and attempted to corelate this value to thermodynamic stability constant through the application of the Debye-Hückel theory. In the second method a constant ionic strength is maintained by swamping i.e. by the addition of an indifferent electrolyte in large excess. Leden (15) used 3M $NaClO_4$ for this purpose and Schwarzenbach (16) used 0.1M neutral salts, while Sillen (17) preferred to use 1M or 3M $NaClO_4$. This method has certain limitations, particularly because no electrolyte is absolutely inert from the point of view of complexation and even perchlorate ion in large excess has been reported to form complexes (18).

The values of the thermodynamic stability constants obtained by extrapolation to infinite dilution may therefore be considered to be 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. Therefore, in the studies described in the thesis, the values of stability constants were determined at various ionic strengths (avoiding very large excess of the electrolyte) and then extrapolated to zero ionic strength. It may be mentioned that this appears to be a comparatively better method particularly when the solutions of the reactants forming the chelate are very dilute.

In 1941, Bjerrum (4) introduced the technique of determining the stability constants by potentiometric titrations. Calvin and Wilson (19) have shown that pH measurements made during the titration with alkali of a solution of a chelating agent in the presence and in the absence of the other metal ions, could be used to calculate the degree of formation $\bar{n}$, the free ligand exponent, pL and then the stepwise stability constant K_n of the system. Experimental methods developed by Leden, Bjerrum and Fronaeous have been discussed by Sullivan and Hindman (20). Irving and Rossotti (21) have developed a correction term method.

In the potentiometric studies, reported here, the Bjerrum-Calvin pH-titration technique (4,19) as described by Irving and Rossotti (21,22) was used because it is neither necessary to convert the pH readings to stoichiometric hydrogen ion concentration, nor to know the stoichiometric concentration of the neutral salt added to maintain the ionic strength constant. Moreover, the acid dissociation constants of the reagents, which are required in calculations, are determined under the same conditions as formation constants.

Titrations were carried out in aqueous media and sufficient $NaClO_4$ was added to give a definite overall ionic strength. The titrant was NaOH in all the cases. A large number of titrations were carried out maintaining different ionic strengths, different temperatures, employing different ligand and metal ion concentration ratios.

To determine a chelate stability constant, the following mixtures were titrated against standard alkali, added in small increments, and corresponding change in pH was recorded:

Mixture A : 5 ml of (0.1M)$HClO_4$ + x ml (according to desired ionic strength) of 1M $NaClO_4$.

Mixture B : Mixture A + 50 ml (M/200) ligand solution

Mixture C : Mixture B + 10 ml (M/200) metal ion solution.

The mixtures were diluted with double distilled water to a constant volume of 100 ml. The metal ligand ratio was kept at 1:5, to fulfil the maximum coordination number of the metal. Three titration curves were obtained by plotting pH (B) against volume of alkali added.

Proton-Ligand Stability Constant

Irving and Rossotti's method of calculation was used. The average number of protons attached per ligand molecule ($\bar{n}_A$) can be determined by using the following equation:

$$\bar{n}_A = y + \frac{(v' - v'')(N^o + E^o)}{(V^o + v')\, T_L} \qquad (2.8)$$

where v' and v" denote the volume of alkali required to reach the same pH in titrations of the mixture A and B, respectively, T_L is the total concentration of the ligand, y is the total number of dissociable protons attached per ligand molecule, N^o and E^o are the normality of alkali and the initial concentration of the free acid, respectively and V^{o} is the total initial volume of the mixture.

This $\bar{n}_A$ is given by:

$$\bar{n}_A = \frac{\text{total concentration of proton bound to ligand}}{\text{total concentration of ligand not bound to metal}}$$

$$= \frac{C_{LH} + 2\,C_{LH_2} + \ldots\ldots + j\,C_{LH_j}}{C_L + C_{LH} + C_{LH_2} + \ldots. + C_{LH_j}} \qquad (2.9)$$

This equation can also be transformed in terms of formation constants K_1^{H}, K_2^{H}, etc. as follows:

$$\bar{n}_A = \frac{K_1^{H}\,C_H + 2\,K_1^{H}\,K_2^{H}\,C_H^{2} + \ldots\ldots + j\,\beta_j^{H}\,C_H^{j}}{1 + K_1^{H}\,C_H + K_1^{H}\,K_2^{H}\,C_H^{2} + \ldots. + j\,\beta_j^{H}\,C_H^{j}} \qquad (2.10)$$

where j is the maximum number of associated protons with the ligand. If there is only one replaceable proton in the ligand:

$$K_1^{H} = \frac{\bar{n}_A}{(\bar{n}_A - 1)\,C_H} \qquad (2.11)$$

which may be written in a simpler way as:

$$\log K_1^{H} = \log \frac{\bar{n}_A}{\bar{n}_A - 1} + \text{pH} \ldots.. \qquad (2.12)$$

Thus, the value of the protonation constants can be determined by substituting different values of $\bar{n}_A$ and corresponding pH values in equation (2.12) and then finding the average value.

The calculations of the protonation constants were carried out by plotting a graph between $\bar{n}_A$ and pH, known as formation curve of the ligand and various computational methods (21) viz. interpolation at half $\bar{n}_A$ values, interpolation at various $\bar{n}_A$ values, mid point slope method and least square method were applied to determine the values of the protonation constants.

Metal-Ligand Stability Constants

The stepwise metal-ligand stability constants were obtained from the analysis of the formation curves, which were drawn by plotting $\bar{n}$ against pL. The values of $\bar{n}$, i.e. the average number of ligands attached per metal ion present in whatever form, was calculated from the equation:

$$\bar{n} = \frac{(v''' - v'') \quad N^{o} + E^{o} + T_{L} \, (y - \bar{n}_{A})}{(V^{o} + v'') \, \bar{n}_{A} \, T_{M}} \qquad (2.13)$$

where T_M denotes the total concentration of the metal present in the solution and other terms have their usual meanings.

From the different values of $\bar{n}$, the corresponding values of pL, i.e. the free ligand exponent, were calculated from the equation:

$$pL = \log_{10} \left[\frac{\sum_{n=0}^{n=J} \beta_{n}^{H} \left\{ 1/(\text{antilog } B) \right\}^{n}}{(T_{L} - \bar{n}\, T_{M})} \cdot \frac{V^{o} + v'''}{V^{o}} \right] \qquad (2.14)$$

where β_n^H is the overall proton-ligand stability constant.

Metal-ligand complex formation curves were obtained by plotting $\bar{n}$ vs pL. The formation curves, so obtained, were then analysed and stepwise metal-ligand stability constants were obtained by using various computational methods, described below:

(1) Interpolation at Half $\bar{n}$ Values

According to this method in Bjerrum's approach

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

when $n = 1$, $K_1 = pL_{1/2}$ and (2.15)

when $n = 2$, $K_2 = pL_{3/2}$ (2.16)

The values of log K_1 and log K_2 (and hence log β_2) were obtained by reading the values of pL, corresponding to the points where $\bar{n} = 0.5$ and 1.5 respectively. Unless $K_1/K_2 \gg 10^{2.5}$, this very commonly used approximation, can introduce considerable error and in the case of two dissociation constants, it has the disadvantage of using only two points on the formation curve.

(2) Interpolation at Various $\bar{n}$ Values

To calculate log K_1 and log K_2, use was made of Irving and Rossotti's equation:

$$\log K_1 = pL_{1-d} + \log (1-d)/d \qquad (2.17)$$

$$\log K_2 = pL_{1+d} - \log (1-d)/d \qquad (2.18)$$

where d is assumed to be equal to 0.1, 0.2, ..., 0.9 and values of $\log K_1$ and $\log K_2$ were 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 only justified if $K_1/K_2 > 10^4$ though, in this case, this method is preferable to the first method as it can be applied to several points along the formation curve and mean values of K_1 and K_2 obtained from the results. If $K_1/K_2 < 10^4$, the calculated values of stability constants show a drift which is more pronounced at lower values of d.

(3) Mid-Point Slope Method

At the mid-point of the formation curve, where $\bar{n} = 1$

$$K_1 K_2 [L_1]^2 = 1 \quad \text{or} \quad \log K_1 K_2 = 2\, pL_1 \qquad (2.19)$$

For a system where $n = 2$, the following equation holds good

$$D = - \frac{4.606}{(2 - \sqrt{K_1/K_2})} \qquad (2.20)$$

where D is the slope of the formation curve at the point where $\bar{n} = 1.0$.

Applying equation (2.19) and (2.20), we can calculate the individual values of log K_1 and log K_2.

This method is only applicable where K_1/K_2 lies between 10^3 and 10^{-2} and it uses only a very small portion of the formation curve in the region of the mid-points.

(4) Least Square Treatment

The original equation (for $n = 2$),

$$\bar{n} + (\bar{n} - 1) K_1 C_L + (\bar{n} - 2) K_1 K_2 C_L^2 = 0$$

can be written as

$$\frac{\bar{n}}{(\bar{n} - 1) L} = \frac{(2 - \bar{n}) [L]}{(\bar{n} - 1)} \cdot (K_1 K_2 - K_1) \qquad (2.21)$$

which is the equation which gives a straight line. The line formed through the maximum number of points is used for evaluation of the experimental data using the method of least square .

Evaluation of Thermodynamic Functions

The stability constants of metal chelates are related to the thermodynamic properties such as free energy change (ΔG^o), heat content or enthalpy change ($\Delta \overset{o}{H}$) and entropy change ($\Delta \overset{o}{S}$) 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:

$$\Delta F^{o} = \Delta G^{o} = - RT \ln K \qquad (2.22)$$

where ΔG^{o} is the change in free energy of formation, R is the gas constant, T is the temperature in ^{o}K, of the system and K is the stability constant. The equation $\Delta G^{o} = - RT \ln K$ is known as van't Hoff isotherm.

By finding out the stability constants at different temperatures and plotting log K against 1/T, the enthalpy change, ΔH^{o} of the reaction can be calculated by using the following equation:

$$\Delta H^{o} = \frac{2.303\, R(\log K_2 - \log K_1)(T_1 . T_2)}{(T_2 - T_1)} \qquad (2.23)$$

Assuming this to be constant over the range of experimental temperatures, the entropy change, ΔS^{o} of the reaction can also be calculated by using the Gibbs-Helmholtz equation:

$$\Delta G^{o} = \Delta H^{o} - T\, \Delta S^{o} \qquad (2.24)$$

or $$\Delta S^{o} = \frac{\Delta H^{o} - \Delta G^{o}}{T} \qquad (2.25)$$

Absorptiometric Measurements

The formation of a characteristic colour is one of the important and distinguishing features of chelate compounds. Ley (23) used absorption spectra to distinguish between the free metal ions and their chelates. The colour of the chelate compounds is generally accepted, as being very significant and the intensification of colour is usually considered as an indication that a chelate may be present.

In recent years, investigations on the absorption of light have extensively been used for the study of the coloured chelates in solution, mostly employing the spectrophotometric methods which are based upon Beer-Lambert's law, which holds good only for monochromatic radiations.

$$A = \log \frac{I_o}{I} = \epsilon C d \qquad (2.26)$$

where A = Absorbance of the solution

I_o = Intensity of the incident beam

I = Intensity of the transmitted beam

C = Concentration of the coloured substance in moles/litre

d = Depth of the solution traversed by light in cms

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

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

Discerning the Composition of Metal Chelates

Numerous procedures are known to have been employed successfully using absorption measurements for the calculation of the composition of the complexes. A brief account of some of the methods, used for the present studies, is given below.

Method of Continuous Variation

Job's method (24) of continuous variation involves the use of an additive molecular property as a guide. This method requires a series of solutions of varying mole fractions of the two constituents wherein their sum is kept constant and variation of the physical property (say absorbance) of the mixtures in terms of the composition is studied. The difference between the absorbance of the complex and the total of the absorbance of the ligand and metal (assuming that there is no reduction in volume) is plotted against the mole fractions of one of the constituents. The resulting curve will show a maximum (or minimum) value at the mole fractions corresponding to that in the complex.

Vosburgh and Cooper (25) 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 Gebert (26). In spite of the criticism of the method by some workers (27-32) it is agreed, by all concerned, that the results provide a reliable data when absorbance measurements are used, as the reference property.

Mole Ratio Method

In the mole ratio method of Yoe and Jones (33), a series of solutions of mixtures is prepared containing a constant amount of the metal ion to that of the reagent. The curve of the absorbance plotted against the concentration ratio rises linearly from the origin when both the reactonts 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 variable component is added. This method has been found to be more useful in case of very stable complexes.

Slope Ratio Method

In the slope ratio method of Harvey and Manning (34), 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 component and then the other component in presence of large excess of the second component. This method is more suitable for the study of less stable complexes.

Numerous other methods (35-44) based on absorptiometric measurements have been employed for the study of the complexes. Molland (40) worked out a method which is applicable in cases where more than one central ion is involved in the reaction. The method of proportional absorbance developed by Budešinsky (37) in recent years, is applicable for establishing the existence of binuclear complexes, formed in solution. The method of Frank and Oswalt (38) is effective in the identification of 1:1 complexes. Methods applied for the investigation of stepwise formation of complexes include those of Bjerrum (36), Newman and Hume (41), Janssen (39), Yatsimirskii (43) and Nickless and Anderson (45).

Determination of Stability Constants

Various methods have been reported in the literature for determining the stability constants (46-49). A brief account of some of the methods used in the present studies is described below:

Mole Ratio Method

The stability constant of the complex can be calculated from the mole ratio curve (33). The stability constant K is given by the equation

$$K = \frac{1 - \alpha}{n^n \alpha^{n+1} C^n} \qquad (2.27)$$

where C is the concentration of the complex and α is the degree of dissociation, which is given by the equation:

$$\alpha = \frac{(E_m - E_s)}{E_m} \qquad (2.28)$$

where E_m is the absorbance of the undissociated complex (in presence of an excess of chelating agent) and E_s is the absorbance of the dissociated complex (at equilibrium). Thus for 1:1 complex, from equation (2.27)

$$K = \frac{(1 - \alpha)}{\alpha^2 C} \qquad (2.29)$$

and for 1:2 complex

$$K = \frac{(1 - \alpha)}{4 \alpha^2 C^2} \qquad (2.30)$$

Molecular Extinction Coefficient Method

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

$$\epsilon = A/Cd = A/C \quad \text{(when } d = 1\text{)} \qquad (2.31)$$

where d = length of the absorption cell in cm

C = concentration of the complex in gram moles/litre

A = absorbance

and ϵ = molecular extinction coefficient.

The formation constant K is given by

$$K = \frac{x}{(a - mx)^m \, (b - mx)^n} \qquad (2.32)$$

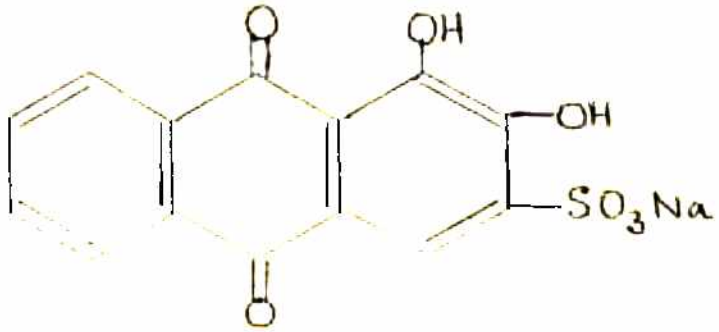
where 'x' i.e. C in equation (2.31) is the concentration of the complex at equilibrium and 'a' and 'b' are the initial concentration of the metal ion and the chelating agent.

THE PRESENT WORK

Among the chromogenic ligands, many dyes are of considerable interest on account of their tendency of forming metal-dye complexes, in solution. The change in colour by interaction between a metal ion and a suitable ligand forms the basis of chromogenic reactions, in which measurement of absorption of light is possible.

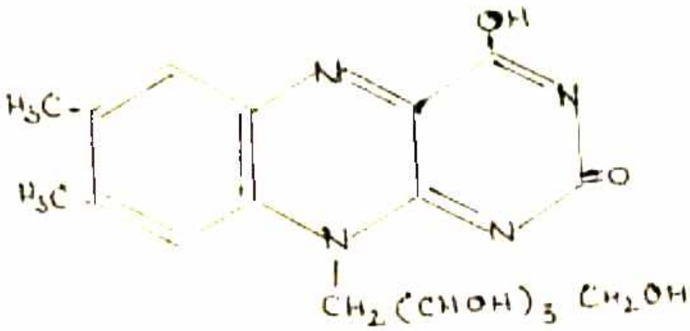
The complexation reactions of three ligands, viz., Alizarin Red S, Nitroso-R-Salt and Riboflavin with some bivalent metal ions i.e. lead, copper, zinc, cadmium, mercury, nickel, cobalt, beryllium and uranyl have been undertaken. Structures of the ligands may be represented as:

A. Alizarin Red S



B. Nitroso-R-Salt

C. Riboflavin



In spite of considerable amount of work reported regarding their use as analytical reagents, not much information regarding their bivalent metal chelates is available. Hence, the aim of the present work has been to investigate systematically the composition, stability and thermodynamic functions of bivalent metal chelates formed in the solution. Attempts have also been made to find further applications of the reagents in the photometric determination of metal ions. Stepwise stability constants, thermodynamic stability constants with their thermodynamic functions have also been found.

Some of the aims of the work presented here are:

1. To find out the stepwise proton-ligand and metal-ligand stability constants, using pH-titration technique.

2. To determine the effect of ionic strength on the stability of the chelates and then its use for the calculation of thermodynamic stability constants.

3. To determine the stepwise thermodynamic functions such as free energy of formation, enthalpy and entropy change during the formation of the metal chelates.

4. To study the order of stability constants amongst bivalent metal ions.

5. To study the composition of the metal chelates.

6. To determine the stability constants of the chelates, using absorbance data.

7. To study the effective pH-range for the stable existence of these chelates.

8. To find out the usefulness of these chelating agents for the spectrophotometric micro determination of metals.

9. To find out the interference of various foreign ions and their tolerance limits

10. To find out the corelation between the ionization of the ligands and the stability of the chelates formed.

11. To study the variation of stability constant and the thermodynamic functions with the properties of metals like electronegativity and ionisation potential.

EXPERIMENTAL DETAILS

PART A

POTENTIOMETRIC STUDIES

Apparatus

A Beckman pH meter (Model H2) with a glass-calomel electrode assembly was used to determine the change in hydrogen ion concentration. Checks were made using a standard Beckman buffer solution before each titration.

A Forma Scientific (Model 2095) precision thermostat was used to circulate the water at a constant temperature. A specially fabricated double walled beaker was used for titrations. The water at a constant temperature was circulated through it to maintain the temperature of the titrating mixture constant within a range of ±0.1°C.

Reagents

All the chemicals used were of 'AnalaR' or reagent grade purity. All the solutions were prepared using carbon dioxide free, double distilled water.

Sodium hydroxide was dissolved in double distilled water and was kept overnight over lime. The solution was filtered and standardised against a standard oxalic acid solution. Perchloric acid (Reidel) was standardised using this NaOH. Sodium perchlorate (Reidel) solutions were prepared by directly dissolving in double distilled water. All the solutions of the ligands and metal ions were prepared in aqueous media and standardised by usual methods.

Procedure

As already mentioned, Bjerrum-Calvin pH-titration technique as modified by Irving and Rossotti was used for all these studies. A number of titrations were carried out maintaining different ionic strengths and different temperatures to calculate the thermodynamic stability constants and various thermodynamic functions. The following three titrations were performed in each case.

Mixture A : 5 ml $HClO_4$ (0.1M) + x ml of 1M $NaClO_4$

Mixture B : Mixture A + 50 ml of ligand (M/200)

Mixture C : Mixture B + 10 ml of metal ion (M/200)

(The volume of sodium perchlorate is dependent on the ionic strength to be maintained).

Double distilled water was added in all the three mixtures to make the volume as 100 ml. The metal-ligand ratio was kept at 1:5, to fulfil the maximum coordination number of the metal ion. All the three mixtures were titrated with progressive addition of a standard NaOH solution ($\sim$1 N) in small increments using a micro burette. The corresponding change in the pH was observed and recorded. First of all these three titrations were performed at a fixed temperature but at 5 different ionic strengths viz. 0.02, 0.05, 0.10, 0.15 and 0.20 to get the thermodynamic stability constants and then at a fixed ionic strength and at five different temperatures viz. 10°, 20°, 30°, 40° and 50°C to determine the various thermodynamic functions.

Stepwise proton-ligand and metal-ligand stability constants were determined by analysing the formation curves using the following computational methods:

1. Interpolation at half $\bar{n}$ values
2. Interpolation at various $\bar{n}$ values
3. Mid-point slope method, and
4. Least square method.

After getting these stepwise stability constants, various thermodynamic functions i.e. change in free energy of formation, enthalpy change and entropy change were determined by using the method as described earlier.

PART B

SPECTROPHOTOMETRIC STUDIES

Instruments

All absorbance measurements were made on UV-VIS Hitachi Perkin Elmer spectrophotometer (Model 139) using one cm matched quartz cells, 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 assembly.

Chemicals

All the chemicals used throughout this work were of 'AnalaR' or reagent grade purity. Double distilled water was used to prepare all the solutions. Aqueous solutions of ligands were used. Stock solutions of diverse ions were prepared from the salts of the corresponding metals.

Conditions of Study

The optimum conditions of study were worked out first, in order to ensure reproducible results. The individual solutions and mixtures were kept in a thermostat maintained at the temperature at which the studies were carried out, for half an hour to attain the equilibrium. pH of all the solutions was adjusted by using an appropriate buffer.

Effect of Time and Temperature

The complex formation was found to be instantaneous in all the cases studied. It was also observed that there was no significant change in absorbance values even after six or eight hours. The temperature change had a little or no effect on the absorbance of the complex. The order of addition of reagents did not have any effect on the absorbance of the chelates.

Effect of pH on Absorption Spectra

In order to study the effect of pH on the absorbance of the chelate, a series of solutions containing a fixed amount of metal and ligand were prepared at different pH values. The pH of the solutions were adjusted to the required value using HCl and NaOH and the total volume was kept constant at 25 ml. The absorption spectra were recorded. The pH range in which the complexes were stable was found out and the measurements were made at a fixed pH (by employing suitable buffer) to avoid any error due to pH variations.

Nature of the Complex Formed

The method of Vosburgh and Cooper was employed to determine the nature of the complex, in solution. Several mixtures containing various proportions of metal and ligand (1:0, 1:1, 1:2, 1:3, 1:4, etc.) were prepared and then the absorbance was measured at different wavelengths. The number of shifts in the λmax, clearly indicated the number of complexes formed. In all the cases studied, only one shift was observed indicating that only one complex was formed under the conditions of study.

Stoichiometry of the Chelate

In order to obtain the composition of the chelate, in solution, three independent methods were applied:

1. Continuous variation method

2. Mole ratio method
3. Slope ratio method

It was considered desirable to use several independent methods for establishing the composition to arrive at a reliable composition. It has been found that all different methods reported here give results which are in good agreement with each other.

Evaluation of Stability Constant

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

1. Mole ratio method
2. Molecular extinction coefficient method.

In order to obtain the thermodynamic stability constant, the stability constants at various ionic strengths were calculated and then the thermodynamic stability constant was calculated by the method of extrapolation of log K to zero ionic strength.

Evaluation of Thermodynamic Functions

The free energy of formation of the chelate was calculated by using the equation (2.22). In order to determine the enthalpy and entropy changes during the complex formation, the stability constants at different temperatures were determined. Since the plots of log K vs 1/T showed no significant departure from linearity,

ΔH was assumed to be constant over the temperature range studied. ΔH of the reaction has been calculated by using the equation (2.23). The entropy change (ΔS) of the reaction was calculated by using the equation (2.25).

Analytical Applications

In order to study the analytical applications of the chelate, the following factors were looked into:

Effect of reagent concentration

The effect of changes in the concentration of ligand on the absorbance of the chelate at suitable pH was determined at λ_{max} of the chelate. It was observed in all the cases that the absorbance increases with increase in the reagent concentration, hence the reagent concentration was kept constant. The concentration of the reagent, essential for the spectrophotometric determination was found out and the determinations were made under these conditions.

Beer's law and effective photometric range

The range of concentration for adherence to Beer's law (in ppm) was determined by plotting a calibration curve between absorbance of various mixtures and the amount of metal ion (in ppm).

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

Sensitivity and molecular extinction coefficient

The sensitivities of the colour reactions have been determined as defined by Sandell (50) in $\mu g/cm^2$ based on an absorbance of 0.01 unit.

The molecular extinction coefficient was calculated for each of the systems investigated, at the λ_{max} of the chelate.

Effect of diverse ions

The effect of diverse ions, in all photometric determinations, was investigated with a solution containing a known amount of metal ion and diverse ion. The pH was adjusted to the required value. The tolerance limit was calculated in each case. The tolerance limit is defined as the concentration of the diverse ion which affects the absorbance of the system by less than ±3%.

Reproducibility and precision

The reproducibility and accuracy of the method was studied by analysing the solutions containing different known amounts of the metal ion in ppm.

Thus the metal in the given alloy or ore, can easily be determined by these methods avoiding the long and tedious wet chemistry methods.

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CHAPTER III

POTENTIOMETRIC STUDIES

POTENTIOMETRIC STUDIES

It is a well-known observation that formation of a metal complex often results in the drop of pH or increase in acidity of the system. The increased acidity is a result of competitive binding tendencies of the two acids (electron acceptors), viz., hydrogen and metal ions, for a base i.e., the ligand. The magnitude of the observed pH change (or alkali needed to neutralise this pH change) forms the basis of one of the well established methods of determining the stability constants of the metal complexes formed in the system.

While working on Alizarin red S, Nitroso-R-salt and Riboflavin, it was felt of interest to study the stepwise stability constants of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Be^{2+} and UO_2^{2+} with these ligands, potentiometrically since no work seems to have been reported in literature on these determinations.

The details of the methods followed have been elaborately described in Chapter II. Bjerrum-Calvin pH-titration technique as used by Irving and Rossotti was employed for these studies. All the calculations of $\bar{n}_A$, $\bar{n}$ and pL were made on IBM Computer 1130, and checked against manual calculations.

PART I

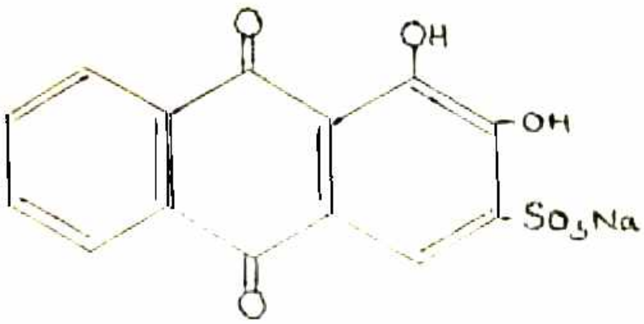
METAL CHELATES OF ALIZARIN RED S

Introduction

A number of hydroxyanthraquinone dyes have been used, for their chromogenic behaviour, as a spectrophotometric reagent for metal ions. The chelating properties of the dyes of this class are due to the presence of = O and -OH groups in adjacent positions which offer suitable coordination sites. Leibhafsky and Winslow (1) studied the interaction of zirconium with Alizarin (1,2-dihydroxyanthraquinone), Purpurin (1,2,4-trihydroxyanthraquinone) and Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone). Though the later two are more sensitive than Alizarin towards cations, they show large deviations from Beer's law. The deviations in these cases are attributed to the scattering of light by the comparatively larger particles of the dye molecules.

During the earlier periods, on the studies of metal dye chelates, there was a confusion about the nature of association of the dye with a metal ion. Several workers like Biltz (2), Weiser and Porter (3) considered these as adsorption compounds. On the other hand, Leibermann and Werner (4) regarded these as definite chemical compounds which have subsequently been substantiated by the studies of Leibhafsky and Winslow (1), Gubli and Jacob (5), who found that the ratio of the reactants were stoichiometric. It is interesting to note that non-stoichiometric compositions for such complexes was found by workers like Green (6), Meyer and Bradshaw (7). Larsen and Hirosawa (8) attributed these deviations to the hydrolysis of metal ions. Dey and coworkers (9) emphasised the nature of the dyes as colloidal electrolytes and explained deviations from stoichiometry due to this aspect. They also recommended the use of very dilute solution for elucidating the true composition of complexes by absorbance measurements, under which condition stoichiometric results are obtainable.

In spite of the excellent chromogenic properties of Alizarin, its use is limited due to its low solubility in water (1 part per 200 parts of water). The sulphonated compound is more soluble in water and possesses additional reactivity. Sodium-1,2-dihydroxyanthraquinone-3-sulphonate has been therefore widely used as a chromogenic ligand. The compound may be represented by the following structure:



Commonly known as sodium alizarin-3-sulphonate (trivial name Alizarin Red S; abbreviated as ARS).

Whilst considerable work has been done on the spectrophotometric studies of metal chelates of ARS, no work on the study of the stepwise formation of bivalent metal chelates of ARS have been reported in literature. Therefore, the present work was undertaken and the chelation reactions of Pb^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Be^{2+} and UO_2^{2+} in aqueous medium, at various ionic strengths and temperatures, have been studied.

EXPERIMENTAL

Apparatus

A Beckman pH-meter (model H2) with a glass-calomel electrode assembly was used to determine the change in hydrogen ion concentration. Checks were made using standard Beckman buffer solution before each titration, to ensure reproducibility.

For the temperature studies, a double walled beaker with one inlet and a outlet, connected to a Forma Scientific (Model 2095) thermostat was used to maintain the desired temperature. Water at constant temperature was circulated in the outer jacket of the double walled beaker to maintain the temperature of the mixture within a range of ±0.1°C.

All the chemicals used were of 'AnalaR' or reagent grade purity. An aqueous solution of ARS (BDH Indicator) was used. BDH 'AnalaR' grade lead nitrate, cupric chloride, zinc sulphate, $HgCl_2$, $NiSO_4$, $CuSO_4$, uranyl nitrate and A.G. Fluka beryllium chloride were used in these studies. Reidel's perchloric acid and sodium perchlorate were used.

All the solutions were prepared using CO_2 free, double distilled water. Sodium hydroxide was dissolved in water and was kept overnight over lime. This solution was filtered and standardised against a standard oxalic acid solution. The overall ionic strength was maintained by using sodium perchlorate solution.

Procedure

Bjerrum-Calvin pH-titration technique as used by Irving and Rossotti was employed for these studies. The details of the methods followed have been elaborately described in Chapter II. A suitable program was framed in the IBM Computer 1130 for the calculations of various values of $\bar{n}_A$, $\bar{n}$ and pL. A number of titrations were carried out maintaining different ionic strengths and temperatures. To determine the chelate stability constants, the following three mixtures were titrated:

Mixture A : 5 ml $HClO_4$ (0.1M) + x ml $NaClO_4$ (1M)

Mixture B : Mixture A + 50 ml of ligand (0.0025M)

Mixture C : Mixture B + 10 ml of metal ion (0.0025M)

(The volume of sodium perchlorate depends upon the ionic strength to be maintained).

The volume of all the mixtures was maintained at 100 ml. The mixtures were titrated with progressive addition of NaOH solution in small increments. The corresponding change in the pH of the mixture was observed and recorded. The metal-ligand ratio was kept at 1:5, to ensure maximum coordination with the metal ion.

These three titrations were performed with the eight metal ions under study, i.e., Pb^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Be^{2+} and UO_2^{2+} at various ionic strengths i.e., 0.02, 0.05, 0.10, 0.15 and 0.20 by keeping the temperature constant i.e. 30°C to get the thermodynamic stability constants. Then these titrations were performed at five different temperatures i.e., 10°, 20°, 30°, 40° and 50°C by keeping the ionic strength constant i.e., 0.10 to calculate the various thermodynamic functions.

RESULTS

The pH readings were plotted against the volume of NaOH added. The titration curves thus obtained at five ionic strengths viz. 0.02, 0.05, 0.10, 0.15 and 0.20 have been graphically represented in figures A and B in Plates 1-5.

Curves 1 and 2 in figures represent the titration curves of the solutions containing perchloric acid and perchloric acid + ligand respectively.

The additional amount of NaOH needed to obtain the same pH in presence of metal ions is clearly due to the liberation of hydrogen ions by complex formation between the ligand and metal ions. It is seen that the titration curves in absence and presence of metal ions almost coincide at higher pH values at which the reagent is completely ionised. This shows that the metal complexes are not hydrolysed even at higher pH values.

Proton-Ligand System

In order to calculate the metal-ligand stability constants, it is necessary to determine the proton-ligand stability constants. Alizarin red S possesses two ionizable hydrogen atoms, in the two-OH groups.

The observations made during the titration of mixtures A and B containing perchloric acid alone and perchloric acid plus ligand respectively, have been utilised to calculate the formation constants of proton-ligand systems. The titration curve 2 in Figure B of Plate 1-5, shows two inflections. The difference in the volume of NaOH used in case of curve 2 as compared to curve 1, to have the same pH-meter readings, is clearly due to the neutralisation of ARS. Two inflections show that dissociation of two hydrogen ions can only take place in the range of pH in which titration is carried out.

Calculation of $\bar{n}_A$ values

As only two hydrogen ions are liberated during the titration, the value of y in the equation below can thus be 2. The expression for $\bar{n}_A$ would be, as used by Irving and Rosotti

$$\bar{n}_A = y + \frac{(v' - v'')(N^o + E^o)}{(V^o + v')\, T_L} \qquad (3.1)$$

where T_L is the total concentration of ligand, E^o is the initial concentration of the perchloric acid (0.1M), V^o is the total initial volume of the solution (100 ml), N^o is the normality of the sodium hydroxide and v' and v" are the volumes of sodium hydroxide added in absence and in presence of the ligand for the same pH meter readings.

T_L, E^o, N^o and V^o are known and the value of $\bar{n}_A$ can be calculated with the knowledge of v' and v". $\bar{n}_A$ values at various pH values were calculated and representative results at ionic strength 0.05 only, are presented in Table 3.1 to reduce the bulk of the thesis.

Plate No. 1

Temperature = 30°C. Ionic strength = 0.02

Fig. A : Titration curves:
(1) $HClO_4$ (2) $HClO_4$ + ARS

Fig. B : Formation curve of proton-ARS system.

Fig. C : Titration curves of ARS metal chelates:
(3) ARS only (4) Pb-ARS (5) Cu-ARS
(6) Zn-ARS (7) Hg-ARS.

Fig. D : Titration curves of ARS metal chelates:
(8) Ni-ARS (9) Co-ARS
(10) Be-ARS (11) UO_2-ARS.

Fig. E : Formation curves of ARS metal chelates:
(1) Pb-ARS (2) Cu-ARS
(3) Zn-ARS (4) Hg-ARS

Fig. F : Formation curves of ARS metal chelates:
(5) Ni-ARS (6) Co-ARS
(7) Be-ARS (8) UO_2-ARS.

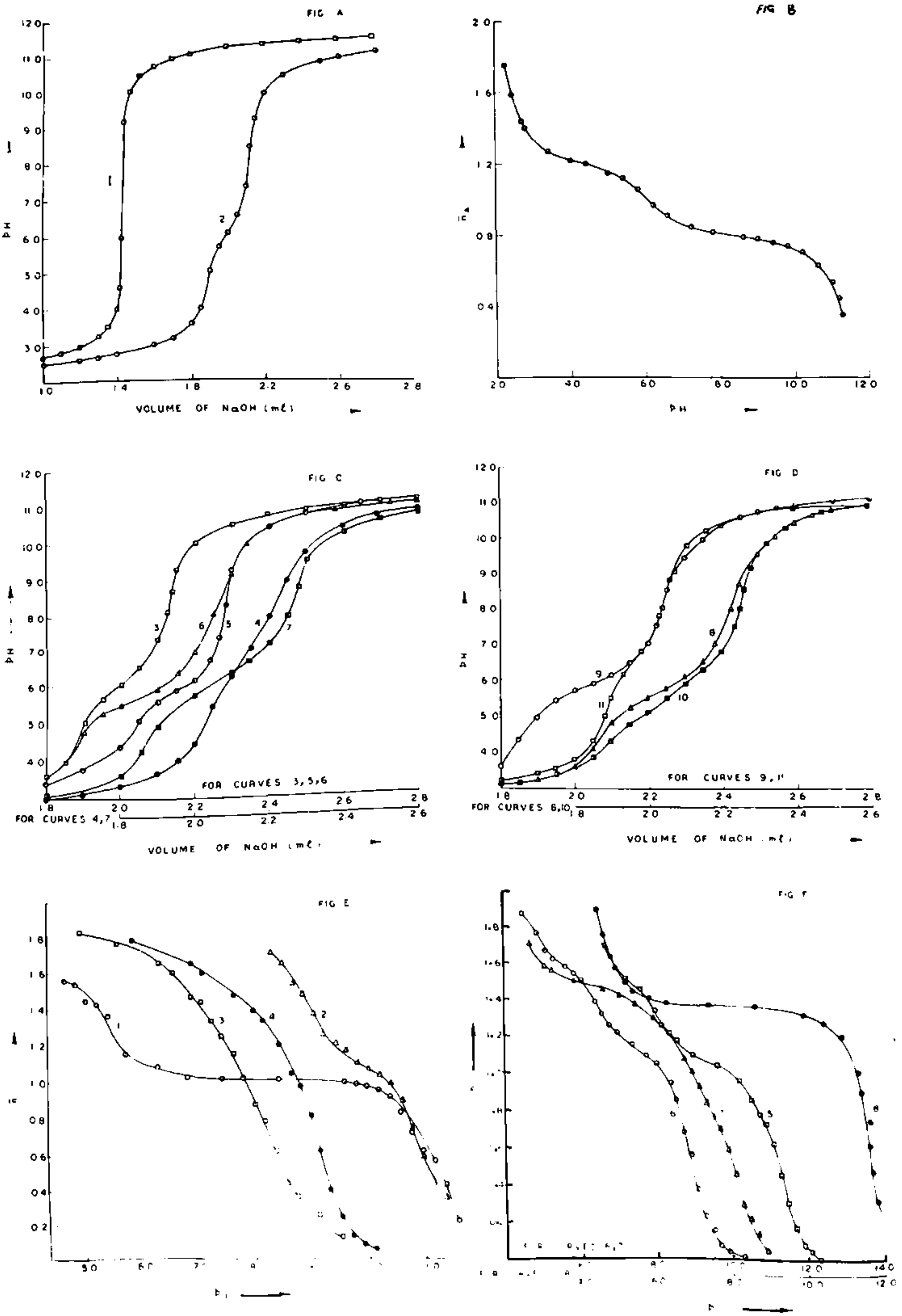


FIG A
pH
12 0
11 0
10 0
9 0
8 0
7 0
6 0
5 0
4 0
3 0
1
2
1 0
1 4
1 8
2 2
2 6
2 8
VOLUME OF NaOH (mℓ)
FIG B
2 0
1 6
1 2
0 8
0 4
2 0
4 0
6 0
8 0
10 0
12 0
pH
FIG C
pH
12 0
11 0
10 0
9 0
8 0
7 0
6 0
5 0
4 0
3
6
5
4
7
FOR CURVES 3, 5, 6
1 8
2 0
2 2
2 4
2 6
2 8
FOR CURVES 4, 7
1 8
2 0
2 2
2 4
2 6
VOLUME OF NaOH (mℓ)
FIG D
pH
12 0
11 0
10 0
9 0
8 0
7 0
6 0
5 0
4 0
9
11
8
10
FOR CURVES 9, 11
1 8
2 0
2 2
2 4
2 6
2 8
FOR CURVES 8, 10
1 8
2 0
2 2
2 4
2 6
VOLUME OF NaOH (mℓ)
FIG E
1 8
1 6
1 4
1 2
1 0
0 8
0 6
0 4
0 2
1
2
3
4
5
6
5 0
6 0
FIG F
1 8
1 6
1 4
1 2
5
6
7
8
12 0
14 0
10 0
12 0

PLATE NO 1

Table 3.1

T_L = 0.0025

v^o = 100.0

μ = 0.05

N^o = 0.34013

Y = 2.0

Figure = Plate 2, B

S.No.	pH	v'	v"	$\bar{n}_A$
1.	2.0	0.712	0.962	-
2.	2.2	0.728	0.978	1.6341
3.	2.4	0.738	0.998	1.6290
4.	2.6	0.876	1.201	1.5081
5.	2.8	1.025	1.400	1.3631
6.	3.0	1.200	1.580	1.3404
7.	3.2	1.280	1.678	1.3097
8.	3.4	1.331	1.735	1.2997
9.	3.6	1.369	1.779	1.2895
10.	3.8	1.391	1.811	1.2724
11.	4.0	1.410	1.832	1.2690
12.	4.2	1.418	1.850	1.2518
13.	4.4	1.419	1.859	1.2379
14.	4.6	1.419	1.868	1.2223
15.	4.8	1.420	1.875	1.2120
16.	5.0	1.420	1.890	1.1860
17.	5.2	1.422	1.900	1.1721
18.	5.4	1.424	1.913	1.1531
19.	5.6	1.427	1.933	1.1237
20.	5.8	1.429	1.958	1.0839

(Contd.)

Table 3.1 (Contd.)

S.No.	pH	v'	v"	$\bar{n}_A$
21.	6.0	1.429	1.983	1.0406
22.	6.2	1.430	2.002	1.0094
23.	6.4	1.430	2.025	0.9696
24.	6.6	1.432	2.046	0.9367
25.	6.8	1.434	2.059	0.9177
26.	7.0	1.437	2.070	0.9039
27.	7.2	1.439	2.080	0.8900
28.	7.4	1.440	2.089	0.8762
29.	7.6	1.440	2.095	0.8658
30.	7.8	1.442	2.100	0.8606
31.	8.0	1.445	2.102	0.8624
32.	8.2	1.448	2.106	0.8607
33.	8.4	1.449	2.110	0.8555
34.	8.6	1.451	2.114	0.8521
35.	8.8	1.451	2.120	0.8417
36.	9.0	1.453	2.127	0.8331
37.	9.2	1.455	2.135	0.8227
38.	9.4	1.459	2.144	0.8141
39.	9.6	1.460	2.157	0.7933
40.	9.8	1.470	2.175	0.7796
41.	10.0	1.482	2.200	0.7572
42.	10.2	1.502	2.235	0.7363
43.	10.4	1.537	2.280	0.7162
44.	10.6	1.590	2.354	0.6790

(Contd.)

Plate No. 2

Temperature = 30°C

Ionic strength = 0.05

Fig. A : Titration curves :

(1) $HClO_4$ (2) $HClO_4$ + ARS

Fig. B : Formation curve of proton-ARS system.

Fig. C : Titration curves of ARS metal chelates:

(3) ARS only (4) Pb-ARS (5) Cu-ARS

(6) Zn-ARS (7) Hg-ARS

Fig. D : Titration curves of ARS metal chelates:

(8) Ni-ARS (9) Co-ARS

(10) Be-ARS (11) UO_2-ARS

Fig. E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

Fig. F : Formation curves of ARS metal chelates

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

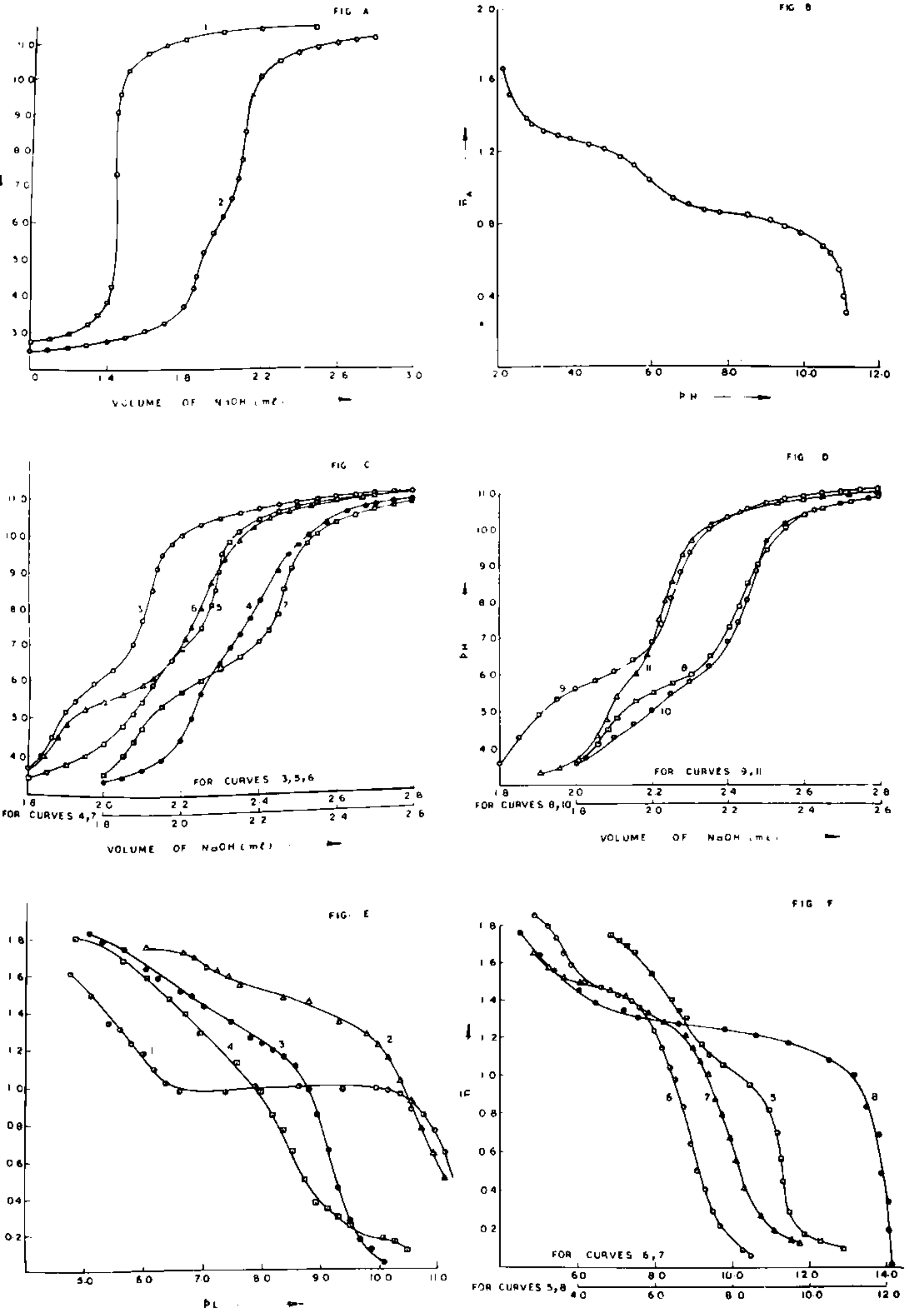


FIG A
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
1
2
0
1.4
1.8
2.2
2.6
3.0
VOLUME OF NaOH (ml)
FIG B
2.0
1.6
1.2
0.8
0.4
2.0
4.0
6.0
8.0
10.0
12.0
pH
FIG C
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3
6
5
4
7
FOR CURVES 3,5,6
1.8
2.0
2.2
2.4
2.6
2.8
FOR CURVES 4,7
1.8
2.0
2.2
2.4
2.6
VOLUME OF NaOH (ml)
FIG D
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
pH
9
11
8
10
FOR CURVES 9,11
1.8
2.0
2.2
2.4
2.6
2.8
FOR CURVES 8,10
1.8
2.0
2.2
2.4
2.6
VOLUME OF NaOH (ml)
FIG E
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
1
2
3
4
5.0
6.0
7.0
8.0
9.0
10.0
11.0
pL
FIG F
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
6
7
5
8
FOR CURVES 6,7
6.0
8.0
10.0
12.0
14.0
FOR CURVES 5,8
4.0
6.0
8.0
10.0
12.0
pL

PLATE NO. 2

Table 3.1 (Contd.)

S.No.	pH	V'	V"	$\bar{n}_A$
45.	10.8	1.671	2.455	0.6455
46.	11.0	1.800	2.642	0.5472
47.	11.2	1.935	2.799	0.4234
48.	11.4	2.100	3.020	0.3310

The proton-ligand formation curves were obtained by plotting the graphs in between $\bar{n}_A$ and pH. Various computational methods viz. interpolation at half $\bar{n}_A$ values (H), interpolation at various $\bar{n}_A$ values (V) and mid-point slope method (M) were applied to determine the stepwise proton-ligand stability constants at different ionic strengths. The thermodynamic stability constants were obtained by extrapolating these values to zero ionic strength. These values are presented in Table 3.2.

Table 3.2

Proton-ligand stability constants at various ionic strengths

	H	V	M	Mean
		$\mu = 0.02$		
log K_1	11.04	11.06	11.14	
log K_2	2.50	2.48	2.52	
log β_2	13.54	13.54	13.66	13.58

(Contd.)

Table 3.2 (Contd.)

	H	V	M	Mean
μ = 0.05				
log K_1	11.01	11.05	11.09	
log K_2	2.46	2.38	2.30	
log β_2	13.47	13.43	13.39	13.43
μ = 0.10				
log K_1	10.88	10.89	10.96	
log K_2	2.58	2.63	2.59	
log β_2	13.46	13.52	13.55	13.51
μ = 0.15				
log K_1	10.55	10.58	10.69	
log K_2	2.33	2.27	2.15	
log β_2	12.88	12.85	12.84	12.86
μ = 0.20				
log K_1	10.32	10.29	10.34	
log K_2	2.26	2.36	2.29	
log β_2	12.58	12.65	12.63	12.62
μ = 0.00 (By the method of extrapolation)				
log K_1	11.13			
log K_2	2.56			
log β_2 (exptl)	13.69			
log β_2 (calc)	13.67			

Metal-Ligand Systems

All the calculations of $\bar{n}$ and pL were made on IBM Computer 1130.

For a metal complex or chelate formation, taking place in steps in a homogeneous solution, the step formation constants are given by:

$$K_n = \frac{C_{ML_n}}{C_{ML_{n-1}} \cdot C_L} \quad (n = 1,2 \text{-----} N) \qquad (3.2)$$

where K_n is called the nth metal-ligand stability constant.

In the present case, the formation constants have been obtained by analysis of the formation curves obtained by plotting $\bar{n}$ against pL. The values of $\bar{n}$ i.e. the average number of ligands attached per metal ion, is calculated from the equation:

$$\bar{n} = \frac{(v''' - v'')(N^o + E^o)\ T_L\ (y - \bar{n}_A)}{(V^o + v'')\ \bar{n}_A \cdot T_M} \qquad (3.3)$$

where T_M denotes the total concentration of metal present in the solution and the other terms have their usual meanings.

The free ligand exponent, pL has been calculated from the equation:

$$pL = \log_{10}\left[\frac{(\beta_1^H\ [H] + \beta_2^H\ [H]^2 + \text{----})}{(T_L - \bar{n}\ T_M)} \cdot \frac{V^o + v'''}{V^o}\right] \qquad (3.4)$$

Plate No. 3

Temperature = 30°C

Ionic strength = 0.10

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

Fig. B : Formation curve of proton-ARS system

Fig. C : Titration curves of ARS metal chelates:

(3) ARS only (4) Pb-ARS (5) Cu-ARS

(6) Zn-ARS (7) Hg-ARS

Fig. D : Titration curves of ARS metal chelates:

(8) Ni-ARS (9) Co-ARS

(10) Be-ARS (11) UO_2-ARS

Fig. E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

Fig. F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

FIG A

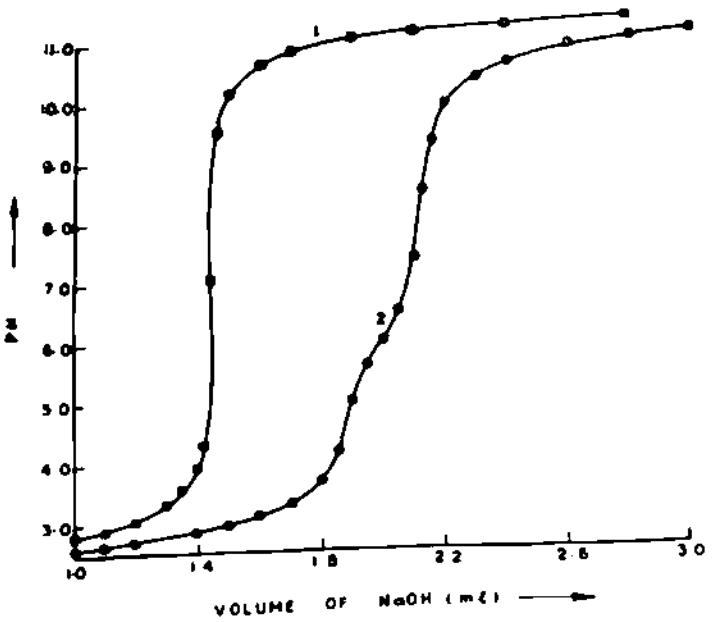


FIG. B

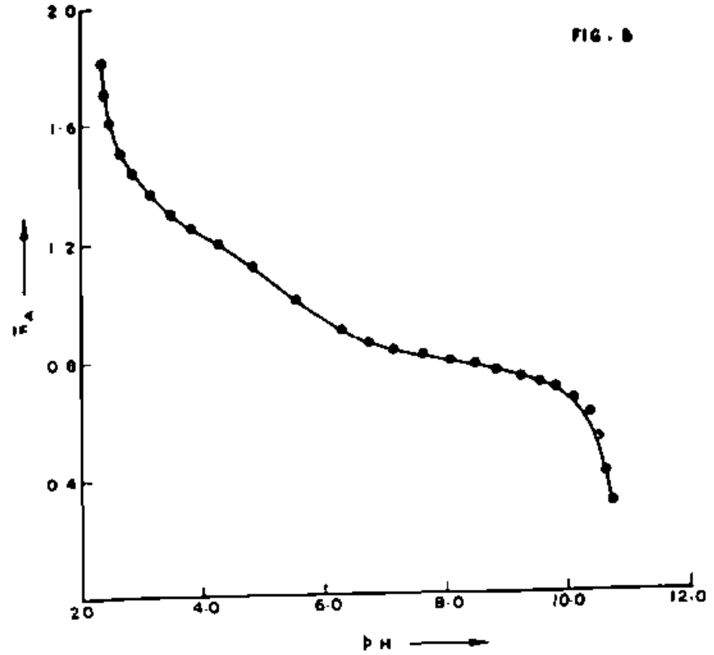


FIG. C

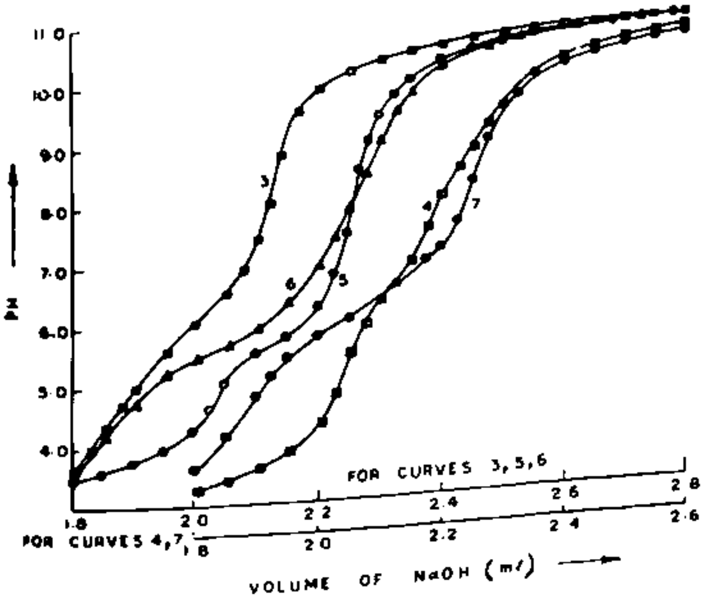


FIG. D

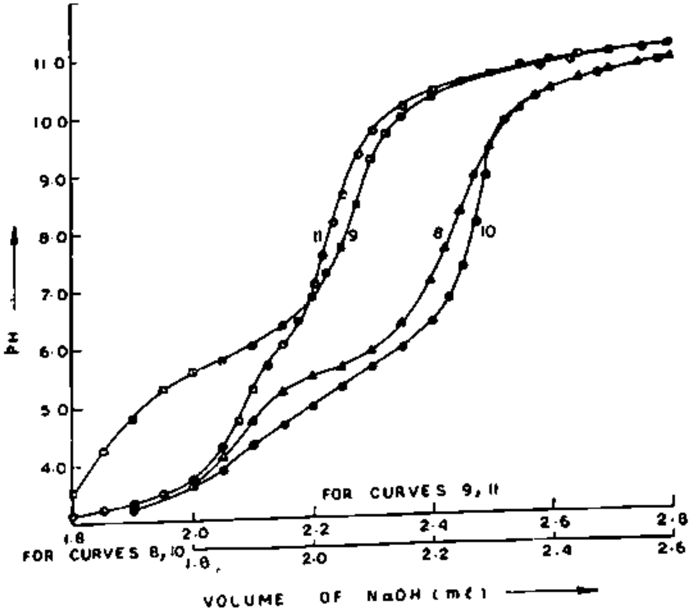


FIG. E

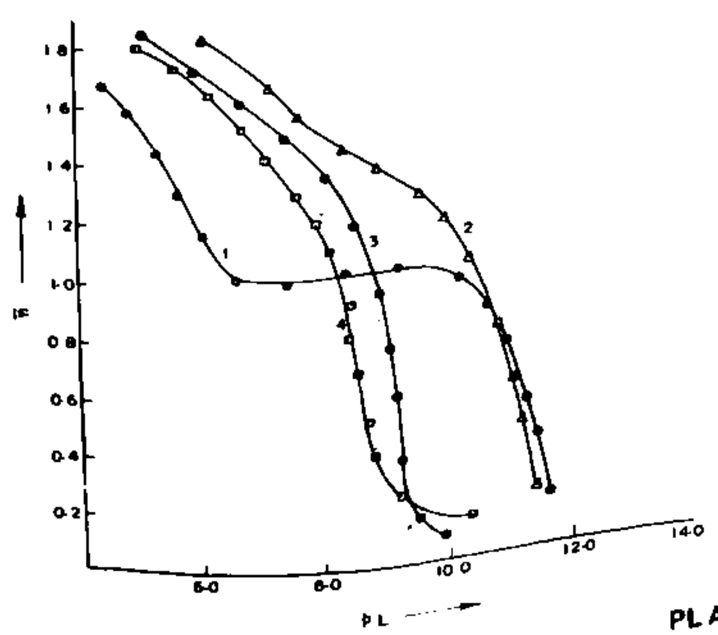


FIG. F

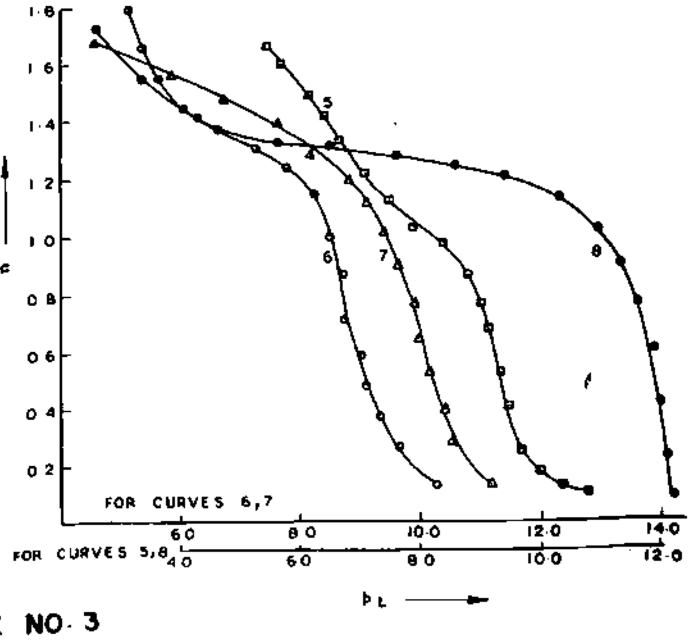


PLATE NO. 3

where β_1^H and β_2^H are the reciprocal acid dissociation constants of the ligand. Results obtained are presented in Tables 3.3-3.6 (only representative results i.e. ionic strength 0.05, are given to reduce the bulk of the thesis).

Table 3.3

T_L = 0.0025 T_M = 0.0005

N^o = 0.34013 V^o = 100.00

μ = 0.05 Figure - Plate 2,E

S. No.	Lead (II)		Copper (II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.145	11.520	0.112	11.783
2.	0.430	11.332	0.365	11.333
3.	0.610	11.131	0.478	11.131
4.	0.724	10.967	0.608	10.929
5.	0.808	10.756	0.738	10.718
6.	0.846	10.549	0.879	10.545
7.	0.915	10.351	0.986	10.398
8.	0.939	10.149	1.112	10.172
9.	0.951	9.954	1.182	9.981
10.	0.952	9.389	1.241	9.789
11.	0.971	8.612	1.311	9.301
12.	0.986	7.834	1.432	8.784
13.	0.986	7.389	1.461	8.333
14.	0.987	6.599	1.540	7.593
15.	1.022	6.392	1.579	7.424
16.	1.099	6.151	1.612	7.214
17.	1.183	5.992	1.641	7.006
18.	1.238	5.785	1.695	6.842
19.	1.318	5.587	1.721	6.639
20.	1.352	5.398	1.755	6.003
21.	1.499	5.101	-	-
22.	1.619	4.762	-	-

Table 3.4

T_L = 0.0025 T_M = 0.0005

N^o = 0.34013 V^o = 100.0

μ = 0.05 Figure - Plate 2,E

S. No.	Zinc (II)		Mercury (II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.035	10.081	0.091	10.482
2.	0.104	9.882	0.141	10.287
3.	0.152	9.743	0.159	10.071
4.	0.258	9.498	0.230	9.501
5.	0.427	9.311	0.272	9.298
6.	0.622	9.112	0.315	9.091
7.	0.818	8.921	0.352	8.902
8.	0.955	8.772	0.470	8.699
9.	1.087	8.551	0.623	8.501
10.	1.139	8.382	0.741	8.333
11.	1.176	8.198	0.823	8.167
12.	1.219	7.998	0.951	7.956
13.	1.245	7.810	1.111	7.504
14.	1.341	7.452	1.281	6.932
15.	1.430	7.001	1.392	6.672
16.	1.479	6.812	1.473	6.411
17.	1.512	6.601	1.588	6.003
18.	1.565	6.209	1.682	5.612
19.	1.641	6.003	1.809	4.804
20.	1.742	5.672	-	-
21.	1.790	5.281	-	-
22.	1.831	5.071	-	-

Table 3.5

$T_L = 0.0025$ $T_M = 0.0005$

$N^o = 0.34013$ $V^o = 100.0$

$\mu = 0.05$ Figure - Plate 2,F

S. No.	Nickel (II)		Cobalt (II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.101	10.911	0.061	10.463
2.	0.142	10.312	0.092	10.285
3.	0.179	9.889	0.218	9.693
4.	0.292	9.462	0.297	9.493
5.	0.456	9.299	0.414	9.299
6.	0.572	9.253	0.512	9.100
7.	0.711	9.141	0.657	8.942
8.	0.831	8.942	0.848	8.751
9.	0.960	8.449	0.987	8.552
10.	1.061	7.762	1.044	8.346
11.	1.112	7.362	1.145	8.194
12.	1.169	7.181	1.238	7.989
13.	1.301	6.812	1.363	7.587
14.	1.343	6.611	1.392	7.401
15.	1.402	6.412	1.424	7.061
16.	1.545	5.898	1.469	6.621
17.	1.656	5.445	1.492	6.198
18.	1.692	5.261	1.589	5.812
19.	1.717	5.008	1.651	5.631
20.	1.744	4.824	1.723	5.440
21.	-	-	1.792	5.223
22.	-	-	1.853	4.851

Table 3.6

$T_L = 0.0025$ $T_M = 0.0005$

$N^o = 0.34013$ $V^o = 100.00$

$\mu = 0.05$ Figure - Plate 2,F

S. No.	Beryllium (II)		Uranyl (II)	
	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.128	11.761	0.021	12.152
2.	0.147	11.542	0.203	12.071
3.	0.197	11.090	0.353	12.060
4.	0.271	10.742	0.499	11.878
5.	0.420	10.291	0.702	11.783
6.	0.560	10.111	0.852	11.511
7.	0.682	9.931	1.013	11.172
8.	0.804	9.722	1.098	10.501
9.	0.885	9.545	1.179	9.453
10.	1.012	9.367	1.221	8.612
11.	1.081	9.171	1.248	7.837
12.	1.149	8.987	1.279	6.599
13.	1.211	8.761	1.307	5.573
14.	1.283	8.211	1.342	5.201
15.	1.333	7.812	1.383	4.421
16.	1.422	7.201	1.452	4.002
17.	1.454	6.804	1.553	3.362
18.	1.493	5.999	1.642	3.001
19.	1.521	5.613	1.755	2.498
20.	1.576	5.199	-	-
21.	1.649	4.811	-	-

Plate No. 4

Temperature = 30°C

Ionic strength = 0.15

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

Fig. B : Formation curves of proton-ARS system

Fig. C : Titration curves of ARS metal chelates:

(3) ARS only (4) Pb-ARS (5) Cu-ARS

(6) Zn-ARS (7) Hg-ARS

Fig. D : Titration curves of ARS metal chelates:

(8) Ni-ARS (9) Co-ARS

(10) Be-ARS (11) UO_2-ARS

Fig. E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

Fig. F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

FIG. A

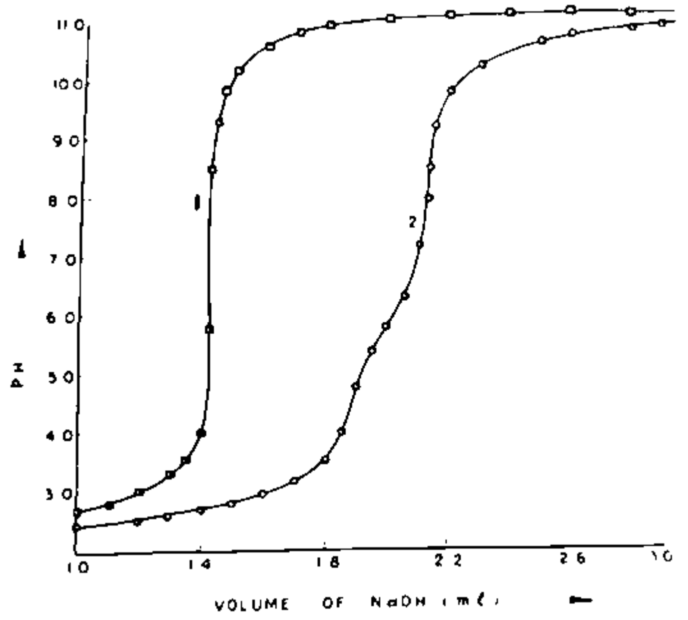


FIG. B

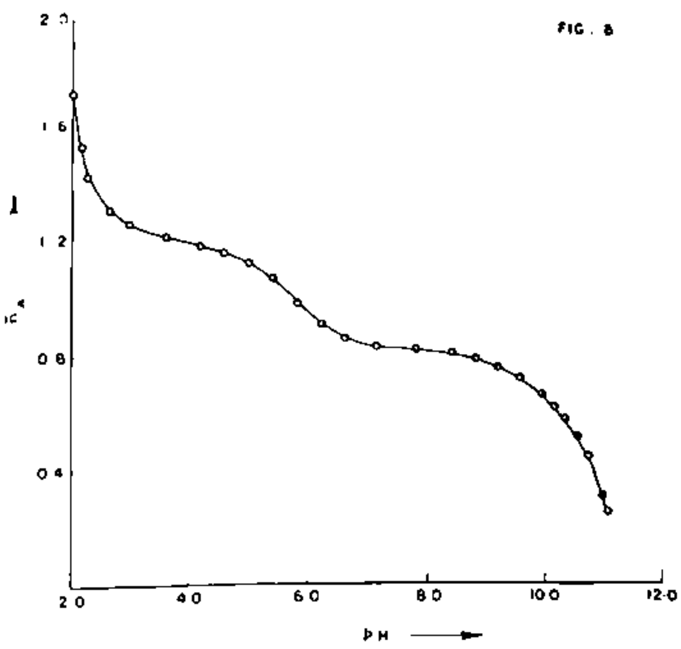


FIG. C

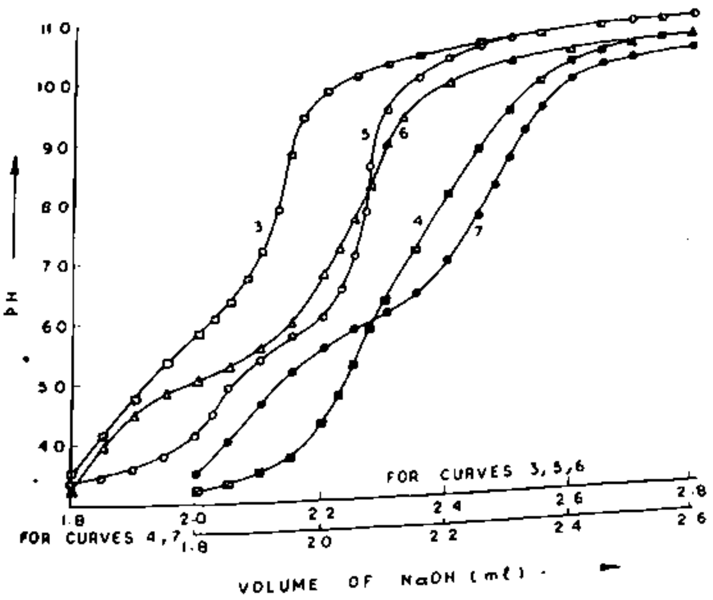


FIG. D

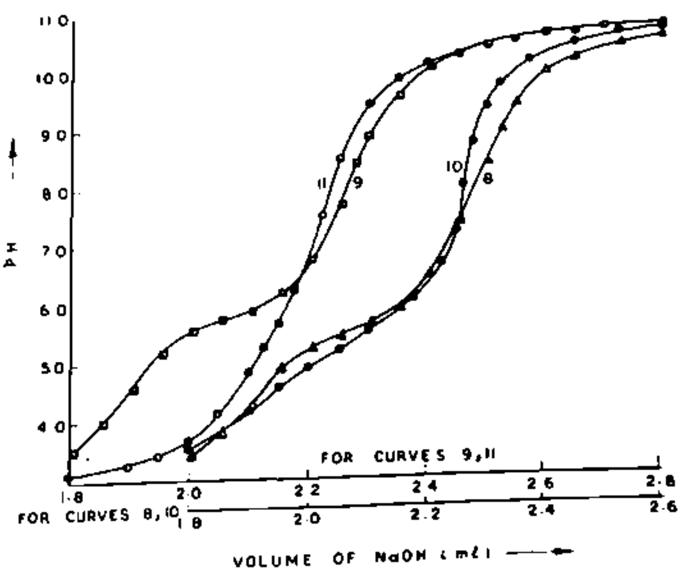


FIG. E

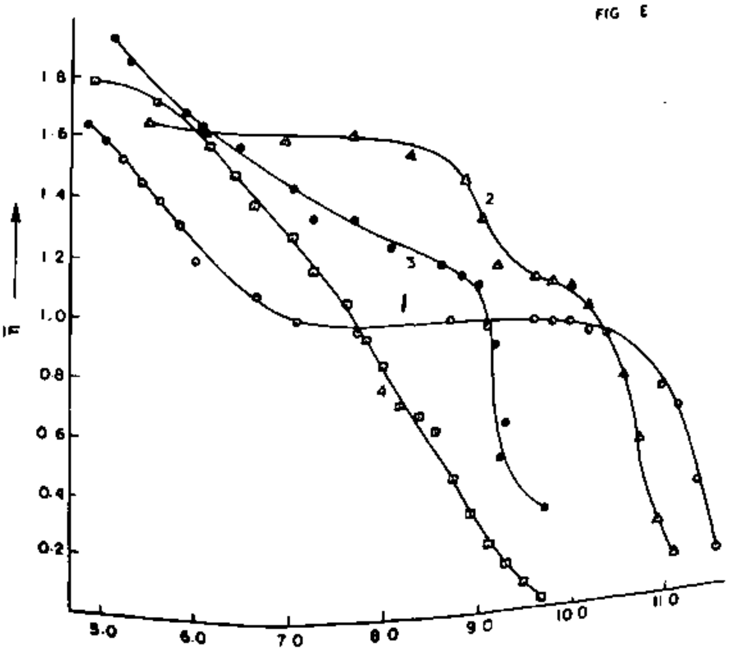


FIG. F

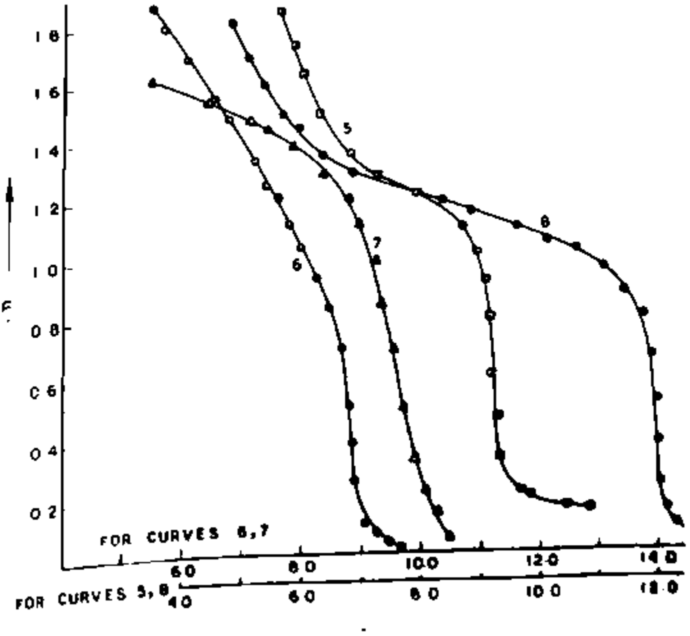


PLATE NO. 4

The metal-ligand formation curves were obtained by plotting $\bar{n}$ against pL and were analysed, as usual, by using various computational methods referred to earlier. The results obtained have been tabulated in Tables 3.7-3.14.

Table 3.7

Values of stability constants of Pb-APS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	11.20	11.16	11.21	
	log K_2	5.04	5.06	5.04	
	log K_c	16.24	16.22	16.25	16.23
0.05	log K_1	11.24	11.21	11.20	
	log K_2	5.11	5.17	5.11	
	log K_c	16.35	16.38	16.31	16.35
0.10	log K_1	11.25	11.25	11.29	
	log K_2	5.18	5.14	5.18	
	log K_c	16.43	16.39	16.47	16.43
0.15	log K_1	11.27	11.12	11.31	
	log K_2	5.25	5.31	5.28	
	log K_c	16.52	16.43	16.59	16.51
0.20	log K_1	11.34	11.38	11.36	
	log K_2	5.65	5.62	5.52	
	log K_c	16.99	17.00	16.88	16.96

Table 3.8

Values of stability constants of Cu-ARS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	11.03	11.16	11.07	
	log K_2	8.74	8.74	8.65	
	log K_c	19.77	19.90	19.72	19.80
0.05	log K_1	11.10	11.13	11.15	
	log K_2	8.12	8.26	8.14	
	log K_c	19.22	19.39	19.28	19.30
0.10	log K_1	10.91	10.90	10.93	
	log K_2	8.31	8.26	8.31	
	log K_c	19.22	19.16	19.24	19.21
0.15	log K_1	10.71	10.71	10.74	
	log K_2	8.40	8.32	8.43	
	log K_c	19.11	19.03	19.17	19.10
0.20	log K_1	10.59	10.61	10.63	
	log K_2	8.35	8.28	8.27	
	log K_c	18.94	18.89	18.90	18.91

Table 3.9

Values of stability constants of Zn-ARS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	9.10	9.13	9.09	
	log K_2	6.70	6.72	6.74	
	log K_c	15.80	15.85	15.83	15.83
0.05	log K_1	9.22	9.25	9.19	
	log K_2	6.72	6.83	6.69	
	log K_c	15.94	16.08	15.88	15.97
0.10	log K_1	9.29	9.34	9.24	
	log K_2	6.70	6.62	6.78	
	log K_c	15.99	15.96	16.02	15.99
0.15	log K_1	9.24	9.39	9.33	
	log K_2	6.69	6.72	6.68	
	log K_c	15.93	16.11	16.01	16.01
0.20	log K_1	8.73	8.73	8.71	
	log K_2	6.28	6.31	6.38	
	log K_c	15.01	15.04	15.09	15.05

Table 3.10

Values of stability constants of Hg-ARS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	8.43	8.45	8.41	
	log K_2	6.68	6.66	6.69	
	log K_c	15.11	15.11	15.11	15.11
0.05	log K_1	8.64	8.68	8.61	
	log K_2	6.34	6.33	6.31	
	log K_c	14.98	15.01	14.92	14.97
0.10	log K_1	8.61	8.59	8.57	
	log K_2	6.22	6.29	6.34	
	log K_c	14.83	14.88	14.91	14.87
0.15	log K_1	8.57	8.59	8.52	
	log K_2	6.26	6.21	6.29	
	log K_c	14.83	14.80	14.81	14.81
0.20	log K_1	8.03	8.08	8.01	
	log K_2	6.10	6.08	6.12	
	log K_c	14.13	14.16	14.13	14.14

Table 3.11

Values of stability constants of Ni-ARS chelate at various ionic strengths

Ionic strength	log K_n	H	V	Mean
0.02	log K_1	9.24	9.22	
	log K_2	5.31	5.54	
	log K_c	14.55	14.76	14.65
0.05	log K_1	9.26	9.31	
	log K_2	5.88	6.11	
	log K_c	15.14	15.42	15.28
0.10	log K_1	9.28	9.37	
	log K_2	6.06	6.01	
	log K_c	15.34	15.38	15.36
0.15	log K_1	9.22	9.24	
	log K_2	6.23	6.21	
	log K_c	15.45	15.45	15.45
0.20	log K_1	8.64	8.77	
	log K_2	6.68	6.85	
	log K_c	15.32	15.62	15.47

Plate No. 5

Temperature = 30°C

Ionic strength = 0.20

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

Fig. B : Formation curve of proton-ARS system

Fig. C : Titration curves of ARS metal chelates:

(3) ARS only (4) Pb-ARS (5) Cu-ARS

(6) Zn-ARS (7) Hg-ARS

Fig. D : Titration curves of ARS metal chelates:

(8) Ni-ARS (9) Co-ARS

(10) Be-ARS (11) UO_2-ARS

Fig. E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

Fig. F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

FIG A

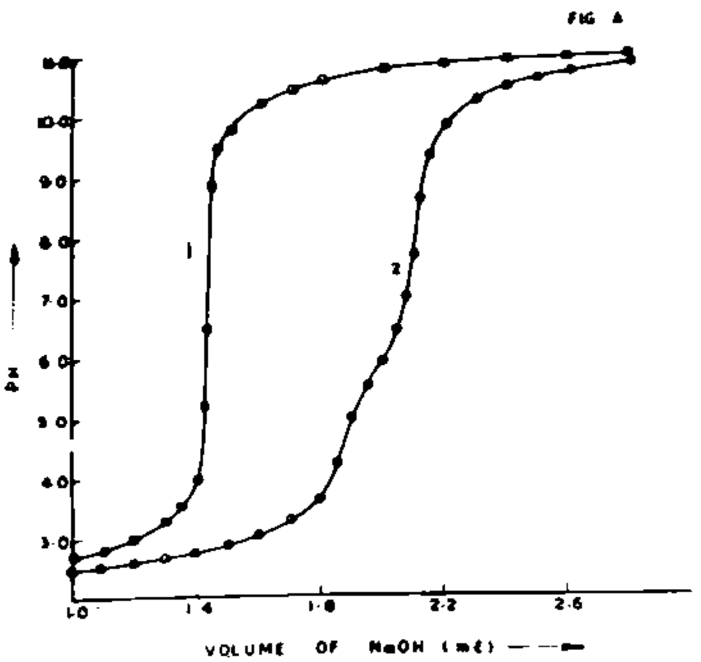


FIG B

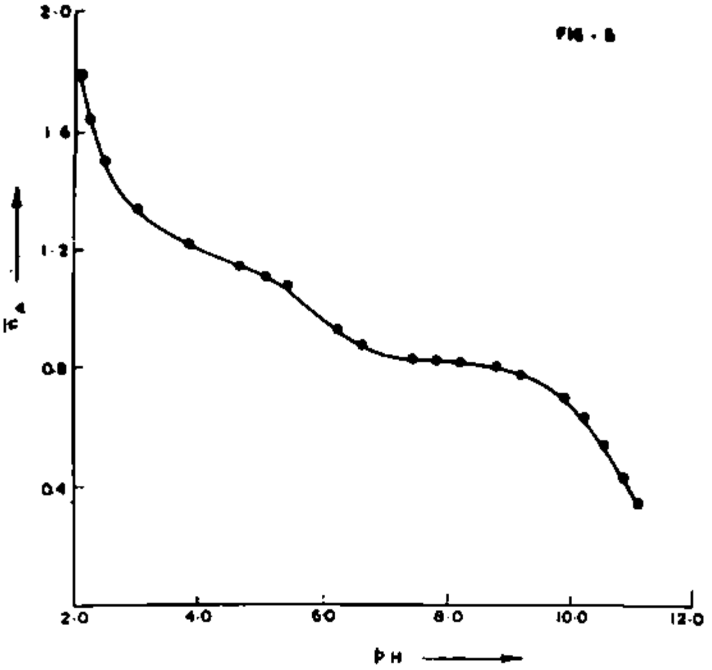


FIG C

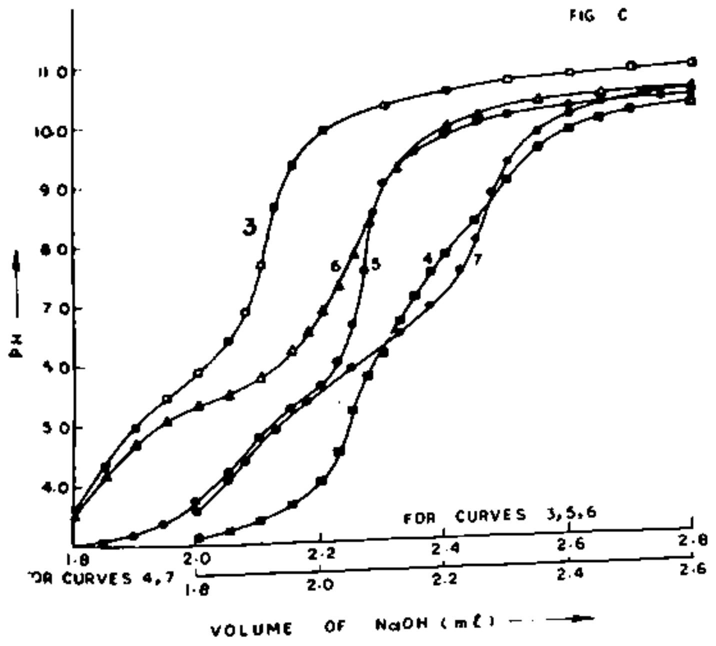


FIG D

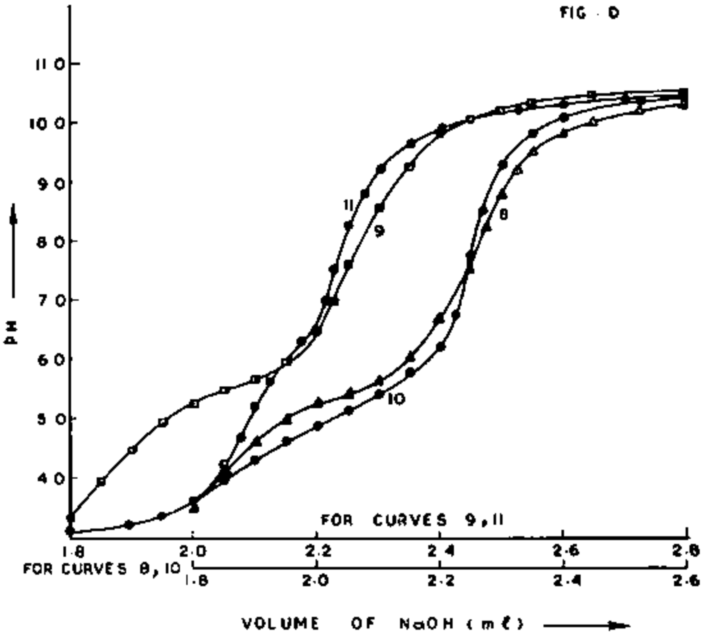


FIG E

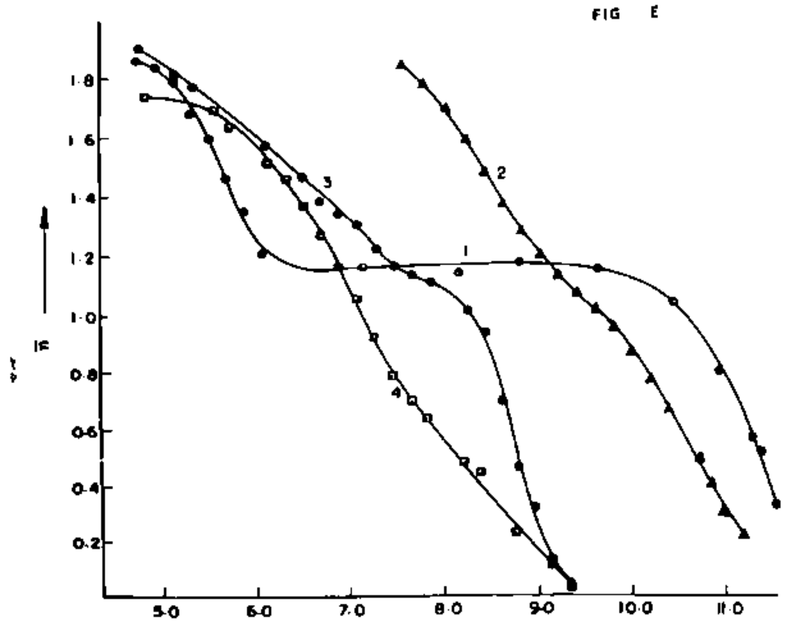


FIG F

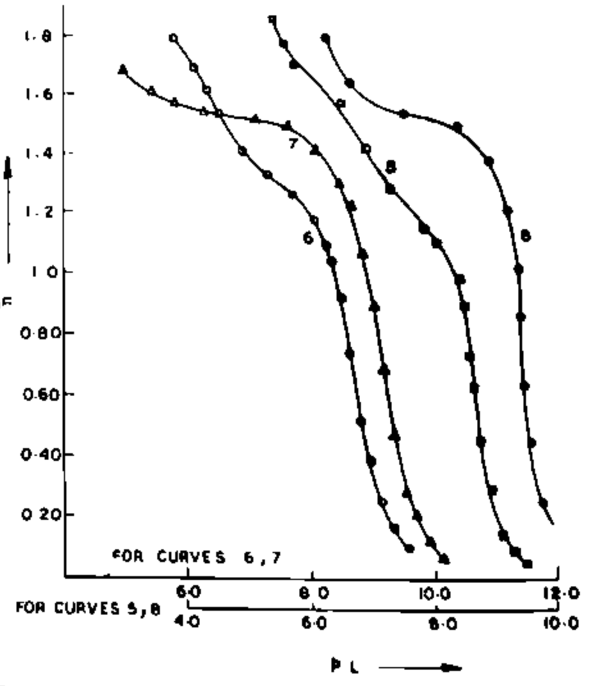


PLATE NO. 5

Table 3.12

Values of stability constants of Co-[illegible] chelate at various ionic strengths

Ionic strength	log	H	V	Mean
0.02	log K_1	8.98	8.99	
	log K_2	6.06	6.23	
	log K_c	15.04	15.22	15.13
0.05	log K_1	9.08	9.22	
	log K_2	6.26	6.38	
	log K_c	15.34	15.60	15.47
0.10	log K_1	9.11	9.17	
	log K_2	6.36	6.36	
	log K_c	15.47	15.53	15.50
0.15	log K_1	8.74	8.68	
	log K_2	6.78	6.72	
	log K_c	15.52	15.40	15.46
0.20	log K_1	8.83	8.89	
	log K_2	6.65	6.81	
	log K_c	15.48	15.70	15.59

Table 3.13

Values of stability constants of Be-ARS chelate at various ionic strengths

Ionic strength	$\log K_n$	H	V	M	Mean
0.02	$\log K_1$	10.07	10.04	10.12	
	$\log K_2$	5.50	-	5.60	
	$\log K_c$	15.57	-	15.72	15.64
0.05	$\log K_1$	10.18	10.21	10.21	
	$\log K_2$	6.23	-	6.30	
	$\log K_c$	16.41	-	16.51	16.46
0.10	$\log K_1$	10.11	10.10	10.13	
	$\log K_2$	6.44	-	6.48	
	$\log K_c$	16.55	-	16.61	16.58
0.15	$\log K_1$	9.67	9.70	9.72	
	$\log K_2$	7.00	-	6.99	
	$\log K_c$	16.67	-	16.71	16.69
0.20	$\log K_1$	9.34	9.41	9.42	
	$\log K_2$	7.68	-	7.80	
	$\log K_c$	17.02	-	17.22	17.12

Table 3.14

Values of stability constants of UO_2-ARS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	11.74	11.86	-	
	log K_2	5.20	-	-	
	log K_c	16.94	-	-	16.94
0.05	log K_1	11.89	-	-	
	log K_2	5.63	-	-	
	log K_c	17.52	-	-	17.52
0.10	log K_1	9.82	-	-	
	log K_2	7.85	-	-	
	log K_c	17.67	-	-	17.67
0.15	log K_1	9.80	10.02	-	
	log K_2	7.80	-	-	
	log K_c	17.60	-	-	17.60
0.20	log K_1	9.54	9.72	9.72	
	log K_2	8.40	-	8.30	
	log K_c	17.94	-	18.02	17.98

Thermodynamic Stability Constants

The thermodynamic stability constants were obtained by extrapolation of the stability constants to zero ionic strength (Plate 6). The values of log step stability constants at various ionic strengths were extrapolated to zero ionic strength to obtain the step thermodynamic stability. These values have been represented as log $K_1^{\mu=0}$ and log $K_2^{\mu=0}$. Their sum has been shown as calculated log $K_c^{\mu=0}$. The values of overall concentration stability constants K_c, at various ionic strengths, were likewise extrapolated to zero ionic strength . The overall thermodynamic stability constants thus obtained have been symbolised as experimental log $K_c^{\mu=0}$. The values of thermodynamic stability constants have been reported in Table 3.15.

Thermodynamic Functions

A thorough study of complex formation processes in solution requires the knowledge of some of the thermodynamic characteristics of the reactions studied viz., changes in enthalpy (ΔH), entropy (ΔS) and free energy of formation (ΔG). In order to have a reliable approach for an investigation of the nature of the forces acting within complex particles when they are formed in solution, it is necessary to know the energy changes in the reactions studied. Stability constants are related directly only to changes in free energy of formation (ΔG). However, one

Plate No. 6

Temperature = 30°C

Fig. 1 : Extrapolation of log K to zero ionic strength (Pb-ARS system)
A - log K_1; B - log K_2; C - log K_c

Fig. 2 : Extrapolation of log K to zero ionic strength (Cu-ARS system)
A - log K_1; B - log K_2; C - log K_c

Fig. 3 : Extrapolation of log K to zero ionic strength ([illegible]n-ARS system).
A - log K_1; B - log K_2; C - log K_c

Fig. 4 : Extrapolation of log K to zero ionic strength (Hg-ARS system).
A - log K_1, B - log K_2, C - log K_c

Fig. 5 : Extrapolation of log K to zero ionic strength (Ni-ARS system)
A - log K_1; B - log K_2; C - log K_c

Fig. 6 : Extrapolation of log K to zero ionic strength (Co-ARS system)
A - log K_1; B - log K_2; C - log K_c

Fig. 7 : Extrapolation of log K to zero ionic strength (Be-ARS system)
A - log K_1; B - log K_2; C - log K_c

Fig. 8 : Extrapolation of log K to zero ionic strength (UO_2-ARS system)
A - log K_1; B - log K_2; C - log K_c

FIG. 1

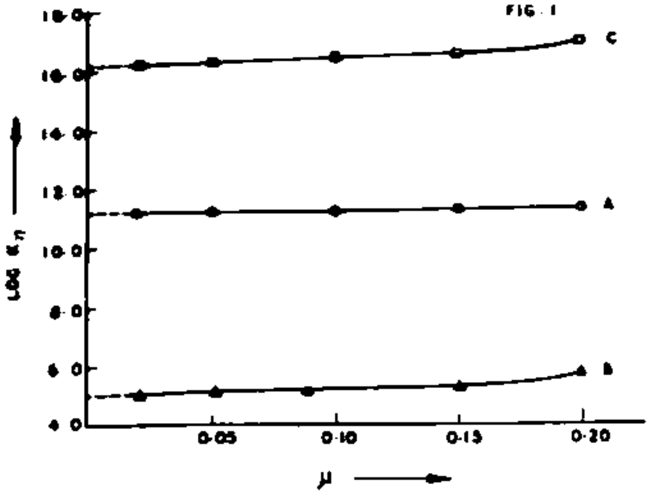


FIG. 2

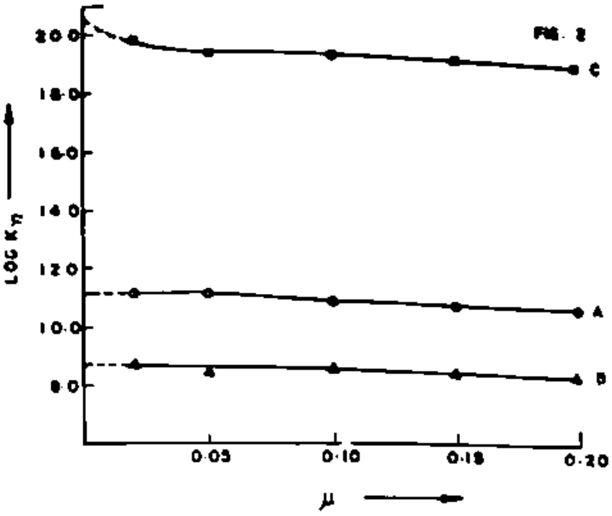


FIG. 3

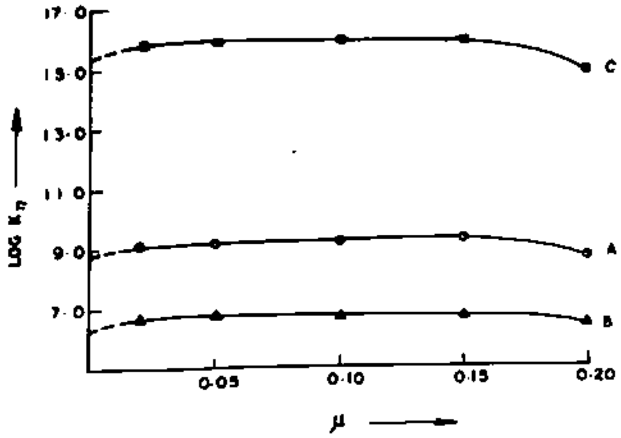


FIG. 4

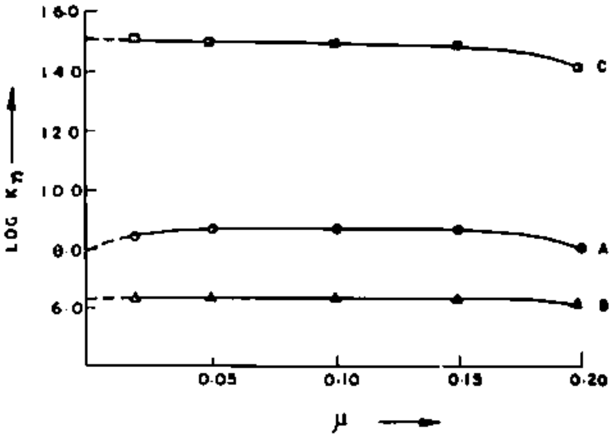


FIG. 5

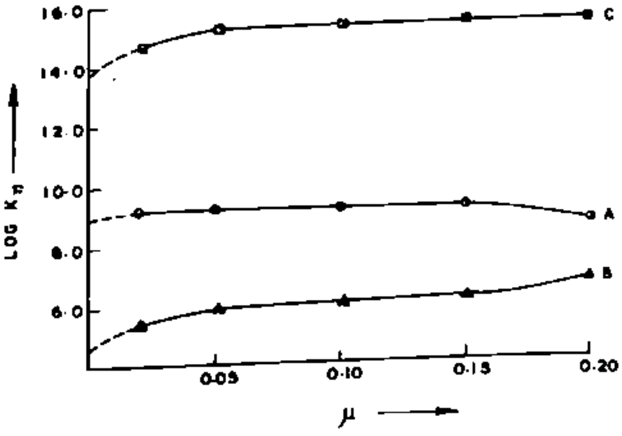


FIG. 6

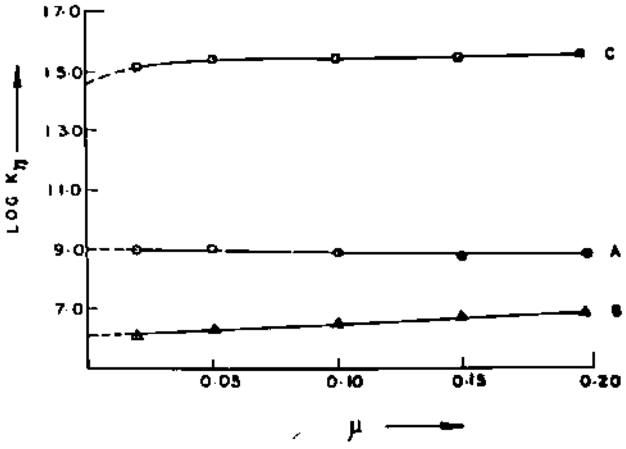


FIG. 7

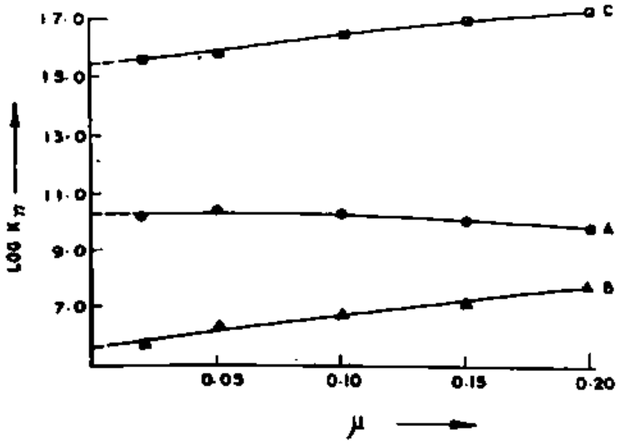


FIG. 8

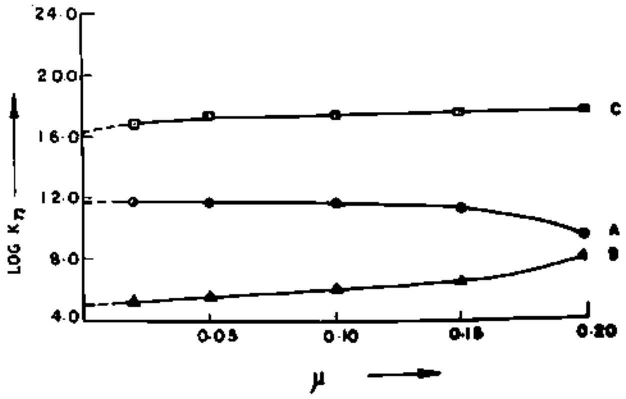


PLATE NO. 6

Table 3.15

Values of thermodynamic stability constants at 30°C

$\log K_n$	Pb^{2+}	Cu^{2+}	Zn^{2+}	Hg^{2+}	Ni^{2+}	Co^{2+}	Be^{2+}	UO_2^{2+}
$\log K_1^{\mu=0}$	11.11	10.80	8.61	8.38	9.33	8.96	10.12	12.05
$\log K_2^{\mu=0}$	5.01	9.55	6.43	6.90	5.27	5.99	5.36	4.81
$\log K_c^{\mu=0}$ (calc)	16.12	20.35	15.04	15.28	14.60	14.95	15.48	16.86
$\log K_c^{\mu=0}$ (exptl)	16.12	20.39	15.09	15.30	14.56	15.00	15.42	16.96

must know the changes in enthalpy during complex formation reactions (thermal effect) to calculate the changes in entropy during complex formation and the changes in stability of the complex particles with a temperature change to evaluate the bond energy and to study the complete reaction of complex formation.

A knowledge of the entropy changes during the reactions makes it possible to have a new approach to the evaluation of certain factors which determine the stability of complex compounds.

Whilst it is true that reliable data can be obtained for thermodynamic stability constants by the method of extrapolation (as described earlier) of the values obtained at different ionic strengths for the purpose of determination of thermodynamic functions, the method of extrapolation has not in many cases yielded reliable results. It was, therefore, thought proper to calculate the thermodynamic functions maintaining a constant ionic strength, which incidently eliminates the effect of variation in ionic strengths.

In the present studies the thermodynamic functions have been determined by keeping the ionic strength constant i.e. 0.10.

The stability constant is related to the change in Gibbs' free energy of formation (ΔG) at a particular ionic strength by the equation $\Delta G = - RT \ln K$.

In order to determine the changes in enthalpy and entropy, the stability constants were determined at various temperatures. As in earlier cases the Bjerrum-Calvin pH-titration technique as modified by Irving and Rossotti was employed to evaluate the stability constants. All the titrations were performed at five different temperatures, i.e., 10°, 20°, 30°, 40° and 50°C to get the thermodynamic functions.

The pH readings of the titrations were plotted against the volume of alkali added. The titration curves thus obtained at five different temperatures are graphically represented in Plates 7-10, A, C and D.

Proton-Ligand System

The $\bar{n}_A$ values were calculated at different pH values to get the formation curves of the proton-ligand systems at five temperatures. All the values are graphically represented in Figure B of Plates 7-10.

The proton-ligand formation curves obtained by plotting $\bar{n}_A$ vs pH were analysed by using various computational methods viz. interpolation at half $\bar{n}_A$ values, interpolation at various $\bar{n}_A$ values and mid-point slope method, to calculate the protonation constants of the ligand at different temperatures. The values obtained by different methods are in fair agreement.

Plate No. 7

Temperature = 10°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

B : Formation curve of proton-ARS system

C : Titration curves of ARS-metal chelates:

(3) Pb-ARS (4) Cu-ARS

(5) Zn-ARS (6) Hg-ARS

D : Titration curves of ARS metal chelates:

(7) Ni-ARS (8) Co-ARS

(9) Be-ARS (10) UO_2-ARS

E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

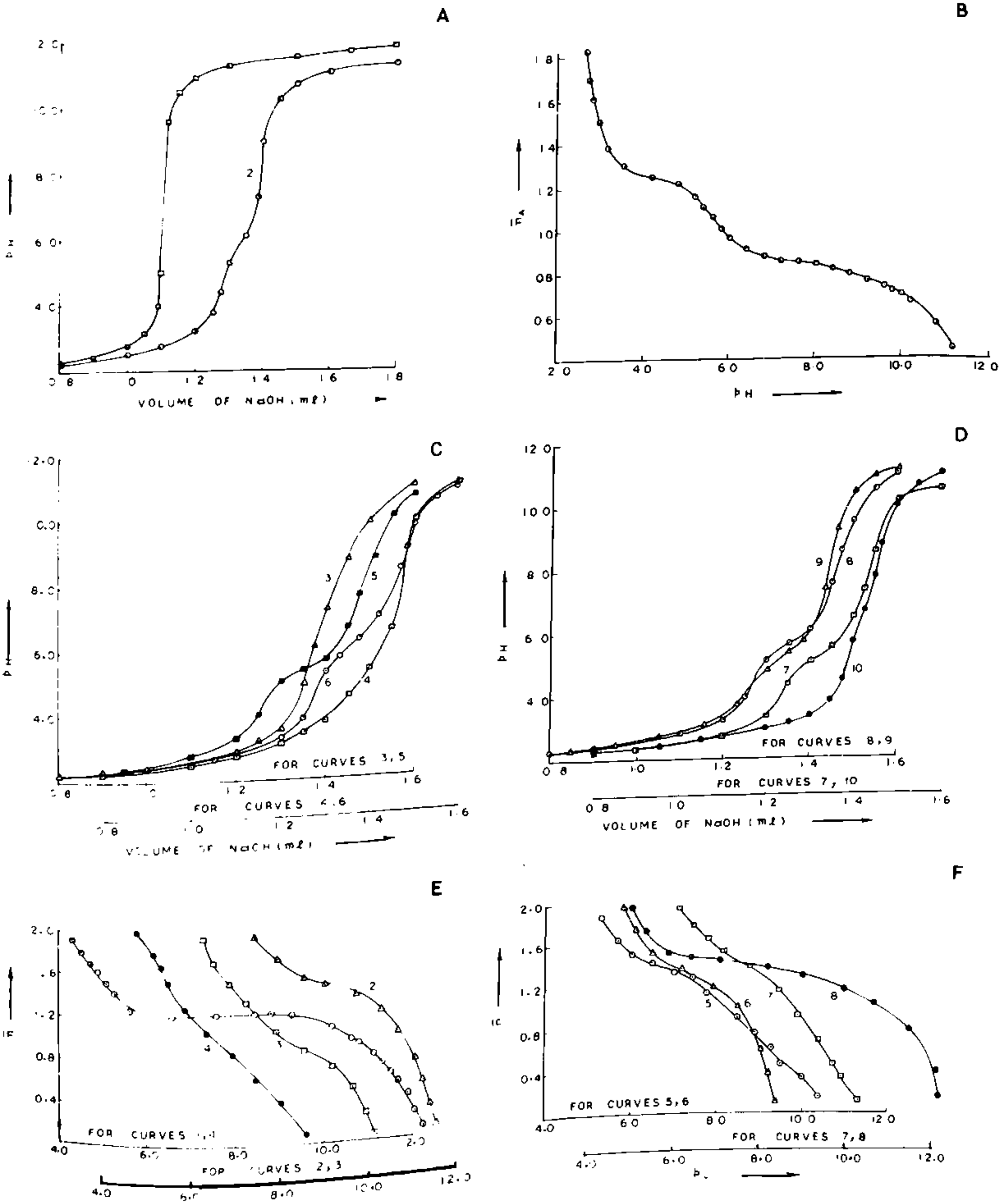

A
2.0
10.0
8.0
6.0
4.0
pH
2
0.8
1.0
1.2
1.4
1.6
1.8
VOLUME OF NaOH (ml)
B
1.8
1.6
1.4
1.2
1.0
0.8
0.6
n̄A
2.0
4.0
6.0
8.0
10.0
12.0
pH
C
12.0
10.0
8.0
6.0
4.0
pH
3
5
6
4
FOR CURVES 3,5
0.8
1.0
1.2
1.4
1.6
FOR CURVES 4,6
VOLUME OF NaOH (ml)
D
12.0
10.0
8.0
6.0
4.0
pH
9
8
7
10
FOR CURVES 8,9
0.8
1.0
1.2
1.4
1.6
FOR CURVES 7,10
VOLUME OF NaOH (ml)
E
2.0
1.6
1.2
0.8
0.4
n̄
1
2
3
4
FOR CURVES 1,4
4.0
6.0
8.0
10.0
12.0
FOR CURVES 2,3
pH
F
2.0
1.6
1.2
0.8
0.4
n̄
5
6
7
8
FOR CURVES 5,6
4.0
6.0
8.0
10.0
12.0
FOR CURVES 7,8
pH

PLATE NO. 7

The Gibbs' free energy of formation (ΔG) was calculated by using the equation $\Delta G = - RT \ln K$. The enthalpy change (ΔH) was calculated either by the slope of the curve obtained by plotting log K vs 1/T or by using the equation (2.23). Assuming ΔH to be constant over the experimental temperature range (10-50°C) the change in entropy (ΔS) was calculated by using the equation (2.25). The average values of the proton-ligand stability constants with their thermodynamic functions are reported in Table 3.16.

Table 3.16

Values of proton-ligand stability constants and thermodynamic functions

$\Delta H_1 = - 6.694$

$\Delta H_2 = - 1.218$

$\Delta H = - 8.204$

(Kcal/mole)

Temperature (°C)	10	20	30	40	50
log K_1	10.98	10.92	10.88	10.50	10.30
log K_2	3.01	2.95	2.63	2.90	2.85
log K_c	13.91	13.75	13.51	13.40	13.15
$-\Delta G_1$	14.22	14.64	15.09	15.04	15.23
$-\Delta G_2$	3.90	3.96	3.65	4.15	4.21
$-\Delta G$ (Kcal/mole)	18.02	18.44	18.74	19.20	19.44

(Contd.)

Table 3.16 (Contd.)

Temperature (^{o}C)	10	20	30	40	50
ΔS_1	26.54	27.10	27.70	26.65	26.40
ΔS_2	9.47	9.34	8.01	9.38	9.27
ΔS (e.u.)	34.66	34.92	34.77	35.12	34.71

Metal-Ligand System

The values of $\bar{n}$ were calculated at different pH values from the equation mentioned earlier and then the corresponding values of pL were computed from this data. The values of $\bar{n}$ were plotted against the corresponding pL values to get the formation curves of metal complexation equilibria and are graphically represented in Plates 7-10, E and F.

Various computational methods were applied to analyse these formation curves i.e. interpolation at half $\bar{n}$ values (H), interpolation at various $\bar{n}$ values (V) and mid-point slope method (M) to calculate the stepwise metal-ligand stability constant. The average values of stability constants with various thermodynamic functions i.e. ΔG, ΔH and ΔS are reported in Table 3.17-3.24. The values of stability constants obtained by different methods are in fair agreement.

Plate No. 8

Temperature = 20°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

B : Formation curve of proton-ARS system.

C : Titration curves of ARS metal chelates:

(3) Pb-ARS (4) Cu-ARS

(5) Zn-ARS (6) Hg-ARS

D : Titration curves of ARS metal chelates:

(7) Ni-ARS (8) Co-ARS

(9) Be-ARS (10) UO_2-ARS

E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

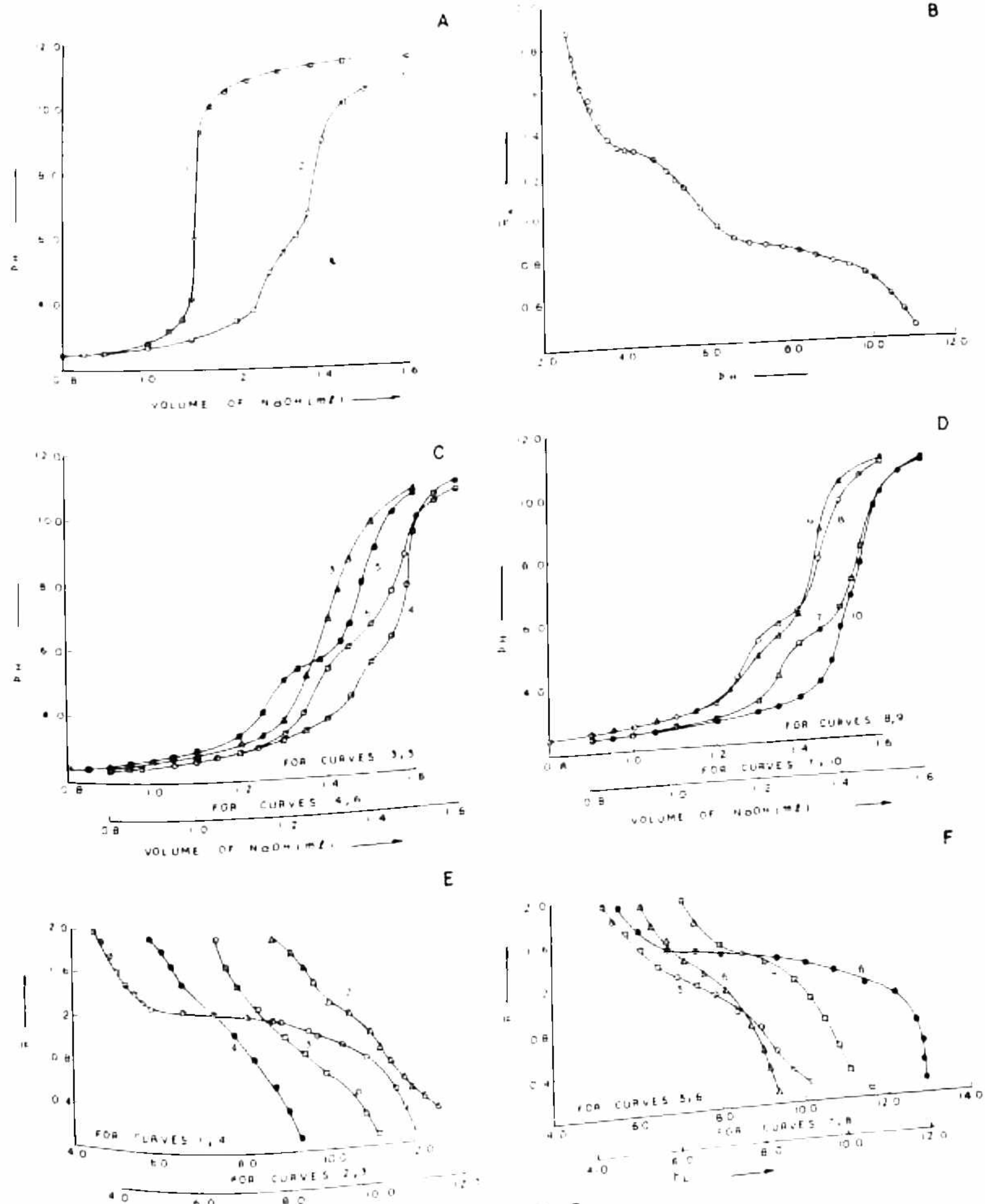

A
pH
12.0
10.0
8.0
6.0
4.0
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH(ml) →
1
2
B
1.6
1.4
1.2
1.0
0.8
0.6
n̄
2.0
4.0
6.0
8.0
10.0
12.0
pH
C
pH
12.0
10.0
8.0
6.0
4.0
3
5
4
6
FOR CURVES 3,5
FOR CURVES 4,6
VOLUME OF NaOH(ml) →
D
pH
12.0
10.0
8.0
6.0
4.0
9
8
7
10
FOR CURVES 8,9
FOR CURVES 7,10
VOLUME OF NaOH(ml) →
E
n
2.0
1.6
1.2
0.8
0.4
1
2
3
4
FOR CURVES 1,4
4.0
6.0
8.0
10.0
12.0
FOR CURVES 2,3
PL →
F
n
2.0
1.6
1.2
0.8
0.4
5
6
7
8
FOR CURVES 5,6
4.0
6.0
8.0
10.0
12.0
14.0
FOR CURVES 7,8
PL →

PLATE NO. 8

Table 3.17

Values of stability constants and thermodynamic functions of Pb(II)-ARS system

$\Delta H_1 = -8.706$

$\Delta H_2 = 4.485$

$\Delta H = -4.240$
(Kcal/mole)

Temperature (°C)	10	20	30	40	50
log K_1	11.67	11.40	11.20	11.01	10.82
log K_2	4.95	5.18	5.25	5.32	5.41
log K_c	16.62	16.58	16.45	16.33	16.23
$-\Delta G_1$	15.12	15.29	15.53	15.77	15.99
$-\Delta G_2$	6.41	6.95	7.28	7.62	8.00
$-\Delta G$ (Kcal/mole)	21.53	22.24	22.81	23.19	23.98
ΔS_1	22.67	22.47	22.53	22.57	22.55
ΔS_2	38.49	39.01	38.76	38.67	38.61
ΔS (e.u.)	61.08	61.44	61.23	60.56	61.12

Table 3.18

Values of stability constants and thermodynamic functions of Cu(II)-ARS system

$\Delta H_1 = - 5.017$

$\Delta H_2 = - 6.972$

$\Delta H = - 12.640$

(Kcal/mole)

Temperature (^{o}C)	10	20	30	40	50
$\log K_1$	11.23	11.02	10.90	10.82	10.73
$\log K_2$	8.61	8.47	8.38	8.14	7.96
$\log K_c$	19.84	19.50	19.20	18.96	18.69
$-\Delta G_1$	14.54	14.79	15.11	15.50	15.86
$-\Delta G_2$	11.15	11.36	11.62	11.66	11.77
$-\Delta G$ (Kcal/mole)	25.70	26.15	26.73	27.16	27.64
ΔS_1	33.73	32.64	33.27	34.57	33.55
ΔS_2	14.75	14.96	15.33	14.94	14.85
ΔS (e.u.)	42.58	48.57	46.46	46.36	46.40

Table 3.19

Values of stability constants and thermodynamic functions of Zn(II)-ARS system

$\Delta H_1 = -7.185$

$\Delta H_2 = -2.821$

$\Delta H = -10.590$
(Kcal/mole)

Temperature (°C)	10	20	30	40	50
log K_1	9.61	9.52	9.30	9.12	8.93
log K_2	6.84	6.78	6.70	6.64	6.57
log K_c	16.45	16.30	16.00	15.76	15.50
$-\Delta G_1$	12.45	12.76	12.90	13.06	13.20
$-\Delta G_2$	8.86	9.09	9.29	9.51	9.71
$-\Delta G$ (Kcal/mole)	21.31	21.85	22.19	22.57	22.91
ΔS_1	18.59	19.01	18.85	18.76	18.61
ΔS_2	21.32	21.39	21.34	21.35	21.32
ΔS (e.u.)	37.82	38.42	38.26	38.12	38.15

Table 3.20

Values of stability constants and thermodynamic functions of Hg(II)-ARS system

$\Delta H_1 = -3.219$

$\Delta H_2 = -2.215$

$\Delta H = -5.223$

(Kcal/mole)

Temperature (°C)	10	20	30	40	50
log K_1	8.78	8.69	8.60	8.51	8.48
log K_2	6.43	6.35	6.30	6.26	6.21
log K_c	15.21	15.04	14.90	14.77	14.69
$-\Delta G_1$	11.37	11.65	11.92	12.17	12.54
$-\Delta G_2$	8.33	8.52	8.74	8.97	9.18
$-\Delta G$ (Kcal/mole)	19.70	20.17	20.66	21.14	21.72
ΔS_1	28.78	28.76	28.69	28.26	28.83
ΔS_2	21.59	21.49	21.51	21.57	21.24
ΔS (e.u.)	51.13	50.99	50.95	50.67	51.05

Plate No. 9

Temperature = 40°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

B : Formation curve of proton-ARS system

C : Titration curves of ARS metal chelates:

(3) Pb-ARS (4) Cu-ARS

(5) Zn-ARS (6) Hg-ARS

D : Titration curves of ARS metal chelates:

(7) Ni-ARS (8) Co-ARS

(9) Be-ARS (10) UO_2-ARS

E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS

(7) Be-ARS (8) UO_2-ARS

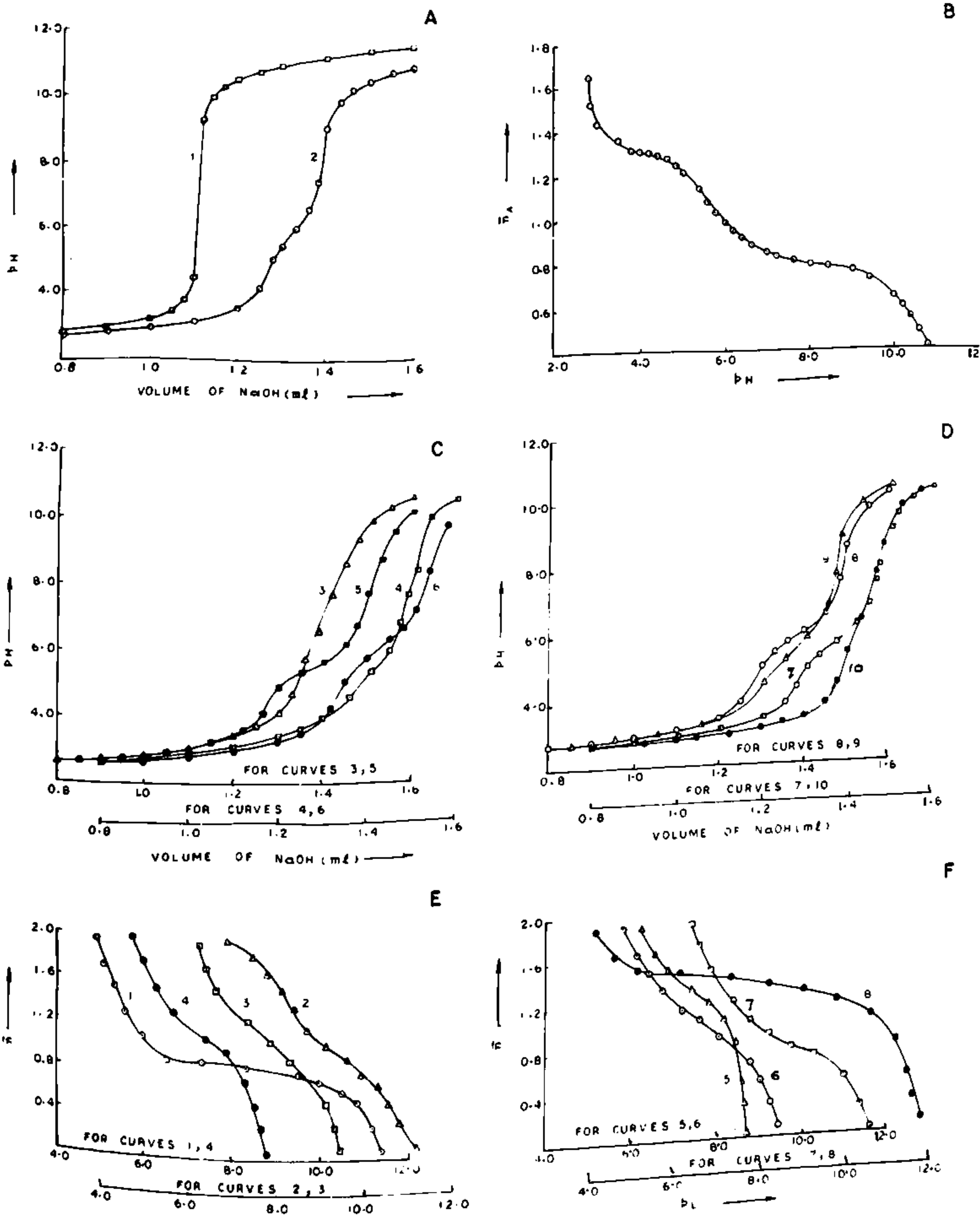

A
pH
VOLUME OF NaOH (mℓ)
1
2
12.0
10.0
8.0
6.0
4.0
0.8
1.0
1.2
1.4
1.6
B
$\bar{n}_A$
pH
1.8
1.6
1.4
1.2
1.0
0.8
0.6
2.0
4.0
6.0
8.0
10.0
12.0
C
pH
3
5
4
6
FOR CURVES 3, 5
FOR CURVES 4, 6
VOLUME OF NaOH (mℓ)
D
pH
9
8
7
10
FOR CURVES 8, 9
FOR CURVES 7, 10
VOLUME OF NaOH (mℓ)
E
$\bar{n}$
1
4
3
2
FOR CURVES 1, 4
FOR CURVES 2, 3
p_L
2.0
1.6
1.2
0.8
0.4
F
$\bar{n}$
8
7
6
5
FOR CURVES 5, 6
FOR CURVES 7, 8
p_L

PLATE NO. 9

Table 3.21

Values of stability constants and thermodynamic functions of Ni(II)-ARS system

$\Delta H_1 = -8.071$

$\Delta H_2 = +3.634$

$\Delta H = -4.448$

(Kcal/mole)

Temperature (°C)	10	20	30	40	50
$\log K_1$	9.58	9.43	9.30	9.02	8.81
$\log K_2$	5.97	6.02	6.10	6.22	6.31
$\log K_c$	15.55	15.45	15.40	15.24	15.12
$-\Delta G_1$	12.41	12.65	12.90	12.92	13.02
$-\Delta G_2$	7.73	8.07	8.46	8.91	9.33
$-\Delta G$ (Kcal/mole)	20.14	20.72	21.36	21.83	22.35
ΔS_1	15.30	15.63	15.92	15.48	15.70
ΔS_2	40.15	39.95	39.91	40.04	40.11
ΔS (e.u.)	55.40	55.49	55.75	55.49	55.42

Table 3.22

Values of stability constants and thermodynamic functions of Co-ARC system

$\Delta H_1 = -\ 7.066$

$\Delta H_2 = \ 3.703$

$\Delta H = -\ 3.357$

(Kcal/mole)

Temperature (^{o}C)	10	20	30	40	50
log K_1	9.18	9.02	8.90	8.73	8.48
log K_2	6.51	6.61	6.70	6.78	6.87
log K_c	15.69	15.63	15.60	15.51	15.35
$-\Delta G_1$	11.90	12.10	12.34	12.50	12.54
$-\Delta G_2$	8.43	8.86	9.29	9.71	10.16
$-\Delta G$ (Kcal/mole)	20.33	20.96	21.63	22.21	22.70
ΔS_1	17.07	17.17	17.30	17.35	16.93
ΔS_2	42.86	42.80	42.85	42.81	42.88
ΔS (e.u.)	60.01	60.02	60.26	60.23	59.84

Plate No. 10

Temperature = 50°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + ARS

B : Formation curve of proton-ARS system

C : Titration curves of ARS metal chelates:

(3) Pb-ARS (4) Cu-ARS

(5) Zn-ARS (6) Hg-ARS

D : Titration curves of ARS metal chelates:

(7) Ni-ARS (8) Co-ARS

(9) Be-ARS (10) UO_2-ARS

E : Formation curves of ARS metal chelates:

(1) Pb-ARS (2) Cu-ARS

(3) Zn-ARS (4) Hg-ARS

F : Formation curves of ARS metal chelates:

(5) Ni-ARS (6) Co-ARS (7) Be-ARS

(8) UO_2-ARS

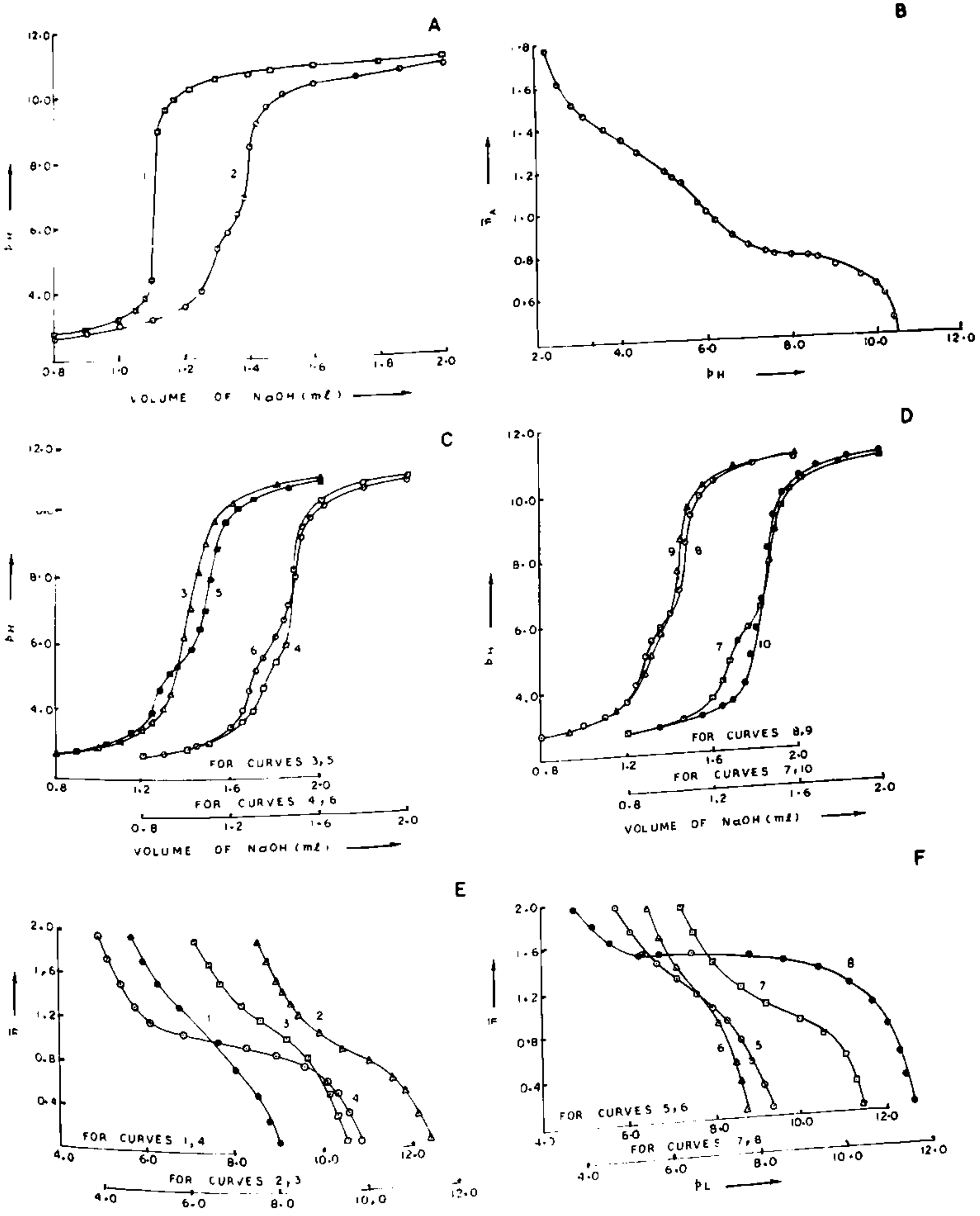

A
12.0
10.0
8.0
6.0
4.0
pH
1
2
0.8
1.0
1.2
1.4
1.6
1.8
2.0
VOLUME OF NaOH (ml)
B
1.8
1.6
1.4
1.2
1.0
0.8
0.6
n̄A
2.0
4.0
6.0
8.0
10.0
12.0
pH
C
12.0
10.0
8.0
6.0
4.0
pH
3
5
6
4
0.8
1.2
1.6
2.0
FOR CURVES 3, 5
FOR CURVES 4, 6
0.8
1.2
1.6
2.0
VOLUME OF NaOH (ml)
D
12.0
10.0
8.0
6.0
4.0
pH
9
8
7
10
FOR CURVES 8, 9
0.8
1.2
1.6
2.0
FOR CURVES 7, 10
0.8
1.2
1.6
2.0
VOLUME OF NaOH (ml)
E
2.0
1.6
1.2
0.8
0.4
n̄
1
3
2
4
FOR CURVES 1, 4
4.0
6.0
8.0
10.0
12.0
FOR CURVES 2, 3
4.0
6.0
8.0
10.0
12.0
pL
F
2.0
1.6
1.2
0.8
0.4
n̄
8
7
6
5
FOR CURVES 5, 6
4.0
6.0
8.0
10.0
12.0
FOR CURVES 7, 8
4.0
6.0
8.0
10.0
12.0
pL

PLATE NO. 10

Table 3.23

Values of stability constants and thermodynamic functions of Be-ARS system

ΔH_1 = 5.283

ΔH_2 = -3.548

ΔH = 1.752
(Kcal/mole)

Temperature ($^{\circ}$C)	10	20	30	40	50
log K_1	9.61	9.77	9.90	10.00	10.13
log K_2	7.06	6.92	6.82	6.77	6.71
log K_c	16.67	16.69	16.72	16.77	16.84
$-\Delta G_1$	12.45	13.10	13.73	14.32	14.97
$-\Delta G_2$	9.14	9.28	9.46	9.70	9.92
$-\Delta G$ (Kcal/mole)	21.59	22.38	23.19	24.02	24.89
ΔS_1	62.61	62.69	62.70	62.59	62.66
ΔS_2	19.75	19.55	19.49	19.64	19.71
ΔS (e.u.)	82.12	82.31	82.22	82.28	82.45

Plate No. 11

Ionic strength = 0.10

A : Variation of log K with 1/T (Pb-ARS system)
A - log K_1; B - log K_2; C - log K_c

B : Variation of log K with 1/T (Cu-ARS system)
A - log K_1; B - log K_2; C - log K_c

C : Variation of log K with 1/T (Zn-ARS system)
A - log K_1; B - log K_2; C - log K_c

D : Variation of log K with 1/T (Hg-ARS system)
A - log K_1; B - log K_2; C - log K_c

E : Variation of log K with 1/T (Ni-ARS system)
A - log K_1; B - log K_2; C - log K_c

F : Variation of log K with 1/T (Co-ARS system)
A - log K_1; B - log K_2; C - log K_c

G : Variation of log K with 1/T (Be-ARS system)
A - log K_1; B - log K_2; C - log K_c

H : Variation of log K with 1/T (UO_2-ARS system)
A - log K_1; B - log K_2; C - log K_c

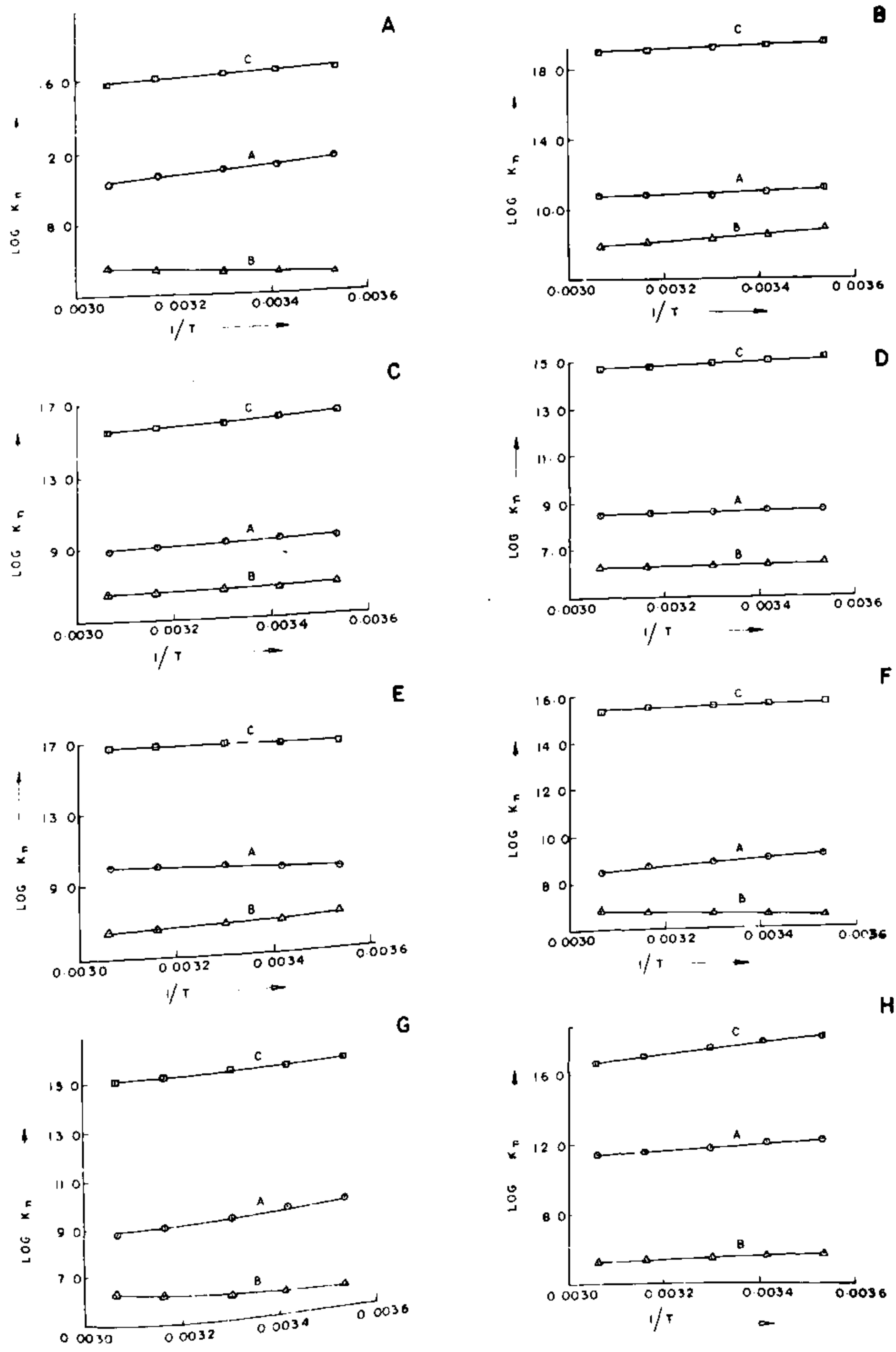

A
C
A
B
.6 0
2 0
8 0
LOG Kn
0 0030
0 0032
0.0034
0.0036
1/T
B
C
A
B
18 0
14 0
10.0
LOG Kn
0.0030
0 0032
0.0034
0 0036
1/T
C
C
A
B
17 0
13 0
9 0
LOG Kn
0.0030
0 0032
0.0034
0.0036
1/T
D
C
A
B
15 0
13 0
11.0
9 0
7 0
LOG Kn
0.0030
0.0032
0 0034
0 0036
1/T
E
C
A
B
17 0
13 0
9 0
LOG Kn
0.0030
0 0032
0 0034
0.0036
1/T
F
C
A
B
16.0
14 0
12 0
10 0
8 0
LOG Kn
0 0030
0 0032
0 0034
0.0036
1/T
G
C
A
B
15 0
13 0
11 0
9 0
7 0
LOG Kn
0 0030
0 0032
0 0034
0 0036
1/T
H
C
A
B
16 0
12 0
8 0
LOG Kn
0 0030
0 0032
0.0034
0.0036
1/T

PLATE NO. II

Table 3.24

Values of stability constants and thermodynamic functions of UO_2(II)-ARS system

$\Delta H_1 = -\ 7.498$

$\Delta H_2 = -\ 5.503$

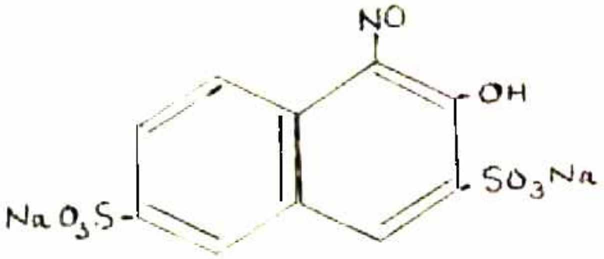
$\Delta H\ = -12.480$
(Kcal/mole)

Temperature (^{o}C)	10	20	30	40	50
log K_1	12.08	11.95	11.80	11.50	11.30
log K_2	5.82	5.71	5.60	5.41	5.32
log K_c	17.90	17.66	17.40	16.91	16.62
$-\Delta G_1$	15.64	16.03	16.36	16.47	16.70
$-\Delta G_2$	7.54	7.60	7.77	7.75	7.86
$-\Delta G$ (Kcal/mole)	23.18	23.69	24.13	24.22	24.56
ΔS_1	28.75	29.09	29.22	28.65	28.47
ΔS_2	7.19	7.35	7.46	7.17	7.31
ΔS (e.u.)	37.82	38.23	38.43	37.53	37.57

PART II

METAL CHELATES OF NITROSO-R-SALT

The excellent chromogenic property of nitrosonaphthols for metal ions is well known. This is due to the presence of a nitroso group adjacent to the phenolic group in the molecule, which imparts the properties of a bidentate ligand to this class of compounds. Thus 1-nitroso-2-naphthol and 2-nitroso-1-naphthol are well known spot and colorimetric reagents. The introduction of sulphonate groups into the molecule enhances the properties of nitrosonaphthols as chromogenic ligands. Nitroso-R-salt, which is the sulphonated form of 1-nitroso-2-naphthol has excellent chelating properties. This compound is commonly known as Nitroso-R-salt (abbreviated as NRS) and its structure may be represented as:



Van Klooster (10) noted the colour reaction of NRS with cobalt and since then the formation of Co-NRS chelate has been studied in detail by various workers. Classein and Westerveld (11) and Willard and Kaufmann (12) made extensive studies on the interaction between Co^{2+} and NRS and studied the characteristics of the coloured complex. Komar and coworkers (13,14) obtained interesting results on the complex and found a composition of 1:3 (Co:NRS) with an instability constant of 7×10^{-35} in a citrate phosphate buffer. The analytical application of the formation of the coloured Co^{2+} complex was made use in the spectrophotometric determination of Co^{2+} by several workers. Volkova and Pakhomova (15) reported the photometric determination of cobalt in an iron ore using Nitroso-R-salt as a reagent.

Besides cobalt, several other metal ions have also been found to form coloured complexes with Nitroso-R-salt. The Cu^{2+} complex of NRS was also studied (16) and Anger and Ofri (17) studied the spot reactions of NRS. Ropars and Viovy (18) made a detailed study of the copper-complex and postulated the structure of the complex based on computed calculation of the spectra.

The iron complex of NRS has received considerable attention. Oka and Miyamoto (19) studied the dissociation constants of NRS and the stability of the iron complex. They (20,21) also described the spectrophotometric determination of Fe(II) with NRS. Yoshinaga and Masatoshi (22) described the determination of traces of iron using NRS as photometric reagent above a pH of 7.2, where a green complex is formed. Quast (23) made a comparative study of various colorimetric reagents for iron and found NRS to be the most sensitive reagent for the spectrophotometric determination of iron. NRS was employed by Ness and Dickerson (24) for the determination of iron in serum. Tolmachev and Barkhinskii (25) used the NRS procedure for the determination of iron in nickel based stainless steel.

Nageswara Rao and Raghava Rao (26) noted that uranium forms a red coloured complex with NRS and the complex may be extracted with chloroform. Spectrophotometric studies of the NRS and the photometric determination of thorium by NRS have been reported (27).

NRS forms coloured complexes with many platinum metals. Dey et al. (28,29) in connection with their studies on the chromogenic reactions of platinum metals studied the colour reactions of Pd(II), Ru(III), Rh(III), Os(III) and Os(VIII) with NRS. Banerji and Garg (30) have reported the formation of a chelate with Pd(II). Dey et al. (31) made a detailed study of the composition of Pd(II)-NRS chelates. The red coloured complex between Pd(II) and NRS was also investigated by Shamir and Schwartz (32), who described the determination of Pd(II) with NRS. Nath and Agarwal (33) have reported the determination of several platinum metals with NRS.

In addition to the study of the coloured complexes and their analytical applications, NRS has also been subjected to several other types of studies. Goldschmeid and Lucena (34) studied the reduction of NRS at the dropping mercury electrode and reported its half wave potential. Podolenko, Chikrryzova and Lyalikov (35) reduced NRS colorimetrically to ammine and found the reduction to be a 4-electron process. Rudolph and Furman (36) reported that NRS could be determined by reduction with chromous chloride.

From the foregoing account, it may be seen that the work on NRS complexes, so far reported in literature is mainly concerned with spectrophotometric studies on coloured metal complexes. Obviously, it has been so, in attempts to evolve suitable methods for the spectrophotometric determination of metals, by exploiting the chromogenic properties of the ligand. Attention however does not seem to have been paid to a rigorous treatment of the equilibria in these metal-NRS complexation reactions, which is of great importance in such studies.

The first systematic study of the stepwise formation of metal-NRS complexes was done by Banerjee and Dey (37). They carried out a study of the proton-ligand and metal-ligand stability constants of NRS complexes of thorium and uranium by the Bjerrum-Calvin pH-titration technique. These authors, however, worked at an ionic strength of 0.1M $NaClO_4$ and did not evaluate the thermodynamic constants. Mandal and Dey (38) studied the Ti(IV), Zr(IV) and Hf(IV) complexes of NRS in media of different ionic strengths but they did not look into the effect of temperature and determination of thermodynamic functions.

In the present work NRS chelates of lead(II), copper (II), zinc (II), cadmium (II), mercury (II), nickel (II), cobalt (II), beryllium (II) and uranyl (II) have been studied in detail. Studies have been carried out in media of varying ionic strengths viz. 0.02, 0.05, 0.10, 0.15 and 0.20 using $NaClO_4$ for maintaining constancy of the ionic strength. The various thermodynamic functions i.e. ΔG, ΔH and ΔS were also calculated by determining the stability constants at five different temperatures viz. 10°, 20°, 30°, 40° and 50°C by keeping the ionic strength constant i.e. 0.10.

The experimental details are same as in the case of metal chelates of ARS and have been described, in detail in Chapter II. An aqueous solution of NRS (E. Merck G.R.) was used for these studies.

RESULTS

Protonation Constants

NRS is a weak acid due to the presence of a phenolic group. The dissociation constant K_H of NRS (which is written here as HNRS) is given by:

$$K_H = \frac{C_{NRS} \cdot C_H}{C_{HNRS}}$$

The formation curves of the proton-ligand system were inverted-S shaped and were extended between 0 and 1 in the $\bar{n}_A$ scale (Plate 12B-16B) showing that only one dissociation was possible in this case. The values of $\bar{n}_A$ were calculated at various pH values to get the formation curves of the proton-ligand systems at various ionic strengths. The values only at one ionic strengths are recorded in Table 3.25, in order to reduce the bulk of the thesis.

Table 3.25

$T_L = 0.005$ $N^o = 0.1838$

$V^o = 100.00$ $Y = 1.0$

$\mu = 0.10$ Figure - Plate 14,B

S. No.	pH	v'	v"	$\bar{n}_A$
1.	3.8	2.538	2.545	0.9961
2.	4.0	2.561	2.571	0.9945
3.	4.2	2.580	2.590	0.9945
4.	4.4	2.590	2.600	0.9945
5.	4.6	2.599	2.609	0.9945
6.	4.8	2.601	2.617	0.9912
7.	5.0	2.606	2.622	0.9912

(contd.)

Table 3.25 (Contd.)

S. No.	pH	v'	v"	$\bar{n}_A$
8.	5.2	2.609	2.634	0.9862
9.	5.4	2.611	2.645	0.9813
10.	5.6	2.612	2.662	0.9725
11.	5.8	2.615	2.690	0.9588
12.	6.0	2.618	2.724	0.9419
13.	6.2	2.619	2.773	0.9155
14.	6.4	2.620	2.842	0.8783
15.	6.6	2.620	2.949	0.8196
16.	6.8	2.620	3.070	0.7533
17.	7.0	2.621	3.247	0.6569
18.	7.2	2.621	3.410	0.5675
19.	7.4	2.621	3.560	0.4853
20.	7.6	2.622	3.600	0.4311
21.	7.8	2.622	3.731	0.3921
22.	8.0	2.622	3.800	0.3543
23.	8.2	2.625	3.835	0.3368
24.	8.4	2.629	3.870	0.3198
25.	8.6	2.630	3.890	0.3094
26.	8.8	2.634	3.901	0.3056
27.	9.0	2.639	3.915	0.3007
28.	9.2	2.647	2.938	0.2926
29.	9.4	2.657	3.951	0.2910
30.	9.6	2.668	3.971	0.2861
31.	9.8	2.680	3.991	0.2818

(Contd.)

Plate No. 12

Temperature = 30°C

Ionic strength = 0.02

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

Fig. B : Formation curve of proton-NRS system

Fig. C : Titration curves of NRS metal chelates:

(3) NRS only (4) Pb-NRS (5) Cu-NRS

(6) Zn-NRS (7) Cd-NRS

Fig. D : Titration curves of NRS metal chelates:

(8) Hg-NRS (9) Ni-NRS (10) Co-NRS

(11) Be-NRS (12) UO_2-NRS

Fig. E : Formation curves of NRS metal chelates

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

Fig. F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

FIG A

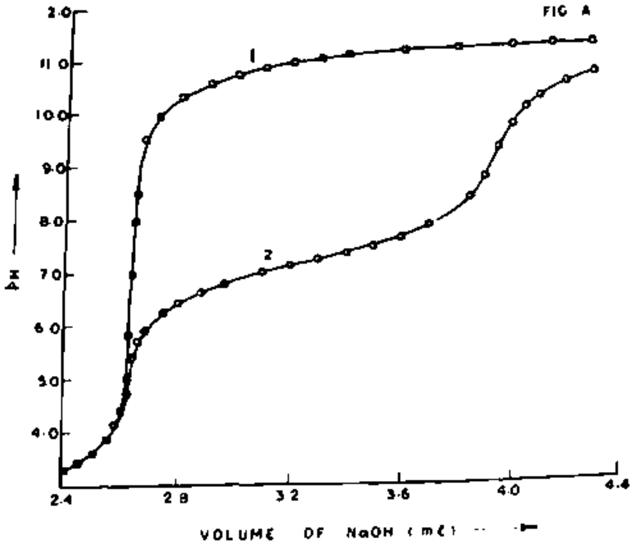


FIG. B

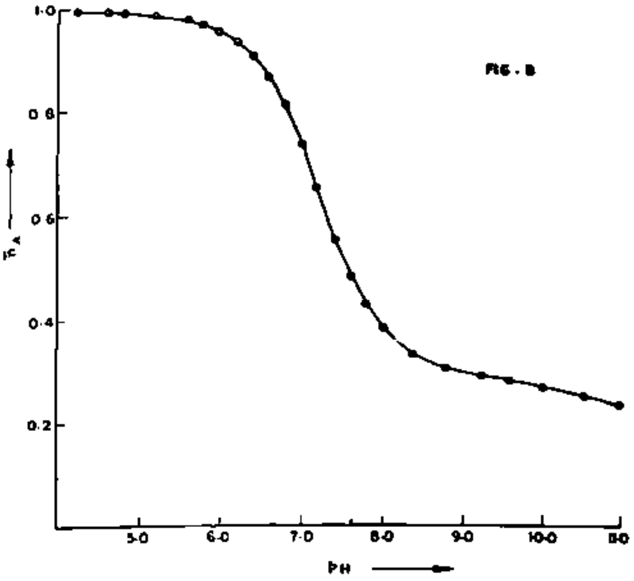


FIG C

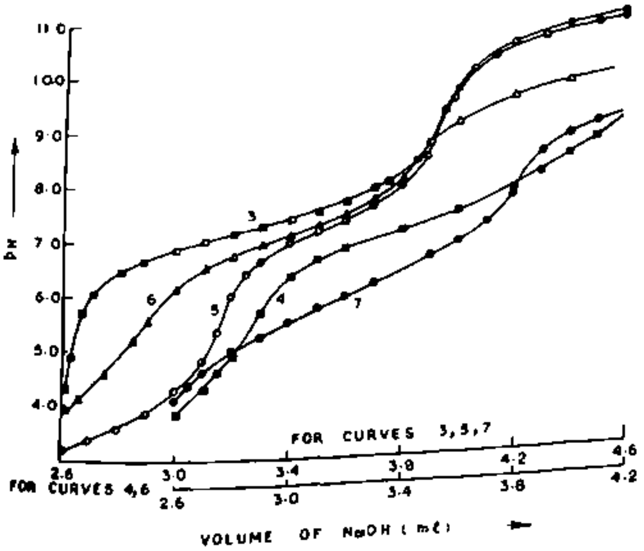


FIG. D

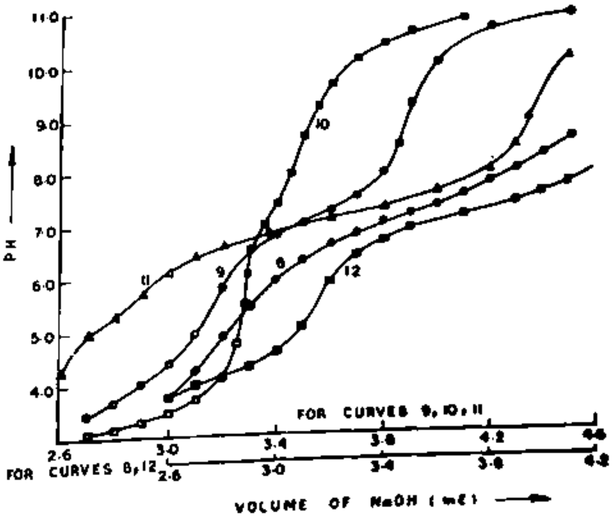


FIG. E

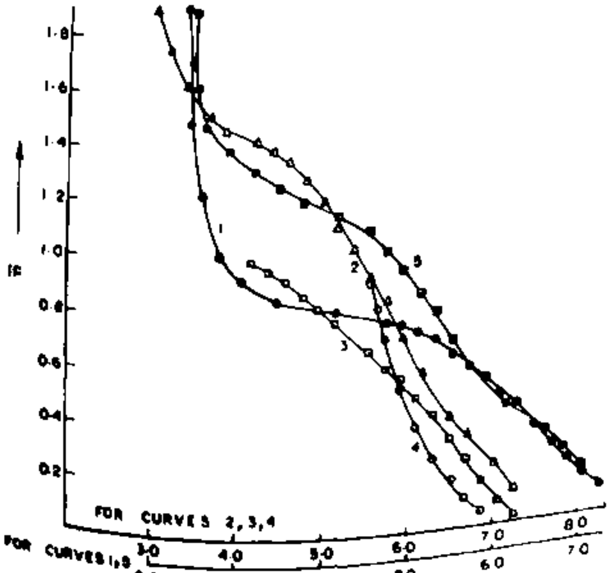


FIG. F

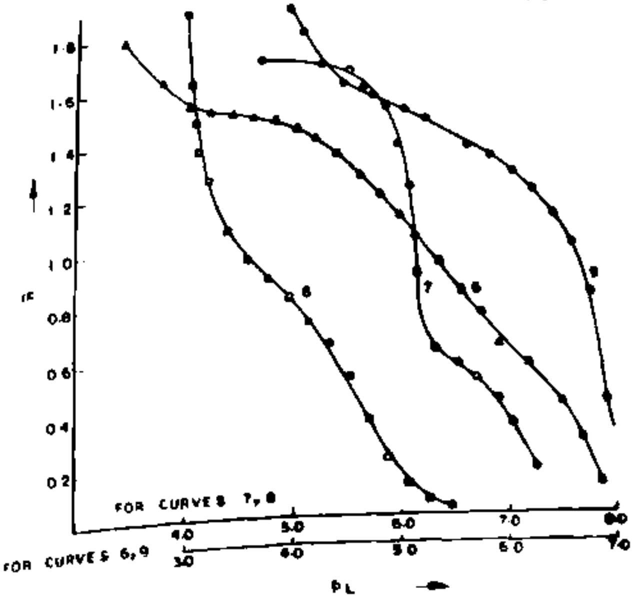


PLATE NO. 12

Table 3.25 (contd)

S. No.	pH	v'	v"	$\bar{n}_A$
32.	10.0	2.710	4.030	0.2771
33.	10.2	2.747	4.080	0.2692
34.	10.4	2.800	4.150	0.2613

The proton-ligand formation curves obtained by plotting $\bar{n}_A$ vs pH were analysed by using various computational methods viz. interpolation at half $\bar{n}_A$ values (H), interpolation at various $\bar{n}_A$ values (V) and least square methods (L), to calculate the protonation constants of the ligand. The values of the protonation constants at various ionic strengths are recorded in Table 3.26.

Table 3.26

Ionic strength	$\log K^H$			Mean $\log K^H$
	H	V	L	
0.02	7.52	7.61	7.55	7.56
0.05	7.52	7.44	7.51	7.49
0.10	7.40	7.35	7.36	7.37
0.15	7.28	7.29	7.34	7.30
0.20	7.16	7.17	7.17	7.17
0.00	-	-	-	7.08

It is interesting to mention here that in the case of ligand titration, colour changes were observed, as follows:

pH	Colour
2.6 - 5.1	Yellow
5.7 - 6.6	Yellowish green to greenish yellow
6.7 and above	Greenish yellow to green

A change in colour from yellow to green is observed within the pH range 6.9-7.7 at various ionic strengths. At this pH range, $\bar{n}_A$ is approximately 0.5, at all the five ionic strengths. This suggests that the transition from yellow LH species to green L^- species takes place in solution.

Metal-Ligand System

All the calculations of $\bar{n}$ and pL were made on IBM Computer 1130.

The values of $\bar{n}$ were calculated at various pH values from the equation mentioned earlier and then the corresponding values of pL were computed from this data. These values of $\bar{n}$ and pL at one ionic strength (to reduce the bulk of the thesis) are given in Tables 3.27-3.29.

Table 3.27

T_L = 0.005 T_M = 0.001

N^o = 0.1836 V^o = 100.0

μ = 0.10 Figure:Plate 14,E

S. No.	Pb(II)		Cu(II)		Zn(II)	
	$\bar{n}$	pL	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.062	6.883	0.131	7.083	0.052	7.099
2.	0.113	6.687	0.272	6.874	0.067	6.857
3.	0.166	6.512	0.379	6.711	0.108	6.709
4.	0.235	6.313	0.478	6.542	0.157	6.501
5.	0.293	6.147	0.608	6.341	0.222	6.300
6.	0.364	5.898	0.682	6.153	0.301	6.102
7.	0.441	5.703	0.798	5.937	0.392	5.927
8.	0.502	5.512	0.959	5.561	0.495	5.711
9.	0.556	5.324	1.057	5.379	0.563	5.532
10.	0.621	5.139	1.136	5.199	0.650	5.343
11.	0.659	4.947	1.202	5.002	0.719	5.151
12.	0.715	4.749	1.267	4.810	0.754	4.972
13.	0.754	4.543	1.321	4.602	0.802	4.743
14.	0.781	4.364	1.348	4.404	0.878	4.571
15.	0.856	3.687	1.385	3.865	0.927	4.387
16.	0.889	3.198	1.449	3.589	0.989	3.969
17.	0.918	2.971	1.499	3.457	-	-
18.	0.987	2.704	1.620	3.272	-	-
19.	1.197	2.411	1.881	3.001	-	-
20.	1.417	2.286	-	-	-	-
21.	1.526	2.246	-	-	-	-
22.	1.781	2.071	-	-	-	-

Table 3.28

T_L = 0.005 T_M = 0.001

N^o = 0.1838 V^o = 100.0

μ = 0.10 Figure=Plate 14,E and F

S. No.	Cd(II)		Hg(II)		Ni(II)	
	$\bar{n}$	pL	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.018	6.872	0.121	7.101	0.079	7.077
2.	0.037	6.649	0.162	6.901	0.098	6.903
3.	0.061	6.483	0.219	6.699	0.129	6.701
4.	0.129	6.312	0.263	6.500	0.265	6.378
5.	0.172	6.111	0.338	6.289	0.439	6.098
6.	0.318	5.887	0.415	6.111	0.699	5.701
7.	0.467	5.701	0.503	5.947	0.827	5.552
8.	0.599	5.542	0.572	5.723	0.948	5.375
9.	0.702	5.398	0.651	5.534	1.055	5.183
10.	0.768	5.273	0.730	5.341	1.158	4.999
11.	0.850	5.101	0.811	5.151	1.241	4.798
12.	0.972	4.699	0.889	4.952	1.328	4.611
13.	-	-	0.982	4.767	1.381	4.401
14.	-	-	1.062	4.597	1.432	4.212
15.	-	-	1.131	4.401	1.489	4.051
16.	-	-	1.239	3.973	1.521	3.898
17.	-	-	1.298	3.457	1.572	3.689
18.	-	-	1.353	3.023	1.601	3.454
19.	-	-	1.555	2.303	1.639	3.243
20.	-	-	1.719	2.124	1.707	2.867
21.	-	-	-	-	1.789	2.463

Table 3.29

$T_L = 0.005$ $T_M = 0.001$

$N^o = 0.1838$ $V^o = 100.00$

$\mu = 0.10$ Figure - Plate 14,F

S. No.	Co(II)		Be(II)		UO_2(II)	
	$\bar{n}$	pL	$\bar{n}$	pL	$\bar{n}$	pL
1.	0.179	7.081	0.039	6.273	0.160	6.901
2.	0.449	6.921	0.083	6.098	0.352	6.771
3.	0.698	6.801	0.138	5.898	0.461	6.701
4.	0.797	6.747	0.212	5.699	0.741	6.549
5.	0.998	6.619	0.302	5.501	0.978	6.351
6.	1.254	6.397	0.419	5.299	1.102	6.199
7.	1.348	6.221	0.546	5.133	1.199	6.001
8.	1.488	6.041	0.704	4.876	1.281	5.802
9.	1.601	5.738	0.802	4.749	1.342	5.603
10.	1.731	5.268	0.973	4.571	1.412	5.421
11.	1.759	5.081	1.118	4.398	1.461	5.232
12.	1.798	4.853	1.301	4.201	1.540	4.832
13.	1.829	4.673	1.442	4.125	1.579	4.648
14.	1.861	4.469	1.561	4.004	1.656	4.448
15.	1.892	4.251	1.756	3.943	1.738	4.273
16.	-	-	1.898	3.826	1.859	4.063

The values of $\bar{n}$ were plotted against the corresponding pL values to get the formation curves of metal complexation equilibria. Various computational methods viz. interpolation at half $\bar{n}$ values (H), interpolation at various $\bar{n}$ values and mid-point slope method (M) were used to determine the stepwise metal-ligand stability constants and the values are reported in Tables 3.30-3.37. The values obtained by different methods are in fair agreement.

Table 3.30

Values of stability constants of Pb^{2+}-ARS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	5.97	5.98	5.96	
	log K_2	2.63	2.59	2.58	
	log K_c	8.60	8.57	8.54	8.57
0.05	log K_1	5.87	5.88	5.91	
	log K_2	2.58	2.58	2.53	
	log K_c	8.45	8.46	8.44	8.45
0.10	log K_1	5.64	5.62	5.60	
	log K_2	2.30	2.32	2.28	
	log K_c	7.94	7.94	7.88	7.92
0.15	log K_1	5.55	5.58	5.61	
	log K_2	2.29	2.25	2.21	
	log K_c	7.84	7.83	7.82	7.83

Plate No. 13

Temperature = 30°C

Ionic strength = 0.05

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

Fig. B : Formation curve of proton-NRS system

Fig. C : Titration curves of NRS metal chelates:

(3) NRS only (4) Pb-NRS (5) Cu-NRS

(6) Zn-NRS (7) Cd-NRS

Fig. D : Titration curves of NRS metal chelates:

(8) Ni-NRS (9) Co-NRS

(10) Be-NRS (11) UO_2-NRS

Fig. E : Formation curves of NRS metal chelates:

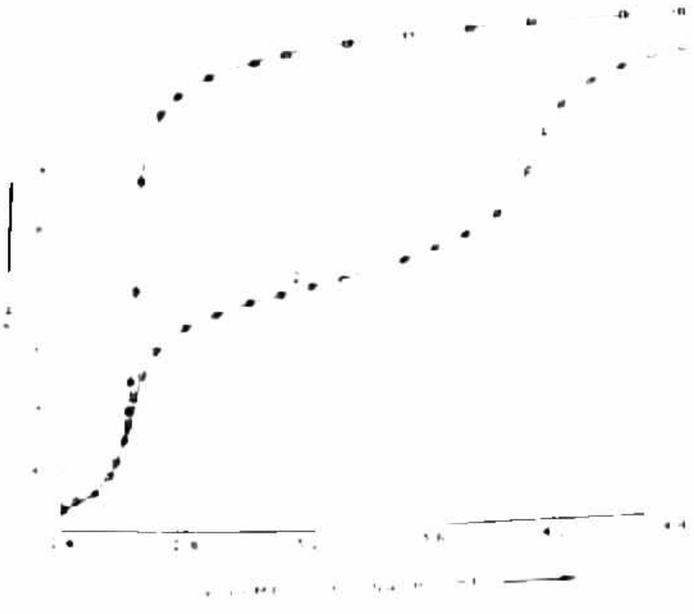
(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

Fig. F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS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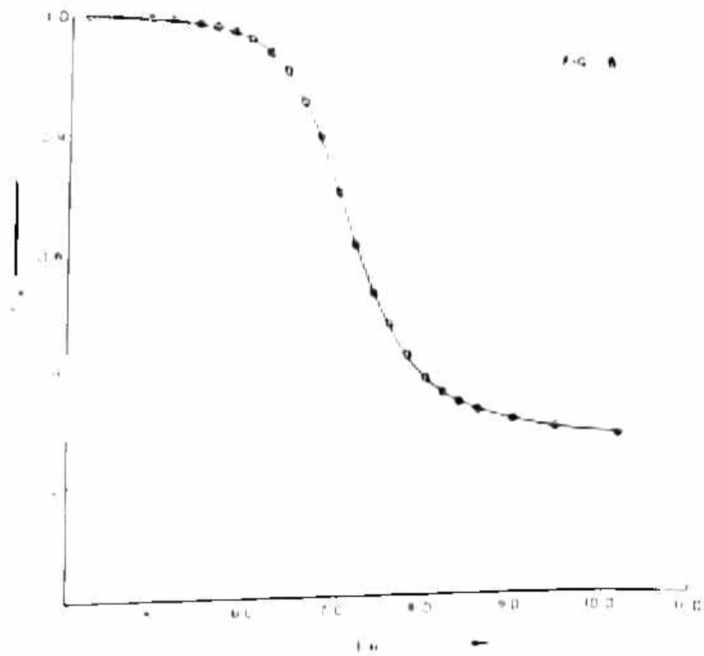
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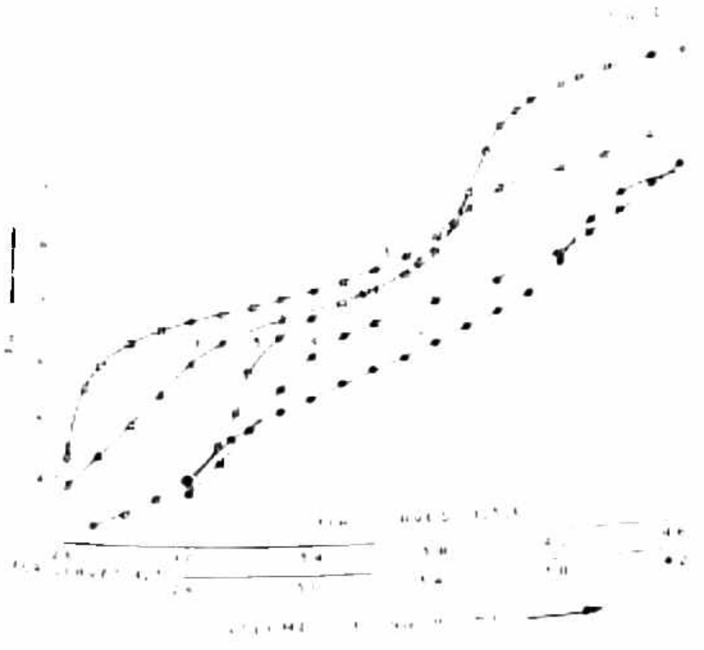
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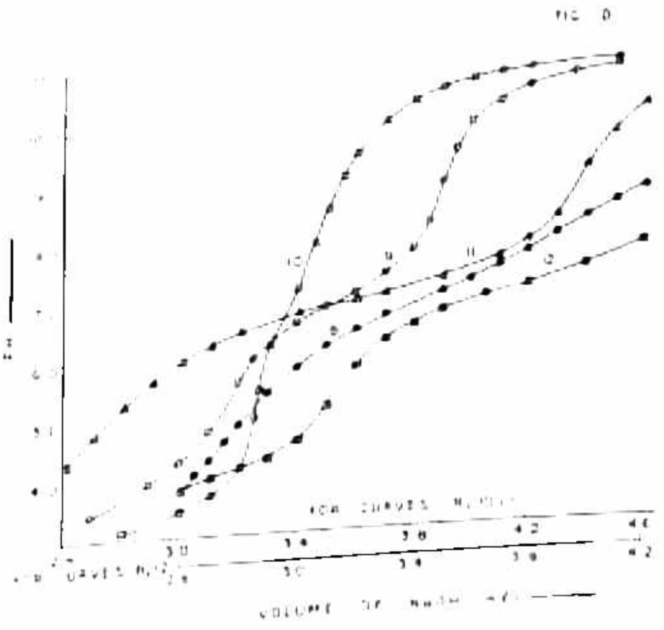
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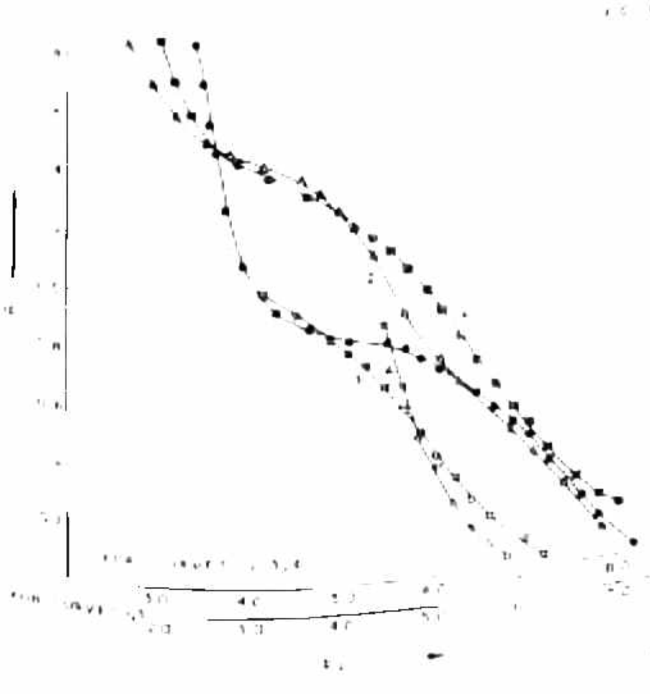
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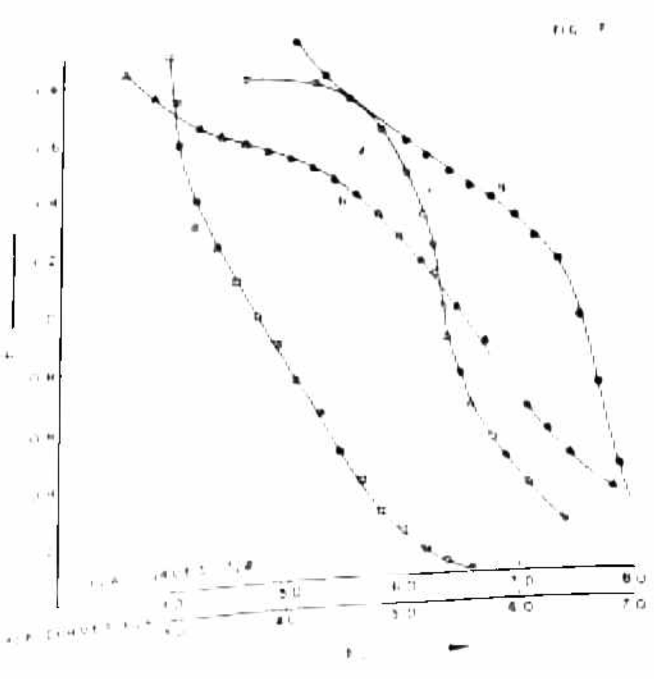

FOR CURVES
5.0
6.0
7.0
8.0

PLATE NO 13

Table 3.30 (contd.)

Ionic strength	log K_n	H	V	M	Mean
0.20	log K_1	5.40	5.42	5.38	
	log K_2	2.21	2.19	2.17	
	log K_c	7.61	7.61	7.55	7.59

Table 3.31

Values of stability constants of Cu-NRS chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	6.77	6.79	6.84	
	log K_2	3.66	3.66	3.63	
	log K_c	10.43	10.45	10.47	10.45
0.05	log K_1	6.74	6.77	6.83	
	log K_2	3.52	3.50	3.48	
	log K_c	10.26	10.27	10.31	10.28
0.10	log K_1	6.52	6.49	6.49	
	log K_2	3.44	3.49	3.42	
	log K_c	9.96	9.98	9.91	9.95
0.15	log K_1	6.31	6.30	6.36	
	log K_2	3.38	3.43	3.38	
	log K_c	9.69	9.73	9.74	9.72
0.20	log K_1	6.18	6.19	6.21	
	log K_2	6.35	6.43	3.37	
	log K_c	9.63	9.62	9.58	9.61

Table 3.32

Values of stability constants of Zn-NRG and Cd-NRG chelates at various ionic strengths

Metal ion	Ionic strength	log K		Mean
		H	V	
Zn^{2+}	0.02	5.94	5.92	5.93
	0.05	5.81	5.87	5.84
	0.10	5.69	5.67	5.68
	0.15	5.53	5.67	5.60
	0.20	5.52	5.53	5.53
Cd^{2+}	0.02	5.94	5.90	5.92
	0.05	5.81	5.87	5.84
	0.10	5.67	5.69	5.68
	0.15	5.63	5.59	5.61
	0.20	5.53	5.55	5.54

Plate No. 14

Temperature = 30°C

Ionic strength = 0.10

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

Fig. B : Formation curve of proton-NRS system

Fig. C : Titration curves of NRS metal chelates:

(3) NRS only (4) Pb-NRS (5) Cu-NRS

(6) Zn-NRS (7) Cd-NRS

Fig. D : Titration curves of NRS metal chelates:

(8) Hg-NRS (9) Ni-NRS (10) Co-NRS

(11) Be-NRS (12) UO_2-NRS

Fig. E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

Fig. F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

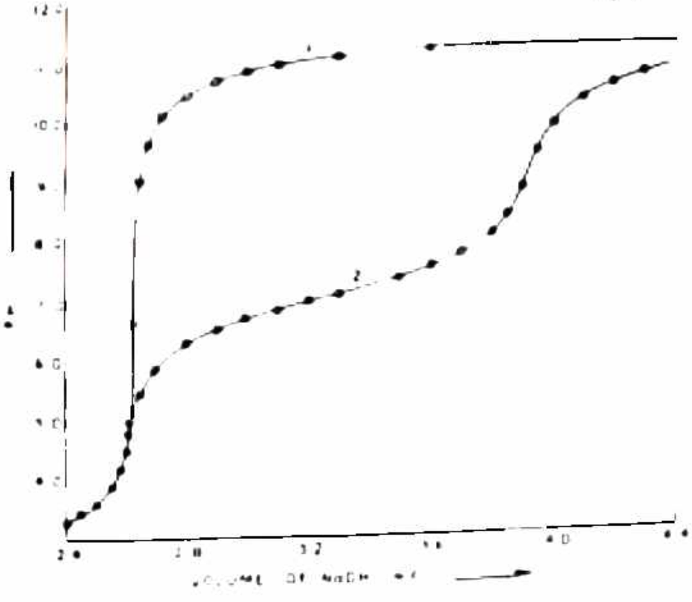


FIG. [illegible]

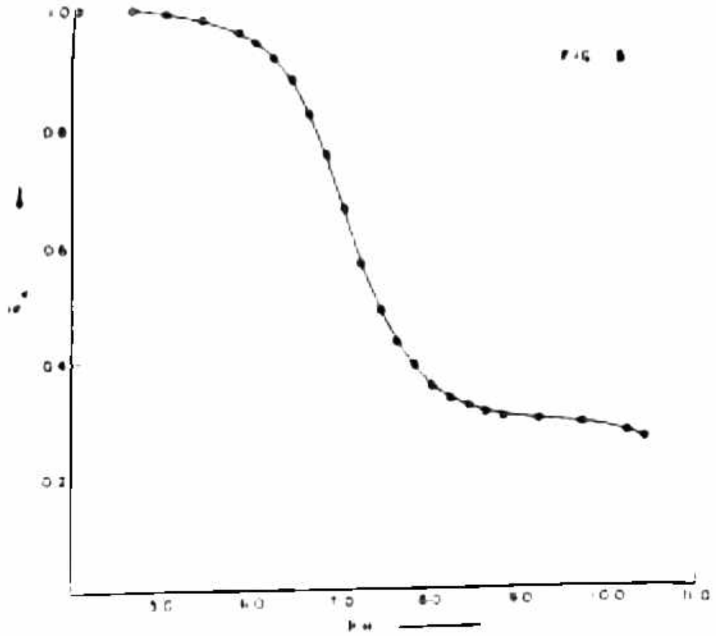


FIG. 8

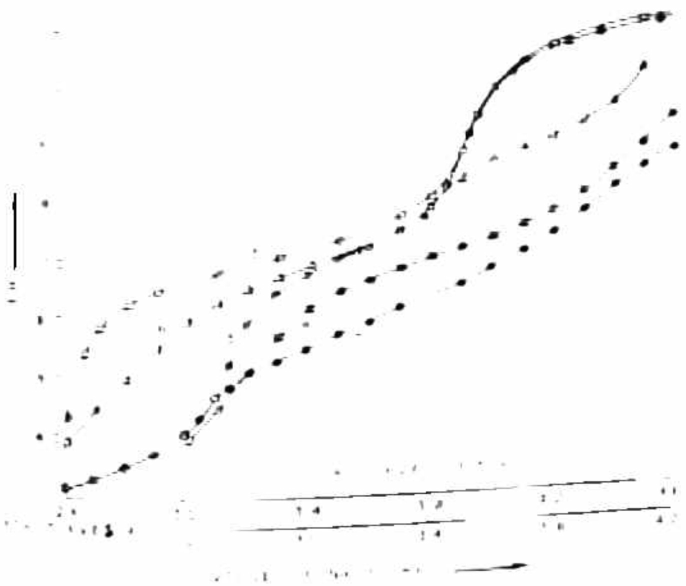


FIG. [illegible]

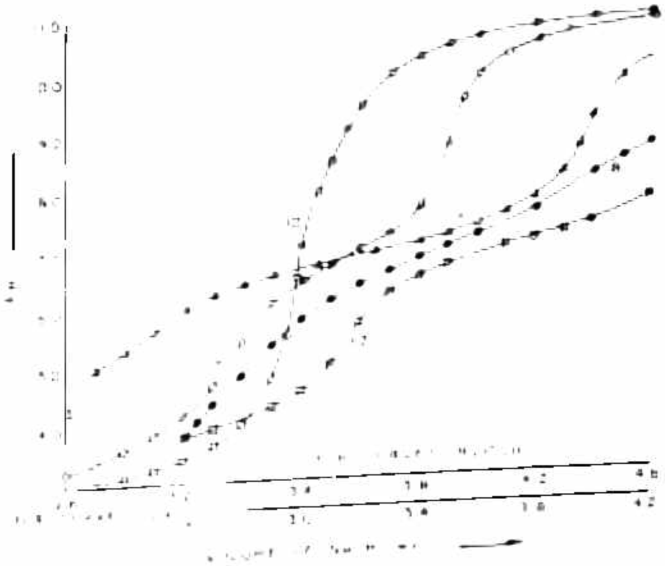


FIG. [illegible]

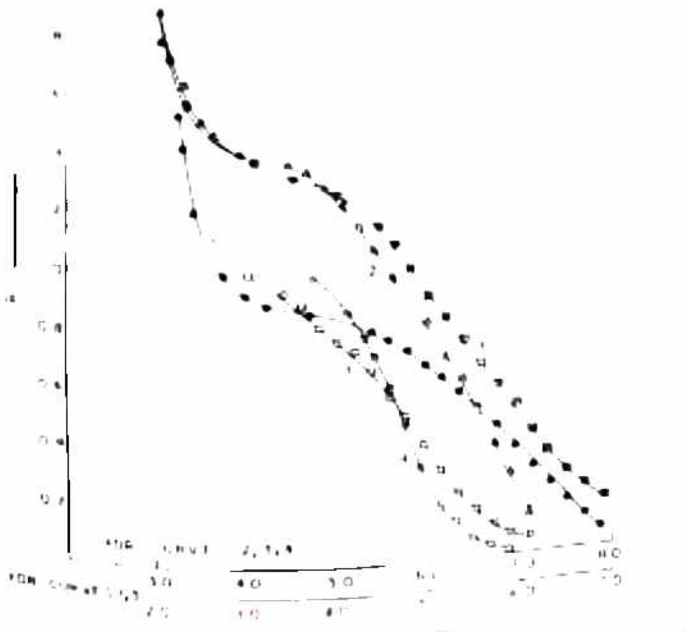


FIG. [illegible]

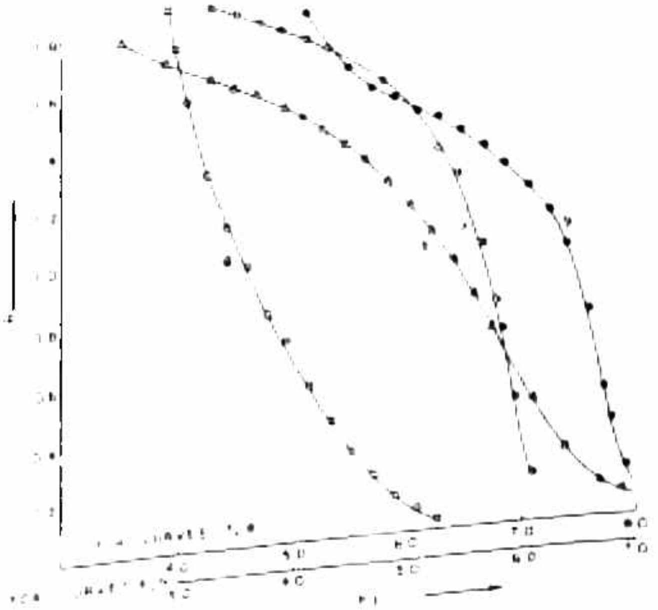


FIG. [illegible]

PLATE NO 14

Table 3.33

Values of stability constants of Hg-NRS system at different ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	5.96	5.97	6.01	
	log K_2	2.61	2.63	2.62	
	log K_c	8.57	8.60	8.63	8.60
0.05	log K_1	5.96	5.97	5.98	
	log K_2	2.59	2.59	2.62	
	log K_c	8.55	8.56	8.60	8.57
0.10	log K_1	5.95	5.96	5.96	
	log K_2	2.54	2.52	2.51	
	log K_c	8.49	8.48	8.47	8.48
0.15	log K_1	5.95	5.96	5.94	
	log K_2	2.23	2.27	2.25	
	log K_c	8.18	8.23	8.19	8.20
0.20	log K_1	5.93	5.95	5.94	
	log K_2	2.21	2.24	2.21	
	log K_c	8.14	8.19	8.15	8.16

Table 3.34

Values of stability constants of Ni-NRS system at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	6.25	6.27	6.31	
	log K_2	3.60	3.61	3.65	
	log K_c	9.85	9.88	9.96	9.90
0.05	log K_1	6.20	6.25	6.22	
	log K_2	3.80	3.78	3.83	
	log K_c	10.00	10.03	10.05	10.03
0.10	log K_1	6.10	6.12	6.17	
	log K_2	3.95	4.00	4.01	
	log K_c	10.05	10.12	10.18	10.12
0.15	log K_1	5.95	5.92	5.97	
	log K_2	4.20	4.23	4.18	
	log K_c	10.15	10.15	10.15	10.15
0.20	log K_1	5.90	5.95	5.97	
	log K_2	4.45	4.41	4.36	
	log K_c	10.35	10.36	10.33	10.35

Plate No. 15

Temperature = 30°C

Ionic strength = 0.15

Fig. A : Titration curves :

(1) $HClO_4$ (2) $HClO_4$ + ARS

Fig. B : Formation curve of proton-NRS system

Fig. C : Titration curves of NRS metal chelates;

(3) NRS only (4) Pb-NRS (5) Cu-NRS

(6) Zn-NRS (7) Cd-NRS

Fig. D : Titration curves of NRS metal chelates:

(8) Hg-NRS (9) Ni-NRS (10) Co-NRS

(11) Be-NRS (12) UO_2-NRS

Fig. E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

Fig. F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

FIG. A

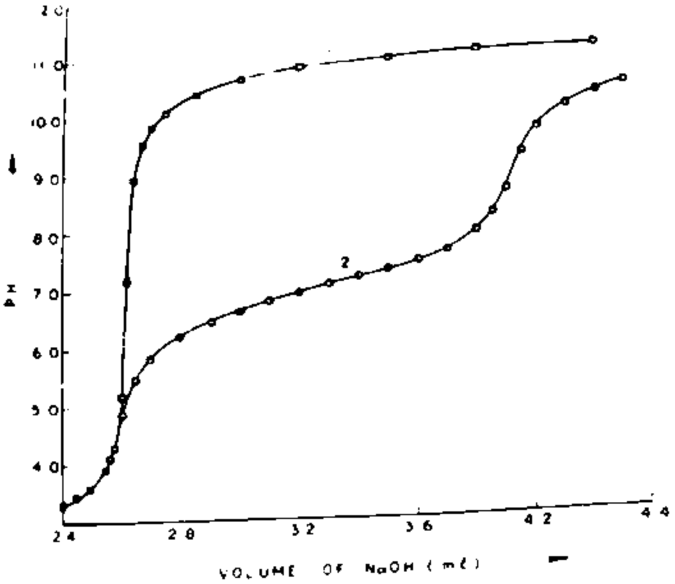


FIG. B

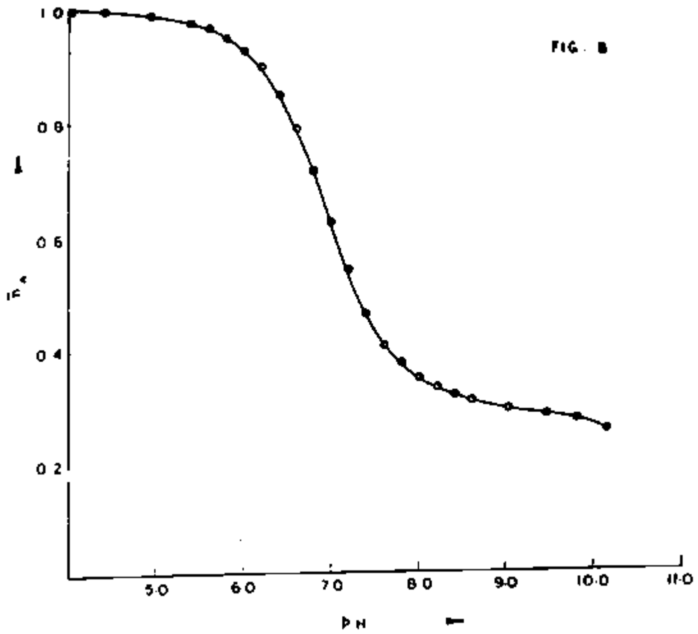


FIG. C

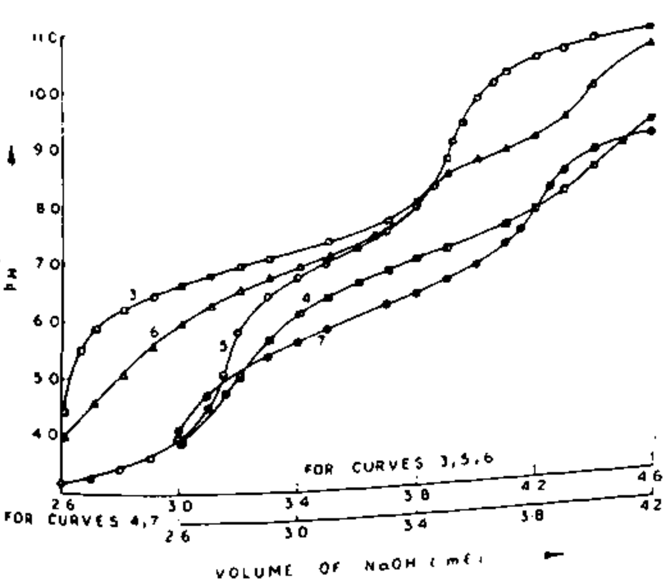


FIG. D

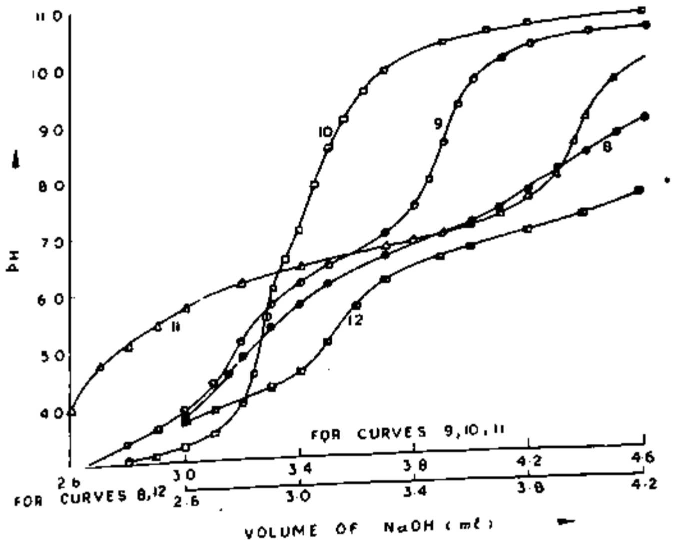


FIG. E

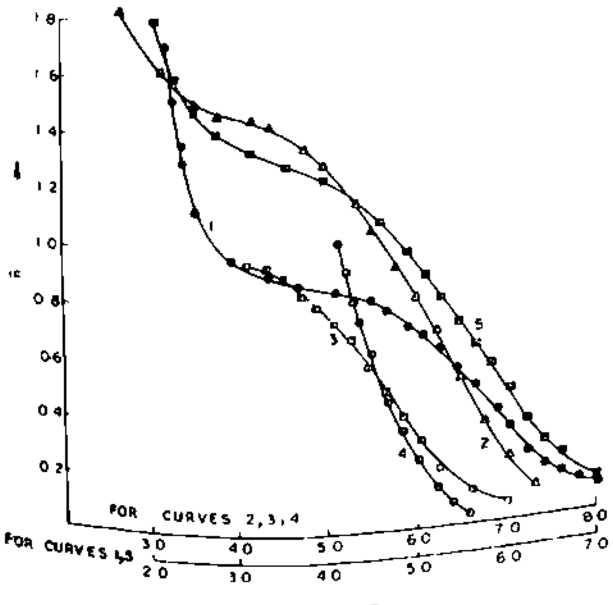


FIG. F

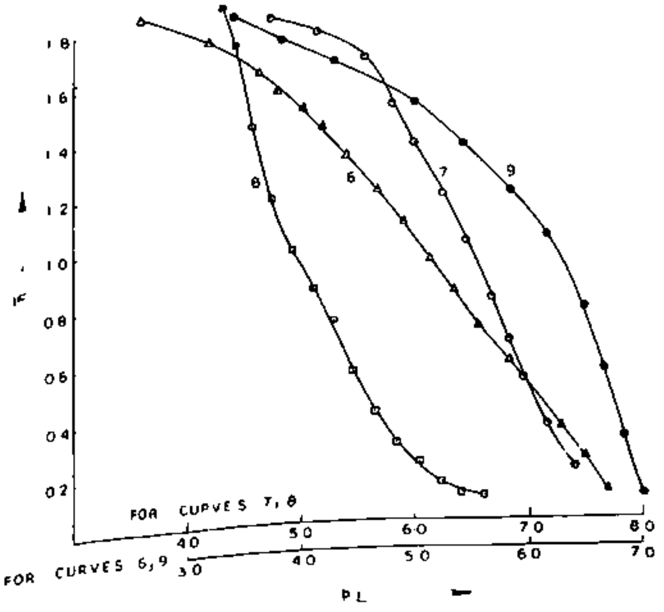


PLATE NO. 15

Table 3.35

Values of stability constants of Co-NRB system at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	6.62	6.70	6.73	
	log K_2	5.89	5.82	5.78	
	log K_c	12.51	12.52	12.51	12.51
0.05	log K_1	6.72	6.80	6.83	
	log K_2	5.95	5.89	5.84	
	log K_c	12.67	12.69	12.67	12.68
0.10	log K_1	6.95	6.91	6.86	
	log K_2	5.99	6.02	6.08	
	log K_c	12.94	12.93	12.94	12.94
0.15	log K_1	6.98	6.95	6.89	
	log K_2	6.04	6.10	6.16	
	log K_c	13.02	13.05	13.05	13.04
0.20	log K_1	7.03	7.00	7.05	
	log K_2	6.18	6.20	6.12	
	log K_c	13.21	13.20	13.17	13.19

Table 3.36

Values of stability constants of Be-NRS system at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	5.38	5.35	5.32	
	log K_2	4.00	4.04	4.09	
	log K_c	9.38	9.39	9.41	9.39
0.05	log K_1	5.46	5.40	5.51	
	log K_2	4.02	4.10	4.08	
	log K_c	9.48	9.50	9.59	9.52
0.10	log K_1	5.51	5.44	5.48	
	log K_2	4.17	4.20	4.13	
	log K_c	9.68	9.64	9.61	9.64
0.15	log K_1	5.39	5.47	5.52	
	log K_2	4.37	4.33	4.29	
	log K_c	9.76	9.80	9.81	9.79
0.20	log K_1	5.58	5.51	5.43	
	log K_2	4.39	4.42	4.49	
	log K_c	9.97	9.93	9.92	9.94

Plate No.10

Temperature = 30°C

Ionic strength = 0.20

Fig. A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

Fig. B : Formation curve of proton-NRS system

Fig. C : Titration curves of NRS metal chelates:

(3) NRS only (4) Pb-NRS (5) Cu-NRS

(6) Zn-NRS (7) Cd-NRS

Fig. D : Titration curves of NRS metal chelates:

(8) Hg-NRS (9) Ni-NRS (10) Co-NRS

(11) Be-NRS (12) UO_2-NRS

Fig. E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

Fig. F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

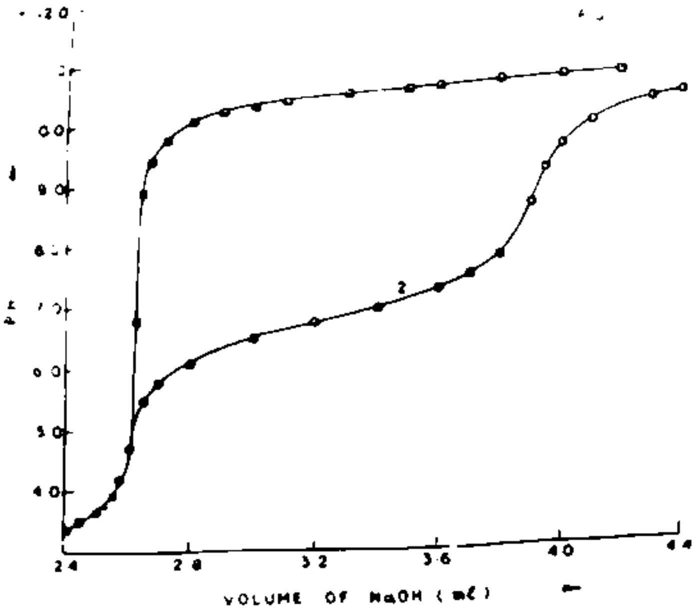


FIG. B

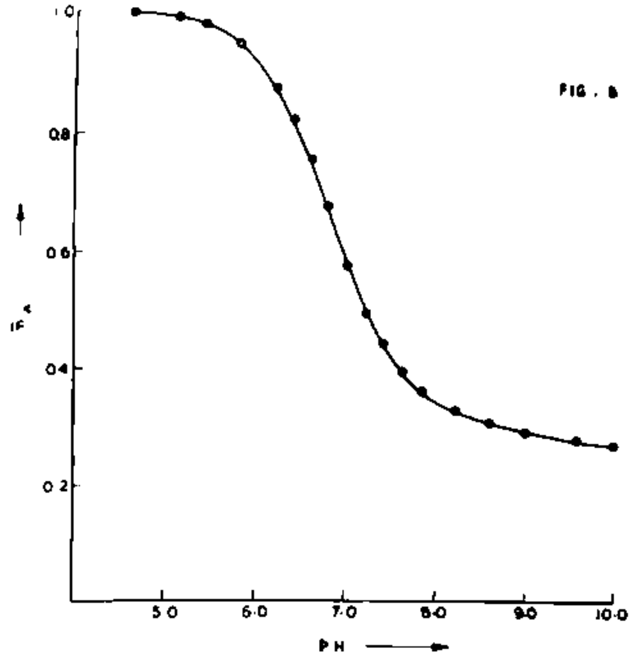


FIG C

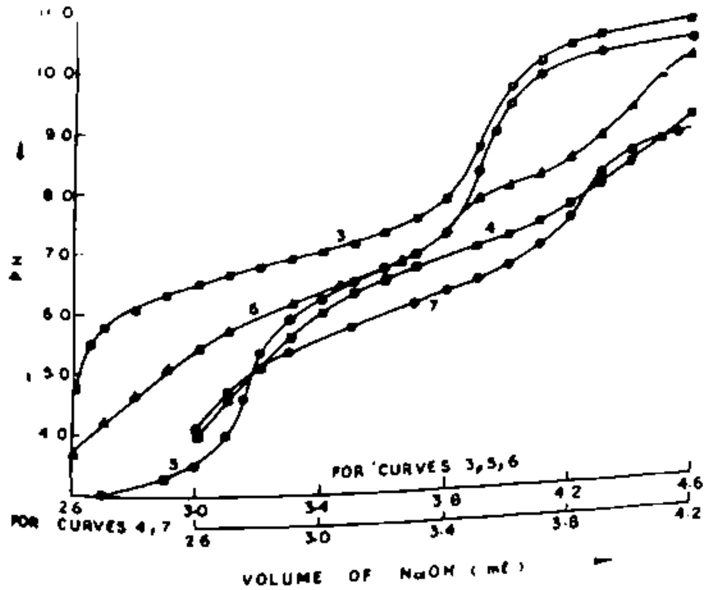


FIG . D

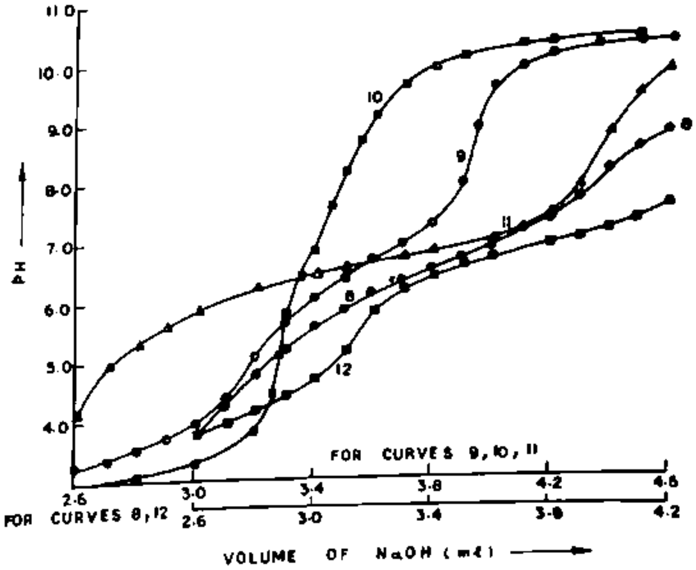


FIG E

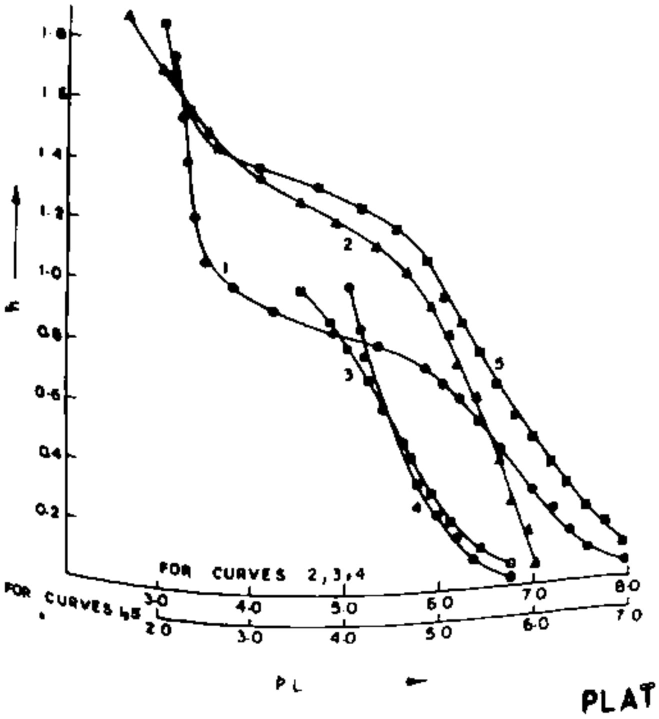


FIG . F

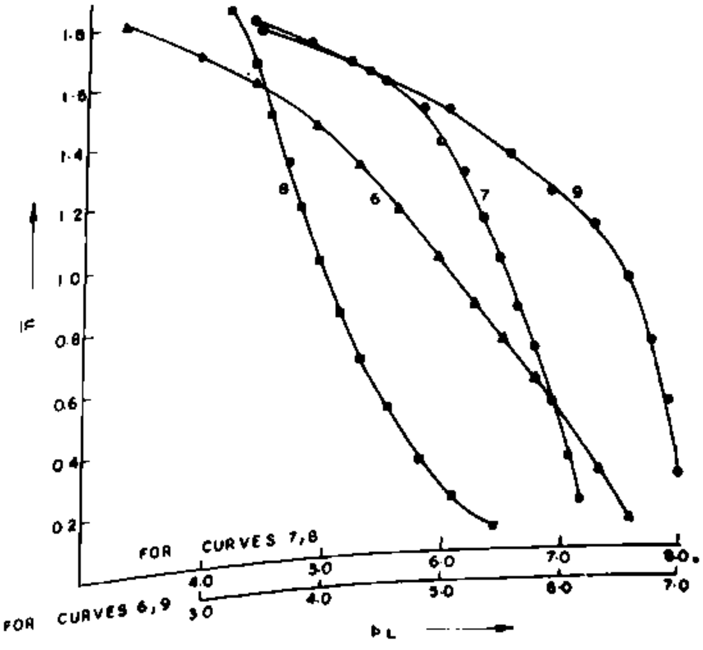


PLATE NO. 16

Table 3.37

Values of stability constants of UO_2-MNS system at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.02	log K_1	6.94	6.85	6.78	
	log K_2	5.11	5.15	5.14	
	log K_c	12.05	12.00	11.92	11.99
0.05	log K_1	6.68	6.74	6.69	
	log K_2	5.26	5.18	5.21	
	log K_c	11.94	11.82	11.90	11.90
0.10	log K_1	6.63	6.69	6.74	
	log K_2	5.07	5.02	5.00	
	log K_c	11.70	11.71	11.74	11.72
0.15	log K_1	6.61	6.67	6.72	
	log K_2	5.10	5.01	4.98	
	log K_c	11.71	11.68	11.70	11.70
0.20	log K_1	6.52	6.60	6.68	
	log K_2	5.02	4.95	4.89	
	log K_c	11.54	11.55	11.57	11.55

Thermodynamic Stability Constants

The thermodynamic stability constants were obtained by extrapolation of the stability constants to zero ionic strength (Plate 17). The values of log step stability constants at various ionic strengths were extrapolated to zero ionic strength to give step thermodynamic stability. These values have been represented as log $K_1^{\mu=0}$ and log $K_2^{\mu=0}$ in Table 3.38. The values of overall concentration stability constants K_c, at various ionic strengths, were likewise extrapolated to zero ionic strength. The overall thermodynamic stability constants thus obtained have been symbolised as experimental log $K_c^{\mu=0}$. The values of thermodynamic stability constants have been reported in Table 3.38.

THERMODYNAMIC FUNCTIONS

Various thermodynamic functions were calculated for a thorough study of complex forming reactions, in solution. The free energy of formation, ΔG, was calculated by using the equation (2.21). To calculate the change in enthalpy and entropy, the stability constants were calculated at five different temperatures i.e. 10°, 20°, 30°, 40° and 50°C, at a fixed ionic strength i.e. 0.10.

The pH readings of the titrations were plotted against the volume of alkali added. The titration curves

Plate No. 17

Temperature - 30°C

A : Extrapolation of log K to zero ionic strength (Pb-NRS system).
A - log K_1; B - log K_2; C - log K_c

B : Extrapolation of log K to zero ionic strength (Cu-NRS system).
A - log K_1; B - log K_2; C - log K_c

C : Extrapolation of log K to zero ionic strength
A - Zn-NRS; B - Cd-NRS

D : Extrapolation of log K to zero ionic strength (Hg-NRS system)
A - log K_1; B - log K_2; C - log K_c

E : Extrapolation of log K to zero ionic strength (Ni-NRS system).
A - log K_1; B - log K_2; C - log K_c

F : Extrapolation of log K to zero ionic strength (Co-NRS system).
A - log K_1; B - log K_2; C - log K_c

G : Extrapolation of log K to zero ionic strength (Be-NRS system).
A - log K_1; B - log K_2; C - log K_c

H : Extrapolation of log K to zero ionic strength (UO_2-NRS system).
A - log K_1; B - log K_2; C - log K_c

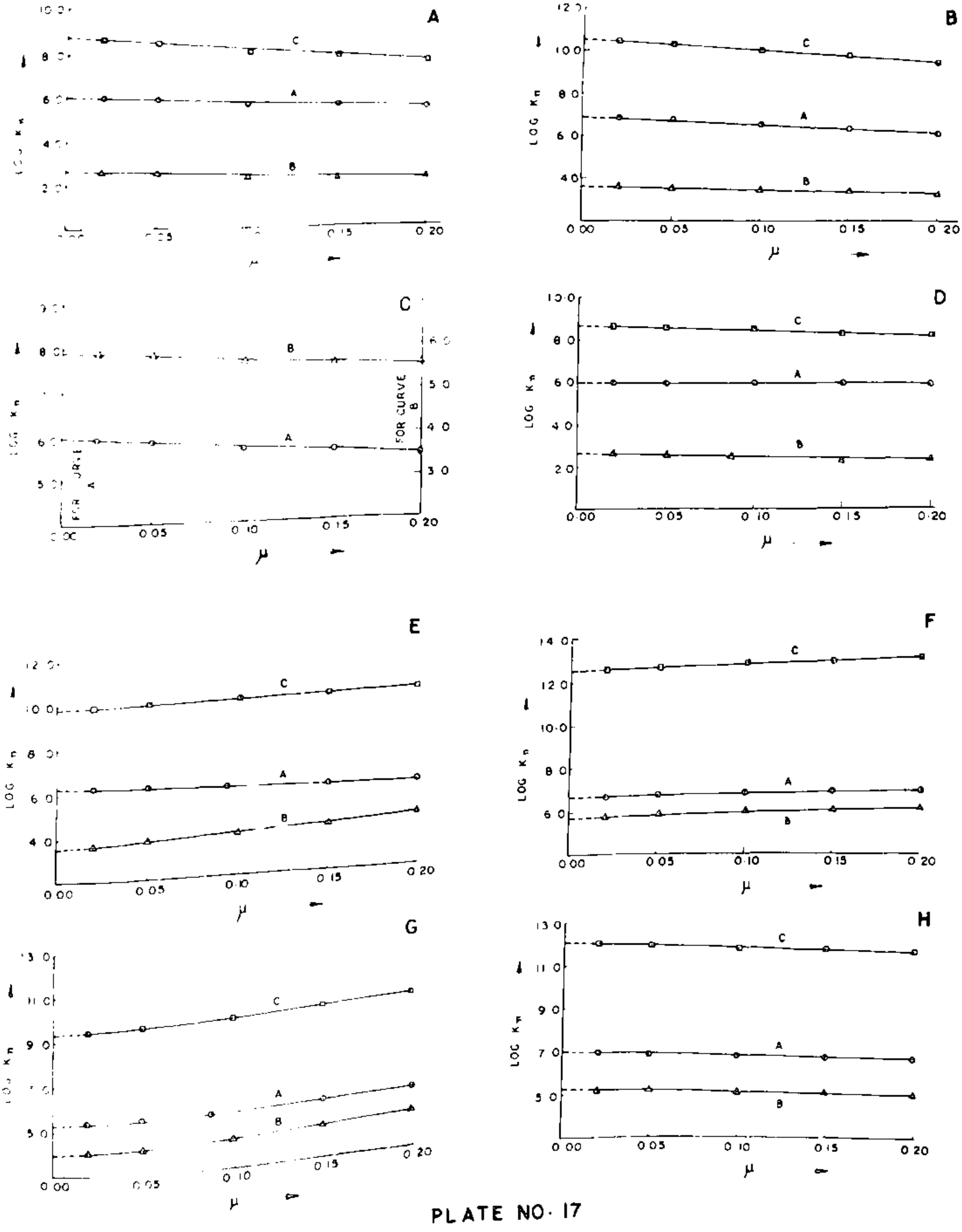

A
10.0
8.0
6.0
4.0
2.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ
B
12.0
10.0
8.0
6.0
4.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ
C
9.0
8.0
6.0
5.0
LOG Kn
FOR CURVE A
FOR CURVE B
6.0
5.0
4.0
3.0
B
A
0.00
0.05
0.10
0.15
0.20
μ
D
10.0
8.0
6.0
4.0
2.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ
E
12.0
10.0
8.0
6.0
4.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ
F
14.0
12.0
10.0
8.0
6.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ
G
13.0
11.0
9.0
7.0
5.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ
H
13.0
11.0
9.0
7.0
5.0
LOG Kn
C
A
B
0.00
0.05
0.10
0.15
0.20
μ

PLATE NO. 17

Table 3.36

Values of thermodynamic stability constants at 30°C

$\log K_n$	Pb^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Ni^{2+}	Co^{2+}	Be^{2+}	UO_2^{2+}
$\log K_1^{\mu=0}$	6.02	6.92	5.97	5.96	5.98	6.27	6.55	5.30	6.90
$\log K_2^{\mu=0}$	2.64	3.69	-	-	2.64	3.60	5.78	4.00	5.20
$\log K_c^{\mu=0}$ (calc.)	8.66	10.61	5.97	5.96	8.62	9.89	12.43	9.30	12.10
$\log K_c^{\mu=0}$ (exptl.)	8.67	10.60	5.97	5.96	8.62	9.65	12.48	9.30	12.05

thus obtained at different temperatures are graphically represented in Plates 18-A, C and D to 21-A, C and D.

Proton-Ligand System

The $\bar{n}_A$ values were calculated at various pH values to get the formation curves of the proton-ligand systems at different temperatures. All the values are graphically represented in Plates 18,B to 21,B.

The proton-ligand formation curves obtained by plotting $\bar{n}_A$ vs pH were analysed by using various computational methods viz. interpolation at half $\bar{n}_A$ values (H), interpolation at various $\bar{n}_A$ values (V) and least square method (L), to calculate the proton ligand stability constants at different temperatures. The values obtained by different methods are in fair agreement and the average values are recorded in Table 3.39.

The free energy of formation(ΔG)was calculated by using the equation $\Delta G = - RT \ln K$. The enthalpy change ΔH was calculated by using the equation (2.23) and assuming ΔH to be constant over the temperature range, in which the experiments were performed, ΔS of the reaction was calculated by using the equation (2.25) and all these values are recorded in Table 3.39.

Table 3.39

Values of proton-ligand stability constants and thermodynamic functions

ΔH (Kcal/mole) = - 4.364

Temperature (^{o}C)	10	20	30	40	50
log K	7.51	7.40	7.30	7.19	7.08
$-\Delta G$ (Kcal/mole)	9.73	9.92	10.13	10.30	10.87
ΔS (e.u.)	18.98	18.95	19.01	18.94	18.89

Metal-Ligand System

The values of $\bar{n}$ were calculated at different pH values from the equation mentioned earlier and then the corresponding pL values were computed from this data. The $\bar{n}$ values were plotted against the corresponding pL values to get the formation curves of metal complexation equilibria (Plates 18, E and F to 21, E and F).

Various computational methods were applied to analyse these formation curves i.e. interpolation at half $\bar{n}$ values (H), interpolation at various $\bar{n}$ values (V) and mid-point slope method (M). The values obtained from these methods are in fair agreement and the average values are recorded in Tables 3.40-3.47. The free energy of formation was calculated from the equation (2.22). The

Plate No. 18

Temperature = 10°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

B : Formation curve of proton-NRS system

C : Titration curves of NRS metal chelates:

(3) Pb-NRS (4) Cu-NRS

(5) Zn-NRS (6) Cd-NRS

D : Titration curves of NRS metal chelates:

(7) Hg-NRS (8) Ni-NRS (9) Co-NRS

(10) Be-NRS (11) UO_2-NRS

E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

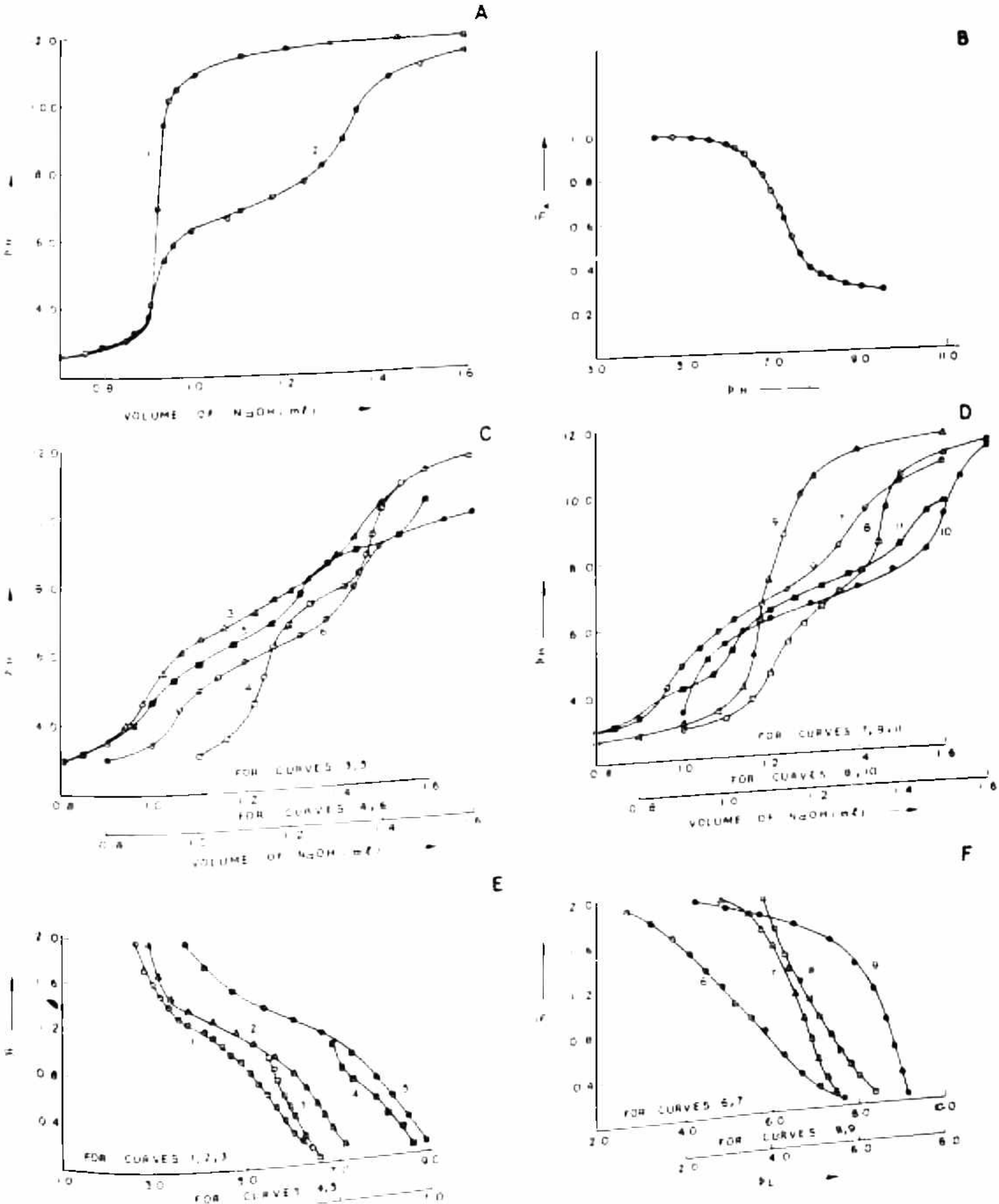

A
12.0
10.0
8.0
6.0
4.0
pH
1
2
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH (ml)
B
1.0
0.8
0.6
0.4
0.2
3.0
5.0
7.0
9.0
11.0
pH
C
12.0
10.0
8.0
6.0
4.0
pH
3
5
4
6
FOR CURVES 3,5
0.8
1.0
1.2
1.4
1.6
FOR CURVES 4,6
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH (ml)
D
12.0
10.0
8.0
6.0
4.0
pH
9
7
8
11
10
FOR CURVES 7,9,11
0.8
1.0
1.2
1.4
1.6
FOR CURVES 8,10
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH (ml)
E
2.0
1.6
1.2
0.8
0.4
1
2
3
4
5
FOR CURVES 1,2,3
1.0
3.0
5.0
7.0
9.0
FOR CURVES 4,5
1.0
3.0
5.0
7.0
PL
F
2.0
1.6
1.2
0.8
0.4
6
7
8
9
FOR CURVES 6,7
2.0
4.0
6.0
8.0
10.0
FOR CURVES 8,9
2.0
4.0
6.0
8.0
PL

PLATE NO. 18

enthalpy change (ΔH) was calculated by using the equation (2.23). Assuming ΔH to be constant over the experimental temperature range, ΔS, the entropy change was calculated by using the equation (2.25). The values of stepwise stability constants with their thermodynamic functions are recorded in Tables 3.40 to 3.47.

Table 3.40

Values of stability constants and thermodynamic functions of Pb-NRS system

ΔH_1 = - 9.585

ΔH_2 = -13.490

ΔH = -22.470

(Kcal/mole)

Temperature (^{o}C)	10	20	30	40	50
log K_1	5.66	5.63	5.62	5.20	4.70
log K_2	3.17	2.55	2.30	2.10	1.90
log K_c	8.83	8.18	7.92	7.30	6.60
- ΔG_1	7.33	7.55	7.79	7.45	6.95
- ΔG_2	4.11	3.42	3.19	3.01	2.81
- ΔG (Kcal/mole)	11.44	10.97	10.98	10.46	9.76
- ΔS_1	8.11	6.94	5.91	6.82	6.16
-ΔS_2	33.13	34.34	33.97	33.45	33.05
- ΔS (e.u.)	38.94	39.22	37.89	38.23	39.32

Table 3.41

Values of stability constants and thermodynamic functions of Cu-NRS system

$\Delta H_1 = -1.950$

$\Delta H_2 = 4.092$

$\Delta H = 3.011$
(Kcal/mole)

Temperature (^oC)	10	20	30	40	50
$\log K_1$	6.53	6.51	6.50	6.42	6.34
$\log K_2$	3.23	3.32	3.41	3.53	3.65
$\log K_c$	9.79	9.83	9.91	9.95	9.99
$-\Delta G_1$	8.46	8.73	9.01	9.20	9.37
$-\Delta G_2$	4.22	4.45	4.73	5.06	5.40
$-\Delta G$ (Kcal/mole)	12.68	13.18	13.74	14.26	14.77
ΔS_1	22.98	23.13	23.30	23.13	22.97
ΔS_2	29.36	29.14	29.10	29.20	29.36
ΔS (e.u.)	34.18	34.67	35.39	35.88	36.39

Plate No. 19

Temperature = 20°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

B : Formation curve of proton-NRS system

C : Titration curves of NRS metal chelates:

(3) Pb-NRS (4) Cu-NRS

(5) Zn-NRS (6) Cd-NRS

D : Titration curves of NRS metal chelates:

(7) Hg-NRS (8) Ni-NRS (9) Co-NRS

(10) Be-NRS (11) UO_2-NRS

E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

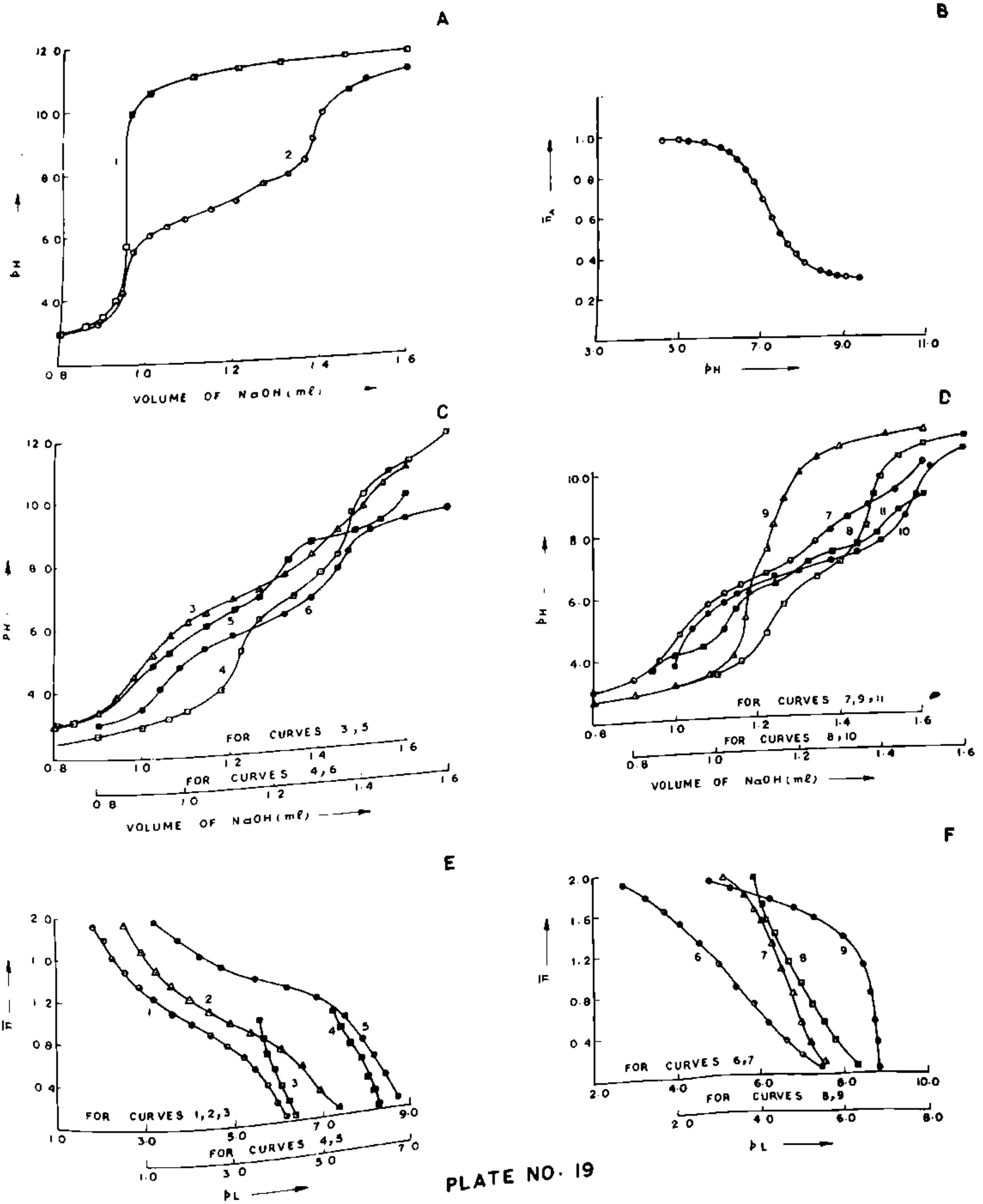

A
pH
12.0
10.0
8.0
6.0
4.0
1
2
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH(ml)
B
$\bar{n}_A$
1.0
0.8
0.6
0.4
0.2
3.0
5.0
7.0
9.0
11.0
pH
C
pH
12.0
10.0
8.0
6.0
4.0
3
4
5
6
FOR CURVES 3,5
0.8
1.0
1.2
1.4
1.6
FOR CURVES 4,6
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH(ml)
D
pH
10.0
8.0
6.0
4.0
7
8
9
10
11
FOR CURVES 7,9,11
0.8
1.0
1.2
1.4
1.6
FOR CURVES 8,10
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH(ml)
E
$\bar{n}$
2.0
1.6
1.2
0.8
0.4
1
2
3
4
5
FOR CURVES 1,2,3
1.0
3.0
5.0
7.0
9.0
FOR CURVES 4,5
1.0
3.0
5.0
7.0
pL
F
$\bar{n}$
2.0
1.6
1.2
0.8
0.4
6
7
8
9
FOR CURVES 6,7
2.0
4.0
6.0
8.0
10.0
FOR CURVES 8,9
2.0
4.0
6.0
8.0
pL

PLATE NO. 19

Table 3.42

Values of stability constants and thermodynamic functions of Zn-NRS and Cd-NRS systems

- ΔH for Zn-NRS = 6.304
(Kcal/mole)

- ΔH for Cd-NRS = 6.956
(Kcal/mole)

Metal ion	Temperature (°C)	10	20	30	40	50
Zn^{2+}	log K	5.90	5.76	5.68	5.45	5.31
	-ΔG (Kcal/mole)	7.64	7.73	7.87	7.81	7.84
	ΔS (e.u.)	4.73	4.85	5.17	4.80	4.74
Cd^{2+}	log K	5.81	5.72	5.64	5.36	5.15
	-ΔG (Kcal/mole)	7.53	7.67	7.82	7.68	7.61
	ΔS (e.u.)	2.01	2.44	2.85	2.31	2.04

Table 3.43

Values of stability constants and thermodynamic functions of Hg-NR3 system

$\Delta H_1 = -8.656$

$\Delta H_2 = -3.569$

$\Delta H = -12.600$
(Kcal/mole)

Temperature (°C)	10	20	30	40	50
$\log K_1$	6.15	6.00	5.96	5.60	5.31
$\log K_2$	2.72	2.61	2.52	2.43	2.37
$\log K_c$	8.87	8.61	8.48	8.03	7.68
$-\Delta G_1$	7.97	8.04	8.26	7.88	7.84
$-\Delta G_2$	3.52	3.50	3.49	3.48	3.50
$-\Delta G$ (Kcal/mole)	11.49	11.54	11.75	11.36	11.34
$-\Delta S_1$	2.43	2.09	1.29	2.48	2.54
$-\Delta S_2$	0.16	0.23	0.25	0.28	0.21
$-\Delta S$ (e.u.)	3.92	3.65	2.77	4.12	3.90

Table 3.44

Values of stability constants and thermodynamic functions of Ni-NRS system

ΔH_1 = - 2.423

ΔH_2 = - 2.665

ΔH = - 5.088
(Kcal/mole)

Temperature (°C)	10	20	30	40	50
log K_1	6.29	6.21	6.14	6.11	6.05
log K_2	4.14	4.09	4.00	3.97	3.88
log K_c	10.43	10.30	10.14	10.08	9.93
$-\Delta G_1$	8.15	8.33	8.51	8.75	8.94
$-\Delta G_2$	5.36	5.49	5.55	5.69	5.74
$-\Delta G$ (Kcal/mole)	13.51	13.82	14.06	14.44	14.68
ΔS_1	20.22	20.15	20.18	19.88	20.18
ΔS_2	9.53	9.62	9.51	9.65	9.50
ΔS (e.u.)	29.74	29.75	29.59	29.82	29.68

Plate No. 20

Temperature = 40°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

B : Formation curve of proton-NRS system

C : Titration curves of NRS metal chelates

(3) Pb-NRS (4) Cu-NRS

(5) Zn-NRS (6) Cd-NRS

D : Titration curves of NRS metal chelates:

(7) Hg-NRS (8) Ni-NRS (9) Co-NRS

(10) Be-NRS (11) UO_2-NRS

E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

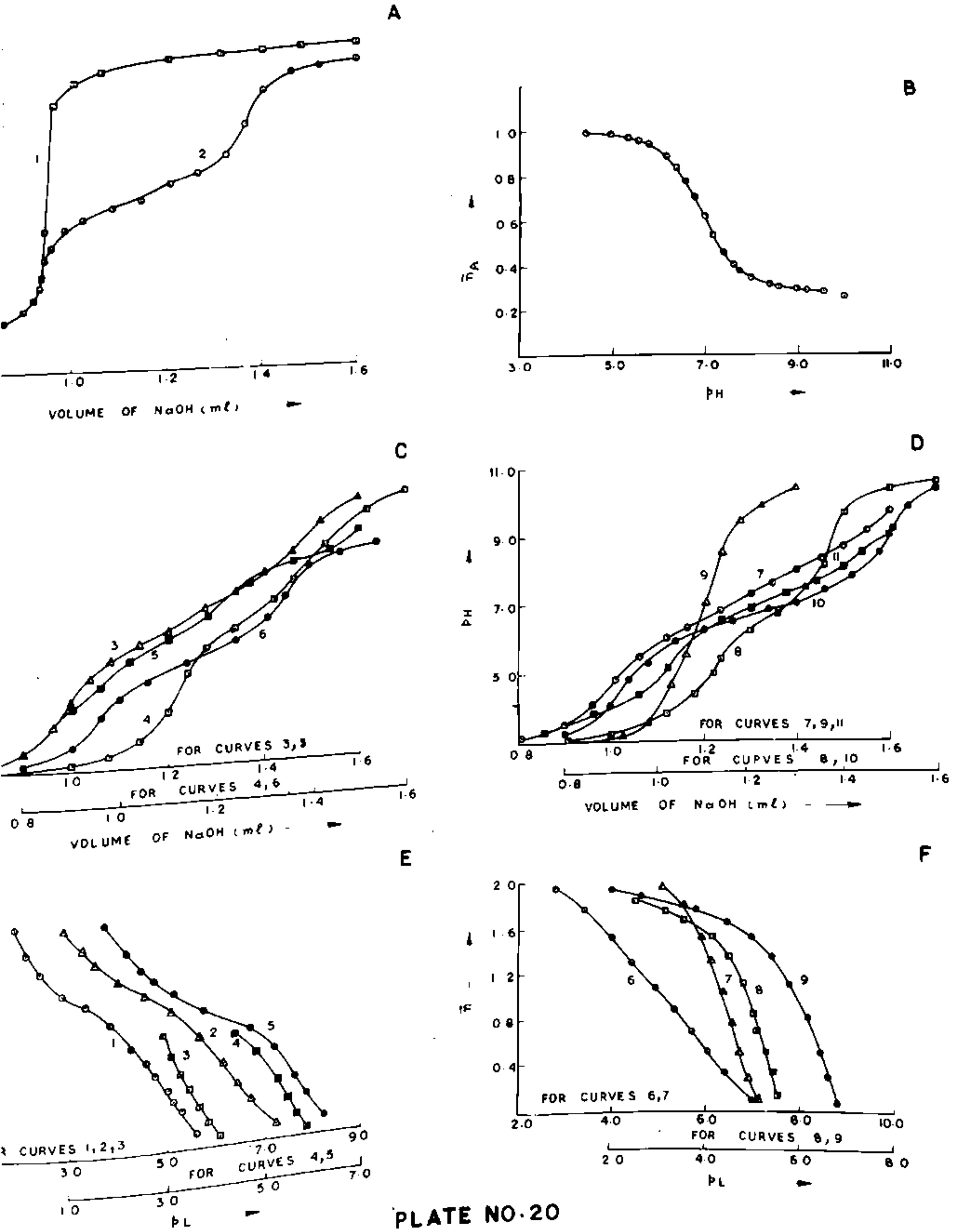

A
1
2
1·0
1·2
1·4
1·6
VOLUME OF NaOH (mℓ)
B
1·0
0·8
0·6
0·4
0·2
FA
3·0
5·0
7·0
9·0
11·0
pH
C
3
5
4
6
FOR CURVES 3,5
1·0
1·2
1·4
1·6
FOR CURVES 4,6
0·8
1·0
1·2
1·4
1·6
VOLUME OF NaOH (mℓ)
D
11·0
9·0
7·0
5·0
pH
9
7
11
10
8
FOR CURVES 7,9,11
0·8
1·0
1·2
1·4
1·6
FOR CURVES 8,10
0·8
1·0
1·2
1·4
1·6
VOLUME OF NaOH (mℓ)
E
1
2
3
4
5
R CURVES 1,2,3
3·0
5·0
7·0
9·0
FOR CURVES 4,5
1·0
3·0
5·0
7·0
pL
F
2·0
1·6
1·2
0·8
0·4
n̄
6
7
8
9
FOR CURVES 6,7
2·0
4·0
6·0
8·0
10·0
FOR CURVES 8,9
2·0
4·0
6·0
8·0
pL

PLATE NO·20

Table 3.45

Values of stability constants and thermodynamic functions of Co-NRS system

$\Delta H_1 = -4.809$

$\Delta H_2 = -1.730$

$\Delta H = -6.542$
(Kcal/mole)

Temperature ($^{\circ}C$)	10	20	30	40	50
$\log K_1$	7.04	6.96	6.90	6.72	6.56
$\log K_2$	6.04	6.02	6.00	5.92	5.88
$\log K_c$	13.08	12.98	12.90	12.64	12.46
$-\Delta G_1$	9.12	9.33	9.57	9.63	9.73
$-\Delta G_2$	7.82	8.06	8.32	8.48	8.69
$-\Delta G$ (Kcal/mole)	16.94	17.39	17.89	18.11	18.42
ΔS_1	15.23	15.40	15.70	15.38	15.22
ΔS_2	21.51	21.60	21.74	21.55	21.55
ΔS (e.u.)	37.03	37.11	37.41	37.07	36.80

Plate No. 21

Temperature = 50°C

Ionic strength = 0.10

A : Titration curves:

(1) $HClO_4$ (2) $HClO_4$ + NRS

B : Formation curve of proton-NRS system

C : Titration curves of NRS metal chelates:

(3) Pb-NRS (4) Cu-NRS

(5) Zn-NRS (6) Cd-NRS

D : Titration curves of NRS metal chelates:

(7) Hg-NRS (8) Ni-NRS (9) Co-NRS

(10) Be-NRS (11) UO_2-NRS

E : Formation curves of NRS metal chelates:

(1) Pb-NRS (2) Cu-NRS (3) Zn-NRS

(4) Cd-NRS (5) Hg-NRS

F : Formation curves of NRS metal chelates:

(6) Ni-NRS (7) Co-NRS

(8) Be-NRS (9) UO_2-NRS

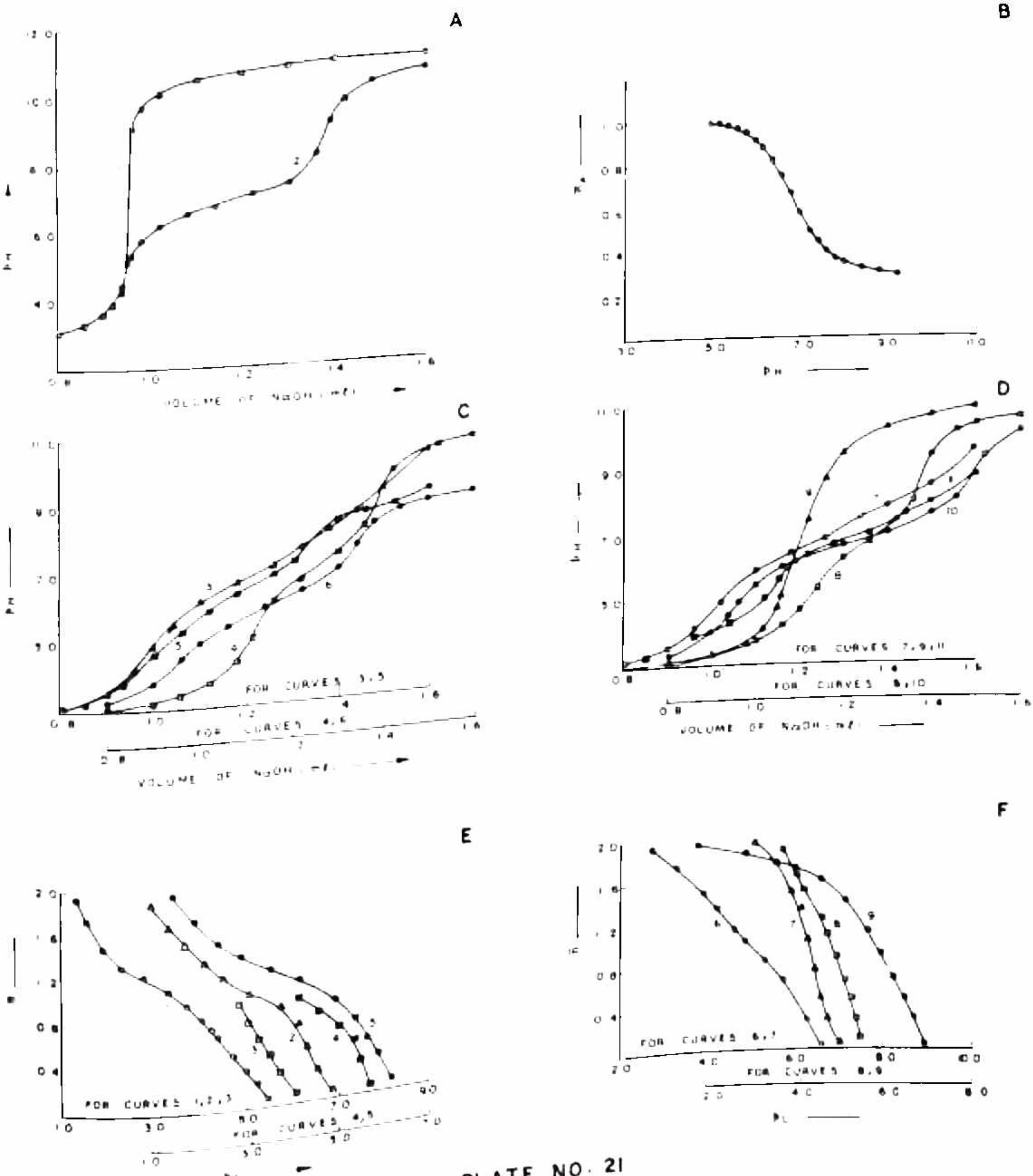

A
B
C
D
E
F
12.0
10.0
8.0
6.0
4.0
pH
0.8
1.0
1.2
1.4
1.6
VOLUME OF NaOH (ml)
1
2
1.0
0.8
0.6
0.4
0.2
3.0
5.0
7.0
9.0
11.0
pH
11.0
9.0
7.0
5.0
FOR CURVES 3,5
FOR CURVES 4,6
FOR CURVES 7,9,11
FOR CURVES 8,10
3
4
5
6
7
8
9
10
11
2.0
1.6
1.2
0.8
0.4
FOR CURVES 1,2,3
FOR CURVES 4,5
FOR CURVES 6,7
FOR CURVES 8,9
pL
4.0
6.0
8.0
10.0

PLATE NO. 21

Table 3.46

Values of stability constants and thermodynamic functions of Be-NRS system

$\Delta H_1 = -3.841$

$\Delta H_2 = -0.523$

$\Delta H = -4.222$
(Kcal/mole)

Temperature (°C)	10	20	30	40	50
log K_1	5.59	5.53	5.48	5.32	5.23
log K_2	4.18	4.17	4.17	4.15	4.14
log K_c	9.77	9.69	9.65	9.47	9.37
$-\Delta G_1$	7.24	7.42	7.60	7.62	7.73
$-\Delta G_2$	5.42	5.59	5.78	5.94	6.12
$-\Delta G$ (Kcal/mole)	12.66	13.01	13.38	13.56	13.85
ΔS_1	12.00	12.19	12.40	12.07	12.03
ΔS_2	17.28	17.29	17.35	17.31	17.32
ΔS (e.u.)	29.80	29.89	29.90	29.82	29.51

Plate No. 22

Ionic strength = 0.10

1. Variation of log K with 1/T (Pb-NRS system)
   A - log K_1; B - log K_2; C - log K_c

2. Variation of log K with 1/T (Cu-NRS system)
   A - log K_1; B - log K_2; C - log K_c

3. Variation of log K with 1/T
   A - Zn-NRS; B - Cd-NRS

4. Variation of log K with 1/T (Hg-NRS system)
   A - log K_1; B - log K_2; C - log K_c

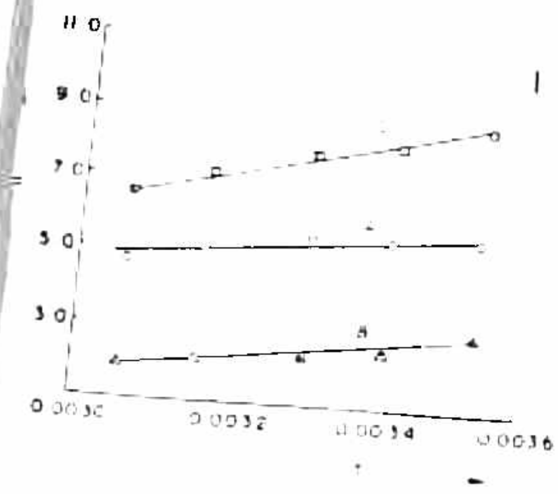
5. Variation of log K with 1/T (Ni-NRS system)
   A - log K_1; B - log K_2; C - log K_c

6. Variation of log K with 1/T (Co-NRS system)
   A - log K_1; B - log K_2; C - log K_c

7. Variation of log K with 1/T (Be-NRS system)
   A - log K_1; B - log K_2; C - log K_c

8. Variation of log K with 1/T (UO_2-NRS system)
   A - log K_1; B - log K_2; C - log K_c

1



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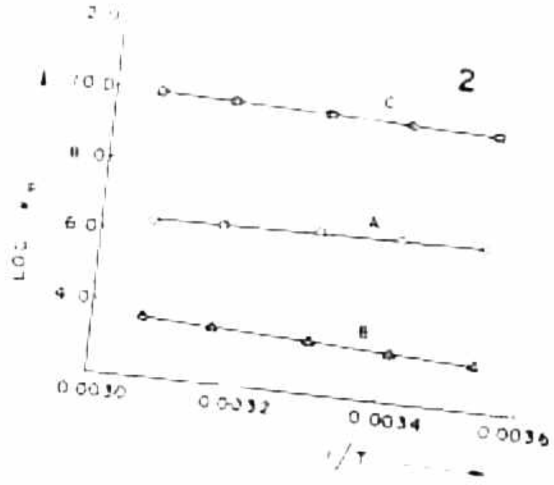

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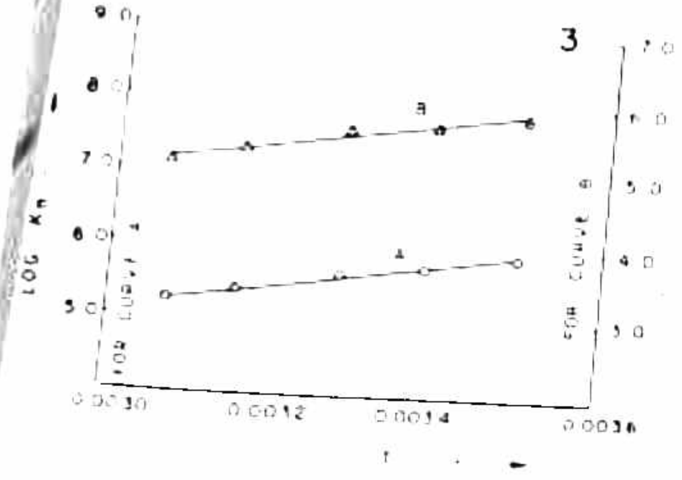

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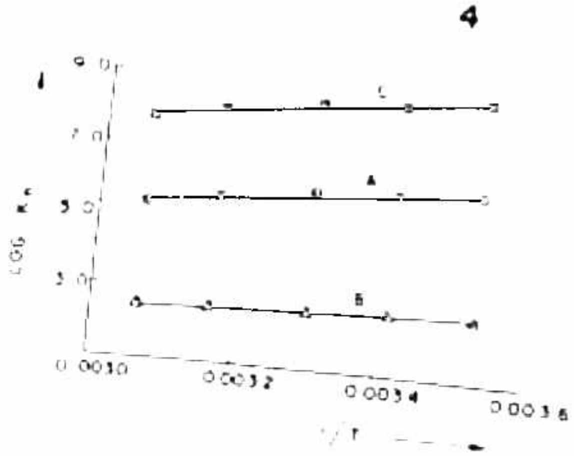

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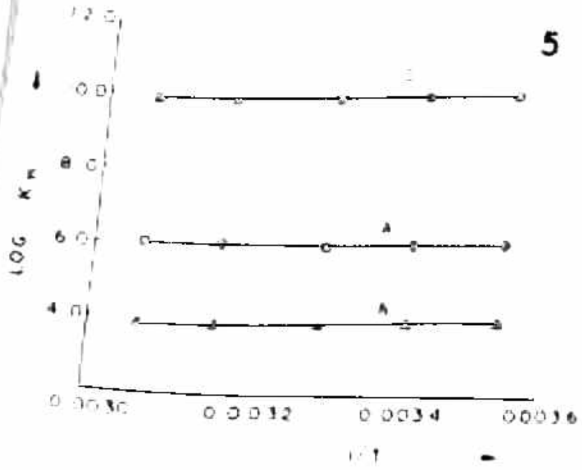

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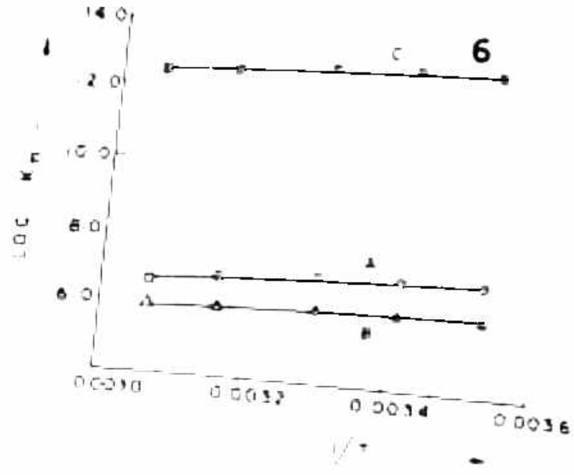

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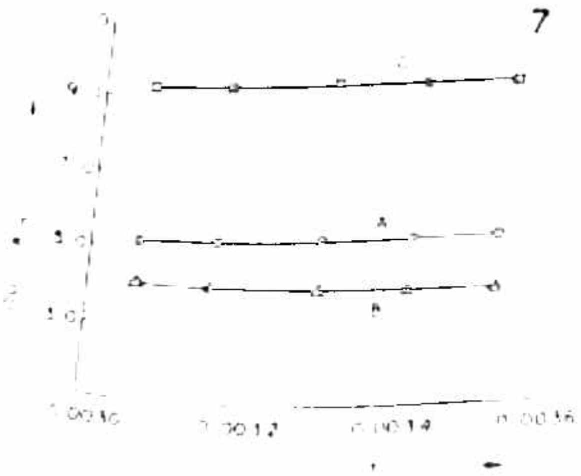

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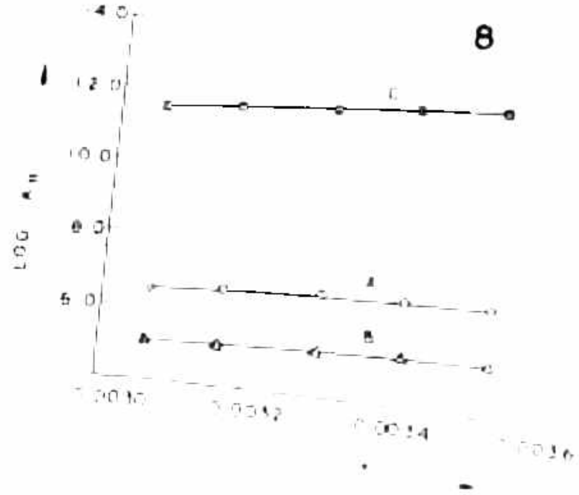

PLATE NO. 22

Table 3.47

Values of stability constants and thermodynamic functions of UO_2-NRS system

ΔH_1 = - 4.498

ΔH_2 = - 4.273

ΔH = - 8.784
(Kcal/mole)

Temperature (^oC)	10	20	30	40	50
log K_1	6.84	6.76	6.69	6.51	6.42
log K_2	5.42	5.29	5.12	5.08	5.01
log K_c	12.26	12.05	11.81	11.59	11.43
- ΔG_1	8.86	9.06	9.28	9.33	9.49
- ΔG_2	7.02	7.10	7.10	7.28	7.41
- ΔG (Kcal/mole)	15.88	16.16	16.38	16.61	16.90
ΔS_1	15.44	15.58	15.76	15.41	15.45
ΔS_2	9.70	9.63	9.46	9.59	9.69
ΔS (e.u.)	25.05	25.11	25.05	24.91	25.11

PART III

METAL CHELATES OF RIBOFLAVIN

Introduction

Nitrogen is one of the most powerful electron donors among the elements. The lone electron pair in nitrogen's hybridised Sp^3 orbitals can be donated to a variety of electron acceptors, to form a host of compounds of widely different nature. This coupled with the availability of a large number of nitrogen containing organic compounds, place nitrogen containing ligands among the most versatile of ligands.

The earlier work on nitrogen containing ligands was mainly centred on a study of co-ordinating behaviour of ammonia, ammines and ethylenediamine. The pioneering work in this field was done by Werner (39), who studied the synthetic and stereochemical aspects of metal ammines and by Bjerrum (40) who studied metal ammine formation in aqueous solution. Recently, interest has been diverted principally towards bidentate and polydentate nitrogen containing ligands.

Nitrogen containing ligands are of immense importance in every aspect of chemistry. The well known reagent for nickel i.e. dimethyl glyoxime co-ordinates through its nitrogens. Extensive advantage is taken of the complexing tendencies of azodyes in the dye industry. Many of the biologically important chelates like chlorophyll and haemin are metal chelates of nitrogen containing ligands. The widespread use of chelates in homogeneous and heterogeneous catalysis has necessitated a rapid development of specific nitrogen containing ligands. Thus, it would be reasonable to assert, with confidence, that there is no facet of chemical science which is untouched by these ligands.

8-hydroxyquinoline owes its well-known avidity for metallic cations to the presence of an ionisable hydroxyl group next to a tertiary heterocyclic nitrogen atom. The presence of a similar configuration in several of the naturally occurring purines i.e. riboflavin, gave rise to a suggestion that these substances also, bind metallic cations (41,42) through the nitrogen atom. The structure of riboflavin may be represented as

and is known as riboflavin (RBF), lactoflavin or vitamin B_2.

Riboflavin has been reported by Albert (43) to form complexes with some metal ions, in solution. Foye and Lange (44) isolated solid metal ion complexes of riboflavin containing two metal ions per riboflavin molecule.

They reported that when a solution of metal salt was added to a solution of riboflavin, initially at pH 9, a substantial drop in the pH was observed and a coloured precipitate was immediately formed. This work has however been questioned by various workers (45-47). A number of metal salts and complexes of riboflavin has been reported to be inhibitory to tumor growth (48).

Biosynthesis and hydrolysis of RBF was discussed by Axelord and Martin (49) and Kumar and Rao (50). Some factors affecting the biosynthesis of RBF were determined by Kanopkaite and Gibaviciute (51). Vaisman (52) studied that RBF cannot be stored for more than 10 days because of its being susceptible to oxidation. Thermal decomposition of RBF was discussed by Kiyohide (53) and Kazuo and Motome (54). Draper and Ingraham (55) determined the pK values of RBF potentiometrically.

Kaderavek and Prati (56) determined RBF in cheese and was extracted from various animal and vegetable food products (57). A review of discussion of the methods of determination for RBF was given by Jancki, Kaminski and Stanicki (58). Some biological applications were studied by Burns and Conney (59). William et al. (60) studied the photochemistry of riboflavin. It changes its colour by ultraviolet and visible light (61).

The chelating tendencies of RBF were discussed by Thomas and Henry (62). Spence and Tocatlian (63) studied of RBF were extracted and their I.R. spectra were studied by Spence and Peterson (64). The properties of complexes of enzymes with riboflavin were studied by Richard and Plaut (65).

The survey of the literature however shows that very little work has been done on the metal complexes of RBF. Recently Nayan and Dey (66) made a systematic study of the stepwise formation of Al(III), Cr(III), Be(II), Pb(II) and U(VI) complexes with riboflavin.

In the present work, the chelates of riboflavin with Cu(II), Zn(II), Cd(II) and Hg(II) have been studied in detail. These studies have been carried out in aqueous media of different ionic strengths viz. 0.01, 0.02, 0.05, 0.10 and 0.15 at a fixed temperature of 25°C. The thermodynamic stability constants were also calculated by extrapolating the values of measured stability constants to zero ionic strength.

The experimental details are the same as given in the case of metal chelates of ARS and have been described, in detail, in Chapter II. Riboflavin is soluble either in hot water or in an alkaline solution. An aqueous solution of riboflavin (E. Merck) was used for these studies.

RESULTS

Proton-Ligand System

In order to calculate the metal-ligand stability constants, it is necessary to determine the proton-ligand stability constants.

The observations made during the titrations of mixtures A and B, containing perchloric acid alone and perchloric acid plus ligand respectively, have been utilized to calculate the stability constants of proton-ligand system. The difference in the volume of alkali used in case of mixture A as compared to B, to have the same pH value, is clearly due to the neutralisation of riboflavin.

The values of v', v" and v"' were obtained from the graphs plotted in between alkali added and pH and then the various values of $\bar{n}_A$ were calculated at different pH values and at five ionic strengths i.e. 0.01, 0.02, 0.05, 0.10 and 0.15. The representative values of v', v" and v"' at one ionic strength only (to reduce the bulk of the thesis) are given in Table 3.48.

Table 3.48

N^o = 0.5263 V^o = 100.00

$T_{\cdot}$ = 0.00075 Y = 1.0

pH	v'	v''	v'''			
			Cu(II)	Zn(II)	Cd(II)	Hg(II)
3.60	0.956	0.962	0.960	0.932	0.960	0.964
4.00	0.963	0.967	0.965	0.941	0.965	0.973
4.20	0.967	0.967	0.970	0.947	0.968	0.980
4.40	0.970	0.970	0.974	0.953	0.973	0.987
4.60	0.973	0.973	0.977	0.958	0.975	0.993
4.80	0.974	0.974	0.978	0.962	0.978	1.000
5.00	0.974	0.974	0.980	0.965	0.980	1.002
5.20	0.977	0.977	0.980	0.967	0.981	1.003
5.40	0.978	0.978	0.981	0.970	0.983	1.004
5.60	0.978	0.978	0.982	0.973	0.984	1.005
5.80	0.979	0.979	0.984	0.977	0.985	1.006
6.00	0.980	0.980	0.988	0.979	0.986	1.007
6.20	0.980	0.980	0.992	0.982	0.987	1.008
6.40	0.981	0.981	0.996	0.986	0.988	1.010
6.60	0.981	0.982	1.000	0.988	0.989	1.011
6.80	0.982	0.984	1.003	0.991	0.990	1.012
7.00	0.982	0.985	1.006	0.994	0.991	1.013
7.20	0.983	0.987	1.010	0.997	0.992	1.015
7.40	0.984	0.987	1.013	1.000	0.992	1.016
7.60	0.984	0.988	1.017	1.004	0.993	1.017
7.80	0.986	0.990	1.020	1.008	0.995	1.018

(Contd.)

Plate No. 23

Temperature = 30°C

A. Formation curve of proton-RBF system (μ = 0.01)

B. Formation curve of proton-RBF system (μ = 0.02)

C. Formation curve of proton-RBF system (μ = 0.05)

D. Formation curve of proton-RBF system (μ = 0.10)

E. Formation curve of proton-RBF system (μ = 0.15)

F. Extrapolation of log K to zero ionic strength (H-RBF system)

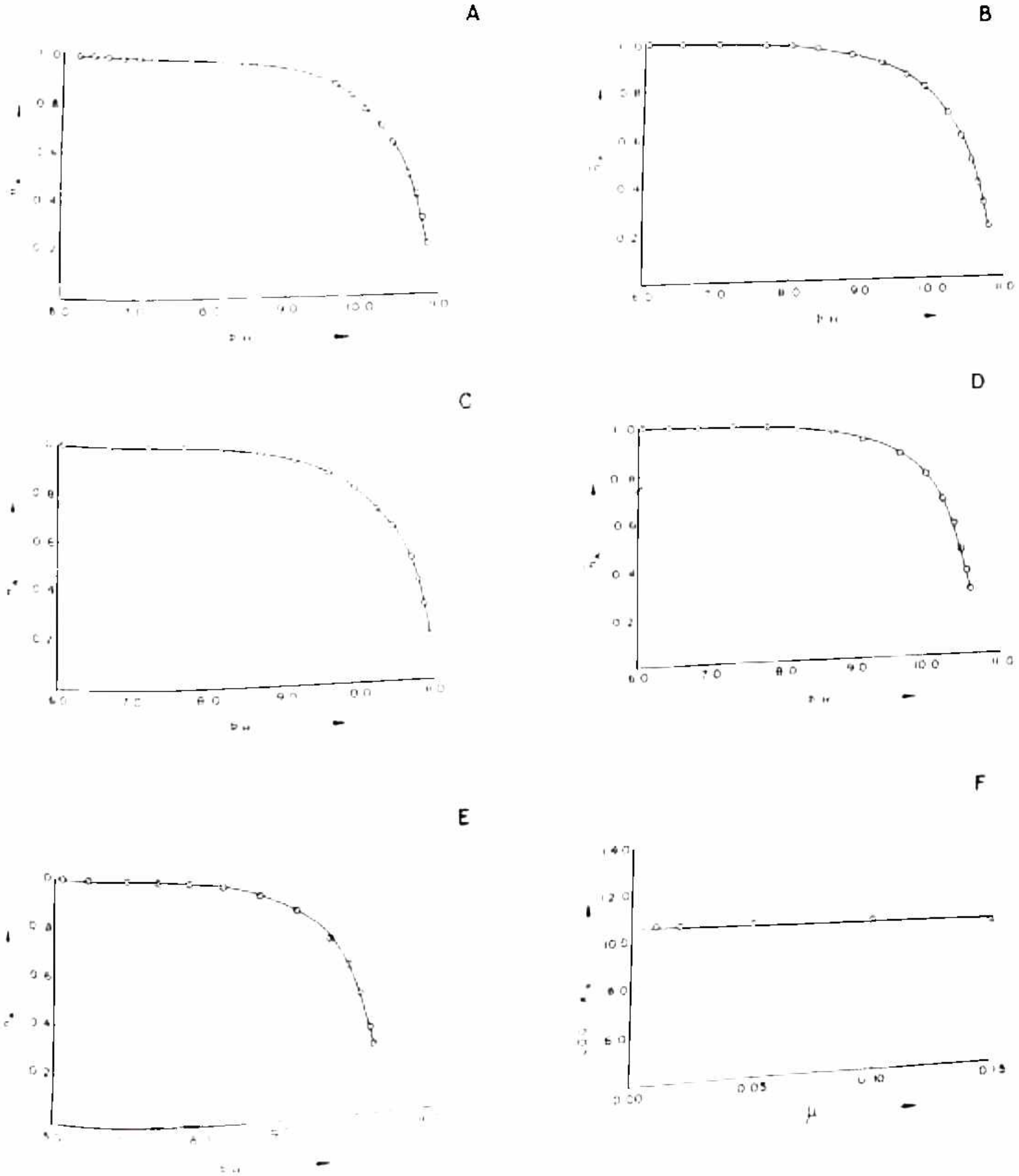
A
B
C
D
E
F
1.0
0.8
0.6
0.4
0.2
6.0
7.0
8.0
9.0
10.0
11.0
pH
14.0
12.0
10.0
8.0
6.0
0.00
0.05
0.10
0.15
μ

PLATE NO. 23

Table 3.48 (Contd.)

pH	v'	v"	v'''			
			Cu(II)	Zn(II)	Cd(II)	Hg(II)
8.00	0.986	0.992	1.021	1.012	0.996	1.020
8.20	0.987	0.993	1.023	1.017	0.998	1.022
8.40	0.988	0.994	1.026	1.022	1.004	1.024
8.60	0.988	0.995	1.028	1.027	1.011	1.027
8.80	0.990	0.995	1.032	1.032	1.022	1.029
9.00	0.992	0.998	1.036	1.037	1.050	1.033
9.20	0.993	1.000	1.041	1.042	1.077	1.036
9.40	0.994	1.005	1.050	1.050	1.093	1.040
9.60	0.997	1.015	1.060	1.060	1.111	1.047
9.80	1.000	1.025	1.072	1.073	1.127	1.057
10.00	1.007	1.040	1.088	1.089	1.140	1.070
10.20	1.017	1.057	1.106	1.110	1.159	1.088
10.40	1.032	1.078	1.127	1.133	1.180	1.110
10.60	1.055	1.120	1.155	1.166	1.208	1.140
10.80	1.092	1.150	1.200	1.210	1.250	1.175
11.00	1.144	1.182	1.260	1.300	1.300	1.245

The proton-ligand formation curves (Plate 23) were obtained by plotting $\bar{n}_A$ at various pH values. Various computational methods viz. interpolation at half $\bar{n}_A$ values (H), and interpolation at various $\bar{n}_A$ values (V) were applied to determine the stepwise proton-ligand stability constants at different ionic strengths. The thermodynamic stability constants were obtained by extrapolating these values to zero ionic strength. All these values are reported in Table 3.49.

Table 3.49

Ionic strength	$\log K^H$		Mean $\log K^H$
	H	V	
0.01	10.62	10.56	10.60
0.02	10.54	10.54	10.54
0.05	10.49	10.51	10.50
0.10	10.42	10.38	10.40
0.15	10.00	10.01	10.00
0.00*	-	-	10.66

* Value extrapolated at zero ionic strength

Metal Ligand System

All the calculations of $\bar{n}_A$, $\bar{n}$ and pL were made on the IBM Computer 1130 and checked.

The values of $\bar{n}$ were calculated at various pH values from the equation mentioned earlier and then the corresponding values of pL were computed from this data. These values of $\bar{n}$ and pL at one ionic strength (to reduce the bulk of the thesis) are reported in Tables 3.50-3.51.

Table 3.50

T_L = 0.00075 T_M = 0.00015

N^o = 0.5263 V^o = 100.0

μ = 0.01 Figure - Plate 24,A

pH	Cu(II)		Zn(II)	
	$\bar{n}$	pL	$\bar{n}$	pL
5.40	0.104	8.338	-	-
5.60	0.138	8.141	-	-
5.80	0.174	7.944	-	-
6.00	0.277	7.754	-	-
6.20	0.416	7.567	0.069	7.535
6.40	0.520	7.377	0.173	7.344
6.60	0.628	7.187	0.209	7.147
6.80	0.668	6.991	0.246	6.951
7.00	0.743	6.799	0.318	6.757
7.20	0.820	6.607	0.356	6.561
7.40	0.920	6.417	0.460	6.371
7.60	-	-	0.570	6.181
7.80	1.069	6.033	0.041	5.988
8.00	-	-	0.723	5.797
8.20	1.085	5.635	0.866	5.612
8.40	1.157	5.433	1.012	5.427
8.60	1.203	5.248	1.166	5.244
8.80	1.328	5.063	1.328	5.063
9.00	1.394	4.871	1.431	4.875
9.20	-	-	1.552	4.690

(Contd.)

Table 3.50 (Contd.)

pH	Cu(II)		Zn(II)	
	$\bar{n}$	pL	$\bar{n}$	pL
9.40	1.714	4.511	1.714	4.511
9.60	1.796	4.322	1.796	4.322
9.80	1.938	4.142	1.979	4.148

Table 3.51

T_L = 0.00075 T_M = 0.00015

N^o = 0.5263 V^o = 100.00

μ = 0.01 Figure - Plate 24,A

pH	Cd(II)		pH	Hg(II)	
	$\bar{n}$	pL		$\bar{n}$	pL
8.00	0.144	5.741	3.80	0.072	9.935
8.20	0.181	5.545	4.00	0.214	9.748
8.40	0.361	5.361	4.20	0.450	9.570
8.60	0.583	5.183	4.40	0.589	9.383
8.70	0.723	5.119	4.60	0.723	9.197
8.80	0.969	5.022	5.20	0.901	8.615
			5.60	0.936	8.219
			5.80	0.942	8.020
			6.20	0.970	7.623

The values of $\bar{n}$ were plotted against the corresponding pL values to get the formation curves of metal complexation equilibria. Various computational methods viz. interpolation at half $\bar{n}$ values (H), interpolation at various $\bar{n}$ values (V) and mid-point slope method (M) were applied to determine the stepwise metal-ligand stability constants and the values are reported in Tables 3.52-3.55. The values obtained by different methods are in fair agreement.

Table 3.52

Values of stability constants of Cu-RBF system at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.01	log K_1	7.38	7.33	7.34	
	log K_2	4.70	4.70	4.72	
	log K_c	12.08	12.03	12.06	12.05
0.02	log K_1	6.94	6.95	6.84	
	log K_2	3.68	3.66	3.85	
	log K_c	10.62	10.61	10.69	10.64
0.05	log K_1	6.78	6.81	6.38	
	log K_2	3.65	3.76	4.06	
	log K_c	10.43	10.57	10.44	10.48

(Contd.)

Table 3.52 (contd.)

Ionic strength	log K_n	H	V	M	Mean
0.10	log K_1	6.48	6.43	6.16	
	log K_2	4.04	4.05	3.98	
	log K_c	10.52	10.48	10.14	10.38
0.15	log K_1	6.64	6.43	6.39	
	log K_2	3.25	3.40	3.35	
	log K_c	9.89	9.83	9.74	9.82

Table 3.53

Values of stability constants of Zn-RBF chelate at various ionic strengths

Ionic strength	log K_n	H	V	M	Mean
0.01	log K_1	6.30	6.39	6.51	
	log K_2	4.90	4.74	4.58	
	log K_c	11.20	11.13	11.09	11.14
0.02	log K_1	6.28	6.33	6.31	
	log K_2	4.03	4.21	4.34	
	log K_c	10.31	10.54	10.65	10.50
0.05	log K_1	6.12	6.38	6.20	
	log K_2	4.05	4.19	4.23	
	log K_c	10.17	10.57	10.43	10.39

(Contd.)

Plate No. 24

Temperature = 30°C

A. Formation curves of RBF-metal chelates ($\mu = 0.01$)
(1) Cu-RBF (2) Zn-RBF (3) Cd-RBF
(4) Hg-RBF

B. Formation curves of RBF-metal chelates ($\mu = 0.02$)
(1) Cu-RBF (2) Zn-RBF (3) Cd-RBF
(4) Hg-RBF

C. Formation curves of RBF-metal chelates ($\mu = 0.05$)
(1) Cu-RBF (2) Zn-RBF (3) Cd-RBF
(4) Hg-RBF

D. Formation curves of RBF-metal chelates ($\mu = 0.10$)
(1) Cu-RBF (2) Zn-RBF (3) Cd-RBF
(4) Hg-RBF

E. Formation curves of RBF-metal chelates ($\mu = 0.15$)
(1) Cu-RBF (2) Zn-RBF (3) Cd-RBF
(4) Hg-RBF

F. Extrapolation of log K to zero ionic strength
(Cu-RBF system)
A - log K_1; B - log K_2; C - log K_c

G. Extrapolation of log K to zero ionic strength
(Zn-RBF system)
A - log K_1; B - log K_2; C - log K_c

H. Extrapolation of log K to zero ionic strength.
A - Cd-RBF; B - Hg-RBF system.

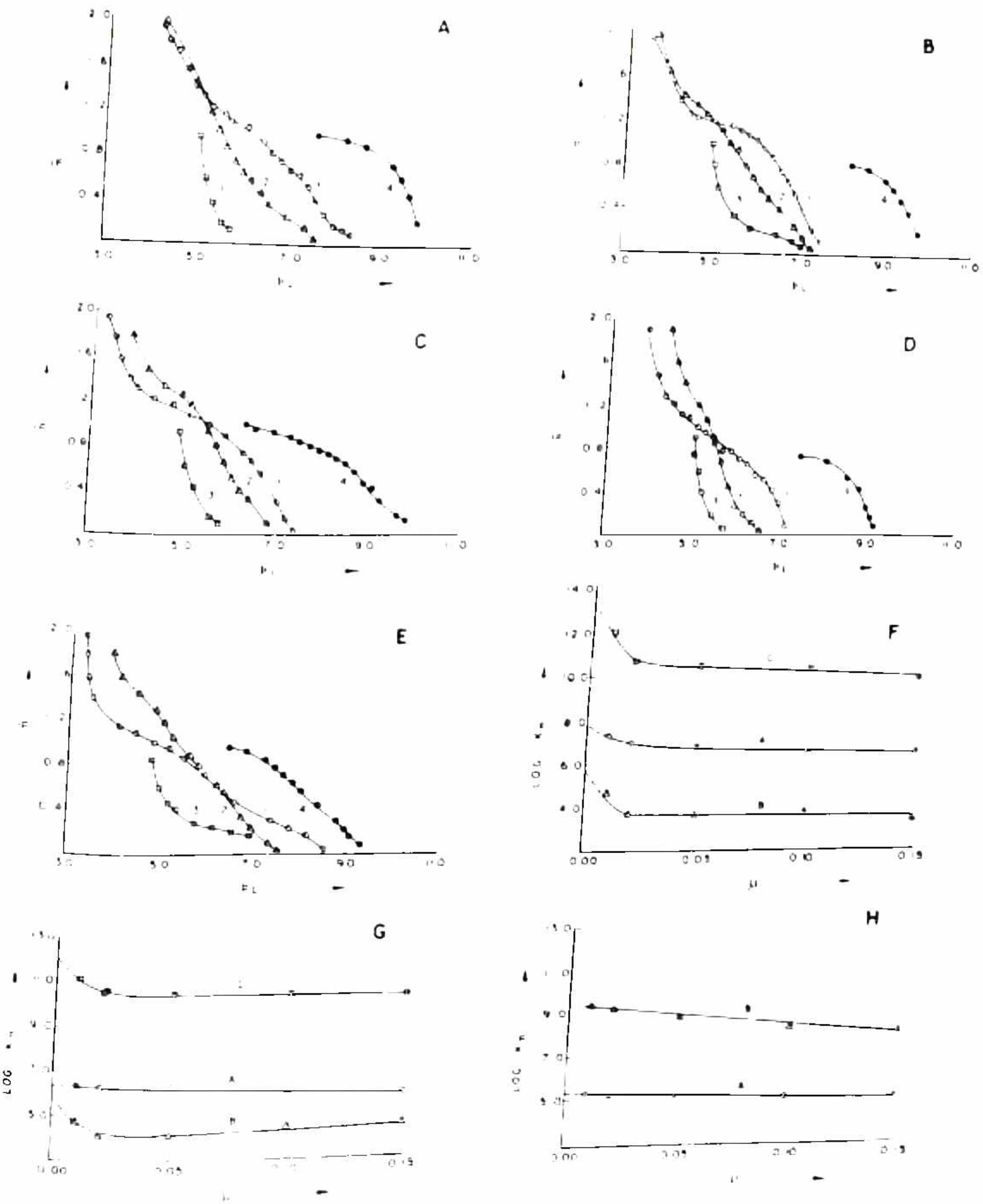
A
B
C
D
E
F
G
H
2.0
1.6
1.2
0.8
0.4
3.0
5.0
7.0
9.0
11.0
pH
LOG K
14.0
12.0
10.0
8.0
6.0
4.0
0.00
0.05
0.10
0.15
μ

PLATE NO 24

Table 3.53 (Contd.)

Ionic strength	log K_n	H	V	M	Mean
0.10	log K_1	5.73	5.83	5.70	
	log K_2	4.58	4.45	4.61	
	log K_c	10.31	10.28	10.31	10.30
0.15	log K_1	5.54	5.50	5.80	
	log K_2	4.40	4.39	4.52	
	log K_c	9.94	9.89	10.32	10.15

Table 3.54

Values of stability constants of Cd-HBF system at various ionic strengths

Ionic strength	log K_n	H	V	Mean
0.01	log K_1	5.23	5.37	5.30
0.02	log K_1	5.21	5.35	5.28
0.05	log K_1	5.20	5.26	5.23
0.10	log K_1	5.15	5.24	5.20
0.15	log K_1	5.10	5.24	5.17

Table 3.55

Values of stability constants of Hg-RBF system at various ionic strengths

Ionic strength	log K_n	H	V	Mean
0.01	log K_1	9.51	9.45	9.48
0.02	log K_1	9.30	9.20	9.25
0.05	log K_1	8.86	8.75	8.80
0.10	log K_1	8.52	8.38	8.45
0.15	log K_1	8.22	8.20	8.21

Thermodynamic Stability Constants

The thermodynamic stability constants were obtained by extrapolation of measured stability constants to zero ionic strength (Plate 24-F, G and H). The values of log step stability constants at various ionic strengths were extrapolated to zero ionic strength to give step thermodynamic stability as log $K_1^{\mu=0}$ and log $K_2^{\mu=0}$. The values of the overall concentration stability constants K_c, at various ionic strengths were likewise extrapolated to zero ionic strength. The overall thermodynamic stability constants, thus obtained, have been symbolised as experimental log $K_t^{\mu=0}$. The values of thermodynamic stability constants have been reported in Table 3.56.

Table 3.56

Values of thermodynamic stability constants at 25°C

$\log K_n$	Cu(II)	Zn(II)	Cd(II)	Hg(II)
$\log K_1^{\mu=0}$	7.81	6.42	5.41	9.49
$\log K_2^{\mu=0}$	5.81	5.71	-	-
$\log K_c^{\mu=0}$ (calculated)	13.62	12.13	-	-
$\log K_c^{\mu=0}$ (experimental)	13.59	12.08	5.41	9.49

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CHAPTER IV

SPECTROPHOTOMETRIC STUDIES

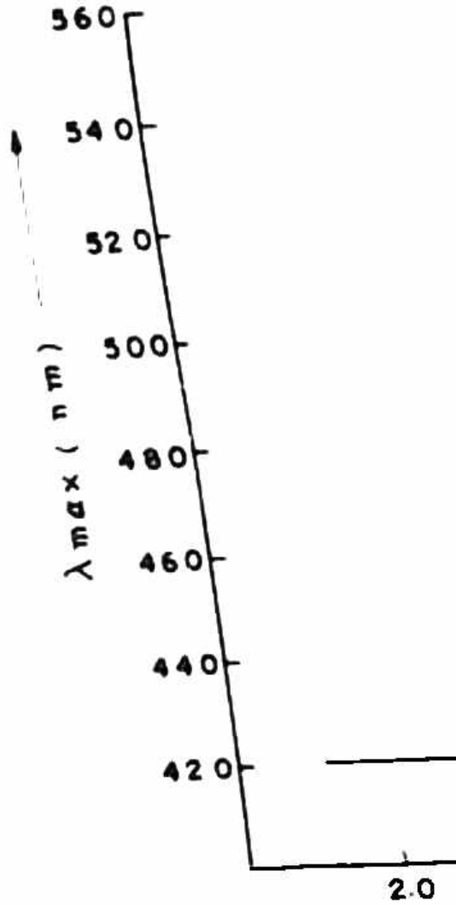
OBJECT OF PHOTOMETRIC STUDIES

The formation of coloured chelates by metals in solution, with various chelating agents has received considerable attention in recent years. It forms the basis of colorimetric analysis by the measurement of the intensity of colour of the solution. Almost all metals can now be determined colorimetrically and Sandell has estimated seventy five per cent of the metals. These methods are superior to the conventional methods because of better selectivity and sensitivity.

Among the chromogenic ligands, many dyes have offered considerable interest on account of their tendency of forming metal dye complexes in solution. The variation in colour by interaction between a metal ion and a suitable ligand in solution, forms the basis of chromogenic reactions in which absorbance measurements are possible.

The divalent metal ions selected here, are those, on which, no work has been reported in the literature. The chelates of Zn(II), Be(II), Ni(II) and Co(II) with Alizarin Red S and Ni(II) with Nitroso-R-salt have been studied.

A detailed study of these systems along with their photometric determinations, has been reported in the present chapter.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540
520
500
480
460
440
420
λmax (nm)
2.0

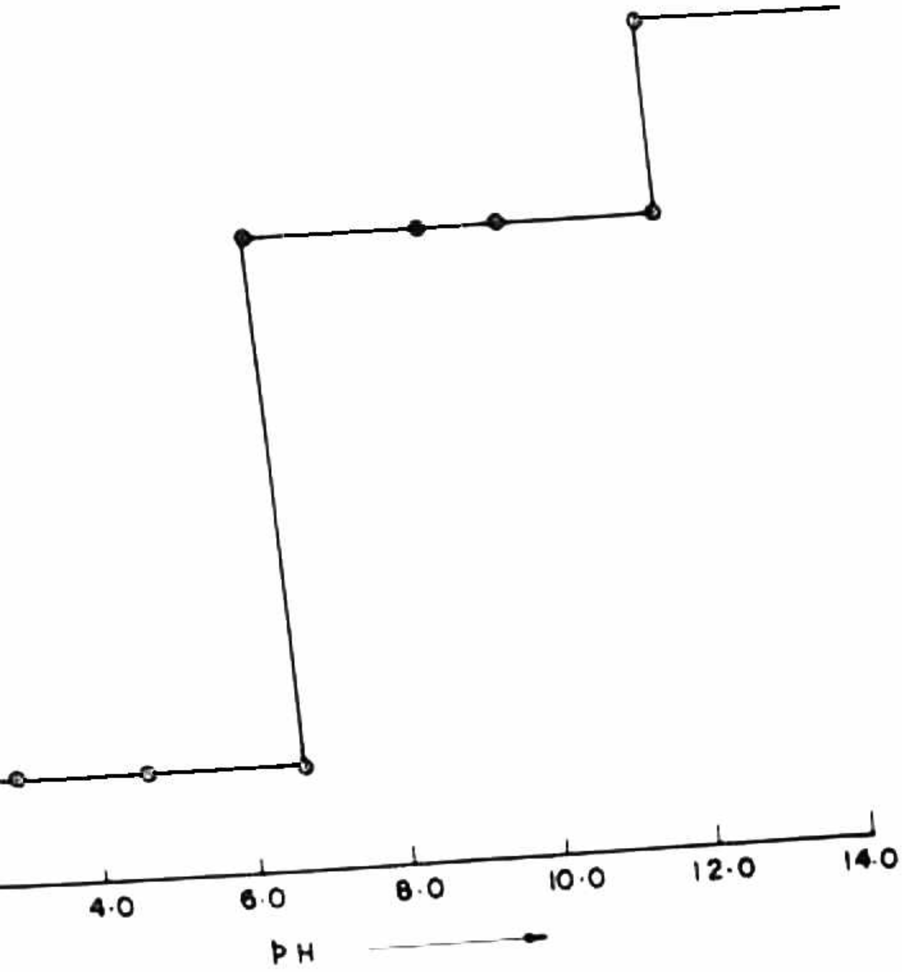


PLATE NO. 25

METAL CHELATES OF ALIZARIN RED S

Characteristics of Alizarin Red S

Alizarin Red S (ARS) changes its colour with the variation in hydrogen ion concentration and a study of the absorption spectrum shows a shift in the λ_{max} with the change in the pH of the medium. A stock solution of ARS was prepared in double distilled water, and a number of solutions were prepared at different pH values by dilution of the stock solution. All the studies were made at 25±0.1°C. The results obtained have been summarised in Table 4.1 and graphically represented in Plate 25.

Table 4.1

Shift in λ_{max} with change in pH of ARS

pH	λ_{max}
1.2 - 6.7	420
5.7 - 12.0	520
> 12.0	555

Instruments

All absorbance measurements were made on UV-VIS Hitachi Perkin Elmer (Model 139) spectrophotometer using one cm matched quartz cells, equipped with thermoplates to stabilize the temperature of the cell holder. pH was measured on a Beckman pH meter (Model H2) using a glass-calomel electrode assembly.

Chemicals

All the chemicals used throughout this work, were of 'AnalaR' or reagent grade quality. All the solutions of the metals and ligand were prepared in double distilled water. Stock solutions of diverse ions were prepared from the corresponding metal salts.

Conditions of Study

Appropriate dilution of the solutions were made by adding double distilled water. All the studies were carried out at 25°C. The individual solutions and the mixtures were kept in a precision thermostat (Forma Scientific Model 2095) maintained at 25±0.1°C, for half an hour to attain the equilibrium. The pH in the chelates of Zn(II) and Be(II) were adjusted using hexamine-perchloric acid buffer and in the chelates of Ni(II) and Co(II) with ARS by using potassium hydrogen phthalate-NaOH buffer solution. The conditions of study of all the chelates are given in Table 4.2.

Effect of Time and Temperature

The chelate formation was found to be instantaneous in all cases. Studies revealed that there was no significant change in the absorbance values even after six or eight hours. The temperature change had no measurable effect on the absorbance of the complex. The order of addition of reagents did not have any effect on the absorbance of the chelates. However, in the present studies, the metal ion solution was taken first in all the cases, to ensure uniformity.

Effect of pH

In order to study the effect of pH on the absorbance of the chelate, a series of solutions containing a fixed amount of metal and ligand were prepared at different pH values. The pH of the solutions were adjusted to the required value and the total volume was made upto 25 ml. The absorption spectra were recorded against reagent blank. The pH range in which the chelates were stable along with the pH at which the studies were carried out are recorded in Table 4.2.

Nature of the Complex Formed

The method of Vosburgh and Cooper (1) was employed to determine the nature of the complex, in solution. Mixtures containing various proportions of metal and ligand (2:1, 1:0, 1:1, 1:2, 1:3, 1:4, etc.) were prepared. The pH of the solutions of Zn(II), Be(II), Co(II) and Ni(II) chelates with ARS were adjusted to within ±0.1 of the required pH. The absorbance of these mixtures at various wavelengths were measured and the results have been graphically represented in Plates 26,A-29,A. The results show that only one complex is formed under the conditions of study, in all the systems. The concentrations employed in the studies are recorded in Table 4.3.

Stoichiometry of the Chelates

In order to obtain the empirical formulae of these chelates, in the solution, three independent methods were applied.

(i) Continuous variation method

Job's method of continuous variation (2) was adopted for the determination of the composition of the coloured complexes. The results and conditions of studies at λ_{max} of each chelate have been summarized in Table 4.4 and are graphically represented in Plates 26,B-29,B.

(ii) Mole ratio method

For the determination of composition by mole ratio method (3), a series of solutions was prepared from metal and ligand at appropriate pH. The mole ratio of metal to ligand was varied from 1:025 to 1:10. The absorbance of these mixtures were measured at λ_{max} of the chelate. In order to economise on the space, only one representative result has been graphically represented in Plate 27,D.

(iii) Slope ratio method

In this method, the volume of the variable component was varied from 0.0 to 5.0 ml in the presence of an excess concentration of the other (4). The concentrations employed and results obtained are given in the Table 4.5. The results are graphically represented in Plate 27,E, 28,D and 29,D.

Evaluation of Stability Constant

The stability constants of these chelates have been determined by two different methods described earlier. The values of the stability constants by different methods are recorded in Table 4.6.

Effect of Ionic Strength on Stability Constant

With a view to obtain the thermodynamic stability constant of the chelates, the stability constant of the chelates at different ionic strengths, at a particular pH and temperature (cf. Table 4.2) have been determined. By the method of extrapolation, using log K values, to zero ionic strength , the thermodynamic stability constant has been calculated and the results have been recorded in Table 4.7.

ANALYTICAL APPLICATIONS

Experiments were performed to test the suitability of the chelate for the photometric determination of the metal.

Standard Procedure

Transfer 5.0 ppm in case of Zn(II), 2.0 ppm for Be(II) and 2.24 ppm of the metal solution for Co(II) and Ni(II) systems to a 25 ml flask and add at least eight fold concentration of ARS for Zn(II), twenty fold concentration for Be(II) and ten fold for Ni(II) and twenty fold concentration of the ligand for Co(II). The solution may then be made upto the mark after adjusting the pH to the required value, allowing 30 minutes for the solutions to attain the equilibrium. The absorbance was measured at the λ_{max} of the chelate.

Effect of Reagent Concentration

The effect of the changes in the concentration of ligand on the absorbance of the chelate, at that pH, was determined at the λ_{max}. It was observed that the absorbance increased with increase in the reagent concentration; hence the reagent concentration was kept constant. It was found that at least eight fold concentration of the reagent was essential for the effective spectrophotometric determination of Zn(II), twenty fold for Be(II), ten fold for Ni(II) and twenty fold for Co(II) with ARS.

Beer's Law and Sensitivity

Calibration curves for the determination of Zn(II), Be(II), Ni(II) and Co(II) with ARS were prepared by using

Plate No. 26

A. Absorption curves of the mixtures of zinc chloride and ARS.

Curve 1 - $ZnCl_2$ = 8.00 × 10^{-5}M, ARS = 8.0 × 10^{-5}M

Curve 2 - $ZnCl_2$ = 4.00 × 10^{-5}M, ARS = 8.0 × 10^{-5}M

Curve 3 - $ZnCl_2$ = 2.66 × 10^{-5}M, ARS = 8.0 × 10^{-5}M

Curve 4 - $ZnCl_2$ = 2.00 10^{-5}M, ARS = 8.0 × 10^{-5}M

B. Variation in absorbance of Zn-ARS chelate with pH

T_M = 4.0 × 10^{-5}M, T_L = 8.0 × 10^{-5}M.

C. Job's curves for Zn-ARS chelate.

Curve 1 - C_M = C_L = 2.0 × 10^{-3}M

Curve 2 - C_M = C_L = 1.0 × 10^{-3}M

Curve 3 - C_M = C_L = 5.0 × 10^{-4}M

D. Job's curves for Zn-ARS chelate

Curve 1 - C_M = 1.0 × 10^{-3}M, C_L = 2.0 × 10^{-3}M

Curve 2 - C_M = 5.0 × 10^{-4}M, C_L = 1.0 × 10^{-3}M

E. Beer's law plot for Zn-ARS chelate

F. Ringbom plot for Zn-ARS chelate

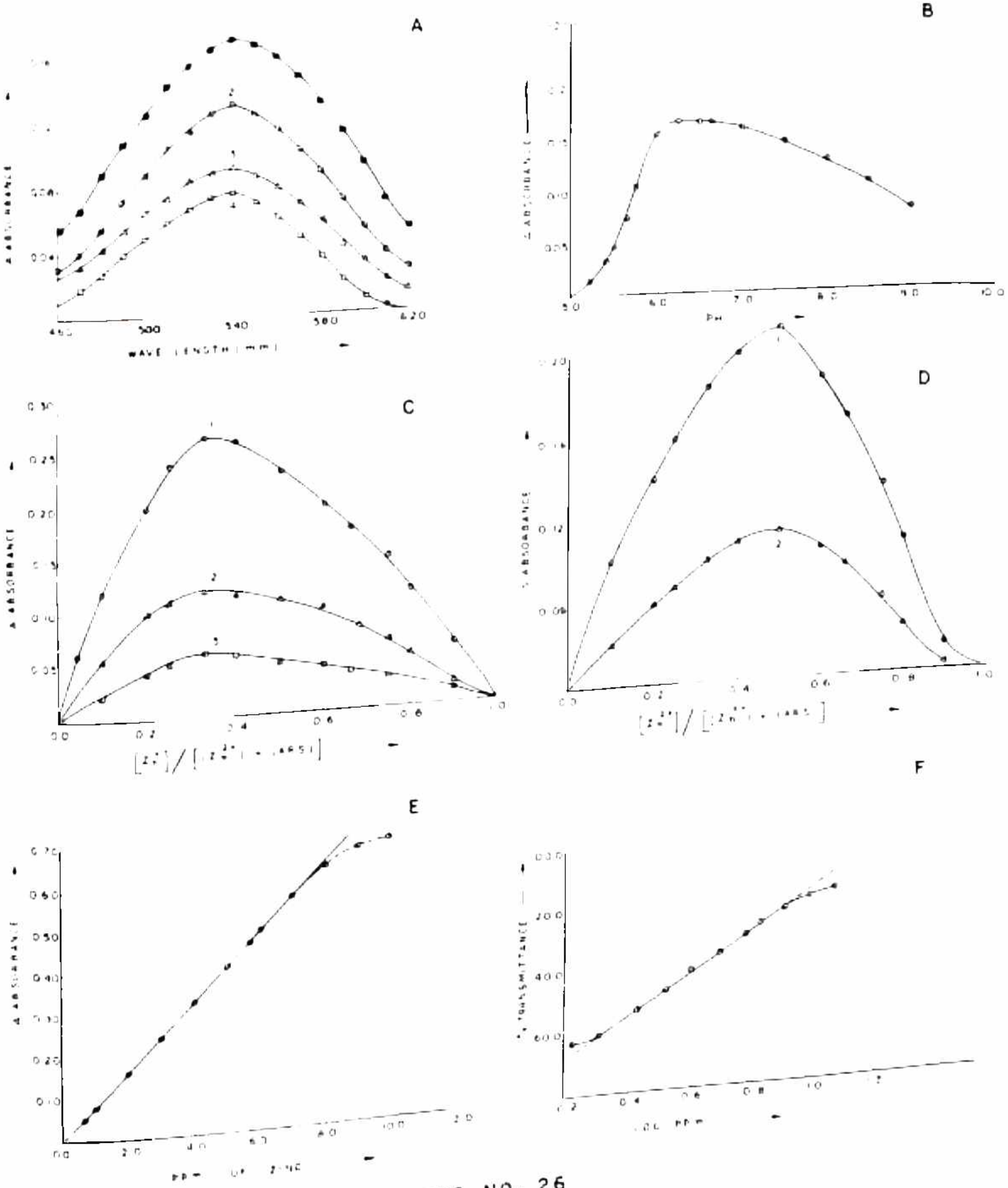
A
ABSORBANCE
WAVE LENGTH (mμ)
460
500
540
580
620
B
ABSORBANCE
0.05
0.10
0.15
0.2
PH
5.0
6.0
7.0
8.0
9.0
10.0
C
ABSORBANCE
0.05
0.10
0.15
0.20
0.25
0.30
0.0
0.2
0.4
0.6
0.8
1.0
D
ABSORBANCE
0.08
0.12
0.16
0.20
0.0
0.2
0.4
0.6
0.8
1.0
E
ABSORBANCE
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.0
2.0
4.0
6.0
8.0
10.0
12.0
PPM OF ZINC
F
TRANSMITTANCE
20.0
40.0
60.0
0.2
0.4
0.6
0.8
1.0
1.2
LOG PPM

PLATE NO. 26

the standard procedure (Plates 26E, 27F, 28E and 29E). The range over which the Beer's law was obeyed has also been studied (Table 4.8). The optimum concentration range for the determination, was obtained by the Ringbom method and is tabulated in Table 4.8. Molar absorptivity and spectrophotometric sensitivity, according to Sandell's notation (5), at the λ_{max} of each chelate for $I_o/I = 0.001$, were calculated and recorded in Table 4.8.

REPRODUCIBILITY

Standard solutions of metal ions were analysed ten times by the standard procedure with ARS to determine the reproducibility. The results were found to be constant with a standard deviation of 0.005. The accuracy of the method was evaluated by analysing solutions containing known amounts of metal ions using the standard procedure.

Effect of Diverse ions

In order to examine the effect of diverse ions on the determination of metals, absorbance measurements were made for solutions containing a fixed amount of metal (in the final solution) in the presence of diverse ions. The tolerance limit was taken as the amount which caused absorbance error not exceeding ±3%.

Zn(II)-ARS System

Absorbance measurements were made for solutions

<u>Plate No. 27</u>

A. Absorption curves of the mixtures of $BeCl_2$ and ARS

Curve L - ARS = $1.6 \times 10^{-5}M$

Curve 1 - $BeCl_2 = 8.0 \times 10^{-5}M$, ARS = $16.0 \times 10^{-5}M$

Curve 2 - $BeCl_2 = 16.0 \times 10^{-5}M$, ARS = $16.0 \times 10^{-5}M$

B. Variation in absorbance of Be-ARS chelate with pH

$T_M = 4.0 \times 10^{-5}M$, $T_L = 8.0 \times 10^{-5}M$

C. Job's curves for Be-ARS chelate

Curve 1 = $C_M = C_L = 2.0 \times 10^{-3}M$

Curve 2 = $C_M = C_L = 1.0 \times 10^{-3}M$

Curve 3 = $C_M = C_L = 5.0 \times 10^{-4}M$

D. Mole ratio curves or spectrophotometric titration of a constant amount of Be(II) and varying amount of ARS.

Curve A - Conc. of Be(II) = $4.0 \times 10^{-5}M$

Curve B - Conc. of Be(II) = $2.0 \times 10^{-5}M$

E. Slope ratio method for Be-ARS chelate

Curve 1 - Ligand varying

Curve 2 - Metal varying

F. Beer's law plot for Be-ARS chelate

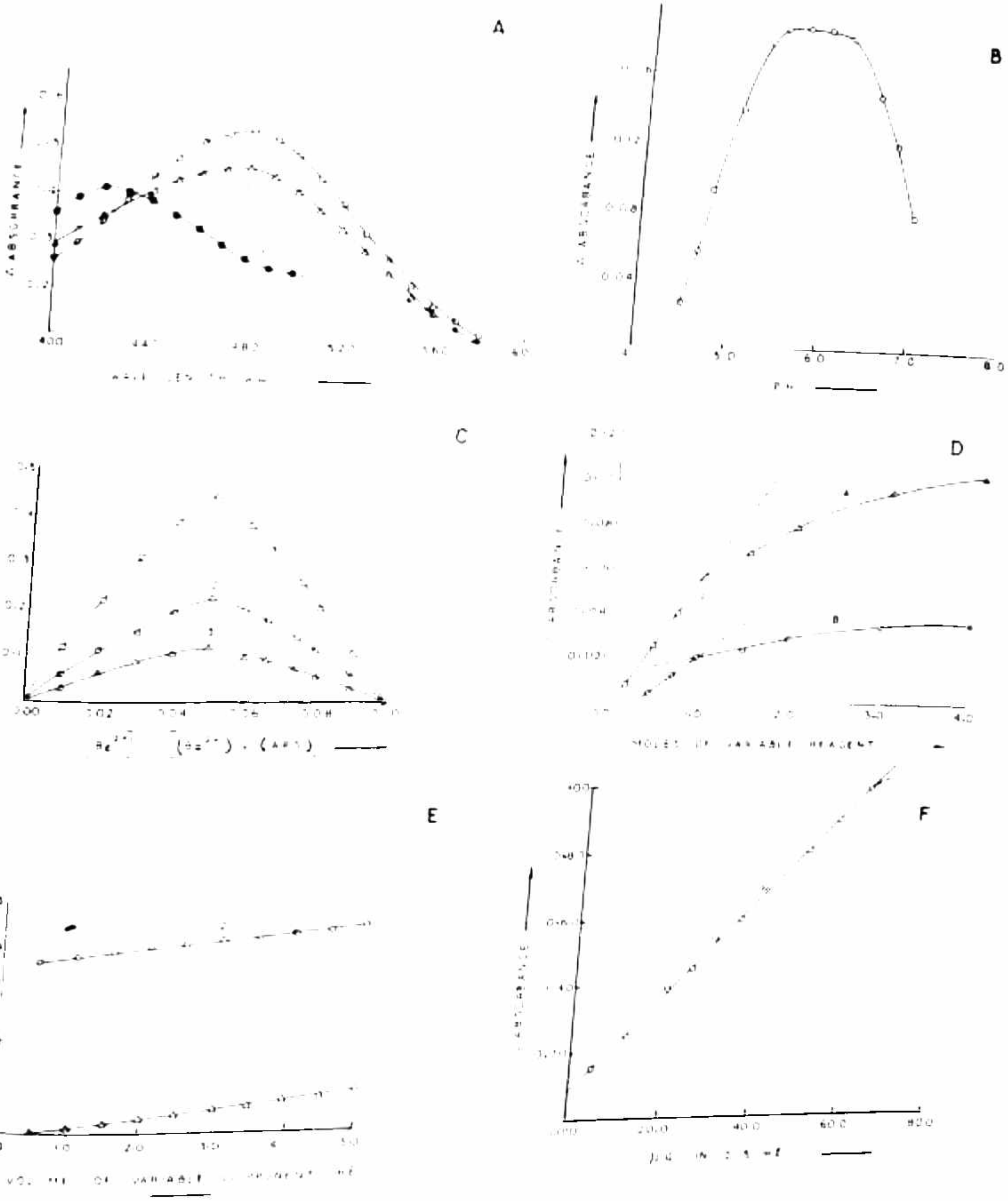

A
ABSORBANCE
400
B
ABSORBANCE
0.12
0.08
0.04
5.0
6.0
7.0
8.0
C
ABSORBANCE
0.1
0.2
0.3
0.4
0.00
0.02
0.04
0.06
0.08
D
B
0.020
1.0
2.0
3.0
4.0
MOLES OF VARIABLE REAGENT
E
ABSORBANCE
0.1
0.2
0.4
0.0
1.0
2.0
3.0
5.0
F
ABSORBANCE
20.0
40.0
60.0
80.0

PLATE NO. 27

Plate No. 28

A. Absorption curves of the mixtures of $NiSO_4$ and ARS

Curve 1 - $NiSO_4 = 16.0 \times 10^{-5}M$, ARS = $16.0 \times 10^{-5}M$

Curve 2 - $NiSO_4 = 8.0 \times 10^{-5}M$, ARS = $16.0 \times 10^{-5}M$

Curve 5 - $NiSO_4$ = - , ARS = $16.0 \times 10^{-5}M$

B. Variation in absorbance of Ni-ARS chelate with pH

$T_L = 4.0 \times 10^{-5}M$, $T_M = 8.0 \times 10^{-5}M$

C. Job's curves for Ni-ARS chelate

Curve 1 - $C_M = C_L = 2.0 \times 10^{-3}M$

Curve 2 - $C_M = C_L = 1.0 \times 10^{-3}M$

Curve 3 - $C_M = C_L = 5.0 \times 10^{-4}M$

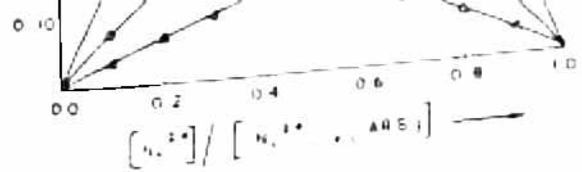
D. Slope ratio method for Ni-ARS chelate

Curve 1 - Ligand varying

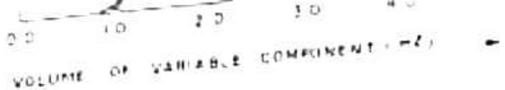
Curve 2 - Metal varying

E. Beer's law plot for Ni-ARS chelate

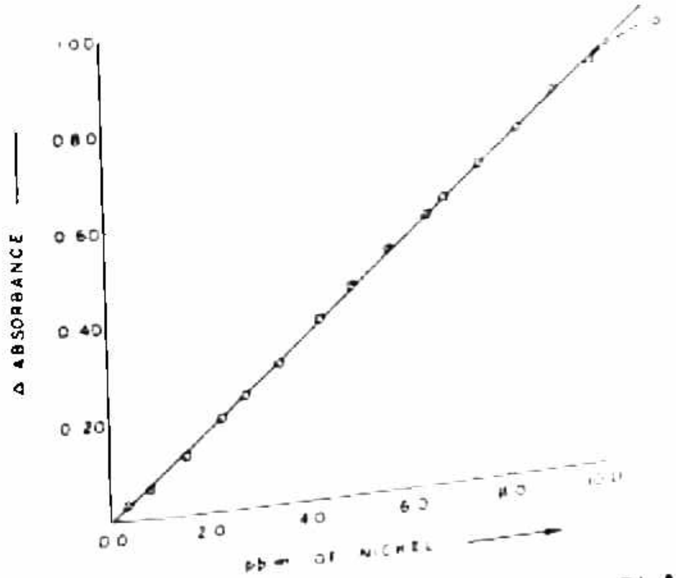
F. Ringbom plot for Ni-ARS chelate



E



F



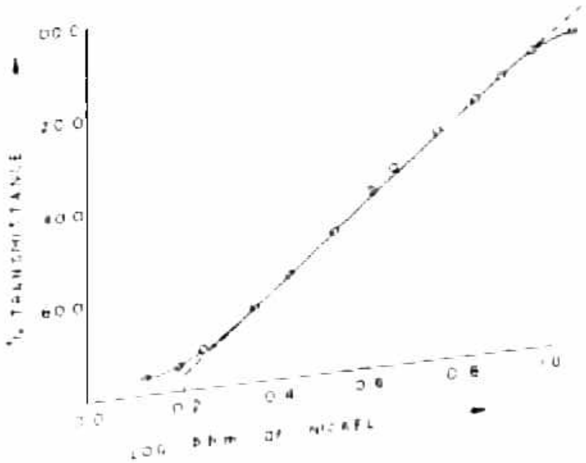
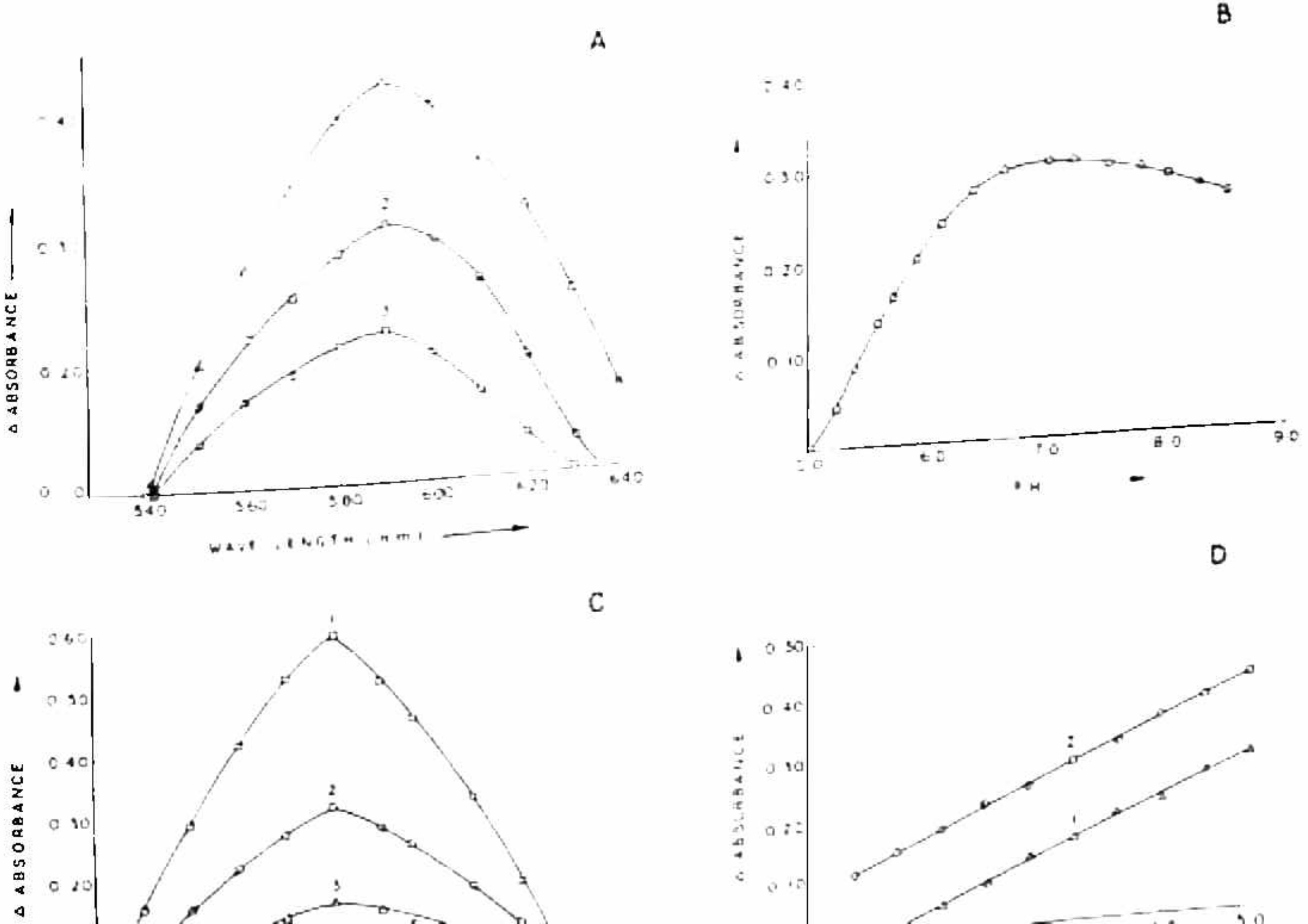


PLATE NO. 28


A
Δ ABSORBANCE
0.0
0.20
0.3
0.4
540
560
580
600
620
640
WAVE LENGTH (nm)
1
2
4
B
Δ ABSORBANCE
0.10
0.20
0.30
0.40
5.0
6.0
7.0
8.0
9.0
pH
C
Δ ABSORBANCE
0.20
0.30
0.40
0.50
0.60
1
2
3
D
Δ ABSORBANCE
0.10
0.20
0.30
0.40
0.50
1
2
5.0

containing 5.0 ppm of zinc in presence of diverse ions. From the results, it can be concluded that ions specially mercury (II), nickel (II), barium (II), chromium (III) and iron (III) interfere seriously while molybdenum (VI), silver (I), sulphate, acetate and oxalate did not interfere, even when the concentration was as high as 50 ppm.

Be(II)-ARS System

Absorbance measurements were made for the solutions containing 2.0 ppm of Be(II) in the presence of diverse ions. The results show that ions specially lead (II), zinc (II), copper (II), cadmium (II), nickel (II), cobalt (II), uranyl (II), vanadyl (II), molybdenum (VI), cerrous (II) and oxalate are not tolerated and interfere seriously while magnesium (II), barium (II), strontium (II), chloride, sulphate, borate, nitrate and iodide did not interfere even when the concentration was as high as 100 ppm.

Ni(II)-ARS System

Absorbance measurements were made for the solutions containing 2.24 ppm of Ni(II) in the presence of diverse ions. From the results it can be seen that ions like copper (II), zinc (II), cadmium (II), cobalt (II), beryllium (II), platinum (II), palladium (II), ferrous, vanadyl, aluminium (III) and cerrous interfere seriously while sulphate, oxalate, nitrate, tartarate, bromide and iodide did not interfere even when the concentration was

Plate No. 29

A. Absorption curves of the mixtures of $CoSO_4$ and ARS

Curve 1 - $CoSO_4$ = 16.00×10^{-5}M, ARS = 16.0×10^{-5}M

Curve 2 - $CoSO_4$ = 8.00×10^{-5}M., ARS = 16.0×10^{-5}M

Curve 3 - $CoSO_4$ = 5.33×10^{-5}M, ARS = 16.0×10^{-5}M

Curve 4 - $CoSO_4$ = 4.00×10^{-5}M, ARS = 16.0×10^{-5}M

B. Variation in absorbance of Co-ARS chelate with pH

$T_M = 4.0 \times 10^{-5}$M, $T_L = 8.0 \times 10^{-5}$M.

C. Job's curves for Co-ARS chelate

Curve 1 - $C_M = C_L = 2.0 \times 10^{-3}$M

Curve 2 - $C_M = C_L = 1.0 \times 10^{-3}$M

Curve 3 - $C_M = C_L = 5.0 \times 10^{-4}$M

D. Slope ratio method for Co-ARS chelate

Curve 1 - Ligand varying

Curve 2 - Metal varying

E. Beer's law plot for Co-ARS chelate

F. Ringbom plot for Co-ARS chelate.

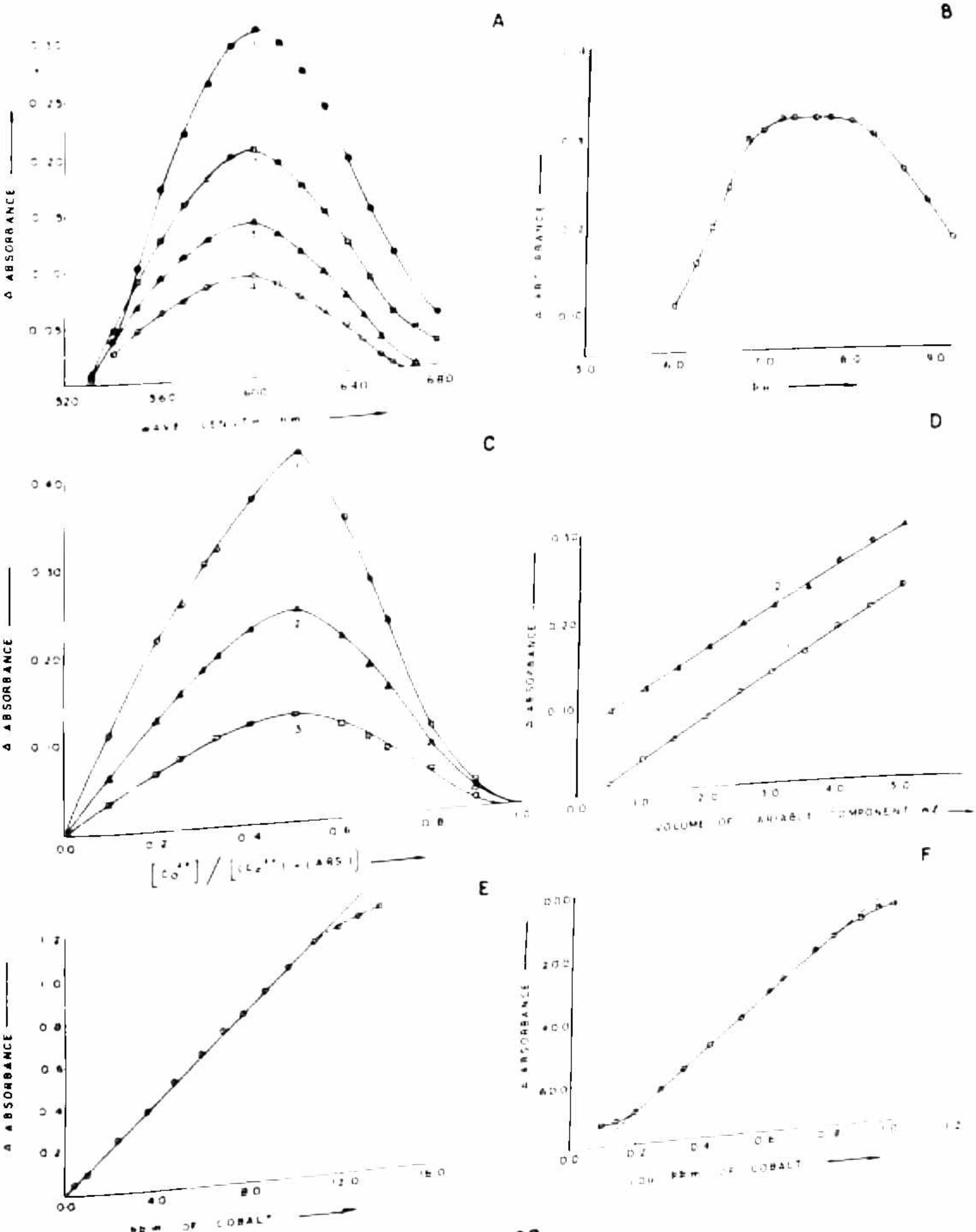

A
Δ ABSORBANCE
0.30
0.25
0.20
0.15
0.10
0.05
520
560
600
640
680
WAVE LENGTH nm
1
2
3
4
B
Δ ABSORBANCE
0.4
0.3
0.2
0.10
5.0
6.0
7.0
8.0
9.0
pH
C
Δ ABSORBANCE
0.40
0.30
0.20
0.10
0.0
0.2
0.4
0.6
0.8
1.0
1
2
3
[Co²⁺] / [Co²⁺] + [ARS]
D
Δ ABSORBANCE
0.30
0.20
0.10
0.0
1.0
2.0
3.0
4.0
5.0
VOLUME OF VARIABLE COMPONENT ml
1
2
E
Δ ABSORBANCE
1.2
1.0
0.8
0.6
0.4
0.2
0.0
4.0
8.0
12.0
16.0
PPM OF COBALT
F
Δ ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.2
PPM OF COBALT

PLATE NO. 29

as high as 100 ppm.

Co(II)-ARS System

Absorbance measurements were made for the solutions containing 2.24 ppm of Co(II) in the presence of diverse ions. From the results it can be inferred that ions specially zinc (II), cadmium (II), nickel (II), beryllium (II), platinum (II), palladium (II), iron (II), vanadium (II), aluminium (III) and cerrous interfere seriously while magnesium (II), silver (I), chloride, sulphate, acetate, oxalate, chlorate, tartarate, bromide and iodide do not interfere even at high concentrations (100 ppm).

Table 4.2

Optimum conditions for the study of metal chelates

Chelate	Temperature (°C)	λ_{max} (nm)	pH range for stable existence	pH (±0.1) at which studies were made
Zn-ARS	25	540	5.8-8.0	6.4
Be-ARS	25	480	4.2-7.6	5.5
Ni-ARS	25	590	5.0-8.5	7.0
Co-ARS	25	600	5.0-8.5	7.0

Table 4.3

Vosburgh and Cooper's method for determining the nature of the chelate

Mixture	Concentration of metal taken (× 10^{-5}M)				Concentration of ARC taken		Metal to ligand ratio
	Zn(II)	Be(II)	Ni(II)	Co(II)	For Zn-ARC	For Be, Ni and Co with ARC	
1	8.00	8.00	16.00	16.00	8.0×10^{-5}M	16.0×10^{-5}M	1:1
2	4.00	16.00	8.00	8.00	8.0×10^{-5}M	16.0×10^{-5}M	1:2
3	2.66	-	-	5.33	8.0×10^{-5}M	16.0×10^{-5}M	1:3
4	2.00	-	-	4.00	8.0×10^{-5}M	16.0×10^{-5}M	1:4
5	-	-	16.00	-	-	8.0×10^{-5}M	2:1

Table 4.4

Job's method for determining the composition of chelates

System	Figure No.	Conditions of study				Metal to ligand ratio corresponding to peaks
		pH (± 0.1)	Temperature ($^{\circ}C$)	Ionic strength	λ_{max} (nm)	
Zn-ARS	Plate 26,C	6.4	25	0.10	540	1:2
Be-ARS	Plate 27,C	5.5	25	0.10	480	1:1
Ni-ARS	Plate 28,C	7.0	25	0.10	590	1:1
Co-ARS	Plate 29,C	7.0	25	0.10	600	1:1

Table 4.5

Slope ratio method for determining the composition

Conditions of study are as described in Table 4.2

System	Figure No.	Concentration in final solution				Metal to ligand ratio
		Metal $\times 10^{-4}$M	Ligand $\times 10^{-6}$M	Metal $\times 10^{-4}$M	Ligand $\times 10^{-5}$M	
Be-ARS	Plate 27,B	1.0	2.0	1.0	2.0	1:1
Ni-ARS	Plate 28,D	4.0	8.0	4.0	8.0	1:1
Co-ARS	Plate 29,D	4.0	8.0	4.0	8.0	1:1

Table 4.6

Values of stability constants (log K)

System	Mole ratio method	Molecular extinction coefficient method	Mean log K
Zn-ARS	8.13	7.65	7.89
Be-ARS	4.22	4.28	4.25
Ni-ARS	4.32	4.38	4.35
Co-ARS	3.91	3.52	3.71

Table 4.7

Variation of stability constant with ionic strength

Conditions of study are same as described in Table 4.2

Ionic strength	Be-ARS	Ni-ARS	Co-ARS
0.02	4.218	4.171	3.744
0.04	4.226	4.148	3.726
0.06	4.230	4.125	3.713
0.08	4.234	4.110	3.702
0.10	4.240	4.087	3.690
0.15	4.256	4.040	3.657
0.20	4.270	3.990	3.620
0.30	4.300	3.890	3.550
0.40	4.330	3.854	3.447
0.00	4.210*	4.185*	3.760*

*Extrapolated values of stability constants at zero ionic strength.

Table 4.8

Optimum concentration range, molar absorptivity and sensitivities of metal chelates

Conditions of study are same as described in Table 4.2

System	Concentration range in which Beer's law obeys (p.p.m)	Optimum concentration range (p.p.m)	Molar absorptivity	Sensitivity (μg/cm²)
Zn-ARS	1.8-9.2	2.0-8.2	5950	0.010
Be-ARS	0.2-4.7	0.2-4.0	4300	0.002
Ni-ARS	0.0-10.0	0.9-9.0	5500	0.010
Co-ARS	0.0-10.0	1.2-8.2	6000	0.009

NICKEL (II) - NITROSO-R-SALT CHELATE

The formation of an orange coloured chelate between bivalent nickel and nitroso-R-salt has been studied in aqueous medium, spectrophotometrically. The composition of the complex, in solution, has been determined by three different methods, mentioned earlier and it has been found that a stable chelate is formed between one mole of nickel and two moles of the ligand. The stability constant of the chelate has been determined by mole-ratio method and the method using molecular extinction coefficient data. The thermodynamic stability constant has been determined and the effect of temperature on the stability was studied. The optimum conditions for the micro determination of nickel have also been worked out.

EXPERIMENTAL

A standard solution of nickel was prepared by dissolving nickel sulphate (BDH 'AnalaR') in double distilled water. An aqueous solution of nitroso-R-salt (E. Merck) was prepared in CO_2 free, double distilled water. All other reagents used were of 'AnalaR' grade.

RESULTS

Conditions of Study

All experiments were performed at 25°C. The individual solutions and mixtures were kept in a precision thermostat (Forma Scientific Model 2095) maintained at 25±0.1°C. The mixtures were allowed to stand for half an hour to attain the equilibrium. The pH of all the solutions was maintained at 7.2±0.1 by using potassium hydrogen phthalate-NaOH buffer.

Nature of the Complex

To determine the nature of the complex formed, Vosburgh and Cooper's method was adopted. Mixtures containing varying proportions of nickel and NRS were prepared. The concentrations employed in the studies are given in Table 4.9.

Table 4.9

Mixture	Concentration of Nickel	Concentration of NRS	Ratio M:L
1	1.6×10^{-4}M	3.2×10^{-4}M	1:1
2	3.2×10^{-4}M	3.2×10^{-4}M	1:2
3	3.2×10^{-4}M	1.6×10^{-4}M	2:1
4	-	3.2×10^{-4}M	0:1

The absorbance of these mixtures at various wavelengths was measured and the results have been graphically represented in Plate 30A. The results showed that only one complex was formed under the conditions of study.

Effective pH range

The solutions containing the same concentration of metal and ligand were prepared at different pH and the absorbance was measured at various wavelengths. The complex showed λ_{max} at 470 nm in the pH range 5.6 to 6.8. The absorbance was almost constant in the pH range 6.9 to 7.4 and so 7.2±0.1 pH was selected for subsequent studies and was adjusted by potassium hydrogen phthalate-NaOH buffer.

Stoichiometry of the Components

(i) Job's Method

To determine the composition of the complex, Job's method of continuous variation was adopted. The studies were performed at two wavelengths but only representative results, obtained from the studies at 470 nm, have been graphically represented in Plate 30,B. The peaks were observed of metal:ligand ratio at 1:2.

(ii) Mole Ratio Method

A series of solutions was prepared from Ni^{2+} and NRS, in such a way that the mole-ratio of Ni^{2+} and NRS varied from 1:0.25 to 1:10. The concentrations employed are given in Table 4.10.

Table 4.10

pH = 7.2±0.1 Temp. = 25°C

Total volume made upto 25 ml

Concentration of nickel (C)	$5.0\times10^{-5}M$	$4.0\times10^{-5}M$
Plate 30,C Curve	A	B

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

(iii) Slope Ratio Method

The volume of the variable component was varied from 1 to 5 ml, in presence of an excess concentration of the other. The concentrations employed are given in Table 4.11.

Plate No. 30

A. Absorption curves of the mixtures of $NiSO_4$ and NRS

Curve 1 - $NiSO_4$ = 1.6×10^{-4}M, NRS = 3.2×10^{-4}M

Curve 2 - $NiSO_4$ = 3.2×10^{-4}M, NRS = 3.2×10^{-4}M

Curve 3 - $NiSO_4$ = 3.2×10^{-4}M, NRS = 1.6×10^{-4}M

Curve 4 - - - , NRS = 3.2×10^{-4}M

B. Job's curves for Ni-NRS chelate

Curve 1 = $C_M = C_L = 2.0 \times 10^{-3}$M

Curve 2 = $C_M = C_L = 1.0 \times 10^{-3}$M

Curve 3 = $C_M = C_L = 5.0 \times 10^{-4}$M

C. Mole ratio curves for Ni-NRS chelate

Curve A - Conc. of nickel = 5.0×10^{-5}M

Curve B - Conc. of nickel = 4.0×10^{-5}M

F. Slope ratio method for Ni-NRS chelate

Curve 1 - Ligand varying

Curve 2 - Metal varying

E. Variation of log K of Ni-NRS chelate with 1/T

(T = absolute temperature)

D. Beer's law plot for Ni-NRS chelate.


A
B
C
D
E
F
ABSORBANCE
0.4
0.2
0.0
2.0
4.0
6.0
8.0
VARIABLE REAGENT
0.8
1.0
NICKEL
9.5
9.4
9.3
.003
0.6
0.4
1.0
2.0
3.0
4.0
5.0
VARIABLE REAGENT

PLATE NO. 30

Table 4.11

pH = 7.2 ± 0.1 Temp. = 25°C

Total volume = 25 ml λ = 470 nm

Concentration of the constant component = 4.0×10^{-4} M

Concentration of the variable component varies from 8.0×10^{-6} to 8.0×10^{-5} M.

Figure	Line	Remark
Plate 30, F	2	Metal varying
Plate 30, F	1	Ligand varying

The results have been graphically represented in Plate 30, F. The slope of the two straight lines provided the Ni:NRS ratio as 1:2.

Determination of Stability Constant

The stability constant of Ni-NRS chelate has been determined by different methods, mentioned earlier. The values of log K obtained by different methods are given in Table 4.12.

Table 4.12

Method	log K
Mole Ratio method	9.68
Molecular extinction coefficient method	9.47
Mean	9.58 ± 0.1

Effect of Ionic Strength

The stability constants were determined at various ionic strengths and thermodynamic stability constant was calculated by extrapolation of stability constants to zero ionic strength and the results are given in Table 4.13.

Table 4.13

pH = 7.2 ± 0.1;   Temp. = 25°C

λ = 470 nm

Ionic strength	log K
0.00	9.313
0.02	9.328
0.04	9.337
0.06	9.351
0.08	9.361
0.10	9.371
0.15	9.371
0.20	9.371

Effect of Time and Temperature

The complex formation was found to be instantaneous at room temperature; maximum colour development was attained in ten minutes after preparation. The absorbance then remained constant for more than six hours.

Thermodynamic Functions

The free energy of chelate formation has been calculated by using the equation $\Delta G = -RT \ln K$. For the determination of enthalpy and entropy changes during chelate formation, the stability constant was determined at different temperatures. From the slope of the curve obtained by plotting log K against 1/T (Plate 30,E) the enthalpy change (ΔH) has been determined and by assuming this to be constant over a range of the experimental temperatures, the entropy change (ΔS) was calculated by using expression $\Delta S = (\Delta H - \Delta G)/T$. The results obtained are given in Table 4.14.

Table 4.14

pH = 7.2±0.1 $\mu = 0.10$

$-\Delta H = 4.239$ Kcal/mole

Temp. (°C)	log K	$-\Delta G$ (Kcal/mole)	ΔS (e.u.)
10	9.542	12.36	28.67
20	9.431	12.65	28.71
30	9.337	12.95	28.75
40	9.253	13.25	28.78
		Mean	28.73

ANALYTICAL APPLICATIONS

Experiments were performed to test the suitability of the chelate for the photometric determination of Ni(II) with NRS.

Standard Procedure

Transfer 2.24 ppm of Ni(II) solution in a 25 ml flask and add eight fold concentration of NRS. The solution has then to be made upto the mark after adjusting the pH to 7.2±0.1 by potassium hydrogen phthalate-NaOH buffer. After 30 minutes, the absorbance was measured at the λ_{max} of the chelate.

Effect of Reagent Concentration

The effect of change in the concentration of ligand on the absorbance of the chelate at 7.2±0.1 pH was determined at 470 nm. It was observed that the absorbance increased with increase in the reagent concentration, hence the reagent concentration was kept constant. It was found that at least eight fold concentration of the reagent is essential for the effective spectrophotometric determination of Ni(II).

Beer's Law and Sensitivity

Calibration curve for the determination of Ni(II) with NRS was prepared by using the standard procedure (Plate 30,D). The Beer's law obeyed over the concentration range of 0.0 to 7.8 ppm. The optimum concentration for the determination was obtained by Ringbom method and was found to be 0.7-6.7 ppm.

The molar absorptivity was found to be 8375 and the spectrophotometric sensitivity as expressed by Sandell's notation was 0.006 μg of nickel per cm^2.

Reproducibility and Precision

The reproducibility and precision of the method was studied by applying the standard procedure to a number of solutions of known concentration of nickel and comparing the results, so obtained, with the calibration curve. The deviation was found to be within a range of 0.005.

Effect of Diverse Ions

The effect of diverse ions on the determination of Ni(II) was examined under the conditions of standard procedure. In every case 2.24 ppm of nickel solution was used. The tolerance limit was taken as the amount that caused the absorbance error not exceeding ±3%. The results show that ions specially zinc (II), mercury (II), cobalt (II), beryllium (II), palladium (II), copper (II), iron (II) and silver (I) interfere and lead (II), cadmium (II), uranyl (II), magnesium (II), strontium (II), molybdenum (VI), lanthanum (III) and thallium (I) do not interfere at low concentrations. Chloride, bromide, iodide, sulphate, chlorate, nitrate, nitrite, sulphite, oxalate, acetate, borate and tartarate do not interfere even at high concentrations (50 ppm).

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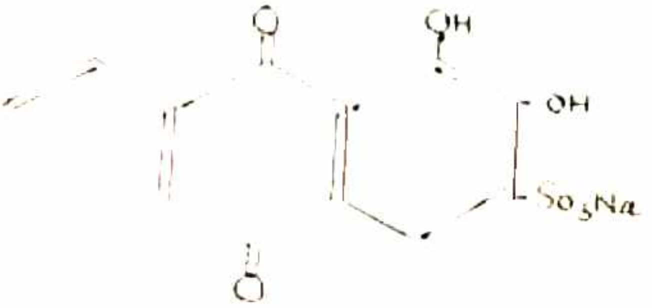
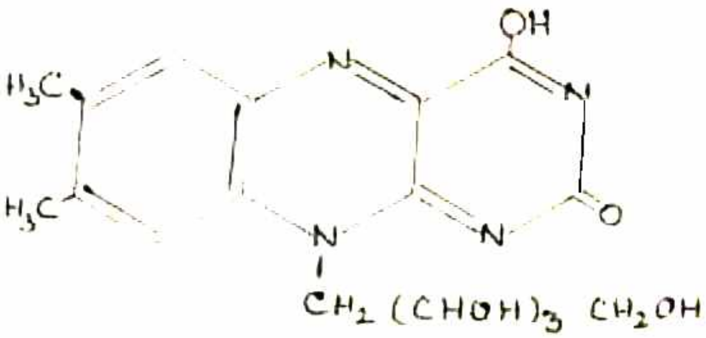
DISCUSSION

In course of these investigations, detailed studies were carried out on some bivalent metal chelates viz. Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Be^{2+} and UO_2^{2+} involvin Alizarin red S, Nitroso-R-salt and Riboflavin having the following structures:



(Alizarin red S)

(Nitroso-R-salt)

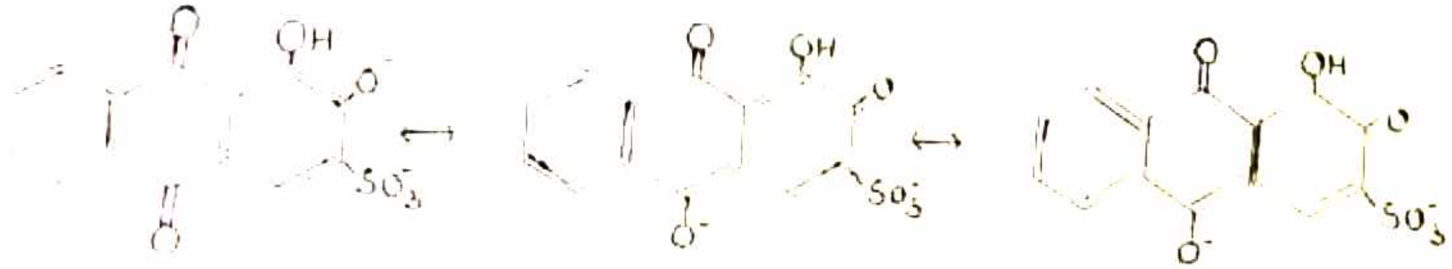


(Riboflavin)

PART I : METAL CHELATES OF ALIZARIN RED S

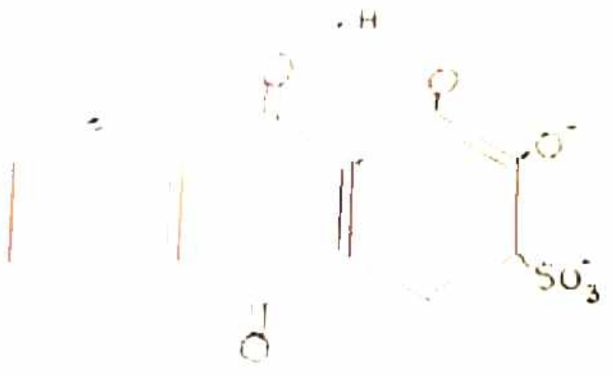
In metal chelates of Alizarin red S (ARS), there are two alternative positions where the chelation ring may be formed. The metal ion may be chelated either (I) between the quinoid oxygen and alpha phenolic oxygen or (II) between the alpha and beta phenolic oxygens. Beech and Drew (1), Larsen and Hirozawa (2) suggested a structure involving (I) while Leichafsky and coworkers (3) held the view of complexation by (II).

Larsen and Hirozawa (2) have proposed the following resonating structure for ARS for the half neutralised form.



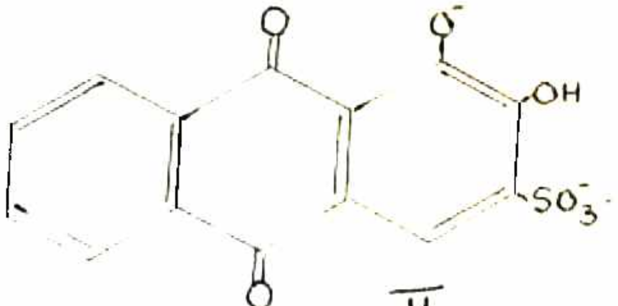
Here the beta hydrogen is ionized at pH ∼ 8. Therefore, chelation by method (I), involving the quinoid oxygen and alpha phenolic oxygen will not affect the resonance and experimentally it has also been reported as not affecting resonance. Spectral and polarographic evidences also support this view.

It has been suggested (4,5), that in the case of ARS, the beta phenolic hydrogen ionises first since the alpha phenolic hydrogen is involved in hydrogen bonding with the quinoid oxygen. This may be represented by the following structure.



I

It is felt that sufficient attention has not been given to the presence of $-So_3^-$ group, adjacent to the beta phenolic group. The presence of this group should hinder the ionization of the beta phenolic hydrogen as the presence of the adjacent negative charges should introduce electrostatic repulsions in the molecule which could overcome the stability due to intramolecular hydrogen bonding. Infra-red studies of ARS in a polar and a non-polar solvent should show a strong splitting of quinoid modes in the non-polar solvent if the quinoid oxygen is intramolecularly hydrogen bonded. But such studies do not seem to have been carried out as yet. In the absence of such evidence, it is difficult to decide which hydrogen ionizes first, though purely electrostatic considerations support the ionization of alpha phenolic hydrogen. The ionized species may then be represented as:

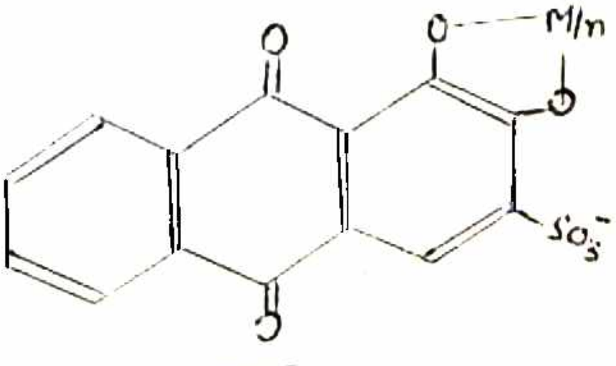


II

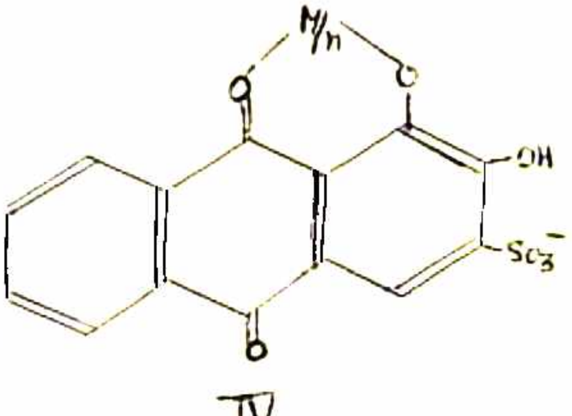
The visible spectrum of ionised species has λ_{max} at around 520 nm. If the chelate has a λ_{max} nearly 520 nm, it is taken to mean that chelation is through the quinoid oxygen and alpha phenolic group, otherwise bonding is assumed to be through the two phenolic groups.

If the alpha phenolic hydrogen ionizes first, then the λ_{max} at 520 nm is due to the ionic species II. Then, the large shifts from the λ_{max} of the ligand to that of the chelates can be justified on the basis of chelation through the quinoid oxygen and the alpha phenolic group.

The two possible structures for the chelates, therefore, are:



III



IV

As the quinoid oxygen has strong donor tendencies, it is suggested that structure IV probably represents the actual species existing in the solution. Further studies are needed to establish the nature of metal-ligand bonding conclusively.

During these investigations, stepwise protonation constants of ARS and stability constants of its metal chelates with Pb^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Be^{2+} and UO_2^{2+} were determined potentiometrically using Bjerrum-Calvin technique as modified by Irving and Rossotti, detailed in Chapter II.

These studies revealed that all the metal ions form 1:2 (M:L) chelates with ARS. The order of stability of bivalent metal chelates was found to be:

$Cu > UO_2 > Be > Pb > Zn > Co > Ni > Hg$

This order is generally in agreement with the order given by Mal ey and Mellor (6). Irving and Rossotti (7) have obtained an order $Cu > UO_2$ in 8-hydroxyquinoline. The higher value of Co^{2+} chelate in comparison of Ni^{2+} chelate can be attributed to the fact that the tetrahedral complex of Co^{2+} is more stable than Ni^{2+} (8). It has also been suggested that higher the ionization potential of the metal atom, the higher should be the stability of its complex. Since cobalt (II) has a higher value of ionization potential than nickel (II), it is quite likely that this plays an important role in determining the order of the stability constants of Co^{2+} and Ni^{2+}-ARS chelates.

In all the cases, $K_n > K_{n+1}$. This is so, for statistical reasons and because of the repulsion of a coordinating ligand for an incoming ligand of similar typ

A consideration of the experimental results would show that the values of ΔH and ΔS are larger in magnitude for the metal-ARS systems as compared to the H-ARS system. This evidently is due to the "chelate-effect", the metal chelates being obviously more stable than the protonated complex.

The chelates of bivalent metal ions with ARS, are all formed spontaneously as evidenced by the negative values of ΔG i.e. free energy of formation. The positive values of ΔS show that a greater amount of disorder exists in the system after chelate formation than before. The values of ΔH are negative except for the first step of chelate formation in Be-ARS and the second step in Pb^{2+}, Ni^{2+} and Co^{2+}-ARS chelates. Only in the case of the Be-ARS system, the overall ΔH is positive. It appears that in the solvated Be^{2+} ion, ligand substitution is not possible except by supplying a quantity of energy for the first step of chelation. The second step is exothermic but the first step is so endothermic as to make the overall process endothermic. The second step in the chelate formation between Pb^{2+}, Ni^{2+} and Co^{2+} with ARS seems to be sterically hindered giving rise to positive ΔH values. It may be because Co^{2+} and Ni^{2+} form tetrahedral complexes resulting in the stability of Co^{2+} chelate being greater than Ni^{2+} chelate with ARS.

PART II : METAL CHELATES OF NITROSO-R-SALT

In the metal chelates of Nitroso-R-salt (NRS), the chelation can take place only at one position i.e. in between the -NO group and -OH group. The tentative structure for the metal chelates of NRS can be represented as:

In these investigations the proton-ligand stability constants and stepwise metal-ligand stability constants of NRS with Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Be^{2+} and UO_2^{2+} were determined potentiometrically.

These studies revealed that all the bivalent metal ions, except Zn^{2+} and Cd^{2+}, form 1:2 metal chelates with NRS. These results are in confirmation with those obtained spectrophotometrically. The order of stability of these bivalent metal chelates, considering $\log K_1$ only, was found to be:

$$UO_2 > Co > Cu > Ni > Zn \sim Cd \sim Hg > Pb > Be$$

The higher value of UO_2^{2+} than Cu^{2+} chelate can be justified on the basis that it has been generally observed with -O-O- donors that UO_2^{2+} forms stronger complexes than Cu^{2+} and this order is reversed in ligands with -O-N- donors (9). According to the Maley and Mellor's order, the stability constants of Zn^{2+}, Cd^{2+} and Hg^{2+} chelates should decrease from Zn^{2+} through Hg^{2+} i.e. Zn > Cd > Hg. In the case of the chelates of these metals with NRS, however, it is found that the order is (considering log K_1 only) Zn ~ Cd ~ Hg. One of the contributing factors may be metal-ligand π-bonding which is likely to be maximum in Hg-NRS and minimum in Zn-NRS chelate. It is well known that π-bonded complexes are more stable than simple σ-bonded complexes. The stability of Co^{2+} chelate is greater than Ni^{2+} which can be justified on the basis of the fact that cobalt has a higher value of ionization potential than nickel and that the tetrahedral complexes of Co^{2+} are very stable in comparison to other bivalent metal ions (8).

The metal chelates of NRS are more stable than the protonated complex which can be justified on the basis of that the values of ΔH and ΔS are larger in magnitude for the metal-NRS systems as compared to the H-NRS system.

The chelate formation between NRS and bivalent metal ions is a spontaneous process as indicated by negative values of ΔG. The ΔH values are all negative except in the case of ΔH_2 of Cu-NRS system. This may be because of steric hinderance to solvent substitution in the second step. Such a hinderance is conceivable if we imagine the geometry of the species formed in the first step i.e. $Cu(H_2O)_2$.NRS to be tetragonally distorted due to the Jahn-Teller effect (10). The ΔS values for all chelates except Pb-NRS and Hg-NRS systems are positive. In the latter two cases, the stepwise as well as overall ΔS values are negative, possibly due to the formation of very symmetric species which interact strongly with the solvent to produce a highly ordered system.

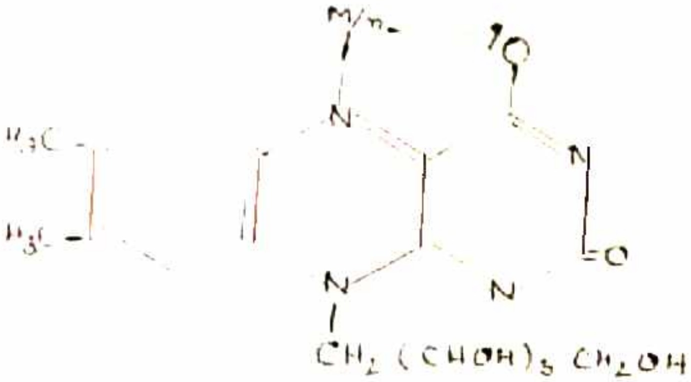
PART III : METAL CHELATES OF RIBOFLAVIN

In the metal chelates of riboflavin (RBF), the chelation can take place in two possible ways:

(I) between the phenolic –OH group and the nitrogen of the same ring.

or (II) between the phenolic –OH group and the heterocyclic nitrogen of the adjacent ring.

In structure (I), there is a four membered ring formation which evidently will be unstable or less stable in comparison to that of a five membered ring. The only possibility, therefore left is, of chelation by the (II) method, forming a five membered ring, which will be stable. Tentatively therefore, the structure of RBF chelates, can be represented as:



In course of these investigations, the protonation constants of RBF and stepwise stability constants of its metal chelates with Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} were determined potentiometrically using Bjerrum-Calvin technique as modified by Irving and Rossotti, detailed in Chapter II.

These studies revealed that RBF forms 1:1 metal chelates with Cd^{2+} and Hg^{2+} and 1:2 chelates with Cu^{2+} and Zn^{2+}. The order of stability of these chelates, considering log K_1, was found to be:

$$Cu > Zn > Cd < Hg$$

This order is generally, in agreement with the order given by Maley and Mellor except in the case of Hg^{2+} chelate. The stability of Hg^{2+} chelate is greater than Zn^{2+} and Cd^{2+}, which can be attributed to the unusually high ionization potential of mercury. It may also be possible that in the Hg-RBF chelate, extensive metal-ligand π-bonding takes place leading to a high value of stability constant for this chelate.

* * *

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SUMMARY

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The thesis concerns itself with discerning chelate formation, in solution, by potentiometric as well as spectrophotometric methods. In course of these studies, metal chelates of Alizarin red S, Nitroso-R-salt and Riboflavin have been investigated potentiometrically whereas spectrophotometric studies have been carried out on some metal chelates of Alizarin red S and Nitroso-R-salt.

PART A : POTENTIOMETRIC STUDIES

The principal aim of the present work has been to investigate systematically, the stepwise proton-ligand and metal-ligand stability constants at various ionic strengths to get the stepwise thermodynamic stability constants and at different temperatures to determine various thermodynamic functions such as free energy of formation, enthalpy and entropy changes associated with the formation of metal chelates in solution. The ligands selected for these studies are Alizarin red S, Nitroso-R-salt and Riboflavin.

PART B : SPECTROPHOTOMETRIC STUDIES

This part of the thesis concerns itself with the study of metal chelates of Alizarin red S and Nitroso-R-salt. The composition, stability and thermodynamic functions were determined. The application of the reagents for the micro determination of metal ions has also been attempted.

The work has been presented in five chapters. The first chapter of the thesis contains a brief introduction of coordination chemistry with special reference to the chemistry of metal chelates.

Chapter two describes the methods of discerning chelate formation in solution potentiometrically as well as spectrophotometrically.

The stepwise proton-ligand and metal-ligand stability constants have been determined using Bjerrum-Calvin titration technique as modified by Irving and Rossotti. The computational methods mainly employed for the analysis of the formation curves, to determine the stepwise proton-ligand and metal-ligand stability constants are:

(i) Interpolation at half $\bar{n}$ values

(ii) Interpolation at various $\bar{n}$ values

(iii) Mid point slope method

(iv) Least square method.

The thermodynamic functions i.e. ΔG, ΔH and ΔS have also been calculated by using Gibbs Helmholtz equation and van't Hoff's isotherm.

In the spectrophotometric studies, the following methods were used for the determination of the composition of metal chelates:

(i) The continuous variation method

(ii) The mole ratio method

(iii) The slope ratio method

The stability constants of the chelates were determined by using following methods based on the absorptiometric measurements:

(i) Mole ratio method

(ii) Method using molecular extinction coefficient data.

The third chapter deals with the determination of proton-ligand and metal-ligand stability constants at various ionic strengths and different temperatures to calculate various thermodynamic functions using pH-titration technique. The chapter is subdivided into three parts: Part I deals with the studies of metal chelates of Pb(II), Cu(II), Zn(II), Hg(II), Ni(II), Co(II), Be(II) and UO_2(II) with Alizarin red S.

Part II deals with the studies of metal chelates of Pb(II), Cu(II), Zn(II), Cd(II), Hg(II), Ni(II), Co(II), Be(II) and UO_2(II) with Nitroso-R-salt.

Part III deals with the studies of metal chelates of Cu(II), Zn(II), Cd(II) and Hg(II) with Riboflavin. All the calculations of stability constants were made on IBM

Computer 1130 and checked with the results obtained manually.

Chapter four describes the spectrophotometric study of Zn(II), Be(II), Ni(II) and Co(II) with Alizarin red S and Ni(II) with Nitroso-R-salt.

The fifth and the last chapter presents the discussion of all the results obtained.

In course of this work, the stepwise proton-ligand and metal-ligand stability constants of Alizarin red S, Nitroso-R-salt and Riboflavin have been determined potentiometrically.

The present work has also been able to throw light on the composition, stability, thermodynamic functions and certain structural aspects of the chelates and also the possibilities of being used for photometric determinations, which have not received sufficient attention earlier.

The stability constants and thermodynamic functions of the chelates have been determined at five different ionic strengths viz. 0.02, 0.05, 0.10, 0.15 and 0.20, and at five different temperatures viz. 10°, 20°, 30°, 40° and 50°C. Some of the representative results have been recorded in Tables I-VI.

Table I

Values of stability constants of ARS and NRS metal chelates

Temperature = 30°C $\mu = 0.1$

Metal ion	$\log K_1$		$\log K_2$		$\log K_c$	
	ARS	NRS	ARS	NRS	ARS	NRS
H^+	10.91	7.37	2.60	-	13.51	7.37
Pb^{2+}	11.25	5.62	5.18	2.30	16.43	7.92
Cu^{2+}	10.91	6.50	8.30	3.45	19.21	9.95
Zn^{2+}	9.29	5.68	6.70	-	15.99	5.68
Cd^{2+}	-	5.68	-	-	-	5.68
Hg^{2+}	8.59	5.96	6.27	2.52	14.88	8.48
Ni^{2+}	9.33	6.12	6.03	4.00	15.36	10.12
Co^{2+}	9.14	5.90	6.36	6.04	15.50	12.94
Be^{2+}	10.12	5.48	6.46	4.16	16.58	9.64
UO_2^{2+}	9.82	6.69	7.85	5.03	17.67	11.72

Table II

Values of thermodynamic stability constants of ARS and NRS metal chelates at 30°.

Metal ion	NRS				ARS			
	log $K_1^{\mu=0}$	log $K_2^{\mu=0}$	log $K_c^{\mu=0}$ (calc.)	log $K_c^{\mu=0}$ (exptl.)	log $K_1^{\mu=0}$	log $K_2^{\mu=0}$	log $K_c^{\mu=0}$ (calc.)	log $K_c^{\mu=0}$ (exptl.)
H^+	7.08	-	7.08	7.08	11.13	2.56	13.69	13.67
Pb^{2+}	6.02	2.64	8.66	8.67	11.11	5.01	16.12	16.12
Cu^{2+}	6.92	3.69	10.61	10.60	10.80	9.55	20.35	20.39
Zn^{2+}	5.97	-	5.97	5.97	8.61	6.43	15.04	15.09
Cd^{2+}	5.96	-	5.96	5.96	-	-	-	-
Hg^{2+}	5.98	2.64	8.62	8.62	8.38	6.90	15.28	15.30
Ni^{2+}	6.29	3.60	9.89	9.85	9.33	5.27	14.60	14.58
Co^{2+}	6.57	5.78	12.43	12.48	8.96	5.99	14.95	15.00
Be^{2+}	5.30	4.00	9.30	9.30	10.12	5.36	15.48	15.42
UO_2^{2+}	6.90	5.20	12.10	12.05	12.05	4.81	16.86	16.96

Table III

Values of thermodynamic functions of ARS-metal chelates

$\mu = 0.10$

Metal ion	$-\Delta G$ (Kcal/mole)	ΔS (e.u.)	ΔH (Kcal/mole)
H^+	ΔG_1 = 14.84	ΔS_1 = 26.88	ΔH_1 = -6.694
	ΔG_2 = 3.97	ΔS_2 = 9.09	ΔH_2 = -1.218
	ΔG^2 = 18.77	ΔS^2 = 34.84	ΔH^2 = -8.204
Pb^{2+}	ΔG_1 = [illegible]	ΔS_1 = 22.56	ΔH_1 = -8.706
	ΔG_2 = 7.25	ΔS_2 = 38.71	ΔH_2 = +4.485
	ΔG^2 = 22.75	ΔS^2 = 61.08	ΔH^2 = -4.240
Cu^{2+}	ΔG_1 = 15.18	ΔS_1 = 33.55	ΔH_1 = -5.017
	ΔG_2 = 11.51	ΔS_2 = 14.97	ΔH_2 = -6.972
	ΔG^2 = 26.68	ΔS^2 = 46.07	ΔH^2 = -12.640
Zn^{2+}	ΔG_1 = 12.87	ΔS_1 = 18.76	ΔH_1 = -7.185
	ΔG_2 = 9.29	ΔS_2 = 21.34	ΔH_2 = -3.821
	ΔG^2 = 22.17	ΔS^2 = 38.15	ΔH^2 = -10.590
Hg^{2+}	ΔG_1 = 11.93	ΔS_1 = 28.66	ΔH_1 = -3.219
	ΔG_2 = 8.75	ΔS_2 = 21.48	ΔH_2 = -2.215
	ΔG^2 = 20.68	ΔS^2 = 51.00	ΔH^2 = -5.223
Ni^{2+}	ΔG_1 = 12.78	ΔS_1 = 15.61	ΔH_1 = -8.071
	ΔG_2 = 8.50	ΔS_2 = 40.03	ΔH_2 = +3.634
	ΔG^2 = 21.28	ΔS^2 = 55.51	ΔH^2 = -4.448
Co^{2+}	ΔG_1 = 12.28	ΔS_1 = 17.16	ΔH_1 = -7.066
	ΔG_2 = 9.29	ΔS_2 = 42.84	ΔH_2 = +3.703
	ΔG^2 = 21.57	ΔS^2 = 60.07	ΔH^2 = -3.357
Be^{2+}	ΔG_1 = 13.71	ΔS_1 = 62.65	ΔH_1 = +5.283
	ΔG_2 = 9.50	ΔS_2 = 19.63	ΔH_2 = -3.548
	ΔG^2 = 23.21	ΔS^2 = 82.28	ΔH^2 = +1.752
UO_2^{2+}	ΔG_1 = 16.24	ΔS_1 = 28.84	ΔH_1 = -7.498
	ΔG_2 = 7.72	ΔS_2 = 7.30	ΔH_2 = -5.503
	ΔG^2 = 23.96	ΔS^2 = 37.92	ΔH^2 = -12.480

Table IV

Values of thermodynamic functions of NHS-metal chelates

$\mu = 0.10$

Metal ion	$-\Delta G$ (Kcal/mole)	ΔS (e.u.)	ΔH (Kcal/mole)
H^+	$\Delta G = 10.19$	$\Delta S = 18.95$	$\Delta H = -4.364$
Pb^{2+}	$\Delta G_1 = 7.41$ $\Delta G_2 = 3.31$ $\Delta G = 10.72$	$\Delta S_1 = -7.19$ $\Delta S_2 = -33.59$ $\Delta S = -38.72$	$\Delta H_1 = -7.585$ $\Delta H_2 = -13.490$ $\Delta H = -22.470$
Cu^{2+}	$\Delta G_1 = 8.95$ $\Delta G_2 = 4.77$ $\Delta G = 13.73$	$\Delta S_1 = 23.10$ $\Delta S_2 = 29.23$ $\Delta S = 55.30$	$\Delta H_1 = -1.950$ $\Delta H_2 = +4.092$ $\Delta H = +3.011$
Zn^{2+}	$\Delta G = 7.78$	$\Delta S = 4.86$	$\Delta H = -6.304$
Cd^{2+}	$\Delta G = 7.66$	$\Delta S = 2.33$	$\Delta H = -6.956$
Hg^{2+}	$\Delta G_1 = 8.00$ $\Delta G_2 = 3.50$ $\Delta G = 11.50$	$\Delta S_1 = -2.17$ $\Delta S_2 = -0.23$ $\Delta S = -3.67$	$\Delta H_1 = -8.050$ $\Delta H_2 = -3.569$ $\Delta H = -12.600$
Ni^{2+}	$\Delta G_1 = 8.54$ $\Delta G_2 = 5.57$ $\Delta G = 14.10$	$\Delta S_1 = 20.12$ $\Delta S_2 = 9.56$ $\Delta S = 29.72$	$\Delta H_1 = -2.423$ $\Delta H_2 = -2.665$ $\Delta H = -5.088$
Co^{2+}	$\Delta G_1 = 9.48$ $\Delta G_2 = 8.27$ $\Delta G = 17.75$	$\Delta S_1 = 15.39$ $\Delta S_2 = 21.59$ $\Delta S = 37.08$	$\Delta H_1 = -4.809$ $\Delta H_2 = -1.730$ $\Delta H = -6.542$
Be^{2+}	$\Delta G_1 = 7.52$ $\Delta G_2 = 5.77$ $\Delta G = 13.29$	$\Delta S_1 = 12.14$ $\Delta S_2 = 17.31$ $\Delta S = 29.78$	$\Delta H_1 = -3.841$ $\Delta H_2 = -0.523$ $\Delta H = -4.222$
UO_2^{2+}	$\Delta G_1 = 9.20$ $\Delta G_2 = 7.18$ $\Delta G = 16.39$	$\Delta S_1 = 15.53$ $\Delta S_2 = 9.61$ $\Delta S = 25.05$	$\Delta H_1 = -4.498$ $\Delta H_2 = -4.273$ $\Delta H = -8.784$

Table V

Values of stability constants of RBF metal chelates

Temperature = 25°C μ = 0.10

Metal ion	log K_1	log K_2	log K_c	log $K_1^{\mu=0}$	log $K_2^{\mu=0}$	log $K_c^{\mu=0}$ (calc.)	log $K_c^{\mu=0}$ (exptl.)
H^+	10.40	-	10.40	10.66	-	10.66	10.66
Cu^{2+}	6.36	4.02	10.38	7.81	5.81	13.62	13.59
Zn^{2+}	5.75	4.55	10.30	6.42	5.71	12.13	12.08
Cd^{2+}	5.20	-	5.20	5.41	-	5.41	5.41
Hg^{2+}	8.45	-	8.45	9.49	-	9.49	9.49

Table VI

Characteristics of ARS and NRS metal chelates

Chelates	pH	λ_{max} (nm)	Composition M:L	Temperature (^{o}C)	Log K	Optimum concentration range (ppm)	Molar absorptivity
Zn-ARS	6.4	540	1:2	25	7.89	2.0-8.2	5950
Be-ARS	5.5	480	1:1	25	4.25	0.2-4.0	4300
Ni-ARS	7.0	590	1:1	25	4.35	0.9-9.0	5500
Co-ARS	7.0	600	1:1	25	3.71	1.2-8.2	6000
Ni-NRS	7.2	470	1:2	25	9.58	0.7-6.7	6375

APPENDIX I

Computer program for the calculations of $\bar{n}_A$ and $\bar{n}$

```
PA[illegible]
//[illegible]
[illegible]       AVAIL  PHY DRIVE
                                 CCCD
V2
//[illegible]
[illegible]
                    [illegible]), NBAR(50)
                 [illegible]),[illegible]1(50)
                 [illegible]). V[illegible](50), V3(50)
        [illegible]
   [illegible],V[illegible],TL,T[illegible]
        [illegible]
[illegible]
      [illegible]
      KCNT=1
      JI=N
      JJ=1
      [illegible]
   28 [illegible]
      JI=25
   29 IPAGE=
      DC 34 IR=1,NCNT
      I[illegible]IP
      WRITE(5,30)KCUNT,IPAGE [illegible]O',I3,30X,'PAGE',I2,/)
   30 FORMAT(1H1,//,15X,'SET[illegible]
      WRITE(5,31)
   31 FORMAT(15X,65('-'))
      WRITE(5,32)[illegible]'--',14X,'-',/,16X,'S NO',10X,'V2-V1',10X,
   32 FORMAT([illegible]'--',14X,'NA',14X,'N',/)
     *[illegible],11X,'NA',14X,
      WRITE(5,31)
      WRITE(5,33)(I,[illegible](I),D1(I),NBARA(I),NBAR(I),I=JJ,JI)
   33 FORMAT([illegible],I5,4F15.4,/)
      JJ=26
      JI=N
   34 WRITE(5,31)
      KCUNT=KOUNT+1
      IF(KCUNT-NSET) 15,15,45
   45 GO TO 1
   46 CALL EXIT
      END

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[illegible]

// [illegible]
```

APPENDIX II

Computer program for the calculations of free ligand exponent, pL

```
//
LC     T                   C  T  VAIL  PHY CRIV
                                1/         COC
                          T   1 K
V
//

*C
*I
                      ),V111(  ),V 3(5C),PL(50)
                                  )

      I  ( )
                   ,  X,'S.NC',20X,'PH',13X,'VO+V3',14X,'NBAR',14X,'PL',/,6
       ,'----'                ,'-----',1  ,'-----',1  ,'--',//)
          ( ,1) (PH(I),I=1,N),(V111(I),I=1,N),(NBAR(I),I=1,N)
    1  F     T  ( F1  .3)

                   111(I)
                   2*H*H)*V 3(I)/((TL-TM*NBAR(I))*VO)
   1                  (PLOG)  .4343
                      )    I,PH(I),VC3(I),NBAR(I),PL(I)
   12                 (//,   .I ,  F1   .F1  .  ))
      GO TO 5
   20 CALL  X
      END

 ICCS
                                   522   PROGRAM     288

ENC CF CC FILATICN
// XEG
```