CHAPTER II

SCOPE OF THE PRESENT WORK

AND

EXPERIMENTAL

Science is nothing but developed perception, interpreted intent, common-sense rounded out and minutely articulated.

— SANTAYANA
The Life of Reason.
CHAPTER II

SCOPE OF THE PRESENT WORK AND EXPERIMENTAL

The complexation equilibria involved in between different metal ions and various ligands have been largely studied. Few metal ions have, however, received lesser attention in this regard due to some problems associated with them, which make their equilibrium study comparatively difficult. Uranium and thorium are the metal ions which belong to this category. These metal ions are generally more susceptible to easy hydrolysis and as such, their complexation reaction in aqueous solution is mostly associated with the hydrolysis of these metal ions.

The present work is an attempt in the direction of the study of complexation reaction of uranium and thorium, taking care that the equilibrium involved is free from hydrolysis,olation and oxolation reactions. The choice of ligands and study of binary complexes of uranium and thorium, along with their very stable mixed ligand complexes, have been undertaken with great care.

In this context it is desirable to discuss the aqueous and complexation chemistry of uranium and thorium from the information available in literature. It is also necessary to know the complexation chemistry of ligands selected for the present course of studies.
The actinide series of elements, beyond actinium in the periodic table, represents fascinating field of modern research. Until the middle of the eighth decade, most of the research undertaken was in support of nuclear power programmes and consequently, largely concerned with Uranium and Thorium.

More recently, interest has been aroused, as Seaborg (1) has emphasised, because of their possible value for power sources in heart pacers, telecommunication, for industrial measuring devices and medical applications, etc.

Many of the studies of the compounds of uranium and thorium have been stimulated by many workers and literature is available in the form of good books and reviews (2–4). Although, the structural aspects and solution equilibria of the coordination compounds of transition metal ions have been explored to a large extent, the complex chemistry of UO$_2$(VI) and Th(IV) and others which exhibit higher coordination numbers is not explored to a required extent.

In the fitness of the present work, chemistry of uranium(VI) and thorium(IV) complexes, particularly in solution, is briefly reviewed in the following text.
II.2: Chemisty of Hexavalent Uranium:

Uranium which is an element of "5f-6d" region exists in four different stable oxidation states, i.e., 3+, 4+, 5+ and 6+. The general nature of its chemistry is determined by two factors. The first, of course, is the relative magnitude of the standard oxidation potential in the aqueous solution and the second is the peculiar stability of the uranyl ion, UO$_2^{2+}$. The potentials of the various oxidation states of uranium are given below:

(1) Formal potentials in 1M HClO$_4$ at 25°C

\[ \begin{align*}
U & \rightarrow 1.8 \rightarrow U^{3+} \rightarrow \text{Oxidation States} \rightarrow UO_2^{2+} \\
U & \rightarrow 2.17 \rightarrow U(OH)_3 \rightarrow \text{Oxidation States} \rightarrow UO_2(OH)\!\!\!_2
\end{align*} \]

(2) In alkaline solution:

These potentials do not imply to infinite dilution in strict thermodynamic sense because on dilution the ions hydrolyze.

II.2-A: Uranium ions in solution:

Uranium ions in solution form one of the most important domain in the chemistry of this element. Uranium exists in solution in four well defined oxidation states. The hydrolytic reactions, oxidation-reduction equilibria and complex formation characteristics of these ions have been the subject of extensive study.
In common with all other ions in aqueous solution, uranium ions react with water to a greater extent. The degree of hydrolysis considerably depends on the charge and size of the ion. Speaking in very general terms, the driving force in hydrolysis is a high electric charge distribution over a small ion. Interaction with solvent forms a larger ion and decreases the density of electric charge. Aqueous solution of uranium salts always have an acidic reaction, indicative of hydrolysis. The order of hydrolysis is \( U^{4+} > UO_2^{2+} > U^3^+ \). Thus, the degree of hydrolysis increases with increasing charge and decreases with decreasing size of the ions. Although uranyl ion carries only 2+ charge, it behaves hydrolytically more like an ion of charge 4+ than simply as doubly charged cation.

**Structure of uranyl ion in solution:**

The 6+ oxidation state is the most stable oxidation state of uranium found in aqueous solution. There is an argument for the non-existence of \( UO_2^{2+} \) ion but all evidences ranging from classical to spectroscopic and crystallographic ones, definitely prove the presence of \( UO_2^{2+} \) ion. Dittrich(5) found that uranyl chloride and uranyl nitrate behave as typical ternary electrolytes in solution. Jones and Penneman (5) carried out IR studies and observed that \( U(VI) \) exists as oxygenated species. X-ray crystallographic studies on Na [\( UO_2(Ac)_3 \)] and \( UO_2F_2 \) were carried out by Fankuchin (7) who observed the existence of the \( UO_2^{2+} \) as a linear group \( O - U - O \). The Raman spectra of saturated
solution of uranyl salts were studied by Conn and Wu (8) and Satyanarayana (9), who observed at least two frequencies, one at 860 cm\(^{-1}\) and another at 200 cm\(^{-1}\), which have been assigned to symmetric \(v_1\) stretching and \(v_2\) bending vibrations, respectively. A third weaker line at 909 cm\(^{-1}\) was also observed which was assigned to asymmetric \(v_3\) vibration. The linear group O - U - O should show only one frequency, \(v_1\), corresponding to symmetric vibration. Therefore, the Raman data have been interpreted as indicating a bent rather than a linear structure. Sutton (10) and Crandell (11) have interpreted the Raman data in another way. According to them, the extra lines observed in Raman spectra may either be due to complex ion formation with an anion or arise from polymeric ions formed by hydrolysis. Thus, uranyl ion may be considered as having linear structure disturbed to certain extent due to strong local fields. Coulter et al (12) on the basis of low entropy of uranyl ion concluded that it, in solution, may exist as \([\text{U(OH)}_4]^{2+}\). Crandell (11) has studied exchange of oxygen atoms between uranyl ion and water. Since no exchange was observed he concluded that the formula of uranyl ion is UO\(_2^{2+}\) rather than \([\text{U(OH)}_4]^{2+}\). Thus, almost all evidences show uranyl ion as having linear structure, O - U - O, disturbed to certain extent due to strong local fields.
II.2-B: **Hydrolytic reaction of $\text{UO}_2^{2+}$ ion:**

The hydrolytic reactions of $\text{UO}_2^{2+}$ have been extensively studied. Uranyl salt solution is distinctly acidic and it has long been known that large amount of $\text{UO}_3^-$ can be dissolved by the aqueous solution of uranyl salts. These solutions show steep rise in the electrical conductance of very dilute solutions in comparison with other salts of similar type. To account for these observations Mac Innes and Longsworth (12) proposed the formation of polymeric species, viz. $[\text{UO}_2(\text{UO}_3^-)]^{2+}$:

$$2 \text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{U}_2\text{O}_5^{2+} + 2\text{H}^+ \quad K_h = 1.1 \times 10^{-6}$$

$$\text{U}_2\text{O}_5^{2+} + \text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{U}_3\text{O}_8^{2+} + 2\text{H}^+ \quad K_h = 5.0 \times 10^{-9}$$

Sutton (14) gave evidence for the formation of a trimer:

$$\text{U}_3\text{O}_8^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{U}_3\text{O}_8(\text{OH})^+]^+ + \text{H}^+ \quad K_h = 2.8 \times 10^{-4}$$

He has also given evidences for the presence of a polymer $[\text{U}_3\text{O}_8(\text{OH})_4]^{2-}$. However, the polymers of the above trimer type are of negligible importance (14).

Heitranen et al (15) have reevaluated the earlier work of Ahrland (16) on the hydrolysis of $\text{UO}_2^{2+}$ from the point of view of the formation of polynuclear complexes and concluded that the hydrolytic data can be best presented by expecting the formation of sheet like complex with double - OH - bridge, e.g., $\text{UO}_2[\text{(OH)}_2\text{UO}_2]_n^{2+}$. 
Sillen (17) while advancing the "Core link" hypothesis for the formation of polynuclear complexes found special interest in the hydrolytic behaviour of $\text{UO}_2^{2+}$. Thus, there is a general agreement that polymeric ions are formed. Despite some difficulties in fitting all the data at low degree of hydrolysis, the core link formation has undeniable attraction.

II,2-C: Coordination number of Uranium in $\text{UO}_2\text{(VI)}$:

This topic has been discussed quite often in terms of the coordination number of the central uranium atom in various complexes (18-26). Even though $\text{UO}_2^{2+}$ seem to be a typical doubly charged species, it is clear from its complexing behaviour that it has rather a special feature. Usually the central atom attains a coordination number of six around it, but evidences are increasing for higher coordination number of uranium in $\text{UO}_2\text{(VI)}$. In solid state, dioxobis(oxalato)urea uranate(VI) is proved (27) to be heptacoordinated around $\text{U(VI)}$.

Golovnya and Bolotova (21) have prepared pentacarbonato $\text{U(IV)}$ which undergoes easy oxidation and gets converted into tricarbonato dioxouranium(VI), indicating coordination number eight around $\text{U(VI)}$ as shown below:

![Coordination Number Diagram](image-url)
According to Zelentov (23), in inner compounds, the coordination number of U(VI) is generally eight, when the structure and size of ligands render possible the formation of coordinatively saturated complexes. For example, uranyl ion forms very stable eight coordinated compounds with tridentate ligands, such as N(2-pyridyl)-salicylideneimine (28), N(o-hydroxy phenyl)salicyldeneimine and N-2-hydroxy-5-nitrophenyl-5-bromosalicylideneimine (23). IR and NMR studies of coordination polymers of uranyl fluoride with neutral ligand, such as tributylphosphine oxide and tributylphosphate showed its structure to be as given below which proved (29) coordination number eight around U(VI).

\[
\begin{array}{c}
\text{L} & \text{O} & \text{F} & \text{L} & \text{O} & \text{F} & \text{L} \\
\text{O} & \text{F} & \text{L} & \text{O} & \text{F} & \text{L} & \text{O}
\end{array}
\]

where \(L\) is tributylphosphine oxide or tributyl phosphate.

Carey and Martell (30) have proved the structure of tris 8-hydroxyquinolino dioxouranate(VI) as shown below in which U(VI) is octacoordinated.
IR and thermal studies of uranyl complexes with some neutral ligands proved \((31, 32)\) coordination number of ten around \(U(\text{VI})\).

In solution for studies of mixed ligand complexes, in most of the cases, the work has been carried out with two bidentate ligands. However, now a days mixture of three bidentate ligands are also used \((33, 34)\) where all the three ligands participate in the reaction. Ramamoorthy and Santappa \((33)\) have also tried a mixture of four bidentate ligands and studied their coordination with \(\text{UO}_2(\text{VI})\) and found that out of the four ligands only three coordinate with the \(\text{UO}_2(\text{VI})\). These investigations indicate that even in solution, the coordination number of the central uranium atom of \(\text{UO}_2(\text{VI})\) can be extended to eight.

Sacconi and Giannoni \((18)\) have investigated the coordinative power of \(\text{UO}_2^{2+}\) and concluded that the ligands
are coordinated to the central metal ion probably by strong covalent bonds and that U(VI) has a tendency to manifest a coordination number greater than six. According to Evans (22), the preference for the coordination number eight around U(VI) is more dependent upon the nature of ligand rather than on the geometry of uranyl ion. It was further stated (22,35) that, (i) uranyl group will be coordinated to four, five or six oxygen atoms about its equator with strong tendency of coplanarity, (ii) uranyl ion prefers six or seven coordination number rather than eight and (iii) eight coordination can occur when the oxygen atoms are the donor and they belong to polarised bidentate anionic groups, where they are pulled very close. Further, Seaborg and Katz (3) have stated that anions of dicarboxylic acids generally appear to have a strong tendency for complexation.

II.3: COMPLEXES OF UO₂(VI) IN SOLUTION:

Quite a large number of references are available on equilibrium studies of hexavalent uranium using different techniques, as described briefly hereafter.

Equilibrium study of UO₂(VI) and acetic acid was performed, using extraction (36) and polarographic technique (37) and the stability constants are reported. Extraction study with acetyl acetone was carried out by Krishen and Friser (38) while spectrophotometric and conductance measurements were done (39) to study equilibrium constant of Alizarin-S with UO₂(VI). Spectrophotometric study was also done for UO₂(VI) oxalic acid system (40).
Some techniques were used to determine equilibrium constant of UO₂(VI) with benzhydroxamic acid (41). Polarographic study of UO₂(VI) with formic and propionic acids was conducted by Hala and Okac (42) while spectrophotometric study was carried out with 1,8-dihydroxynaphthalene-3,6-disulphonic acid by Banerji and Dey (43). Polarography was used to investigate the equilibrium between UO₂(VI) and glutamic acid (44) while extraction at pH 1.9 was used to perform the study between UO₂(VI) and glycine (45). Stray and Prasilova (46) performed extraction and ion exchange studies between UO₂(VI) and NTA in aq. medium whereas spectrophotometric study of UO₂(VI)-pyruvic acid was reported by Ramamoorthy et al (47). Same technique was employed by Bartusek and Sommer (48) to study equilibrium between UO₂(VI) and various ligands.

Recently Salih Hussain et al (49) determined spectrophotometrically the stability constants of uranyl ion complexes with some substituted salicylic acid, at constant ionic strength of 0.1M (KNO₃) in water-dioxane (1:1, v/v) solution. A comparison was made between the constants obtained with those found previously in aqueous solution. From least square treatment of the data, a linear relationship was found between the two sets of constants.

Abdel et al (50) have evaluated the stability constants of uranyl association complexes with fluoride, chloride, bromide, and sulphate anions and also with
phosphate, oxalate, tartarate and citrate anions as ligands in solution of constant ionic strength, using ascorbic acid as an indicator for the determination. They found the order of decreasing complexing power on U in case of the former anions as: $F^- > SO_4^{2-} > Cl^- > Br^-$, while for the latter anions it was: citrate $>$ tartarate $>$ phosphate $>$ oxalate.

II.3-A: Potentiometric study of binary complexes of $\text{UO}_2$(VI):

Lot of work has been carried out on potentiometric study of binary complexes of $\text{UO}_2$(VI). To save space a brief review is given below.

The most widely used ligands for $\text{UO}_2$(VI) binary complexes are probably the mono and dibasic carboxylic acids (51-78). Derivatives of these acids are also widely used under different conditions of study, viz. temperature, dielectric constant and ionic strength (11,79-101). 8-quinolinol and its different derivatives are also used for equilibrium studies of $\text{UO}_2$(VI) complexes (102-106). Among other widely studied ligands for $\text{UO}_2$(VI), are amino acids and their derivatives (107-126) and amino carboxylic acids which are very good complexing agents (127-134). Some workers have used phenols and their derivatives as complexing agents and studied their equilibrium reactions with $\text{UO}_2$(VI) (79,135-143).

Dutt and Singh (144) used tropolon derivatives to study the equilibrium between $\text{UO}_2$(VI) and the ligands while alumina was used as ligand by Bernatow and
Dey (145). [UO$_2$(VI)-Nitroso-$R$-salt] and [UO$_2$(VI)-Arsenazo III] systems were studied by Goyal and Banerjee (146) and Suchanek et al (147), respectively. Potentiometric equilibrium studies on UO$_2$(VI)-2,3-pyridinediol (148), UO$_2$(VI)-bisisopropylethanethiol (149), UO$_2$(VI)-5-chloro-2,4-dihydroxypropiophenone (150), UO$_2$(VI)-o-hydroxyacetophenone oxime and its substituted derivatives (151), UO$_2$(VI)-2-hydroxy-1-acetonaphthone (152), UO$_2$(VI)-3-bromo-2-hydroxy-5-methyl acetophenone and its oxime and hydrozone (153), UO$_2$(VI)-8-formyl-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (154), UO$_2$(VI)-$\beta$-furan-2-aldoxime (155), UO$_2$(VI)-(N-salicylidenoacetylhydrazino pyridinium) chloride (156) and UO$_2$(VI)-ferron (157) have also been performed under different experimental conditions. Various $\beta$-keto esters (158), 8-amino-1-naphthol and its derivatives (159), p-mercapto acetamidochlorobenzene (160), and some azo compounds (161,162) were also used as ligands for similar potentiometric studies.

Formation constants of the chelates of 2-hydroxy-1-naphthalidene-$\alpha$-naphthylamine; 2-hydroxy-1-naphthalidene-2',6'-diethylaniline (163), 2-hydroxy-1-naphthalidene-thiosemicarbazone (164) and 2-hydroxy-1-naphthalidene-o-fluoroaniline (165) with some bi and tri valent metal ions, including UO$_2^{2+}$ were determined pH-metrically by Bjerrum's method at 25° and ionic strength 0.1M in 75:25 percent (v/v) dioxane-water medium. Similar studies with $N(-2$ hydroxy-5-phenylbenzylidene)-2'-fluoroaniline (166); $N(-2$ hydroxy-1-naphthalidene)-2-
benzoylaniline (167); N(2-hydroxy-5-phenylbenzylidene)-
2-methylaniline and N-(2-hydroxy-5-phenylbenzylidene)-2,6-
dimethylaniline (168) as ligands were also reported by the
same group of workers. Das et al (169) performed potenti­
metric studies of some bivalent metal chelates (including
UO$_2^{2+}$ also) in aq. 42 vol % EtOH solutions with 0.2 M ionic
strength (NaClO$_4$) containing Na-4-hydroxy-3-formylazoben­
ze-4'-sulfonate at 25°C while Pannu et al (170) have
studied effect of variation in temperature and dielectric
constant on [UO$_2$(VI)-salicylanilide] system. Some
other ligands used for the determination of proton-ligand
stability constants and stability constants of their
complexes with some metal ions, which also included UO$_2$(VI),
were o-benzarseneous oxide (171); 2-[(o-hydroxynaphthylimino-
methyl)pyridine (172); 3,5-dichloro-2-hydroxyacetophenone
(173) and o-hydroxyphenylhydrazonoaceto acetanilide (174).
These measurements were carried out in mixed solvents and
at varying ionic strengths. El-Shetery et al (175) have
reported the synthesis and characterization of urenyl
hydrazon-$\beta$-diketone complexes while coordination studies
of some new azopyrazolones ligands with uranyl (2+) were
carried out by Adam et al (176).

Binding ability of acetamide oxime with proton
and UO$_2$(VI) in aq. solutions was studied by Hirotsu et al
(177) while the stability constants of some transition
metal and UO$_2^{2+}$ complexes with the Schiff bases N-2-hydroxy-
phenyl-2-(methoxy, nitro, chloro)benzylimine were deter-
mined by using the Calvin and Bjerrum pH titration technique.
as modified by Irving and Rossotti by Dubey et al (178). The stability constant for the complex of UO$_2^{2+}$ with a macrocyclic aminoether ligand, 1,7,10,16-tetraoxa-4,13-diazocyclotradecane was determined in aq solution by Sub et al (179) while a study of formation equilibria of the complexes of some metal cations including UO$_2^{2+}$, with macrocyclic polyethers (18-crown-6, benzo-15-crown-5, and dicyclo-hexyl-18-crown-6) were investigated potentiometrically in (90% vol) ethanol-water solutions at 25$^\circ$ and an ionic strength 0.1M ($Bu_4$ NC1O$_4$) by Luca and Azab (180).

Lingaiah and Sundarum (181) have studied equilibrium of UO$_2$(VI) by substituted naphthols in aqueous-dioxane medium while the effect of change in ionic strength was studied on the stability of UO$_2$(VI) complexes with 2-hydroxy-1-naphtholdehyde by Ratolikar (182). The stability constant of the chelates formed by 2-(N-pyrrdylmethyleneamino)ethane sulfonic acid in an aq medium (0.01M, 0.05M, 0.1M NaClO$_4$) at 25$^\circ$, 35$^\circ$ and 45$^\circ$ (183) and 2-acetylpyridine semicarbazone (184) in 75% (v/v) aq dioxane at various temperatures with UO$_2^{2+}$ and other metal ions were determined pH-metrically and the thermodynamic functions were also calculated.

Comparison of data on stability constant of different UO$_2$(VI) systems shows that the values of stability constants for a particular system obtained under more or less same conditions of temperature and ionic strength seem to differ much beyond experimental errors.
For example, Feldman and Koval (54) have reported log $K_1 = 1.61$ for 1:1 uranyl-aspartate system while for the same complex Cefola et al (57) reported the value of 8.00. For [UO$_2$(VI)-malonic acid] system Hajan and Martell (64) reported log $K_1 = 5.66$ and log $K_2 = 4.0$ while Athawale et al (53) reported the values of 4.84 and 3.76 for log $K_1$ and log $K_2$, respectively. For [UO$_2$(VI)-maleic acid] system Ramamoorthy and Santappa (61) reported 1:1 complex with log $K_1 = 5.15$, Cefola et al (57) reported 1:1 and 1:2 complexes with log $K_1 = 5.50$ and log $K_2 = 3.63$ while Hajan and Martell (64) noticed 1:1 complex with log $K_1 = 4.46$ and did not observe formation of 1:2 complex. Similar discrepancies were observed in case of itaconic acid (51, 185), citric acid (7, 186), 5-sulphosalicylic acid (63, 72) and some other ligands also.

II.3-B: Potentiometric study of mixed ligand complexes of UO$_2$(VI):

There seems to be no report on the potentiometric study on mixed ligand complex formation of UO$_2$(VI) till 1970. The first report appeared in 1970 by Ramamoorthy and Santappa (185), who reported mixed ligand complex formation of UO$_2$(VI) with mixed dibasic acids such as succinic acid, adipic acid, thiomalic acid and itaconic acid. After this report about twenty to twenty five reports have appeared on equilibrium study of the mixed ligand complex formation of UO$_2$(VI). Most of the work was carried out using different combinations of mono and
bidentate carboxylic acids, substituted carboxylic acids and phenols. Ramamoorthy and Santappa reported on various combinations of bidentate ligands (33, 185). Balkrishnan and Santappa (187) studied mixed ligand complex formation equilibria with the metal ion using different combinations of monobasic-monobasic, monobasic-dibasic and dibasic-dibasic acids. Khanolkar et al. (188) used bidentate carboxylic acids and phenolic acids as primary and secondary ligands, respectively. Simple and mixed ligand complex formation of UO$_2$(VI) with dipicolinic acid (189), catechol (190), aspartic and glutamic acid (191, 192), pyridine carboxylic acids (193, 194), thiocarboxylic acids (195), malic, maleic, chlorosuccinic, dimercaptosuccinic, methyl malonic, dimethyl malonic, picolinic, dipicolinic and quinolinic acids as secondary ligands and 3,5 dinitrosalicylic acid as primary ligand (196, 197) have also been reported. Selvraj and Santappa (198, 199) have studied mixed ligand complexes of UO$_2$(VI) with other ligands. They considered simultaneous equilibria and solved the equations with the help of computer. Ramamoorthy and Santappa (33) during investigations have tried mixture of UO$_2$(VI) with three and four carboxylic acids and found that UO$_2$(VI) combines with only three dibasic acids, thus, limiting the coordination number of the central uranium atom to eight. Kumari and Chaturvedi (34) have studied the formation of quaternary complexes with carboxylic acids, again by considering the simultaneous equilibria.
and computing the data by computer. Mittal et al (200) have used 2,2'-bipyridine, 1,10-phenanthroline and NTA as primary ligands and 8-azoguanine as secondary ligand to study UO₂(VI) complexes at 25°C and ionic strength of 0.1M NaClO₄ in 50% ethanol.

Parveen and Dubey (201) have used 2,2'-bipyridine and ethylenediamine as the primary ligand and glutamic acid as the secondary ligand and reported log K_{MAL} values of UO₂(VI) complex at 25°C as 8.15 and 7.50 respectively. They also reported on U(VI)-ascorbic acid-ethylenediamine/2,2'-dipyridyl mixed ligand systems (201). The values of equilibrium constants of some mixed protonated hydromoly complexes of UO₂(VI) with xylencyl orange were evaluated by Nayan (202). The ternary complexes of uranyl ion with phthalic acid (common ligand) and different ligands capable of complexing through O-, O-(oxalic, maleic, fumaric, succinic and salicylic acids and pyrocatechol), O-, N-(8-hydroxyquinoline and o-aminophenol) or N-, N-(2,2'-bipyridyl and ethylenediamine) were investigated pH-metrically at 25°C and ionic strength 0.1M (KNO₃) in aq medium by Venkatnarayana et al (203). Mixed-ligand complex studies of UO₂²⁺ using nitrilotriacetic acid (NTA) ethylenediamine N,N'-diacetic acid (EDDA) and iminodiacetic acid (IMDA) as primary ligands and various bidentate carboxylic acids, kojic acid, picolinic acid and nitroso-α-salt have been carried out potentiometrically at 5°C, 25°C and 45°C and μ = 0.2M (KNO₃) and the thermodynamic
parameters, viz., $\Delta G$, $\Delta H$ and $\Delta S$ were evaluated by Katkar and Munshi (204). They also reported similar studies with EDDA as primary ligand and succinic, malic, maleic, fumaric, malonic, adipic, itaconic, phthalic and mundelic acids as secondary ligands. The $\Delta G$ and $\Delta H$ values were separated into their electrostatic ($\Delta G_e$) and cratic ($\Delta G_c$) components. The effect of change in dielectric constant and change in ionic strength of the medium were also investigated. The sequence of stability constants was correlated with the properties of the secondary ligands.

Igea et al (205) have determined stability constants of the $\text{UC}^{2+}$-glycolate-lactate system in aq. solutions by two different methods (potentiometry and polarography) at $25^\circ$ and ionic strength 1M (NaClO$_4$). On the basis of the divergence of $B_{11}$ obtained by the two methods and the agreement between statistical and polarographic values they postulated the importance of determining stability constants by $\geq$ 2 independent methods. Sharma et al (206) applied modified form of Irving-Kossotti titration technique to study the formation constants of mixed ligand complexes of the type $\text{M}^{2+}\text{L}$ where $\text{M} = \text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{VO}^{2+}$, $\text{UO}^{2+}$; $\text{A} = \text{bipyridyl}$ and $\text{L} = (\text{L})$-2-aminobutenedioic acid-4-amide at $35^\circ$ ($\mu = 0.1$M). They observed the values of the formation constants for the mixed ligand system to be little lesser than the first formation constant of $\text{M-L}$ simple system. Bandiwadkar and Chavan (207) studied the
mixed ligand complexes of UO$_2^{2+}$ with bidentate carboxylic acid and phenolic acids potentiometrically at 30 ± 1° and $\mu = 0.2$M (NaClO$_4$). They noticed the stability of mixed ligand (1:1:1) complexes to depend on the size of the chelate ring and the stabilities of the binary complexes. Formation constants for mixed metal complexes $K_{MML}^{\text{D}}$ between U(VI) as the central metal ion and each one of the metal ion Fe(III), Al(III) and Cu(II), were determined by using data from potentiometric measurements (208). In each case one of the hydroxycarboxylic acids, citric, tartaric or malic, was used as a ligand.

Most recently binary and ternary complexes of UO$_2^{2+}$, Ni$_2^{2+}$ and Zn$_2^{2+}$ with uracil and NTA were studied at 35° and ionic strength 0.1M (HClO$_4$) by Mishra (209) using ionophoretic technique. The stability constants of the 1:1:1 mixed ligand complexes have been reported. Prabhu and Nair (209a) determined the stability constants of the complexes formed by U(VI) and Pu(VI) with succinate ions in 0.5M NaClO$_4$ medium at 30° following the Bjerrum-Calvin pH titration technique. U(VI) complexes have stabilities higher than the corresponding Pu(VI) complexes in accordance with the acidities of the cations. Complexation of UO$_2^{2+}$ by phenylene-1,2-dioxydiacetic acid was studied by potentiometry, calorimetry, solvent extraction and $^1$H-NMR spectroscopy (209b). Complexation parameters at 298K and ionic strength 0.1 (NaClO$_4$) were determined.
The stepwise stability constants of $\text{UO}_2^{2+}$, $\text{Mn}^{2+}$, $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Zn}^{2+}$, $\text{Fe}^{3+}$ and $\text{UO}_2^{2+}$ ions with hydrazone $\beta$-diketone ligands were determined at $30^\circ$ by pH-titrations in 75% (v/v) dioxane-water solvent (209c). Stability constants of some bivalent metal (including $\text{UO}_2^{2+}$) ion complexes with 2-hydroxy-3,5-dimethylacetophenone oxime were determined at different ionic strengths by Neman et al (209d). By the application of suitable spectrophotometric methods and pH metric measurements, Malesev et al (209e) established that $\text{UO}_2^{2+}$ ion and 3-hydroxyflavone form a 1:1 complex. The concentration stability constant of the complex $[\text{UO}_2(C_{15}H_{9}O_3)]^+$ was determined by Bent-French's ($\beta_1 = 8.59$ at $\text{pH}=3.5$) and Bjerrum's (from 8.68 at $\text{pH}=4$ to 6.14 at $\text{pH}=7$) methods. All the investigations were carried out with 80% ethanolic solutions at 20°, the spectrophotometric measurements being performed at a constant pH (3.5) and a constant ionic strength (0.01M).

II.4: CHEMISTRY OF TETRAVALENT THORIUM:

Thorium, the first member of the actinide series (valence shell electronic configuration, $6d^{2}7s^{2}$), usually shows only one stable oxidation state, the 4+ state, in ionic or covalent compounds. Other oxidation states, 2+ and 3+ also exist. Numerous attempts have been made to prepare compounds in which thorium has an oxidation state lower than 4+. Efforts by Ward (210) to prepare $\text{TnF}_3$ have been unsuccessful. Anderson and D'Eye (211) and Hayek (212,213) have reported the preparation of lower iodides of thorium.
by reduction of ThI₄ with metallic thorium. These lower iodides have been assigned the formula ThI₂ and ThI₃.

The normal oxidation state of thorium is 4⁺ and Th⁴⁺ is one of the least hydrolysed tetrapositive ion, having a first acid dissociation constant equal to 10⁻³.₅(Ca). As a highly charged cation Th⁴⁺ undergoes extensive interaction with water and many anions. It forms a complete range of anhydrous and hydrated salts, together with an extensive range of complexes, especially with oxygen, nitrogen and halogen donor atoms. Reported coordination numbers of Th⁴⁺ ion are 11, 10, 9, 8 and occasionally 6. According to Løtiker (214) the oxidation potential of Th⁴⁺ ion in acid and basic solution is given by

\[ \text{Th} \rightarrow \text{Th}^{4+} + 4e^- ; E^0_A = 1.90 \]

\[ \text{Th} + 4 \text{OH}^- \rightarrow \text{Th(OH)}_4^{4+} + 4e^- ; E^0_B = 2.48 \]

Thorium metal is thus, slightly more electropositive than uranium.

II. 4.A: Hydrolysis of Th⁴⁺:

All the investigators are in agreement that Th⁴⁺ undergoes extensive hydrolysis. However, there is a considerable divergence of opinion regarding the product of hydrolytic reaction.

Tomnet and Chauvenet (215), by measuring the change in conductivity and the evolution of heat on mixing Th⁴⁺ and OH⁻ in various proportions, concluded that the species
Th(OH)$_2^{2+}$ is formed. The conclusion was also drawn by Souteyrand and Chauvenet (216) from a study of nitrate solutions, who reported that the hydrolysis of Th$^{4+}$ proceeds according to the following reactions:

\[
\text{Th}^{4+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Th(OH)}_2^{2+} + 2 \text{H}_3\text{O}^+
\]

\[
\text{Th}^{4+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{ThO}^{2+} + 2 \text{H}_3\text{O}^+
\]

With the help of pH-measurements, Schall and Faucherre (217) have, however, concluded that a tetramer Th$_4^{0+}$ is formed on hydrolysis of Th$^{4+}$. Kraus and Holmberg (218) investigated the hydrolysis of Th$^{4+}$ by emf measurements in perchlorate and chloridesolutions, using a glass electrode.

In acid solution, evidence was found for the presence of hydrated unhydrolysed Th$^{4+}$. In the concentration range, $2.5 \times 10^{-4}$ to $1.5 \times 10^{-2}$ M, hydrolysis of Th$^{4+}$ is reported to be negligible below pH 3 and it is strongly dependent on the concentration of thorium ions (218). No evidence was found for appreciable existence of the monomeric species, Th(OH)$_3^{3+}$, even in the early stage of the hydrolysis. For the formation of Th(OH)$_3^{3+}$ the equilibrium constant is equal to $5 \times 10^{-5}$. They also found it necessary to postulate the formation of at least a dimeric species, in order to account for their hydrolysis data. The following reactions and equilibrium constants fitted their data fairly well.

\[
\text{Th}^{4+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Th(OH)}_2^{2+} + 2 \text{H}_3\text{O}^+; K = 3.4 \times 10^{-8}
\]

\[
2\text{Th}^{4+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Th}_2\text{(OH)}_2^{6+} + 2 \text{H}_3\text{O}^+; K = 2.6 \times 10^{-6}
\]
They have concluded that as the hydrolysis proceeds, higher polymeric complexes must also be formed. Equilibrium systems with polynuclear complex formation have been treated by Sillen (219) under the title of the 'Corelink' hypothesis. Hietmen (220) studied in detail hydrolysis of Th$^{4+}$, according to the 'Corelink' hypothesis of polynuclear complex formation. According to his interpretation a series of complexes of the type $\text{Th} \left[ (\text{OH})_3 \text{Th} \right]^{(n+4)+}_n$ is formed with $n = 1, 2, 3$ etc. It would appear plausible to assume that the complexes are chain-like, although, the hydrolysis data permit no conclusion for the shape of the complexes.

The existence of the products of hydrolysis of Th$^{4+}$ as chainlike complexes is supported by the results of study on colloidal thorium hydroxide, prepared by dialysis of thorium chloride (221). Kraus concluded that in the early stages of hydrolysis, monomolecular species may be important. In the latter states, however, there is agreement regarding the predominance of polynuclear complexes. It has been pointed out by Kraus et al (222) and Kilpatrick (223) that, other anions, which may be present in solution, must also be taken into account. Anions compete with water and OH$^-$ ions for the available positions in the coordination sphere of the metal ion and thus, destroy the bridges and reduce the degree of polymerisation. Anrland (224) found that uranyl ion formed polynuclear complex in perchlorate solution but no sign of polynuclear complex formation was evident when anions were thiocyanate, monochloroacetate, etc.
II.5: **COMPLEXING TENDENCY OF THORIUM(IV) IN SOLUTION:**

The literature survey reveals limited studies on Th\(^{4+}\) complexes involving pH-metric titration technique.

Various workers have reported the stability constants of 1:1 complex of Th(IV) with EDTA, HEDTA, NTA and polyaminocarboxylates (225-229). The stability and thermodynamic properties of Th(IV) chelates of ethylene bis-(oxyethylenenitrilo)-tetraacetic acid at constant ionic strength 0.10 (KClO\(_3\)) have been reported by Hseu and Jyi (230). Srivastava et al (231) determined the stability constant of the complex formed between some metal ions, including Th(IV), and diethylenetriamine, by pH measurements and correlated them with the chromatographic behaviour of the metal ions on silicagel G plates, impregnated with the ligand. Some thermodynamic parameters (\(\Delta G\), \(\Delta H\) and \(\Delta S\)) for the formation of Th(IV) complexes with some polydentate ligands, such as oxydiacetate, iminodiacetate, thiodiacetate and succinate, were determined by potentiometric and calorimetric titrations at 25\(^\circ\) in aqueous 1 mol/dm\(^3\) KClO\(_4\) by DiBernado et al (232).

The study of Th(IV)-ARS complex was done by potentiometric method (233) and spectrophotometric method (234, 235). Studies on equilibrium of Th(IV) complexes with quinizarine and its sulphonatic acid derivatives was reported by Issa et al (236). Potentiometric study on Th(IV)-thiovanol system was carried out by Kanth et al (237). They suggested 1:2 complex formation. According to Saxena
and Sheetwant (238), furfuryl mercaptan formed 1:4 complex with Th(IV). Saxena and Dhawan (239) used DL-norleucine, to study the equilibrium with Th(IV). Thorium(IV)-glycine system was studied by Tomat et al (240). The stability constants of some metal ions including Th(IV) with α,α′-dimethylcaproic acid (241); p-aminobenzoic acid (242) and anions from some carboxylic and aminopolyoxyacids and glycine or oxychinaline (243), have also been determined. Kedrovskaya et al (244) determined the stability constants for [Th(OH)₂⁺ (HA = carboxylic acid, such as HCOOH, HOAC, butyric, hexanoic acids) complexes at 25°C and ionic strength 1.0(NaCl). They attributed the additional stability of [Th(OH)₂⁺ complexes to the H-bond stabilized 6-membered ring structure, involving Th⁴⁺, OH⁻ and the COO⁻ group.

The instability constant of the cation [D₃Th]⁴⁺, where D = diantipyrylmethane, in weakly acidic medium (pH 2), was determined to be 1.09x10⁻¹⁷ by Zhivopistev and Pyatosin (245). Sharma and Sharma (246) have reported the stability constant of 1:2 (metal/ligand) complex of Th(IV) with succinimide at pH 5.0. Sergeev (247) has reported the use of anion-exchange method to determine the stability constants of Th(IV)-amino acid 1:1 chelates at 20°C and ionic strength 0.5. According to Kiraly and Martin (248), the anthracycline containing antibiotic daunorubicin binds metal ions (including Th⁴⁺) with stabilities similar to those of quinizarin. The ionization constants of Th(IV)-3-[(bis(carboxymethyl)amino) methyl]-5-[(diethylamino)
methyl-phenylpyrocatechol (H₄A) were determined by potentiometric titration with NaOH by Zhu et al (249). They also determined the stability constants of Th(IV)–H₄A complexes, [ThA], [ThA⁺], [Th(H₂A)₂] and [Th(H₃A)₂]²⁺ potentiometrically. The complexation equilibrium of Th(IV) with 1,4-bis(4'-methylaniline)anthraquinone was studied spectrophotometrically in 40 vol% DMF at 20° and an ionic strength of 0.1 M (NaClO₄) by Jeleim et al (250).

Formation constants of Th(IV) mixed-ligand complexes were determined by pH-metric measurements at 25° and ionic strength 0.50 M (NaNO₃) by Nayan (251). The species formed are ThAH₂B with NTA(H₄A) and thoron (H₅B) and ThAHB and ThAB with NTA and methyl thymol blue. The later two species are more stable than ThAH₂B, which breaks into simple species above pH ~ 5.5. The stability constants of ternary Th(IV) complexes containing alizarin maroon (AZM) and as a secondary ligand, salicylic acid, 5-sulphosalicylic acid, 5-nitrosalicylic acid, 2,2'-bipyridine or 1,10-phenanthroline, were determined potentiometrically at 25° in 20% and 40% v/v ethanol-water medium at ionic strength 0.1 M (NaClO₄). The mixed ligand complexes showed unexpectedly high stability with an absorption band in solution with λ max 580 nm (252-254). They developed a sensitive method for micro-determination of Th, based on the formation of its ternary complex AZM and 5-sulphosalicylic acid. The mixed ligand complexes of Th(IV) with quinizarin (quim) and as a second ligand, L, salicylic acid (sa), thioxalicylic acid (tsa)
or anthranilic acid (ant), were also studied potentiometrically in 40% v/v ethanol-water medium
\[ \frac{M}{V} = 100 \text{ mol/dm}^3 (KNO_3), 25 \pm 0.1^\circ \] by Idrias et al (255). They characterized the ternary stability constants of the 1:1:1 Th-quin-L complexes and observed the order of their stability to be in accordance with the calculated \( \pi \)-charge densities of the varying ligating group in the ligand L.

Potentiometric studies of mixed ligand complexes of Th(IV), with NTA and EDTA as primary ligands and anthranilic acid as secondary ligand, have been reported by Kale and Mhaske (256). Shetty et al (257) used a fluoride ion sensitive electrode in the study of mixed ligand chelates of Th(IV) with HEDTA and fluoride ions. They reported that the polynuclear Th-HEDTA primary complex forms a mononuclear Th-HEDTA-F_2 complex in presence of fluoride, liberating 3 acetate protons from HEDTA (hydroxyethylene diaminetriacetic acid). Zaidi and Islam (258) studied the equilibrium between Th(IV) and bismuthiol in 70% (v/v) ethanol-water medium. Jain and Sharma (259) reported 1:2 complex for Th(IV)-diphenic acid system, studied in dioxane-water medium. Th(IV)-n-butylthioglycollate system was investigated in 40%(v/v) ethanol while 50% (v/v) ethanol medium was used for equilibrium study between Th(IV) and tetrahydroxy-p-benzoquinone by Hammam and Ibrahim (106).

The complexing behaviour of Th(IV), Pu(IV), Am(III) and Eu(III) with ionizable macrocyclic ligands were
investigated by potentiometric and solvent extraction techniques (259a). Increase in steric constraints with a decrease in metal ion radius as well as increase of ring size, was observed. Grant et al (259b) studied the thermodynamics of the aqueous coordination of thorium with the iodate anion at 25°C.

However, there are some references available in literature where the complexing characteristics of UO₂(IV) and Th(IV) have been reported jointly. Barocas et al (260) determined the stability constants of the complexes of benzohydroxamic acid with Th⁴⁺ and U⁴⁺.

Stability constants of complexes formed between optically pure isomers of methionine and UO₂²⁺, Th⁴⁺ and some divalent cations at 25°C and an ionic strength 0.1M(KNO₃) were determined by potentiometric titrations (261). The stabilities of UO₂²⁺ and Th⁴⁺ complexes with N(-2-carboxy-phenyl)amino diacetic acid (ADA), iminodiacetic acid (IDA) and [(ethylene dioxy)diethylenedinitro] tetra-acetic acid (EGTA), were studied potentiometrically in 0.1M (KNO₃) solutions at 25°C (262). The complexes of Th⁴⁺ ion with IDA and ADA were more stable than those of UO₂²⁺ ions, while EGTA formed more stable complexes with the latter. Sharma et al (263) investigated the interaction between UO₂²⁺ and Th⁴⁺ with (L)2-aminobutanedioic acid-4-amide at 25°C-45°C and ionic strengths 0, 0.1, 0.2, 0.5 and 1.0 M (KNO₃) in aq media by a pH-titration technique. The data suggested the formation of 1:1
complex with $\text{UO}_2^{2+}$ and 1:1 and 1:2 complex with $\text{Th}^{4+}$ ions at pH 3.3 - 6.0 and 2.5 - 5.5, respectively. They evaluated the formation constants by using Calvin and Melchior's extension of Bjerrum's method. The thermodynamic stability constants and other functions accompanying complexation were also evaluated.

Bismondo et al (264) carried out potentiometric and calorimetric investigations of $\text{UO}_2^{2+}$ and $\text{Th}^{4+}$ complexes with glycine in 1.0 M aq $\text{NaClO}_4$ at 25°. They suggested that glycine acts as unidentate ligand through the carboxylate group, while the amino group is not involved in coordination. Complex formation of $\text{UO}_2^{2+}$ and $\text{Th}^{4+}$ and DL-norleucine was studied by pH-titration at 20°, 30° and 40° in aq solution of ionic strength 0.1M ($\text{NaClO}_4$) and metal/ligand ratio 1:5 (265). Stability constants of 1:1 and 1:2 complexes of $\text{UO}_2^{2+}$ and 1:2, 1:3 and 1:4 complexes with $\text{Th}^{4+}$ were calculated. They (265) have also reported a similar study of the metal ions with methylguanidoacetic acid and used the Calvin and Melchior's extension of Bjerrum's method for the calculation of the stability constants of 1:1 and 1:2 complexes of $\text{UO}_2^{2+}$ and 1:1, 1:2 and 1:4 complexes of $\text{Th}^{4+}$. Askalami and Milkhaib (266) determined the stoichiometries and stability constants for $\text{U}^{(VI)}$ and $\text{Th}^{(IV)}$ complexes with 1-substituted-2-naphthol and 4-substituted resorcinol (substituents = 2 pyridylazo, 2-thiazolylazo) by the mol-ratio and/or continuous variation methods. Kumar and Narain (267)
determined formation of sulfathioazole complexes of some metal ions, including U(VI) and Th(IV), by pH-metric titration at 35° and 45° in aq EtOH at ionic strength 0.1M (KNO₃) and calculated the stability constants by the Bjerrum and the Šonin-Majorova methods.

El-Haty and Adam (268) studied the formation, structure and stability constants of 19 UO₂⁺ and Th⁴⁺ chelates with Schiff bases derived from salicylaldehyde and 6-aminopicoline 2-, 3- and 4-aminopyridine, 3-amino-1,2,4-triazine or 2-amino-3-hydroxypyridine. They suggested the coordination through N-atom of azomethine group and O-atom of the phenolic group. Spectrophotometric studies supported the use of some of these ligands for microdetermination of UO₂⁺ and Th⁴⁺ ions in solution.

Morozumi and Hiroshi (269) considered the chloro complexes of uranyl and thorium ions, to be the typical outer-sphere complexes, due to abrupt decrease in their stability constants with increasing ionic strength, their obeying the Fuoss equation and their remarkably low heat of formation.

Ramlingam and Krishnamoorthy (270) determined the formation constants of mixed-ligand complexes of UO₂⁺ and Th⁴⁺ with EDTA as primary ligand and various nucleosides and their bases as secondary ligands, in a 1:1:1 ratio in aq solution (μ = 0.1M, KNO₃) at 35° by potentiometric measurements. Formation constants of 1:1 binary complexes of UO₂⁺ and Th⁴⁺ with the secondary ligands were also
reported. They observed a good correlation between the basicity of secondary ligands and stability of their 1:1 binary complexes. The binary complexes of Th$^{4+}$ showed greater stability in comparison to the corresponding UO$_2^{2+}$ complexes. The binary complexes were more stable than their corresponding ternary complexes. Niu and Whoppin (271) measured the stability constants for the reaction $MX + L \rightleftharpoons MXL$ where $M = $ Gd$^{3+}$, UO$_2^{2+}$ and Th$^{4+}$, $X = $ nitrolactic acid and $L = $ malonate, succinate, glutarate and adipate, in solutions of ionic strength 0.1 ($NaClO_4$) at 25°. These stability constants for a particular $L$, followed the order: Th$X_L > $ UO$_2X_L > $ Gd$X_L$. They have discussed the results in terms of formation, by the ternary ligand $L$, of monodentate or bidentate complexes.

Stability constants, enthalpies and entropies of formation of UO$_2$(VI) and Th(IV) complexes with aspartic acid were determined at 25°C in 1.0 mol/dm$^3$ aq solutions of NaClO$_4$ by means of potentiometric and calorimetric techniques (126). Because of precipitation of solid compounds, only two complexes of 1:1 and 1:2 stoichiometry were observed in the UO$_2$(VI)-aspartate system and only one complex of 1:1 stoichiometry in the Th(IV)-aspartate system. They suggested bonding of both the metal ions to involve one carboxylate group only, the one farthest from the positive amino group.

Stabilities of chelates of sulfanilic acid and 8-hydroxyquinoline were determined for the ions Th$^{4+}$,
UO$_2^{2+}$, Pr$^{3+}$, Nd$^{3+}$ and La$^{3+}$ in order to study the effects of structural changes and other related properties on chelate stability (271a). Metal stability sequence showed an increase in chelate stability with the transition electron shell becoming more filled.

II.6: COMPLEX CHEMISTRY OF THE LIGANDS USED IN THE PRESENT INVESTIGATION:

II.6-A: Primary Ligands:

1. Iminodiacetic acid: Aminopolycarboxylic acids are the excellent complexing agents and the study of their binary complexes with many metal ions have been carried out. Iminodiacetic acid (IMDA) has been used as a ligand with rare earths by Thompson and Lorras (272). Grenthe and Garohamman (273) and Kurkina et al (274) have also studied complexation of rare earths with IMDA. Potentiometric study of UO$_2$(VI) with IMDA was carried out by Rajan and Martell (275) at 25$^\circ$ and ionic strength 0.1M (KNO$_3$). They concluded that IMDA acts as a tridentate ligand and represented the structure of its uranyl complex as:

![Diagram of Uranyl Complex](image)

While investigating on mixed ligand complexes of rare earths with C$_2$DTA as primary ligand, IMDA was used as a
secondary ligand by Marathe and Munsbi (276). Kumari and Chaturvedi (34), while investigating on quaternary complexes of UO₂(VI), have used IMDA as one of the ligands. Katkar and Munsbi (204) have used IMDA as primary ligand and Kojic acid, picolinic acid, nitroso-R-salt and various bidentate carboxylic acids as secondary ligands in physico-chemical investigation of mixed-ligand complexes of UO₂²⁺.

2. **Nitrilotriacetic acid**: NTA is a widely used ligand mostly acting as tetradeptate (277). Studies on the binary complexes of III B group elements have been carried out with NTA as a ligand (278, 279). Binary complexes of Th(IV) with NTA was studied by Sergeev and Korshunov (114), while Gritmon et al (280) have studied complexes of lanthanides with NTA. Stray and Prasilova (46) have reported ion exchange and extraction studies of UO₂(VI) with NTA. Cabell (281) tried potentiometric study of UO₂(VI) with NTA but was not able to give successful mathematical treatment.

Nitrilotriacetic acid has been used as a primary ligand for the study of mixed ligand complex formation. Carey and Martell (30) have reported the mixed ligand complexes of Th(IV) with NTA as a primary ligand and some hydroxy acids as secondary ligands. Carey et al (282) also studied mixed ligand complexes of Th(IV) with NTA as a primary ligand and 5-sulphosalicylic acid, salicylic acid and cromotropic acid as secondary ligands. Formation constant of some mixed ligand complexes, resulting from the
interaction of divalent metal ions with NTA as primary ligand and some bidentate ligands, were reported by Israeli (283). Tandon and Sharma (284) and Bhattacharya and Parikh (285) have reported potentiometric studies of Cu(II), Ni(II) and Zn(II) complexes, using NTA as a primary ligand. Mixed ligand complex formation studies involving NTA as a primary ligand with various metal ions, have been carried out by different workers (286-291). Krishna et al (292) have reported stabilities of Bi(III) complexes with NTA, as a primary ligand, while Jacobs and Margerum (293) have studied the mixed ligand complexes of Ni(II) and reported the free energy charges of these reactions. Simple and mixed ligand complexes of Fe(II) with NTA, as a primary ligand and some oxygen bonding organic anions, as secondary ligands, were reported by Ramamoorthy and Mannir (294) and Morin and Scharff (295). Mhaske and Munshi (296) have reported mixed ligand complexes of Pr(III) with NTA, as a primary ligand, while Pujari and Munshi (297) have studied mixed ligand complexes of Y(III) with NTA, as a primary ligand. Uixit and Munshi (298) and Uixit et al (299) have also reported mixed ligand complexes of Eu(III) and In(III) with NTA, as a primary ligand, using various bidentate ligands, as secondary ligands.

Singh et al (300) studied the formation of Cu(II), UO₂(II), Co(II) and Zn(II) complexes with NTA and valine by paper electrophoresis at 35⁰ and ionic strength 0.1M. Tarelkin et al (301) studied the complexation of Pb²⁺ with
NTA (H₃L) potentiometrically at pH 1.6 - 12.9, ionic strength 1 (KNO₃ + HNO₃) at 25°. Stability constants of binary complexes of UO₂(II) with NTA, suberic (I) and azelaic (II) acids, as ligands, and of mixed ligand complexes of UO₂(II) with NTA, as a primary ligand, and I and II, as secondary ligands, at 5°, 25° and 45° and in different ratios of water to non-aqueous solvents and at different ionic strengths, have been reported by Andhare et al (302). Similar studies using kojic acid, picolinic acid and nitroso-R-salt, as secondary ligands, have also been reported by Katkar and Munshi (204).

3. Ethylenediaminetetra-acetic acid: EDTA is the most outstanding reagent of a series of aminopolycarboxylic acids possessing the characteristic group \( \text{CH}_2\text{COOH} \). The metal complexes of EDTA are of the chelate variety, but the overall complex remains anionic and usually very soluble. Considerations of chelate chemistry indicate that five or six membered rings are the most stable. Its complexing power lies in the ligand forming nitrogen atoms and the carbonyl oxygen of the acetic acid groups. It is well known that acetate ion forms complexes with nearly every metal ion and that the nitrogen atom in amines exerts a similar influence. In EDTA these ligands are built into a molecule which is flexible and in such a position that they are easily accessible and correctly spaced to ensure the
formation of five-membered rings with cations, both across the iminodiacetic acid groups and ethylenediamine bridge.

EDTA forms 1:1 binary complex with all metals. Thus, divalent metals react with the disodium salt $\text{Na}_2\text{H}_2\text{Y}$ according to the scheme:

$$\text{M}^{2+} + 2 \text{H}_2\text{Y}^2- \rightleftharpoons \text{MY}^2- + 2\text{H}^+$$

This reaction results in the metal cation replacing a hydrogen atom from an acetic acid group on each of the two nitrogen atoms in the molecule. In addition, coordinate bonds are developed with the two nitrogen atoms and sometimes also with the carbonyl oxygens of the remaining two acetic acid groups. In this way the metal ion becomes a part of at least three five-membered chelate rings. If the coordination requirements of the central cation require it, coordination can also occur with the remaining carbonyl oxygens, i.e., EDTA is maximally hexadentate. Usually EDTA is capable of forming a coordination saturated complexes with most ions. pH has a marked effect on the stability of the various EDTA-metal complexes.

The studies on binary and mixed ligand complexes of EDTA with metal ions have been reported along with those of HEDTA, in order to avoid repetition of the text.

4. $\text{N-Hydroxyethyl-ethylenediamine-NN'N'-triacetic acid}$

HEDTA corresponds to EDTA with one acetic acid replaced by a hydroxyethyl group. Predictably it has been observed that its complexes are invariably less stable than those of EDTA, except that of Cu(II) and Ni(II) retain a pronounced
ability to react more firmly (relatively speaking) than most others. HEDTA is a pentadentate ligand.

Ternary complexes of rare-earth ions with several multidentate complexones and number of bidentate ligands have been studied spectrophotometrically by Pouluektov et al (303,304). pH-metric investigations on 1:1:1 complex formation of Y(III) with EDTA, HEDTA and NTA, as primary ligands, and acetylacetone and kojic acid as secondary ligands, has been reported by Pujari and Munshi (305). Potentiometric and spectrophotometric studies of mixed-ligand complexes of some rare earth ions with certain complexones and acetylacetone, β-isopropyltropolone and kojic acid have also been carried out (306,307). La(III), Nd(III), Ho(III) and Er(III)-EDTA-lactic acid/CO$_3^{2-}$ complexes have also been investigated (308,309). Abou et al (310) carried out the pH-metric studies on Lanthanide(III)-EDTA-malic acid complex formation. Intorre and Martell (311) reported the tendency of Zr(IV) for formation of mixed-ligand complexes with HEDTA and some bidentate hydroxy acids. Dobrynina et al (312) investigated the formation of rare earth-EDTA-tartaric acid complexes. Potentiometric studies on mixed-ligand complex formation of La(III), Pr(III) and Nd(III) with HEDTA and some dicarboxylic acids have also been reported (313-317).

A quantitative approach to stability correlation of some lanthanide-EDTA-aliphatic hydroxy acid complexes have been attempted by Limaye and Saxena (318). They have discussed the entropy stabilised nature of the 1 : 1 : 1
complexes on the basis of the results obtained from the pH-metric studies. Tripathi et al. (319) carried out the pH-metric investigations on formation of ternary complexes of rare earths-NTA/HEDTA-catechol and other oxygen donors. Complexing tendencies of some lanthanide (III) ions, with NTA, HEDTA, EDTA and some diphenoxy compounds, have also been studied, pH-metrically (320-322). Solution studies on mixed-ligand complex formation of Y(III) using NTA/EDTA/HEDTA as primary ligands and some aromatic oxygen donors as secondary ligands have been reported by Pujari and Munshi (305). Complex forming tendencies of some metal ions with NTA and EDTA, as primary ligands, and dinitro, dibromo-derivatives of salicylic acid and cresotic acid, as secondary ligands have also been studied (323,324). Spectrophotometric investigations on Ho(III)-EDTA-5-sulphosalicylic acid complex have been carried out (308,309). Importance of oxygen donors and five membered ring structure in formation of Ho(III)-EDTA-Tiron complex have been studied by Shetty and Sathe (307).

pH-metric investigations on mixed-ligand complex formation, using NTA (319), EDTA (325) and HEDTA (326) with aromatic oxygen donor ligands, have been studied extensively. The trends in stabilities of mixed-ligand complexes of some lanthanide ions with aminopolycarboxylates and aromatic oxygen donors have also been reported (327). Entropy stabilised nature of lanthanide-EDTA-aromatic oxygen donors has been discussed, on the basis of the results obtained from
pH-metric studies, by Limaye and Saxena (318,328). Dvorakova et al (329) determined potentiometrically stepwise stability constants of rare earth metal complexes with EDTA type ligands at 20° and ionic strength 0.1. Nazarenko and Polukhontov (330) studied the interaction of F⁻ with Ln⁢³⁺-EDTA complexes at 20° and ionic strength 0.2, using potentiometric and spectrophotometric techniques. They calculated stability constants for formation of 1:1:1 and 1:1:2 Ln⁢³⁺ : EDTA : F⁻ complexes.

Lurdes et al (331) have discussed the nature of EDTA complexes of UO₂(VI) and concluded that there is no need to postulate stabilization of the complex by H-bonding between a protonated H-atom and uranyl ion. Limaye and Saxena (332) carried out a pH-metric study of 1:1 binary and 1:1:1 mixed ligand complexes of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) in aq. medium using EDTA as primary ligand, and alizarin red sulphonlic acid (ARS), as secondary ligand (H₂L), employing Irving–Rossotti titration technique, at 25° and ionic strength of 0.2 mol dm⁻³ NaClO₄. The effect of electrostatic repulsion between [Ln(III)-EDTA] and L²⁻ species on the stability of the ternary complex has been studied. They observed the order of stability for the binary and ternary complexes to be: \( \log K_{MA}^A \gg \log K_{ML}^A > \log K_{MAL}^A \), whereas the trend in log \( K_{MAL}^{A} \) values with respect to metal ions was: La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III).
Singh and Saxena (333) have determined potentiometrically by the Irving-Rossotti approach, at 25°C and at an ionic strength $1 = 0.2$ (mol dm$^{-3}$, KNO$_3$), the formation constants ($\log K_{MAL}$) of the mixed complexes of the type MAL, where $M = UO_2^{2+}$ or Th$^{4+}$, $A = IMDA$, NTA, HEDTA, EDTA, CDTA or DTPA and $L =$ catechol (Cat), 4-methylcatechol (m-cat), tiron (tir), 2,3-dihydroxynaphthalene (DHN) or chromotropic acid salt (CS). The observed trends in solution stabilities are: (i) Th$^{4+} > UO_2^{2+}$, (ii) CS $>$ Tir $>$ DHN $>$ m-cat $>$ Cat and (iii) IMDA $>$ NTA $>$ HEDTA $>$ EDTA $>$ CDTA $>$ DTPA, with respect to metal ions, secondary ligands (L) and primary ligands (A), respectively. The $\Delta \log K$ values are negative. Similar observations have recently been reported by the same authors (334) for the above systems, using resorcinol or its derivatives as secondary ligands. The stability sequence observed with respect to the secondary ligands was: 4-Cl-res $>$ 5-Me-res $>$ 2-Me-res $>$ res.

II.6.B: Secondary Ligands

1. Lactic acid: The acid dissociation constants of lactic acid at various temperatures were reported by Martin and Tartar (335). Later on, Davies and Monk (336) reported the acid dissociation constants, along with the formation constants of alkaline earth metal ions. Proton ionization heats and related thermodynamic quantities of various carboxylic acid, including LA, were evaluated in formamide at 25°C by Dash (337). Uddin (338) determined the dissociation constant of LA and other aliphatic and aromatic
monocarboxylic acids at zero ionic strength by the spectrophotometric technique, using methyl orange as an indicator. Spectrophotometric and potentiometric determination of the concentration equilibrium constant of LA in solutions of 0.1 ionic strength (NaCl) at 20.5°, 25.8° and 30.8°C was reported by Ho, Wu-Hsiung (339). Stability constants of Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Fe³⁺ and Pb²⁺ Complexes, formed with LA in aqueous and organic solvent-water media, have been determined, using spectrophotometric and potentiometric techniques, by various workers (340-355). Strezov and Mikhallow (356) investigated the influence of the substituent group in the molecule of aliphatic monocarboxylic acids, including LA, on their interaction with Cd²⁺ and Zn²⁺ ions. They observed the presence of OH group to stabilize the complexes.

Tedesco and De Rumi (357) have reported the stability constants and thermodynamic parameters for Be²⁺, Al³⁺ and Cr³⁺ lactate systems at 25° - 45°C and ionic strength 1.0 (NaCl⁰₄), using potentiometric, pH and ion exchange analytical procedures. Chakravarti and Sharma (358) studied potentiometrically, thermodynamic parameters of Al, In and Tl complexes with some of the α-hydroxy acids—glycolic, lactic and mandelic, and discussed their stability in terms of these parameters. The stability order was: Tl > In > Al, with reference to the metals and lactates > glycolates > mandelates, with reference to the ligands. Potentiometric study, involving redox electrode, of Tl(III) complexes has also
been reported (359). Using the polarographic technique (360, 361), electron migration technique (362), potentiometric technique (363), and ion-exchange methods (364), the complexing properties of In(III) with LA have also been reported. Formation of heteroligand complexes in In(III)-xylenol orange-lactic acid system has been reported by Pyatnitskii and Kolomiets (365). Stepwise formation constants of Ga(III) with LA were determined at 25°, 35° and 45°C and ionic strength 0.2 (NaClO₄), by using Irving-Rossotti pH-titration technique, by Ambulkar and Munshi (366). Sahu (367) carried out conductometric and spectrophotometric studies of Tl(I)-lactate, glycolate and mandelate complexes, and showed formation of 1:1 complexes, with all the three ligands. Proton-ligand formation constants of LA and its formation constants with Tl(III) were found, by using Irving-Rossotti method at 30°, 35° and 40°C, and their thermodynamic parameters were calculated by Cholap et al (368).

By potentiometric study, Chakrawarti and Sharma (369) showed Ti(III) to form 1:1, 1:2 and 1:3 complexes with LA in solution. Thermodynamic parameters were also calculated for the complex formation reaction at 30°C in 0.1 M (NaClO₄) solution (369). The relative strength of the complexes of Ti(IV) with some carboxyl and hydroxyl-containing organic compounds, including LA, was determined, using the UV absorption spectra of the complexes and the metal-indicator method (370). The reaction of Mo(VI) and
Ge(IV) with LA in dilute aqueous solutions were studied, using potentiometric titration technique, by Mikonova and Bartusek (371) and the equilibrium constants were determined. The composition and stability constants of LA complexes of Zr(IV) were determined in 1 M HCl, by an ion-exchange method, by Gnatyshin and Popovich (372). Complexes of W(VI) and Mo(VI) with LA were studied by proton and $^{13}$C NMR spectroscopy (373). Water soluble Nb and Ta chelates with LA have also been reported (374).

Formation constants of rare earth complexes with LA have been reported by various workers (375-378), using the potentiometric titration technique. In order to study the chelating properties of LA with Ln$^{3+}$ ions, Choppin and George (379) have obtained the thermodynamic data. Stability constants of lactate complexes of Ln(III) in aqueous media have been reported by Mohanty and Patnaik (380). The cationic complexes formed at lower pH values dissociate at higher pH values. Lisovoy and Skorik (381) observed the stability constants ($\beta$) of $[\text{LnA}]^{2+}$ (where Ln = La, Lu, Sc and $^{2+}$, and HA = lactic acid), at 25° in water or in water-ethanol solutions, containing 19.8 - 40.3 wt % EtOH, to increase with the increase of the ionic potential of the metal ions. Spectroscopic properties and stability constants of Ho$^{3+}$ - LA complex have been reported by Bukietynska et al (382).

Complex formation constants of actinides ($\text{Am}$, $\text{Cm}$) and lanthanides ($\text{Pr}$, $\text{Eu}$, $\text{Lu}$) with LA were determined by the
electrophoretic method (383). Lundqvist et al (384) studied
the complexation of Am$^{3+}$, Eu$^{3+}$, U$^{4+}$ and UO$_2^{2+}$ by lactate ion
in a 1 M NaClO$_4$ medium at 25°, through liquid-liquid distri-
bution and potentiometric titration measurements. The
synergistic solvent extraction system, Np(V)-TTA-Capriquat
was applied to determine the stability constants of complexes
of NpO$_2^+$ ion with 7 hydroxy acids (including LA) and 5 poly-
carboxylic acids (385). UO$_2^{2+}$ ion forms polymerised chelates
with LA (386). Chelate compounds of uranyl ion with LA have
also been studied by Cefola et al (387). Iega et al (388)
determined the stability constants of uranyl (II)-glycolate-
lactate system in aqueous solutions at 25° and ionic strength
1.0 (NaClO$_4$), by two different methods (potentiometry and
polarography). Kakihana et al (389) studied the interaction
of uranyl ion with some carboxylic acids (including LA) in
aqueous solution by IR and $^{13}$C NMR spectroscopy. Equilibrium
constants for Am(III) in its interaction with lactate,
pyruvate and the Zwitterion from α-alanine, were presented
and compared with corresponding values (previously reported
as free energy changes) for Eu(III) by Aziz and Lyle (390).
The measurements were carried out at 25° in a NaClO$_4$ medium,
ionic strength 2.0, using a partition method. Magon et al
(391) have determined the stability constants of Th(IV)
complexes with α, β and γ hydroxymonocarboxylate ligands
(including LA) in aqueous 1.0 M perchlorate solution at
20° by a potentiometric method. The ligand dissociation
constants were also determined. The β and γ-OH groups, unlike
the α-OH group are not involved in chelate formation.
Lactic acid has also been used in the study of some mixed ligand systems, using potentiometric and spectrophotometric techniques. Concentration formation constants \( K \) of ordinary and mixed \( \text{Cu}^{2+} \) compounds with salicylic, lactic, and phthalic acids, in solution were determined by Sarbaev (392). Joshi et al (393) have reported the formation constants of \( \text{Ni}^{(II)} \) or \( \text{Zn}^{(II)} + \text{dipyridyl} + \text{hydroxy or mercapto acid (including LA)} \) systems in aqueous perchlorate solutions with ionic strength 0.2 M at 35°C. In aqueous solution with ionic strength 0.1 M at 25°C, the acid dissociation constant for \( [\text{Co(en)}_2\text{LA}]^{2+} \) was found to be \( pK_a = 3.4 \) and so, an increased acidity was noticed for protic chelate complexes in comparison with its monodentate analogue (394). Bolotov et al (395) performed polarographic study of the mixed complexes of \( \text{Cd(II)} - \text{benzimidazole-organic acids (including LA)} \) at 25°C and ionic strength 0.1 \( (\text{KNO}_3) \) in 20% water-ethanol medium and have reported stability constants for both simple and mixed complexes. Ramanujam and Krishnan (396) have determined the formation and stability constants of mixed-ligand complexes of \( \text{Cu}^{2+} \) with LA as primary ligand and some amino acids as secondary ligands, by \( \text{pH}\)-metry and spectrophotometry at 30°C and \( \mu = 0.25 \) \( (\text{KNO}_3) \). Kuznik (397) has established the formation of mixed ligand complexes in the systems: \( \text{M C}_2\text{O}_4 \) (solid) - \( \text{NaL} - \text{H}_2\text{O} \) \( (\text{M} = \text{Cd}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Pb}^{2+}, \text{L} = \text{CH}_2\text{OHCOO}^-, \text{CH}_3\text{CH} \cdot \text{OHCOO}^-) \) by solubility method. Solvent extraction and ion-exchange studies on \( \text{Cd} \) and \( \text{Tl} \) complexes with glycollic and lactic acids have
also been reported (398). In solvent extraction K dinonylnaphthalenesulfonate was used as an auxiliary ligand. Spectrophotometric study of Ti(IV)-gallic acid/sulfosalicylic acid systems in presence of LA at different pH has been reported by Murugaiyan et al (399) and formation of mixed complexes was indicated.

Formation constants of 1:1:1 Ln(III)(La, Pr, Nd) complexes with HEDTA and hydroxy acids (glycolic, lactic, malic acid) were determined pH-metrically at 30 ± 1°C by Rana and Tandon (400). They have also reported (401) the formation constants and thermodynamic data for the biligand chelates at 30°C and 35°C, resulting by the interaction between 1:1 M(III)_L binary chelates (M = La, Pr, Nd; L = Cyclohexane-1,2-diamino-N,N',N'-tetraacetic acid) and glycolic, lactic and malic acids. The stability order of M(III) was La > Pr > Nd and of the hydroxy acid was: 

$\text{MA} > \text{LA} > \text{GA}$. Abou et al (402) studied the formation of the mixed-ligand complexes of Nd(III) with LA and EDTA by pH-metric and spectrographic methods at 20°C and pH = 2 - 5 and reported the formation and stability constants. Mixed-ligand complexes of the type Ln-EDTA-X (Ln = La, Ge, Pr, Nd, Sm, X = O-O, O-N, O-S donor ligand, including LA) were studied pH-metrically, by using Irving-Rossotti titration technique at 25°C and ionic strength 0.2 M (NaClO₄), by Limaye and Saxena (403). They used the formation constants of 1:1:1 mixed complexes to test the validity of the Born relation. The authors (404) have also studied the relative complexing tendencies of O-O, O-N and O-S donor (secondary)
ligands (including LA & PCA) in some Ln(III)-EDTA mixed-ligand complexes, under similar conditions, and reported the sequence $0 - 0$ donor (arom.) $> 0 - N$ donor $> 0 - 0$ donor (aliph.) $> 0 - S$ donor. For ternary complexes of the type Ln(III)-EDTA-L, where L = $0 - 0$ donor aliphatic or aromatic hydroxy acids (including LA & PCA), saturated dicarboxylic acids, unsaturated carboxylic acids, phenols or phenolic acids, Limaye and Saxena (318) utilized the stability data to demonstrate that, these complexes are primarily entropy stabilized. They (405) have also used the stability constant data, to study the electrostatic and statistical factors, involved during the formation of these mixed complexes.

Two new stability parameters, 'relative stabilization' and 'relative astatisticality', were introduced. Ln(III)-EDTA-LA/C02− complexes have been reported (308, 309).

Complex formation constants of Np(V) with various organic ligands, including LA, NTA and EDTA also, were determined in 1 M NaClO4 at 25°C, by using the solvent extraction with TTA and 1,10-phenanthroline (406). Mixed ligand complexes of uranyl lactate, with some simple and heterocyclic amines, were prepared and characterised by electronic and IR spectral data as well as elemental analyses (407).

2. Protocatechuic acid: In protocatechuic acid the two phenolic groups are present in ortho positions and one - COOH group is at the meta position, with respect to one - OH group and para, with respect to second - OH group.
Ishimitsu et al (408) have reported that the dissociation constant and thermodynamic parameters of the 1st phenol group of PCA are almost the same, as those of phenol. For dissociation of the 2nd phenol group of PCA, formation of an intramolecular H-bond is indicated. In pH region 7.0-7.5, PCA is present as the carboxylate form and the 2 possible monophenolate anions are present to the extent of 30 and 35% at pH 11.0. Rodante et al (409) studied the contribution of each of the 2 hydroxyl groups to the ionization and solvation process for PCA, by considering the enthalpy values of these processes and a linear combination of those, related to the same processes for the 2,3-dihydroxy and 2,4-dihydroxy derivatives in water-DMSO mixtures, with the mole fraction of DMSO, ranging from 0 to 0.8. They reported that the introduction of a hydroxyl group in position 3- destabilizes the benzene ring, overcoming the stabilization effect, caused by the hydroxyl on position 4-.

The stability constants of complexes of bivalent metal ions with PCA were determined by potentiometric method, using Calvin-Bjerrum technique (410). Potentiometric titration curves were used to study chelate formation of \( UC_2^{2+} \), \( ZrO^{2+} \), \( TeO_4^{2-} \), \( Th^{4+} \) and \( Tl^+ \) with PCA (411). PCA has been reported to form complexes with a number of metal ions and so, potentiometric and/or spectrophotometric studies of the complex formation equilibria for Mn(II) (412); Mn(II), Co(II), Ni(II) & Fe(II) (413); Cd(II) (414); Tl(I), Mg(II), Cd(II), Co(II), Zn(II), Be(II), Ni(II), \( Ud_2^{(VI)} \) & Al(III) (415);
Fe(II) & Fe(III) (416-418); Al(III) & Fe(III) (419); MoO$_4^{2-}$ & WO$_4^{2-}$ (420), WO$_4^{2-}$ (421), Cu(II) (422) and Ti(IV) (423), have been reported.

The Irving-Rossotti technique was applied by Mavani et al (424) to the study of formation constants of the reaction $[\text{MA}]^- + \text{L}^3^- \rightarrow [\text{MAL}]^{4-}$, where L$^3^-$ represents coordination of PCA; M = Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ & Cd$^{2+}$; A = anion of NTA. With NTA 1:1 complexes are formed at lower pH which are stable at higher pH. The values of formation constants, obtained for the mixed ligand system, $K_{\text{MAL}}^M$, are found to be lesser than the 1st formation constant in the binary system $K_M^M$. Formation constants of mixed-ligand complexes, log $K_{\text{MAL}}^M$, where M = Ni(II), A = o-phenanthroline and L = catechol, PCA, or mercapto acids, were also determined by Joshi et al (425), using a modified form of Irving-Rossotti titration method. They found the $K_{\text{MAL}}^M$ to be almost equal to $K_{M}\text{-ophen}$. Krishnamoorthy et al (426) performed spectrophotometric study of Ti(IV) system in the presence and absence of oxalate and tartarate in the pH-range 3.0 to 6.0, which revealed the formation of mixed-ligand complexes.

Stepwise formation constants of the Ga(III)-PCA complexes have been determined potentiometrically by Ambulkar et al (427). Stability constants and thermodynamic parameters were evaluated at 25° - 45° and ionic strength 0.2 M (NaClO$_4$). Stability constants and structure of Nd chelate with PCA has been reported by Agrawal et al (428). They suggested that, one phenol H$^+$ of PCA is released by
complex formation and Nd(III) is chelated by the phenolate O and by the adjacent OH group, which results in the formation of a five membered ring. A polarographic study of the composition and stability constants of benzoate, protocatechuate and salicylate complexes of Nd(III), has been conducted by Chitale and Pitre (429) at 26°, $\mu = 1.0$ (KCl), pH 2.75 + 0.02 (HCl) and ligand concentrations 0.25 to 30 mM. Nd(III) forms 1:1, 1:2 and 1:2 complexes with BA, PCA and SA, with stability constants (log $\beta n$) of 3.45, 7.54 and 7.70, respectively. Formation constants of $\text{UO}_2^{2+}$, $\text{NpO}_2^{2+}$ and $\text{PuO}_2^{2+}$ complexes with hydroxycarboxylic acids (including PCA) were determined by pH-metric titration at 20° in M HClO$_4$ solutions (430).

The uranyl and vanadyl complexes formed with PCA were studied potentiometrically, at 25° in 0.10, 0.40 and 0.70 M NaClO$_4$ solution, by Simoes Gancalves and Mota (431).

Binary and ternary complex formation constants $K_{\text{ML}}^M$ and $K_{\text{MAL}}^M$, respectively, where $M = \text{Pr}^{3+}$, $H_4\beta^+ = \text{EDTA}$ and $H_nL = \text{pyrogallol, pyrocatechol, PCA or protocatechualdehyde}$, were determined at 25°, 35° and 45° and $\mu = 0.2$ M, using a modified form of Irving-Rossotti technique (432). The 1:1:1

\[
\left[ \text{Pr(III)} - \text{EDTA} - L \right]
\]

chelates were less stable than the 1:1

\[
\left[ \text{Pr(III)} - L \right]
\]

chelates. The overall changes in $\Delta G$, $\Delta H$ and $\Delta S$ were also calculated. The metal ligand stability constants of 1:1 binary and 1:1:1 ternary complexes of some lanthanides- EDTA-L- systems, where $L = \text{PCA}$ or $\beta$-resorcylic acid, were determined pH-metrically by Limaye and Saxena (433).

The general trend of stability constants are: $\log K_{\text{MA}}^M \gg \log K_{\text{ML}}^M > \log K_{\text{MAL}}^M$. 
Recently Abu-Bakr et al (434) have reported pH-metric studies on binary and mixed ligand complexes of UO$_2$(VI) with Sudan violet as primary ligand and o-aminophenol, picolinic acid, 8-hydroxyquinoline or 2,2'-bipyridyl as a secondary ligand, in acetone-water (50% v/v) medium at 20° and $\mu = 0.1$ (NaClO$_4$). They found the stability of ternary complexes to increase within the following series of ligands:

$$o\text{-}AP < B_{\text{py}} < 8\text{-}HQ < \text{Pic}.$$  

II.7: **PRESENT WORK**

Ternary or mixed ligand complexes are made up of a central metal ion and two different ligands in addition to the solvent molecules, required to make up the coordination number. Such metal ion mixed ligand complexes are quite common in biological and analytical systems (435-439). Thus, an understanding of the significance of the metal ion in biological systems, may unravel the mysterious surrounding of the protein-substrate interaction and the controlled mechanism that determines the coordination tendency of metal ions bound at the active sites of many enzymes in enzyme-metal ion substrate reaction (440,441). Due to high affinity of uranyl ion for donor atoms like oxygen, uranyl compounds, such as uranyl acetate, are employed as a tool for the elucidation of the structure of proteins (442,443). The interaction of enzymes with substrates or inhibitors in biological milieu, leads to the formation of enzyme-metal ion substrate ternary complex (444-447). As well, the considerable
importance of mixed-ligand complexes in biological fluids have been proved \((439)\). Moreover, the formation of mixed-ligand complexes is important in understanding the behaviour of pollutants in natural water \((448)\). Thus, in recent years the complexation in aqueous solution of actinide ions by charged oxygen donors has been extensively studied. Due to the high affinity of oxygen donors towards actinide ions, discriminating tendencies of metal-aminopolycarboxylates towards aliphatic and aromatic donors (in complexes of the type MAL), also the growing importance of mixed-ligand complexes in biological and analytical systems, it was thought worthwhile to undertake study of complexing tendency of \(\text{UO}_2\)(VI) and \(\text{Th}(IV)\) with some new complexing ligands.

The present study was also planned to find out the coordination number of \(\text{UO}_2\)(VI) and \(\text{Th}(IV)\). As discussed earlier in this Chapter, the coordination number of the central atom in \(\text{UO}_2\)(VI) is six and that of \(\text{Th}(IV)\) is eight. These numbers, however, can be extended beyond six and eight for \(\text{UO}_2\)(VI) and \(\text{Th}(IV)\), respectively, provided that the ligands are sufficiently strong \((204)\). To explore this, two primary ligands were used in case of \(\text{UO}_2\)(VI), 2-iminodiacetic acid and nitrilotriacetic acid, which are tri and tetra dentate, respectively. For \(\text{Th}(IV)\) three primary ligands used were ethylenediamine-tetra-acetic acid, \(\text{N}(2\text{-hydroxy ethyl})\text{ethylenediaminetriacetic acid}\) and nitrilotriacetic acid. The secondary ligands chosen are: lactic acid and protocatechuic acid, which are mostly bidentate. The former being an
aliphatic and the later an aromatic monocarboxylic acid and they have different coordination sites. In order to compare the stability of binary and ternary complexes, the ligands lactic acid and protocatechuic acid, used in binary systems, have been used as secondary ligands in the ternary systems. The binary systems employing the primary ligands were not studied in detail, since they have been reported earlier, by other investigators. However, in each case a few experiments were performed to confirm the earlier results, under the present set of experimental conditions.

In order to form stable ternary complexes, the requirement of large central ion is fulfilled by selecting UO₂(VI) and Th(IV) for the present course of study. UO₂(VI) was found to be better as its hydrolysis starts at comparatively higher pH.

The potentiometric (pH-metric) titration technique has been employed for the present investigation. Determination of stepwise proton-ligand stability constants of lactic acid (LA) and protocatechuic acid (PCA), the ligands used as secondary ligands, and metal-ligand stability constants of binary complexes, formed by the ligands with UO₂(VI) and Th(IV), at three temperatures (20°, 35° and 50°), have been attempted, using modified form of Irving-Rossotti's titration technique, involving the pH measurements. The important thermodynamic parameters namely, change in Gibb's free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS), have been evaluated for these binary complex formation
reactions, using temperature coefficient method and Gibbs-Helmholtz equation. Further, the $\Delta G$ and $\Delta H$ values have been separated into their cratic and electrostatic components. The method of calculation of these parameters is given in detail in Chapter I (Section 1.5-F).

The mixed-ligand complexes of $\text{UO}_2(\text{VI})$ have been studied using iminodiacetic acid (IMDA) and nitrilotriacetic acid (NTA), as primary ligands and the ligands used in binary systems, i.e., LA and PCA, as secondary ligands. For $\text{Th(IV)}$ the primary ligands were EDTA, HEDTA and NTA, while LA and PCA were the secondary ligands, for the above study. Metal-ligand stability constants of these ternary systems have also been evaluated at three different temperatures and from these data the thermodynamic parameters were calculated.

In addition to the above work the effect of variation of ionic strength and the effect of change in dielectric constant of the medium on complexation equilibrium, have also been studied. It is important to note that all the binary and mixed-ligand complexing systems, incorporated in the present Thesis, have been explored for the first time, using potentiometric technique, under the present set of experimental conditions.

The ligands used in the present work, with their structures and abbreviation, have been listed in Table 2.1.
# TABLE 2.1

**THE LIGANDS USED IN THE PRESENT WORK**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of the ligand</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Iminodiacetic acid</td>
<td>IMDA</td>
<td><img src="" alt="Iminodiacetic Acid" /></td>
</tr>
<tr>
<td>2.</td>
<td>Nitrilotriacetic acid</td>
<td>NTA</td>
<td><img src="" alt="Nitrilotriacetic Acid" /></td>
</tr>
<tr>
<td>3.</td>
<td>Ethylenediamine tetraacetic acid</td>
<td>EDTA</td>
<td><img src="" alt="Ethylenediamine Tetraacetic Acid" /></td>
</tr>
<tr>
<td>4.</td>
<td>N(-2 hydroxyethyl)ethylene-diamine-tri-acetic acid</td>
<td>HEDTA</td>
<td><img src="" alt="N(-2 hydroxyethyl)ethylene-diamine-tri-acetic Acid" /></td>
</tr>
<tr>
<td>5.</td>
<td>Lactic acid</td>
<td>LA</td>
<td><img src="" alt="Lactic Acid" /></td>
</tr>
<tr>
<td>6.</td>
<td>Protocatechuic acid</td>
<td>PCA</td>
<td><img src="" alt="Protocatechuic Acid" /></td>
</tr>
</tbody>
</table>
It was planned to discuss the results obtained, on the basis of the following points:

(1) Expansion of coordination number of the central uranium and thorium atom in UO₂(VI) and Th(IV) from six and eight, respectively, to higher numbers, with the use of multi-dentate primary ligands and bidentate secondary ligands.

(2) The different factors favouring and opposing mixed-ligand complex formation.

(3) The donor characteristics of the various ligands used.

(4) The participation of covalent and ionic bonding in the formation of complexes.

(5) The effect of variation of ionic strength of the media and applicability of Brönsted equation at lower ionic strength.

(6) The thermodynamic stability constants of the various systems studied.

(7) Correlation of chemical equilibria and dielectric constant of the medium.

Some important trends and generalisation were obtained, on the basis of the above study.

II.8: EXPERIMENTAL:

The ligands used in the present study contain such groups which are either acidic or basic. Hence, the Irving-
Rossotti's pH-titration technique (449) modified by Movani et al (450), has been employed in the entire study. It was revealed from the preliminary study that, all the ligands are soluble in water. The experiments were carried out at four different ionic strengths, and at three different temperatures, in order to determine the thermodynamic stability constants and the thermodynamic parameters, for the complex formation reactions. For the study of the effect of dielectric constant, various ratios of dioxane-water, ethanol-water and methanol-water media were used. The experimental details of the study have been given below:

II.8-A: Solvents and Chemicals used:

(1) Water: Carbon dioxide free double-distilled water was used. It was obtained by redistilling the distilled water over alkaline permanganate. The dissolution of carbon dioxide in double-distilled water was prevented during distillation. The resulting distillate was boiled to expel oxygen and then it was cooled in well stoppered Pyrex glass vessel. Finally, before using it, nitrogen was bubbled through it. pH of this water was found to be 6.90 ± 0.02.

(11) Dioxane: BDH 'AnalaR' dioxane was purified, before use, by the method described below: One litre of the dioxane, 14 ml of concentrated hydrochloric acid and 100 ml of water, were refluxed for 6-12 hr whilst a slow stream of nitrogen was bubbled through the solution, to remove acetaldehyde formed. The cold solution was then treated with potassium
hydroxide pellets with shaking, until some of them remained
undissolved and the aqueous layer, which separated out,
was run off. Most of the residual water was removed by
keeping dioxane over fresh potassium hydroxide pellets
for 24 hr. This was followed by refluxing it over excess
of sodium for 6–12 hr, i.e., until reaction ceased and the
sodium added remained bright. Finally dioxane was distilled
from sodium and was stored in well fitted ground glass
bottle, which was out of contact with air. The purity was
checked by determining its refractive index (Reported 1.437
at 25°; observed 1.439 at 25°).

(iii) Ethanol: Purified ethanol was obtained by the
following method: About 1 litre of commercial absolute
ethanol (Bengal Chemicals, Calcutta) was taken in a 2 litre
round bottomed pyrex flask and then about 250 g of quick-
lime was introduced into the flask. The quick-lime used
was of commercial grade which was heated for 1–2 hr,
immediately before use. The flask fitted with a condenser,
carrying a drying tube (containing anhydrous CaCl₂), was
then gently heated on a water bath for 6 hr and the contents
were allowed to stand overnight. Purified glass wool was
packed in the wide mouth glass tube (receiver head),
attached at the receiver. The glass wool helped in retain-
ing any finely divided line which tend to pass over with
the alcohol. The distillation was carried out on a steam
bath and the distillate collected was stored in a ground
glass stoppered bottle. The purity was checked by density
measurement (Reported 0.7850 at 25°; observed 0.7863 at 25°).
(iv) Methanol: Purified methanol was obtained by the following method: A mixture of 500 ml of methyl alcohol (BDH, AnalaR), 25 ml of furfural and 60 ml of 10% sodium hydroxide solution, was refluxed in a two litre round-bottomed flask, fitted with a double surface condenser for 6-12 hr. A resin was formed which carried down all the acetone, if present. The alcohol was then carefully fractionated through an efficient column, rejecting the first few ml (5 ml), since it may contain traces of formaldehyde. The purity was checked by density measurements (Reported 0.7872 at 25°; observed 0.7886 at 25°).

(v) Sodium hydroxide solution: Carbon dioxide free sodium hydroxide solution was prepared (451) by dissolving 50 g of sodium hydroxide (E. Merck, G.R.) in 50 ml of double-distilled water in a pyrex flask. This concentrated solution was allowed to stand overnight. As the carbonate remains insoluble in concentrated alkali, it settles down and the clear supernatant liquid was filtered rapidly through a sintered pyrex glass crucible, using a high vacuum pump. Suitable volume of this filtrate was diluted to prepare stock solution of desired strength, ranging from 1.0 to 1.5 M. The concentration of the stock solution was determined by titrating it potentiometrically, against standard potassium hydrogen phthalate. The normality of the stock solution was
(vi) **Nitric acid**: From the commercially available AnalaR (BDH) nitric acid, the required stock solution (0.2 M) was prepared by diluting it with distilled water. This solution was standardised by titrating it potentiometrically against standard sodium hydroxide solution. The normality of the stock solution was checked from time to time, during its use.

(vii) **Potassium nitrate solution**: 2 M stock solution of potassium nitrate (BDH, AnalaR) was prepared by dissolving the requisite quantity in double-distilled water. The pH of this solution was checked and adjusted to pH 7.0, if required. This solution was used within a week's time, to avoid age effect.

(viii) **Uranyl nitrate solution**: 0.02 M uranyl nitrate \[ \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \] solution was prepared by dissolving the requisite quantity of the sample (BDH, AnalaR), in 0.2 M nitric acid, to prevent hydrolysis of the metal ions. The metal content was estimated gravimetrically, by the method of Erdey (452).

(ix) **Thorium nitrate solution**: 0.02 M thorium nitrate \[ \text{Th(NO}_3)_4 \cdot 4\text{H}_2\text{O} \] solution was prepared by dissolving the requisite quantity of the sample (BDH, AnalaR), in 0.2 M nitric acid, in order to avoid hydrolysis of the metal ion. The metal content was estimated by complexometric titration with EDTA, using pyrocatechol violet as an indicator (453).

(x) **Ligand solution**: The solution of (0.01 M) iminodiacetic acid (Sigma), nitrotriacetic acid (BDH), disodium
salt of ethylenediamine tetra acetic acid (BDH, AnalaR), N(2-hydroxyethyl)ethylenediaminetetra acetic acid (Koch-Light Lab, AR) and protocatechuic acid [3,4-dihydroxybenzoic acid] (Fluka), were prepared by dissolving the requisite quantity of the recrystallised samples in double-distilled water and estimated potentiometrically. Lactic acid (0.01 M) solution was prepared by diluting the known volume of commercially available (BDH, AnalaR) sample with double-distilled water. This solution was standardized by titrating it against standard sodium hydroxide solution, potentiometrically. All the above solutions were always prepared fresh, before use.

All other chemicals used such as potassium chloride, borax, agar-agar were of AnalaR grade.

II.8-B: Instruments used:

(1) **pH-Indicator and accessories:** The "SYSTRONICS" Digital pH-meter, model No. 335, with glass-calomel electrodes assembly, was employed for pH-measurements. The instrument was capable of measuring pH from 0 to 14, with a resolution of ± 0.01 pH-units and was provided with temperature compensation control from 0°C to 100°C, with ± 2°C accuracy. The instrument was operated on stabilised voltage of 230 volts, obtained by the use of Suvic Static Voltage Regulator.

The electrode assembly consisted of the reference electrode (Calomel electrode) and an indicator electrode (Glass electrode). The glass electrode (Cambridge) had negligible sodium ion error, up to pH 12.0 in the temperature
range 0° to 85°. The calomel electrode was dipped in the saturated KCl solution and the presence of saturated KCl solution in the electrode was checked from time to time. In order to prevent the formation of chloro complexes of the metal ions, used in the present study, the calomel electrode was not dipped directly in the experimental vessel but it was connected to the titrating vessel, through an inverted U-shaped, narrow glass tube containing a low resistance salt bridge, formed by setting a mixture of saturated potassium nitrate and agar-agar (3%). One end of the glass tube, containing salt bridge, was dipped in a wider mouth casing which contained saturated KCl solution and the calomel electrode. The other end, having a small narrow orifice, was dipped into the experimental solution. Care was taken in the experimental arrangement that, the height of the KCl solution in the wider mouth casing, containing calomel electrode, was always more than the height of the solution in the experimental vessel. The narrow orifice of the tube, containing agar bridge, was useful in cleaning the agar-agar tip. After every experiment, the glass electrode and the agar-agar bridge were washed thoroughly, with double-distilled water. Particular care was taken in washing the agar bridge, to remove the adhering ions. When the agar bridge was not in use, it was kept dipped in saturated solution of potassium nitrate. This arrangement prevented the agar bridge from shrinking and kept it saturated with KNO₃, at all times. Such a treatment prolonged the life of the bridge and thus, it could be used for as many as thirty
experiments. The absence of the chloride ions, at the narrow orifice of the agar-agar bridge, was checked by dipping it in silver nitrate solution, which showed no turbidity.

Before starting the pH measurements, the pH-scale was calibrated in acidic range, by using 0.05 M potassium hydrogen phthalate solution and in alkaline range, by using 0.01 M solution of borax (Na$_2$B$_4$O$_7$·10H$_2$O). For standardization purpose, the pH-values recommended by U.S. National Bureau of Standards were referred (454). Calibration of the pH-indicator scale, in the case of water-organic solvent media, was also made by using aqueous buffers and the pH-meter readings obtained were directly used in the calculations. As explained in Chapter I (Section 1.5-6), this did not give any error in the determination of the stability constants of the metal complexes.

Before adjusting the asymmetry potential knob for calibration of the pH-indicator scale, the temperature compensation knob on the pH-meter, was set at that temperature, at which the actual experiments were to be carried out. The buffer solution used for calibration was also allowed to attain the same temperature. For this purpose, the vessel containing buffer solution, was immersed in a thermostat, maintained at the desired temperature. The calibration was done before starting with every set of readings and after the completion of the whole set, the calibration was again checked with the buffer solution.
Experimental vessel and maintenance of inert atmosphere: The experimental vessel used, was made from corning beaker of 250 ml capacity, to which a side tube was attached at the lower side. The height of the side tube was more than that of the beaker and through this tube nitrogen can be bubbled, which helped in maintaining an inert atmosphere over the solution, in the experimental vessel. The mouth of the vessel was covered with a rubber bung through which the arrangements were made to insert a glass electrode, one glass rod for stirring, limb of the salt bridge and stem of microburette (± 0.01 ml), with which alkali was added, during titration. The glass stirrer was constructed by connecting a glass rod, having a glass pedal at its lower end, to the steel rod attached within a 9 volt D.C. motor. The speed of the glass stirrer was controlled by feeding the current to the motor through a step-down transformer, attached in an eliminator.

All experiments were carried out in an atmosphere of oxygen free nitrogen gas. The gas was found to be free from all traces of oxygen, as the alkaline pyrogallol solution remained colourless by its passage. The nitrogen gas, before passing into the experimental solution, was allowed to pass through the solvent, to get it presaturated with the solvent. The gas was supplied by M/s. Indian Oxygen Company, Bombay, India.
(iii) **Thermostatic arrangements:** All the experiments were carried out at controlled temperatures. For this purpose an electrically maintained thermostat, which was fabricated in the laboratory, and having a regulating accuracy of \( \pm 0.2^\circ \text{C} \), was used. The thermostat was provided with an electrical heater, in order to work at temperatures above the room temperature. But in order to work at temperature below the room temperature, it was necessary to supplement the thermostat by the following arrangement:

To the thermostat an additional contact relay operating on 12 volts D.C. was attached. When the contact thermometer contacted, the relay helped in the appearance of mains voltage 220 volts A.C. Across the contact points of this relay, was connected a circulating pump (0.5 h.p.). The pump was actuated when the contact thermometer contacted and in the process it pumped cold water through a long radiation coil suspended in the thermostat, in a spiral form, thereby cooling the thermostatic bath. The cold water was very conveniently obtained from an aluminium pot, which was placed in the freezer compartment of a domestic refrigerator. The radiation losses from conveying tubes, which sucked and discharged cold water from and to the pot, were prevented by keeping them as short and as near the thermostat as possible. When not in use the sucking and discharging tubes were removed from the pot. The accuracy in the attainment of temperature of experimental solution was checked by suspending a microthermometer (\( \pm 0.1^\circ \text{C} \)), very near the experimental vessel, in the thermostat.
It should be mentioned here that it was necessary to earth the contact temperature bath, stirring motor and heater, in order to obtain reproducibility in readings on ph-meter. The glass stirrer was also stopped while taking the readings.

Hindustan Computers Limited (HCL), 8 C-2/52 System No. 1800/1, Computer was employed for calculation of stability constants, by using "FORTRAN" programme.
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