CHAPTER I

INTRODUCTION

The discovery of what is true and the practice of that which is good, are the two most important objects of philosophy.

- VOLTAIRE
CHAPTER - I

INTRODUCTION

Coordination Chemistry is one of the most active research fields in inorganic chemistry. This is because, in recent years, coordination compounds have found extensive use in various fields of human interest. These comprise of extraction, purification, electrodeposition, separation of metals, mordant dyeing, water softening, etc. Many methods have been developed for the separation and purification of metals (1-3). Complexing agents like oxine, EDTA and its analogues have been studied for influencing plant growth (4). Metal ions, which are known to form olefine complexes, have been found to act as effective catalysts for hydrogenation, hydration and polymerisation reactions of olefines (5). The research in the field of co-ordination chemistry has not only progressed in experimental work but very extensive theoretical treatment is also given. The scope of this field has now become very broad and number and kinds of compounds with which it is concerned are numerous, as it is apparent from the number of articles and books (6-13) published on this subject.
1.1: IMPORTANCE OF STABILITY CONSTANTS OF THE COMPLEXES:

In coordination compounds, metal ions can attach themselves with one or more than one type of ligands, resulting in the formation of binary or mixed-ligand complex species, respectively. In all the above mentioned fields where coordination compounds have found their applications, the first and the foremost requirement is the knowledge of stability constants of the complexes. By determining the stability constants of a given system it is possible in principle, to calculate the equilibrium concentration of each of the species present under a known set of experimental conditions. This exact knowledge of the composition of a solution is essential for the correct interpretation of its optical and kinetic properties, partition equilibria and biological behaviour. The values of the stability constants are also necessary to predict the conditions required for complete or maximal formation of a given complex. Reliable information of stability constants is of great importance in planning analytical and separative procedures. Thus, determination of stability constants of metal-complexes has received much significance in analytical (14), industrial (15), environmental (16) and medical chemistry (17). How rapidly this type of determination has gained importance can be judged by comparing the very limited number of quantitative equilibrium data known before 1941, with the numerous articles published since 1950 (18-25) and from proceedings of a series of International Conferences (26-30). An immense number of data is tabulated in two volumes of
"Stability Constants" published by Chemical Society (31) and in the book of "Instability Constants of Complex Compounds" by Yatsimirskii and Vasil'ev (32). During the last twenty five years an enormous amount of information concerning complex equilibria has been published (7,31) and thousands of important papers and some excellent reviews and books have appeared.

The stepwise formation of complexes was first proved by Niels Bjerrum (33). The fundamental importance of Bjerrum's investigation is the furnishing of clear cut evidence for stepwise complex formation. Jaques (34) was the first to point out that from a series of electrode potential measurements, the composition, dissociation constants and concentration of all the complexes present in the solution can be determined. These results led to the superb results obtained in the work on complex equilibria. Simultaneously with the publication of Bjerrum's work, Leden published a paper (35) on the determination of stability constants of cadmium halide complexes by means of e.m.f. measurements. After the articles of Bjerrum and Leden have appeared, there began a vast development in the field of "Potentiometric Study of Complex Equilibria".

1.2: IMPORTANCE OF THERMODYNAMIC FUNCTIONS:

Though the determination of stability constants has led to the important discoveries on the structure, reactivity and analytical applications of complex compounds, but in
order to have the most accurate approach for an investigation of the nature of the forces acting within the complex species formed in solution, it is necessary to know the energy changes accompanying the reactions. Stability constants are related directly only to changes in isobaric thermodynamic potential. However, it is necessary to know the changes in enthalpy and entropy during complex formation and the changes in stability of the complex species with a temperature change, to evaluate the bond energy. Since, complex formation is favoured by entropy changes and negative heat changes, it is required to evaluate these functions for a complete understanding of the subject.

Much stress has thus, been laid on the determination of thermodynamic functions during the last twenty five years. A number of reviews on the thermochemistry of transition metal complexes have appeared (16,35,37). This was followed by Rossoottti's contribution on the thermodynamics of metal ion complex formation in solution (38). In 1970, a critical review by Ashcroft and Mortimer (6) has appeared which clearly shows the importance of enthalpy and energy data for better interpretations. The presentation of a wonderful collection "Hand-Book of Metal Ligands Heats and Related Thermodynamic Quantities" by Cheristensen and Izatt (39) gives a sound evidence of increasing interest taken in the determination of thermodynamic parameters.
1.3: METHODS FOR THE STUDY OF STABILITY OF COMPLEXES:

There are many properties in solution which change measurably as a result of complex formation. In principle all these measurements can give information on the existence and stability of the different species. By a careful selection, it is possible to find one or more experimental methods for the investigation of all kinds of complexes. This careful consideration is necessary to know, whether the effects of complex formation are quantitatively reflected in the measured property or not. Besides the classical methods such as, spectrophotometry and potentiometry, the armoury of experimental methods has now been enriched by new approaches, such as NMR and ESR spectroscopy. Some of the important physico-chemical methods have been briefly discussed here.

1. Optical methods: When complex formation takes place excitation of the electrons of both the metal ion and the ligand is influenced. The electrons of transition metal ions are easily excited and consequently, they absorb in the visible region whereas, the electron system of non-transition metal ions are much more stable, hence the excitation of these electrons require much greater energy. These species absorb radiations in ultraviolet region of the electromagnetic spectrum. The studies of absorption spectra in the visible and ultraviolet regions give useful information about equilibria in solution. This method can also be used to determine the concentration of the bound and unbound complexing agent or metal ion in solution.
2. **Ion-exchange measurements:** Both cation and anion exchangers have been used to study the stability constants of complexes in solution. But cation exchangers are more often used for quantitative determination of formation constants of metal complexes. Schubert and Richter (40) were among the first to utilise this method. The method is essentially based on the measurement of the partition of uncomplexed ions between resin and solvent phase in the presence and absence of a complexing agent. When equilibrium is attained the concentration of cation attached to the cation exchanger is proportional to the concentration of the free ions in solution. The reliability of the stability constants obtained by these methods is decreased by the introduction of arbitrary assumptions, due to the chemisorption effects.

3. **Polarographic measurements:** The method was introduced by Lingane (41) and Deford and Hume (42). In recent years this method is gaining much importance because of the quickness with which the equilibrium is studied. The reduction potential of a metal at the dropping mercury electrode is shifted towards a more negative value during complex formation. Stability constants can be computed from potential and concentration measurements under a certain set of conditions.

4. **Conductivity measurements:** The change in conductance due to complex formation has not been widely used because of the limitations in quantitative study of formation of
complexes \((43,44)\). If more than one complex is formed, the exact calculations of stability constant is not possible. The theory and application of this method has been discussed by Davies \((45)\).

5. **Potentiometric methods**: The concentration changes caused by complex formation are reflected in the potential of well known electrodes. Various potentiometric methods have been applied, very frequently, in the study of complex equilibria. In fact, most of the recorded stability data were determined by potentiometric methods. By potentiometric measurements both the metal ion and the ligand concentration can be determined. A number of electrodes have been used for determination of metal ion concentration. They are (i) metal electrodes, (ii) metal amalgam electrodes, (iii) redox electrodes and (iv) membrane electrodes. The order also reflects the present frequency of their application.

However, if the ligands are protonated and the conjugate acid of the ligand is weak, which is usually the case, then the complex formation means a competition between protons and metal ions for the ligand. In such cases the stability constants can be derived from pH measurements. This approach to the study of stability constants was first introduced by Bjerrum \((18)\) and since then this technique has become one of the most frequently applied and dependable method of studying stability constants. This method has also been used in the present work and hence will be dealt in more details in the following text of this Chapter.
6. **Solubility measurements**: Lamers and Goldman (46), Bailey (47), and Keefer et al (48) have used the increase in solubility of a sparingly soluble salt in aqueous solution containing the complexing anion as the basis of the determination of the stability of amino-acid complexes.

7. **Gas Chromatography**: Gas chromatography offers a convenient method for the determination of stability constants of complexes involving volatile liquids (49). Gil-Av and Herling (50) studied the equilibria between sixteen different olefines and Ag(I) ions. Cvetanovic et al (51) determined the equilibrium constants of a number of Ag(I)-olefine complexes at different temperatures and studied the effect of deuteration of olefine on the stability.

8. **Miscellaneous methods**: Some other methods occasionally used for stability constant determination are reaction kinetics (52), liquid-liquid partition (53), colligative properties (54), electrophoresis (55), biological assay (56), displacement reactions (57), boiling point and vapour pressure measurements (58), dielectric polarization measurements (59), magnetic susceptibility (60), ultrasonic absorption (61), ultracentrifugation (62), dialysis and filtration (63) and light scattering methods (64).

I.4: METHODS FOR EVALUATION OF THERMODYNAMIC PARAMETERS:

Only two methods have been used, till now, for the determination of the changes in the thermodynamic parameters, occurring during complex formation. Out of the two methods
known, the 'temperature coefficient' method has been very widely used by numerous workers (38) whereas, the other one, the 'Calorimetric' method, was developed by Rossotti (39).

The values of free energy changes (ΔG) have easily been calculated using the 'temperature coefficient' method, whereas 'calorimetric' method leads to an indirect approach of calculating the same parameter. For the evaluation of enthalpy changes (ΔH), though the calorimetric method is finding better place because it gives precise values of smaller changes in enthalpy, but still the temperature coefficient method is being very widely applied since the stability constants at various temperatures, required for this method, can be calculated by applying physico-chemical methods. For evaluating the entropy changes (ΔS), Gibbs-Helmohlitz equation has always been used. More details of the temperature coefficient method, which has been used in the present work, are described in the subsequent text of this Chapter.

I.5: POTENTIOMETRIC STUDIES OF COMPLEX EQUILIBRIA:

I.5-A: Introduction:

The stepwise formation of complexes was first proved by Niels Bjerrum. He studied the chemistry of chromium(III) complexes and published in 1915 a long paper (33) on the kinetic and equilibrium study of chromium(III) thiocyanate complexes. As these complexes are very inert, he was able to analyse the solutions for
the free thiocyanate ions and also for each of the species Cr$^{3+}$, [Cr(ScN)]$^{2+}$, ....... [Cr(ScN)$_6^-$]. The six step stability constants $K_1$, $K_2$ ....... $K_6$ could then be calculated. Though the Bjerrum's investigations furnished clear cut evidence for stepwise complex formation but the method applied was of very limited applicability.

Jacques was the first to point out in the appendix of his book (34), that from a series of electrode potential measurements, the composition, stability constant and concentration of all the complexes present in solution can be determined. The total concentration of the metal ion is evidently the sum of the concentration of each species.

$$T_M = [\text{M}] + [\text{ML}] + \ldots \ldots [\text{ML}_N] \quad \ldots \ldots (1.1)$$

where $N$ denotes the maximum number of ligands $L$, coordinated to the metal ion $M$. Considering the overall stability constant ($K_N$) the following set of quantities are obtained:

$$T_M = [\text{M}]_1 + [\text{M}]_1 [\text{L}]_1 K_1 + [\text{M}]_1 [\text{L}]_1^2 K_1 K_2$$
$$\quad + \ldots \ldots + [\text{M}]_1 [\text{L}]_1^N K_1 K_2 \ldots \ldots K_N \quad \ldots \ldots (1.2)$$

$$T_M = [\text{M}]_1 [1 + [\text{L}]_1 K_1 + [\text{L}]_1^2 K_1 K_2 + \ldots \ldots$$
$$\quad \ldots \ldots + [\text{L}]_1^N K_1 K_2 \ldots \ldots K_N] \quad \ldots \ldots (1.3)$$

Similarly;

$$T_M = [\text{M}]_2 [1 + [\text{L}]_2 K_1 + [\text{L}]_2^2 K_1 K_2 + \ldots \ldots$$
$$\quad \ldots \ldots + [\text{L}]_2^N K_1 K_2 \ldots \ldots K_N] \quad \ldots \ldots (1.4)$$
\[ T_M = [M]_N \{ 1 + [L]_N K_1 + [L]^2 N K_1 K_2 + \ldots \]
\[ \ldots + [L]^N_{N} K_1 K_2 \ldots K_N \} \quad \ldots (1.5) \]

Hence, the measurement of the free metal ion concentration at \( N \) different ligand concentrations enables one to calculate the stability constants. Jaques was aware of some difficulties of his "theoretical method" namely, the small errors in the potential measurements become greatly magnified in the calculation and that the ligand has to be added in great excess, otherwise the basic condition \([L] \sim T_L\) would not be fulfilled. Naturally the problem of activity intrupted his discovery and thus, his method was not realised until the early 1940's due to the world wars.

Between the world wars only a few articles were published on the quantitative study of complex equilibria. The most important among these are Jannik Bjerrum's (18) papers on stability of copper ammine complexes and Meller's (65) Dissertation on the iron(III) thiocyanate complexes, which, however, created only little stir at that time.

After the war, the investigations of electrolyte solutions were directed towards the problem of activity. These investigations were initiated by Niele Bjerrum (66) and many others. These studies soon led to superb results in the work of complex equilibria. The discovery of glass electrode made the measurement of pH very easy and this gave Jannik Bjerrum the idea of potentiometric investigation
of complex equilibria. Simultaneously with the publication of Bjerrum's Dissertation, Ido Leden published a paper (25) on the determination of the stability constants of cadmium halide complexes by means of e.m.f. measurements. Leden's work also solved the problem originally raised by Jaques. After the articles of Bjerrum and Leden had appeared there began a vast development in the field of potentiometric study of complex equilibria.

1.5-B: Basic Principles Involved in Potentiometric Study of Binary Complexes:

The stepwise formation of parent complexes consisting of central group (metal ion) M and N ligands (L) can be represented by the equations (1.6 to 1.9). Charges being omitted for the sake of clarity and simplicity.

\[
\begin{align*}
M + L & \rightleftharpoons ML \quad (1.6) \\
ML + L & \rightleftharpoons ML_2 \quad (1.7) \\
ML_{n-1} + L & \rightleftharpoons ML_n \quad (1.8) \\
ML_{n-1} + L & \rightleftharpoons ML_n \quad (1.9)
\end{align*}
\]

Stepwise formation constants for these equilibria are given by the equations (1.10 to 1.13)
\[ K_1 = \frac{[M][L]}{[M][L]} \] .. (1.10)

\[ K_2 = \frac{[ML_2]}{[ML][L]} \] .. (1.11)

\[ K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \] .. (1.12)

\[ K_N = \frac{[ML_N]}{[ML_{N-1}][L]} \] .. (1.13)

The product of individual stability constants gives a characteristic constant, called overall or cumulative formation constant usually denoted by \( \beta \).

\[ \beta_1 = K_1 = \frac{[ML]}{[M][L]} \] .. (1.14)

\[ \beta_2 = K_1 K_2 = \frac{[ML_2]}{[M][L]^2} \] .. (1.15)

\[ \beta_N = K_1 K_2 \cdots K_N = \frac{[ML_N]}{[M][L]^N} \] .. (1.16)
The individual stability constants mentioned above cannot be calculated directly. To obtain them it is necessary to find a suitable relationship between the individual constants and the experimentally measurable parameters. Most of the numerical and graphical methods developed for the calculation of stability constants are based on or related to the quantity, called complex formation function and denoted by \( n_A, \bar{n} \) and \( p_L \). For the evaluation of these functions the three mixtures (i) acid, (ii) acid + ligand and (iii) acid + ligand + metal, were prepared and titrated against standard alkali potentiometrically. The resultant titration curves were referred to as (i) acid, (ii) ligand and (iii) metal titration curves.

(a) **Proton-Ligand Stability Constants**: In the present work Bjerrum-Calvin titration technique (18,67) modified by Irving and Rossoitti (68) has been adopted to study the complex equilibria of binary systems. In order to calculate the formation constants of the metal complexes by this method, it is essential to have a prior knowledge of the "Practical proton-ligand stability constants". In the large number of cases and in the present case also, the \( L \) is either the conjugate base of weak acid or a conjugate acid of weak base. The complex forming system therefore, contains two series of complexes (a) \( ML_n \) in which \( L \) acts as a ligand and (b) \( H_jL \) in which \( L \) acts as central group and \( H \) as ligand; in other words the ligand can take \( j \) protons. Assuming the protonation of \( L \) also to take place in steps, the average number of protons bound per free
(which is not complex bound) ligand molecule can similarly be written as:

\[ n_A - \frac{\text{Total concentration of proton bound to ligand}}{\text{Total concentration of ligand not bound to metal}} \]

The value of \( n_A \) at various pH meter readings (B) have been calculated from the acid and ligand titration curves. The equation (1.17) as used by Irving and Rossotti (68) has been employed.

\[ n_A = Y - \frac{(N + E^0) (V_2 - V_1)}{(V^0 + V_1) T^{0}_{CL}} \]

where \( V^0 \) is the initial volume of the solution; \( V_1 \) and \( V_2 \) denotes the volume of alkali needed to reach the same value of pH in the titration of acid and ligand, respectively. \( T^{0}_{CL} \) is the total concentration of ligand, \( N \) normality of alkali, \( E^0 \) the initial concentration of free acid, \( Y \) the total number of replaceable protons attached to the ligand and \( n_A \) is the average number of protons attached per ligand ion. The calculation of 'Practical' stability constant of the proton complexes was carried out by plotting a graph of \( n_A \) against pH or B and then employing various computational methods (69). These constants have no physical significance, but are convenient intermediates for evaluating the stability constants of the metal complexes.
(b) **Metal-ligand Stability Constants**: For a metal complex or chelate formation, taking place in homogeneous solution, the stepwise formation constants are given by the equation (1.18):

\[ K_n = \frac{C_{ML_n}}{C_{ML_{n-1}} \cdot C_L} \quad (n = 1, 2, 3, \ldots, N) \quad \ldots \quad (1.18) \]

where \( K_n \) is called \( n^{th} \) metal-ligand stability constant.

Bjerrum (18) introduced the concept of degree of formation or ligand number \( \overline{n} \), which is defined as the average number of ligand bound per metal ion present in whatever form, i.e.,

\[ \overline{n} = \frac{\text{Average number of ligands } L \text{ attached to per central group } M}{\frac{\text{Total number of ligands } L \text{ bound to } M}{\text{Total number of metal } M \text{ present in system}}} \]

\[ = \frac{\text{Total concentration of ligand } L \text{ bound to } M}{\text{Total concentration of metal } M \text{ in the system}} \]

The total concentration of the metal ion \( (T_{CM}^0) \) and ligand \( (T_{CL}^0) \) are evidently known and the concentration of the free (uncomplexed metal ion and of the free ligand appear to be more or less rapidly accessible by potentiometric measurements. The value of \( \overline{n} \) is calculated from the equation (1.19):

\[ \overline{n} = \frac{(N + E^0)(V_3 - V_2)}{(V^0 + V_1) \frac{\overline{n}_A}{A} \cdot T_{CM}^0} \quad \ldots \quad (1.19) \]
where, \( V_3 \) is the volume of alkali required in metal titration curve to reach the same pH value as in initial two cases and other terms have their usual meaning.

The free ligand exponent \( pL \) has been calculated from the equation (1.20):

\[
\begin{align*}
p_L &= \log_{10} \left[ \frac{n = J}{\sum} B_n \frac{V^0}{\left( \text{anti log PH} \right)^n} \right] \\
&= \log_{10} \left[ \frac{n = 0}{\left( T_{CL} - \frac{1}{n} \right)} \frac{(V^0 + V_3)}{V^0} \right] \\
&= \log_{10} \frac{(V^0 + V_3)}{V^0} \\
&= \log\left( \frac{V^0 + V_3}{V^0} \right) \\
&= \log\left( 1 + \frac{V_3}{V^0} \right)
\end{align*}
\]

where, \( B_n \) is the overall 'Practical' proton-ligand stability constant.

In case of water-organic solvent media, for the calculation of \( pL \), the 'B' values are used instead of pH values, where 'B' denotes pH meter reading and not the actual pH, as the pH meter is calibrated with aqueous buffers. Therefore, \( B_n \) is substituted by \( P_{B_n} \) which is the "Practical" proton ligand stability constant in non-aqueous solvent. The use of pH-meter reading 'B' instead of true pH-values does not make any difference in the calculation of \( pL \) (69), is clear from the following explanation.

Van Uitert and Haas (70) have shown the general relationship (1.21) between hydrogen ion concentration and pH-meter readings 'B', which is usually valid for water and water-dioxane mixtures -

\[
\log_{10} [H^+] = B + \log f + \log U^0_H 
\]

.. (1.21). The use of the relation (1.21) can also be
extended to pure ethanol or water-ethanol mixtures (71). Here $f$ is the activity coefficient of hydrogen ions in the solvent mixture under consideration at the same temperature and ionic strength and $U^0_H$ corresponds to the correction at zero ionic strength. For water, $U^0_H = 1$ and at unit activity coefficient $[H^+] = 1/\text{anti log } B$. If then the values of $1/\text{anti log } B = [H^+] f. U^0_H$, in general case, are substituted in equation (1.22), in place of less easily determinable value of $[H^+]$, there will result

\[ \bar{n}_A = \frac{n = j}{\sum_{n=1}^{n=1}} n B_n^H [H^+]^n \]

\[ 1 + \frac{n = j}{\sum_{n=1}} B_n^H [H^+]^n \]

values for proton-ligand stability constants which can be termed as "practical constants", denoted by $P B_n^H$. These are related to the stoichiometric constants by the expression:

\[ B_n^H = (f U^0_H) n P B_n^H \]

Replacing the value of $B_n^H$ and $[H^+]$ from the equation (1.21) and (1.23) in equation (1.20) the relation (1.24) is obtained.

\[ pL = \log_{10} \left[ \sum_{n=0}^{n=j} P B_n^H (f U^0_H)^n \left( \frac{\text{anti log } B}{T^0_{CL} - \bar{n} T^0_{CM}} \right)^n \left( V^0 + V_3 \right) \right] \]

\[ (T^0_{CL} - \bar{n} T^0_{CM}) \]

... ... (1.24)
Therefore,

\[
\text{PL} = \log_{10} \left[ \frac{\sum_{n=0}^{\infty} \frac{P_{BH}^n}{n!} \left( \frac{1}{\text{antilog} B} \right)^n}{(T_{CL} - \bar{n} T_{CM})} \left( \frac{v^0 + v_2}{v_2} \right) \right] \quad \text{(1.25)}
\]

Thus, the equation (1.25) remains of the same form as the equation (1.20) provided that (a) values of \(1/\text{antilog} B\) are used in place of \([H^+]\) and (b) the practical overall stability constants \(P_{BH}^n\), previously obtained for the proton-ligand complexes, are used in place of stoichiometric values of \(B_n^H\). Further, \(\log f \text{U}^0\) may be obtained as the intercept of the linear plot of pH against B, using solutions of known hydrogen ion concentration. Lahiri and Aditya (72) have suggested the correction factors in terms of pH values directly which can also be conveniently adopted to do calculations in water dioxane medium.

The formation curves obtained by plotting \(\bar{n}\) against pL were analysed as usual and various computational methods (73) were applied to evaluate the stepwise formation constants.

I.5.C: Potentiometric Study of Mixed Ligand Complexes:

The study of coordination compounds has now gained much importance because of their extensive uses in the various fields of human interest. The type of complex formed depends much on the presence of various ligands in the solution. The coordination sphere of a central metal ion is called as homogenous if all the donor atoms are identical, whether
the ligand is unidentate or bidentate. However, if the donor atoms are different, the coordination sphere is called as heterogeneous. If different donor atoms belong to the same ligand molecule, the complex is termed as mixed donor complex. However, when more than one type of ligands, other than solvent molecule, participate in the innermost coordination sphere of the central metal atom, the complex formed is known as mixed ligand complex. In most of the cases at least one of the ligand participating is a chelating agent. From the number of studies carried out, it may be stated that the formation of mixed ligand complex is quite common, whenever two or more ligands are present in the solution containing a metal ion.

Sillen's and Martell have pointed out that the formation of polynuclear and mixed ligand complexes has not met with the same interest as mononuclear (binary) complexes. They have been considered as an annoying disturbance impending measurements of the interesting mono-nuclear equilibria and have not been studied for their own sake.

The formation of complexes containing two different ligands has now become of interest to coordination chemists and formation constants of some of these complexes have been determined. Mixed ligand complex formation is now considered of special interest since it offers an alternative reaction to hydrolysis and olation of metal ions. Only two methods have been widely used for the determination of stability constants of mixed ligand complexes. Out of the two methods,
spectrophotometric method depends on spectral characteristics of the system. The treatment is particularly easy if only one mixed ligand complex is formed. If the conjugate acids of the ligands are weak, the study of mixed ligand complexes can be followed by pH-titration technique. This method is applicable if certain conditions are fulfilled. In fact most of the data reported on the stability of the mixed ligand complexes have been determined by potentiometric method.

I.5.D: Basic Principles Involved in the Study of Ternary Complexes:

The simplest case of mixed ligand complex formation can be considered when only two ligands are coordinated to the central metal ion. For this study, the ligands which form quite stable 1:1 rare earth chelates were chosen as primary ligands (A) and the tendency of these primary complexes (MA) to bind a secondary ligand (L) is measured. The necessary condition for the study of mixed ligand complexes by potentiometric method is that, the complex formation between the metal (M) and the primary ligand (A) should be complete at low pH and this primary complex (MA) once formed at lower pH should be stable up to high pH, where the combination of secondary ligand (L) with the primary complex takes place. The reaction can be represented as follows (omitting charges):

\[ M + A \rightleftharpoons MA \quad \text{and} \quad MA + L \rightleftharpoons MAL \quad \ldots (1.26) \]
In the range of the combination of secondary ligand, the dissociation of primary complex should not take place and in presence of the complexing secondary ligand the formation of \([ MA (OH)_n ]\) is suppressed. The addition of secondary ligand to form the mixed chelate therefore, turns out to be the only matter under consideration. The reactions of the system containing the mixture of two ligands and metal ion can be classified into five basic types as follows:

1. Combination of the metal ion with both the ligands simultaneously to form a mixed ligand chelate in single step:

\[
M + A + L \rightleftharpoons MAL \quad \ldots (1.27)
\]

2. Formation of a mixed ligand chelate in two overlapping steps, reflecting slight difference in the affinities of the ligands for the metal ion:

\[
M + A + L \rightleftharpoons MA + L \rightleftharpoons MAL \quad \ldots (1.28)
\]

3. Formation of mixed ligand chelate in two distinctly separate steps, reflecting a wide difference in the affinities of the ligands for the metal ion:

   (i) \[ M + A \rightleftharpoons MA \]  (ii) \[ MA + L \rightleftharpoons MAL \] \ldots (1.29)

4. Formation of mixture of two simple chelate compounds rather than the mixed ligand chelate, containing two different ligands bound to the same metal ion:

\[
2M + nA + mL \rightleftharpoons MAN + ML \quad \ldots (1.30)
\]
5. Instead of forming a mixed ligand chelate, a simple complex is formed between one ligand and the metal ion, while the other ligand remains unbound in the solution:

\[ M + A + L \xrightarrow{\text{formation}} MA + L \] \hspace{1cm} (1.31)

The type 3 reaction mentioned above is operative in the present work.

It should be noted that the above discussion is not intended to be an exhaustive classification system, but merely one which classifies the possible reactions of various mixed ligand chelate systems.

It is of interest at this point to consider some of the factors which control the formation of the mixed ligand chelate (MAL) in solution relative to the competing formation of hydroxy metal chelate \([MA(\text{OH})_n]\). In presence of complexing secondary ligand (L), the formation of \([MA(\text{OH})_n]\) is suppressed with the formation of MAL. Formation of \([MA(\text{OH})_n]\) is more frequent, when more coordination positions of the metal ions are vacant. After the formation of primary complex \([MA]\), secondary ligand satisfies these coordination positions, and hydrolysis of primary complex is suppressed. Hydrolysis of the metal ion is suppressed due to the formation of primary complex.

The secondary ligands (L) were chosen on the basis that the stability of the secondary ligand complex (ML) should be quite less than that of primary complex \([MA]\), so that the replacement reaction such as (1.32) is not possible:

\[ MA + L \xrightarrow{\text{replacement}} ML + A \] \hspace{1cm} (1.32)
For the determination of stability constants of the mixed ligand complexes four mixtures were prepared as follows and titrated against standard sodium hydroxide solution using pH-meter at a constant temperature:

(A) Acid  (B) Acid + Secondary ligand,
(C) Acid + Primary ligand + Metal, and
(D) Acid + Primary ligand + Metal + Secondary ligand.

The ratio of the concentrations of \( M : A : L \) was kept as \( 1 : 1 : 1 \) and the ionic strength was maintained constant at \( \mu = 0.2 \, \text{M} \) (KNO\(_3\)), in all the four mixtures. The pH values of the solution were plotted against the volume of the alkali added. In case of organic solvent-water mixture, the pH-meter readings (B) were plotted against the volume of sodium hydroxide added. The curves so obtained were referred as: (A) Acid titration curve, (B) Secondary ligand titration curve, (c) Primary complex titration curve and (D) Mixed ligand complex titration curve.

The stability constants of ternary complexes \( \log K^\text{MA} \) were evaluated using Irving-Rosetti's pH-titration technique \((68,69)\) modified to accommodate mixed ligand complex formation by Movani et al \((74)\). The same method has been used by various other workers \((75-77)\). The formation of ternary complex can be represented as follows:

\[
\text{MA} + L \xrightleftharpoons{} \text{MAL} \quad \text{.. (1.33)}
\]

and hence,

\[
\frac{[\text{MAL}]}{[\text{MA}][L]} = K^\text{MAL} \quad \text{.. (1.34)}
\]
As the secondary ligands used were weak acids and hence for the calculation of the formation constant of the complex, $K_{MA}^{MA}$, the prior knowledge of "Practical" proton-ligand stability constants of secondary ligands was essential. These constants ($\log K_H^N$) were calculated using titration curve (A) and (B) with the help of Irving-Rossotti's method as applied in the case of binary systems, i.e., the relation (1.17).

The horizontal distance ($V_2$) between curve (A) and curve (B) was measured and subtracted from the horizontal distance ($V_3$) between curve (C) and (D). The difference ($V_3 - V_2$) which gives the amount of alkali corresponding to the formation of the mixed ligand complex at various pH values, is a measure of the ternary complex formation. In titration curve (D), the release of proton will be due to primary and ternary complex formation, but ($V_3 - V_2$) will give the amount of alkali required for the neutralisation of the protons released due to ternary complex formation. Using the values of ($V_3 - V_2$), the average number of secondary ligand molecules bound to the primary complex [MA] were calculated using the equation (1.35):

$$n = \frac{(V_3 - V_2)(N + E^\circ)}{(V^\circ + V_1)\bar{n}_A \cdot T^\circ CM} \quad \ldots \quad (1.35)$$

Since the dissociation of the primary complex [MA] does not take place in the range of combination of secondary ligand, it can be considered that secondary ligand combine with primary complex [MA] just as it does with [M (aq)]$^{n+}$.
in simple system. Hence, the concentration of the primary complex will be equal to the initial concentration of the metal ion. Here it is assumed that due to the strong complexing affinity, at the start of ternary complex formation, metal (M) and primary ligand (A) is completely in the form of \([MA]\) and \(T^0\) is equal to the initial concentration of the metal ions. Other terms in equation (1.35) have their usual meaning.

The free ligand exponent \(p_L\) values were calculated at corresponding \(\bar{n}\) values using the same equation as in original paper of Irving and Rossotti, i.e., the relation (1.20) with the only difference that \(V_3\) is to be replaced by \(V_4\) in this case. The formation curves were obtained by plotting \(\bar{n}\) against \(p_L\). At \(\bar{n} = 0.5\), in the formation curve, 

\[
p_L = \log K_{MAL}^{MA}\n\]

The formation curves obtained were analysed as usual and the formation constants of the mixed ligand complexes have been evaluated.

I.5.E: Computation of Stability Constants from the Formation Functions:

From the experimental data obtained from the plots of pH against volume of the alkali added, the values of \(\bar{n}_A\), \(\bar{n}\) and \(p_L\) are calculated as discussed above. Thus, there are two sets of formation functions (i) \(\bar{n}_A(pH)\) and (ii) \(\bar{n}(p_L)\). Graphs are then plotted between \(\bar{n}_A\) and pH and \(\bar{n}\) and \(p_L\). These plots are known as formation function curves for proton ligand and metal-ligand stability constants, respectively. By solving the formation function curves
either graphically or numerically one can obtain proton-ligand and metal-ligand stability constants (7).

Methods for solving formation function have received considerable attention due to following reasons:

(i) The shape of formation curves depend on the number and nature of complexes; hence all the formation curves cannot be solved by one method.

(ii) A large number of values are available from the experimental data and all values should be utilised to have the most representative values of the stability constants.

(iii) Sometimes the experimental data may not be fully represented in formation curves.

Hence, various methods have been developed by various workers to suit the data.

Out of the different methods, the important ones are: (i) interpolation at half \( n \) values, (ii) interpolation at various \( n \) values, (iii) graphical method, (iv) elimination method, (v) spreading factor method, (vi) correction term method, (vii) least square method, etc. These methods have been reviewed by Martell and Calvin (12), Irving and Rossotti (62), Rossotti and Rossotti (76) and Hearson and Gilbert (77). To economise the space theoretical basis, of only two methods, which have been used in the present course of study, have been given. These are (i) interpolation at half \( n \) value and (ii) interpolation at various \( n \)
values. These methods serve the purpose only in cases when 1:1:1 mixed ligand complexes are formed, which is actually observed for all the systems reported in this thesis.

(A) **Interpolation at half \( \bar{n} \) values:** In a complex forming system, if \( n > \bar{n} > \bar{n} - 1 \), the ratio of two successive complexes is given by:

\[
\frac{ML_n}{ML_{n-1}} = \frac{\bar{n} + 1 - n}{n - \bar{n}}
\]  

Thus,

\[
K_n = \frac{(\bar{n} + 1 - n)}{(n - \bar{n})} \cdot \frac{1}{[L] \bar{n}}
\]  

From the equation (1.37) it follows that if \( 1 > \bar{n} > 0 \), then

\[
K_1 = \frac{\bar{n}}{1 - \bar{n}} \cdot \frac{1}{[L] \bar{n}}
\]  

If, \( 2 > \bar{n} > 1 \) then,

\[
K_2 = \frac{\bar{n} - 1}{2 - \bar{n}} \cdot \frac{1}{[L] \bar{n}}
\]  

Similarly, if \( 3 > \bar{n} > 2 \), then

\[
K_3 = \frac{\bar{n} - 2}{3 - \bar{n}} \cdot \frac{1}{[L] \bar{n}}
\]

The equations (1.38), (1.39) and (1.40) are valid for calculation of \( K_1, K_2 \) and \( K_3 \), if \( Kn/K_{n+1} \gg 10^3 \).

Because in this case the contribution of \( ML_{n-1} \) may be neglected in the region \( \bar{n} < n-1 \). Also at points \( \bar{n} = n-1/2 \), approximately equal amounts of \( ML_{n-1} \) and \( ML_n \) will be present in the solution. It thus follows from the equations (1.38), (1.39) and (1.40) that:
\log K_1 = pL, \text{ at } \overline{n} = 0.5 \\
\log K_2 = pL, \text{ at } \overline{n} = 1.5 \\
\text{and } \log K_3 = pL, \text{ at } \overline{n} = 2.5 \quad \cdots (1.41)

These are very commonly used expressions in the cases where \( n = 3 \), but it suffers from the drawback because only three points are used on the formation curve for the evaluation of the stepwise stability constants of complexes.

(b) Interpolation at various \( \overline{n} \) values: Using equation (1.38), (1.39) and (1.40) and substituting different values of \( \overline{n} \) and \([ L ](\overline{n}_A \text{ and } [ H^+] \) many values of \( K_1 \) can be obtained in the region \( 1 > \overline{n} > 0 \), of \( K_2 \) in the region \( 2 > \overline{n} > 1 \) and \( K_3 \) in the region \( 3 > \overline{n} > 2 \). The mean of all the values gives the most suitable values of \( K_1, K_2 \text{ and } K_3 \). The use of the equations (1.38, 1.39 and 1.40) over the whole range of formation curve is only justified when \( K_n/K_{n+1} > 10^3 \), otherwise the calculated values of the stability constants show a drift which is more pronounced as the values of \( K_n/K_{n+1} \) become lower. This method is preferable to the method (A) because it can be applied at several points along the formation curve.

In the present study only one complex is formed and the log \( K \) values read from formation curves are quite in agreement with the values calculated by the method (B).

1.5-F: Evaluation of Thermodynamic Parameters:

The values of change in free energy ( \( \Delta G \) ), change in enthalpy ( \( \Delta H \) ) and change in entropy ( \( \Delta S \) ) for complex
formation can be calculated using the temperature coefficient and Gibb’s-Helmholtz equation (30).

The direct-relationship (1.42) relating the stability constant, K and the free energy change \( \Delta G \) (kJ mol\(^{-1}\)) for the complex formation reaction can be employed for evaluation of the value of \( \Delta G \).

\[
\Delta G = - RT \ln K
\]

or \( \Delta G = - 2.303 RT \log K \)

or \( \Delta G = - 4.576 T \log K \) \hspace{1cm} (1.42)

The value of \( \Delta H \) (kJ mol\(^{-1}\)) can be evaluated with the help of equation (1.43)

\[
\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}
\]

where \( T \) is the absolute temperature and \( R \) is the gas constant. The equation (1.43) can be written conveniently as follows:

\[
\frac{d \log K}{d \left( \frac{1}{T} \right)} = \frac{\Delta H}{4.576}
\]

Therefore, for the calculation of \( \Delta H \) (kJ mol\(^{-1}\)) a graph of \( 1/T \) against \( \log K \) is plotted. If comparatively a narrow temperature range is chosen, the value of \( \Delta H \) remains approximately constant and the relation of \( \log K \) to \( 1/T \) is expressed by a straight line. The slope of the line on the graph is numerically equal to \(- \Delta H/4.576\). If the graph is not a straight line, then a tangent is
drawn at a point corresponding to any desired temperature at which \( \Delta H \) is to be calculated. In this case gradient at the tangent is equal to \(- \Delta H/4.576\).

The value of \( \Delta S \) (cal degree\(^{-1}\)mole\(^{-1}\)) for the formation reaction can be calculated with the help of Gibb's Helmholtz equation (1.45).

\[
\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad \ldots \quad (1.45)
\]

In the present work an attempt has been made to refine the free energy change (\( \Delta G \)) and enthalpy change (\( \Delta H \)) into their electrostatic and cratic components. The separation of the thermodynamic functions into temperature dependent and temperature independent components was first suggested by Gruney (78) for proton ionisation reaction. The method was extended to metal complex formation by Nancollas (72). The method has been applied by Andergg (80) and Degischer and Nancollas (81). According to Gruney (78) the work required for the dissociation of a metal complex can be written as:

\[
W = K T \ln K - \Delta n K T \ln 55.5 \quad \ldots \quad (1.46)
\]

where the term \( \Delta n K T \ln 55.5 \) is dependent upon the amount of solvent and the composition of the solution and represents the cratic part of the free energy and is characteristic of a reaction in solution in which the number of solute particles is decreased by \( \Delta n \), 55.5 being the number of moles contained in 1000 grams of water (78). It is convenient to
divide \( W \) into two parts, \( W_{\text{env}} \) representing the long-range electrostatic forces, depending upon the environment and increasing with the temperature and \( W_{\text{non}} \) representing short range or quantum mechanical forces, insensitive to environment and independent of temperature, i.e., \( W = W_{\text{env}} + W_{\text{non}} \). The corresponding contributions to the total free energy change are written as \( \Delta G_e \) reflecting the electrostatic contribution and \( \Delta G_c \) representing the covalent component, together with any other temperature independent terms. Thus,

\[
\Delta G = \Delta n \, RT \ln 55.5 + \Delta G_e + \Delta G_c \quad (1.47)
\]

For purely electrostatic interactions, the free energy will be inversely proportional to the dielectric constant, \( \varepsilon \), whose variation with temperature may be expressed empirically by equation (1.48) in which \( \alpha \) is a constant and \( \nu \) is a temperature characteristic of the solvent (219 K for water). Equation (1.47), then becomes equation (1.49) or (1.50).

\[
\varepsilon = \alpha \, e^{\nu/T}
\]

\[\Delta G = \Delta n \, RT \ln 55.5 - \alpha \, e^{\nu/T} + \Delta G_e \quad (1.49)\]

\[
\ln k = -\Delta n \ln 55.5 + \alpha \, e^{\nu/T} / RT - \Delta G_c / RT \quad (1.50)
\]

For a number of association reactions which have been studied over a wide range of temperature it is observed (82) that there is a measured association temperature, \( T^* \). The value of \( T^* \) by differentiation of equation (1.50) is given by the equation (1.51):
\[ T^* = \gamma \left[ 1 + \frac{\Delta Ge}{\Delta Ge^*} \right] \quad \ldots \quad (1.51) \]

where \( \Delta Ge^* \) is the value of \( \Delta Ge \) at \( T^* \).

It is interesting to note that \( T^* \) depends upon the ratio of covalent to electrostatic free energies of interaction. If \( T^* \) lies below freezing point of the solvent, \( \log K \) will rise over whole of the accessible temperature range corresponding to an endothermic heat of interaction. Conversely a \( T^* \) value above the boiling point of the solvent will lead to an exothermic \( \Delta H \). The former condition corresponds to an essentially electrostatic interaction and the latter to a major contribution from covalent forces. The corresponding enthalpy change is given by the equation (1.52).

\[ \Delta H = \Delta Gc - \alpha e^{T/\gamma} \left( 1 - T/\gamma \right) \quad \ldots \quad (1.52) \]

The electrostatic components, \( \Delta Ge \) and \( \Delta He \) may be calculated with the help of the equations (1.53) and (1.54).

\[ \Delta Ge = \alpha e^{T/\gamma} = - \left( \Delta S + \Delta n R \ln 55.5 \right) \quad \ldots \quad (1.53) \]

\[ \Delta He = (T - \gamma) \left( \Delta S + \Delta n R \ln 55.5 \right) \quad \ldots \quad (1.54) \]

The cratic components, \( \Delta Gc \) and \( \Delta Hc \) may be calculated with the help of the equation (1.55) and (1.56).

\[ \Delta Gc = \Delta G - \Delta Ge - \Delta n RT \ln 55.5 \quad \ldots \quad (1.55) \]

\[ \Delta Hc = (\Delta H - \Delta He) \quad \ldots \quad (1.56) \]
Making use of the equations (1.53, 1.54, 1.55 and 1.56) the electrostatic and ionic components of free energy change and enthalpy change are calculated.

1.5-G: Effect of Change in Ionic Strength on the Stability of Binary and Mixed Ligand Complexes:

In solution which contains an electrolyte, it is expected that besides short range van der Waal's forces and ion-dipole interaction, long range electrostatic attraction and repulsion, obeying the inverse square law, will also be existing. A complete understanding of the thermodynamic properties of an electrolyte requires an adequate knowledge of both, the long range interionic forces and short range interaction between the ions and solvent molecules.

The net effect of interionic attraction and repulsion is to decrease the free energy of the solute, as compared to that of the uncharged particles and decrease the activity coefficient. The forces between the ions and solvent dipoles will tend to hold the solution due to which the solvent vapour pressure will be lower than the ideal value of vapour pressure and hence corresponding increase in the activity coefficient of the solute will occur. The short range effects depend approximately linearly on concentration, while the interionic effect changes linearly with the square root of concentration. The short range forces are negligible and hence can be ignored upto one thousandth molar concentration of an electrolyte. Debye and Hückel
have given a theory for ion-ion interactions of dilute solution. According to this theory the mean rational activity coefficient, $f_\pm$, of an electrolyte dissociating into cations of valency $Z_1$ and anions of valency $Z_2$ is given by:

$$\log f_\pm = -\frac{A/Z_1 \cdot Z_2 / \sqrt{\mu}}{1 + B \cdot a\sqrt{\mu}} \quad .. (1.57)$$

where 'A' and 'B' are constants for a given temperature and dielectric constant of the medium, and 'a' is the distance of closest approach of the ions. The numerator in equation (1.57) gives the effect of long range coulombic forces while the denominator shows how these are modified by the short range interactions.

According to Untelberg (83), for aqueous solution, the equation (1.57) assumes the form (1.58):

$$\log f_\pm = -\frac{A / Z_1 \cdot Z_2 / \sqrt{\mu}}{1 + \sqrt{\mu}} \quad .. (1.58)$$

This equation gives a fair representation of the behaviour of a number of electrolytes upto $\mu = 0.1$ M (84). At very low values of $\sqrt{\mu}$ i.e., in very dilute solutions, the term, $B \cdot a \sqrt{\mu}$ will ultimately become negligible and equation (1.57) will then be reduced to equation (1.59).

$$\log f_\pm = -\frac{A / Z_1 \cdot Z_2 / \sqrt{\mu}}{1 + \sqrt{\mu}} \quad .. (1.59)$$

This is known as Debye–Hückel limiting law, according to which $\log f_\pm$ approaches linearity in the square root of concentration at high dilutions.
The study of the effect of change in ionic strength on the stability of complexes is now increasing. Thus, Gewal et al (85), Sandhu et al (86) and Ratolikar (87) have studied the effect of change in ionic strength on the stability of UO$_2$(VI) complex with thioglycolic acid, 3-hydroxynaphthalene-2-carboxylic acid and salicylaldehyde, respectively. Dixit et al (88), Marathe and Munshi (89), Katkar and Munshi (90) have also performed similar studies for the mixed ligand complexes of rare earths and UO$_2$(VI), respectively.

1.5-H: Effect of Dielectric Constant on Stability of Binary and Mixed Ligand Complexes:

The study of the effect of dielectric constant is now gaining much importance. The equilibria of proton-ligand and metal-ligand complexes are influenced considerably by the dielectric constant of the medium because of the fact that at least one of the constituents are either charged or have dipole moment. A number of studies (91-98) have been carried out on the dependence of proton-ligand and metal-ligand formation constants of the complexes, on the properties of solvent. In the study of complex equilibria in different mixed solvents, the organic solvent certainly plays an important role. On introduction of organic solvent in water, the solvent characteristics gradually undergo a change. According to Braudo and Stern (99), on addition of an organic solvent to water, the tetrahedral lattice of water is gradually broken down and owing to the denser packing and smaller extent of
hydrogen bonding between water molecules, the stability of hydroxonium ions increases and the proton donating property of the medium falls or proton accepting property of the solvent increases. Gergeli and Kiss (94) have indicated that the dioxane molecules progressively break down the hydrogen bonded structure of water. Paaba et al (100) and Rorabatcher et al (97) indicated that the basicity of water increases to a great extent in dioxane-water mixture which they attributed to the progressive break down of hydrogen-bonded structure of water by dioxane molecules.

Ions in a binary solvent are assumed to be surrounded by molecules of more polar solvent, i.e., water in partially aqueous medium. Water is an uniquely structured liquid and supposed to have a three dimensional ice-like frame work. Addition of a little organic solvent leads to an increase in the degree of order of the system (101). The degree ordered structure increases, until it reaches to a maxima. After this composition, the highly ordered solvent structure begins to collapse and the system behaves as an ordinary binary system. However, in dioxane-water system no perfect maxima is observed. According to Franks and Ivas (101) most of the ions immediately surround them, thus creating an order, but at a certain distance from the ions, there is a region where the three dimensional structure collapses.

Thus, it is essential to distinguish between the macroscopic dielectric constant of the medium and the dielectric constant of the layer. A study of solvation of
electrolytes in dioxane-water has shown that (i) ions are solvated by both the solvents (102) and (ii) the dioxane-water mixture despite their much lower polarity are more basic than other solvent mixtures. Coetzee and Calvin (103) have concluded from their work on relative solvation in dioxane-water mixtures that most of the anions show a preference for solvation with water.

In most cases, the extent of dissociation is not solely dependent on the dielectric constant of the medium. There is at least an additional factor of the chemical role of the solvent. It has been reported that an acid in solvent of similar dielectric constant exhibits different strengths (104).

Stager and Corisini (105) measured the protonation constants and stability constant of the metal complexes of some 5-substituted derivatives of oxine in 40%, 50%, 60% and 75% (v/v) dioxane-water mixture. They observed that variation of log K as well as average formation constant (log $B_n$) are linear with mole fraction of dioxane.

Chaudhary and Ghosh (91) have studied Cu(II) acetate system in dioxane-water media. They obtained linear plots of log $B_n$ vs $1/\epsilon$. Chaudhary and Kole (106) measured the protonation constant and stability constant of the metal complex of N-Benzoylphenylhydroxyamine in different percentage of methanol, ethanol, isopropanol, acetone and dioxane. They observed the log $P_{K_1}$, log $P_{K_2}$ values to vary linearly with $1/\epsilon$ or mole fraction. Agrawal (107) has determined proton-ligand and metal-ligand stability
constants of N (6-methylbenzoyl)phenylhydroxyl amine in different dioxane-water media. He also observed that 
log $K_1$, log $K_2$ and log $B_2$ values bear linear relationship 
with mole fraction of dioxane. Proton-ligand stability 
constants of DCHAO and stability constant of chelates have 
been determined in 75% (v/v) ethanol, dioxane and acetone 
by Lal and Gupta (108). They observed the plot of log $K^H_1$ 
vs 1/$\varepsilon$ to be linear. Gergely and Kiss (94) have studied 
the formation constant of proton, copper and Nickel complexes 
of alanine in dioxane-water and methanol-water media. They 
observed that the plots of log $K$ vs 1/$\varepsilon$ were not linear. 
They have explained the solvent effect by joint considera-
tion of electrostatic and solute-solvent interactions as 
done earlier by Paaba et al (100) and Rorabatcher et al (97). 
They have also determined $\Delta S$ and $\Delta H$ values of the 
systems. Bhattacharya et al (109) studied equilibrium 
constant and other properties of ferric-salicylate and 
sulphosalicylate in dioxane-water mixtures. Hala and Okac 
(110) have studied the effect of dielectric constant on 
[ UO$_2$(VI)-malonic acid ] system, using different percentage 
of dioxane in water while Hotolikar (87) has studied the 
effect of change in dielectric constant on [ UO$_2$(VI)- 
salicyldehyde ] system. Verma and Patel (111) have studied 
protonation constants of acetophenone and its oxime in 
different dioxane-water media and evaluated $\Delta G$, $\Delta H$ and 
$\Delta S$ values. Arbad et al (112) studied the effect of 
dielectric constant on [ UO$_2$(VI)-CMSTA ] system using 
different percentage of dioxane. They observed the relation
between $\log B_n$ vs $1/\varepsilon$ to be nonlinear, while with mole fraction, it is linear. The effect of dielectric constant on the stability constant of mixed ligand complexes is sporadically studied. Thus, Dixit et al (88) and Marathe and Munshi (89) have studied effect of dielectric constant on the mixed ligand complex systems of Ga(III), In(III), Sm(III) and Ho(III). Similar studies of several ternary complexes of UO$_2$(VI) have also been performed by Katkar and Munshi (90).
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