Chapter V

Conclusion

5.1 Conclusion:

Equillibrium studies involving simultaneous attachment of three different ligands to Lanthanide ions require specific conditions mainly due to statistical unfavour of Lanthanide ions to get coordinated to more than one ligand[1-3]. In order to get clear understanding in this direction it is imperative that such system should be studied in more details and the factors that governs the complex formation of higher order must be studied by investigating some new systems. This involves selection of appropriate structural combinations with peculiar physical characteristic which will enable us to explore some new facts during studies on simultaneous equillibria resulting in the formation of 1:1:1:1 quaternary complexes in solution.

Apart from pK values, basicity of ligands, coordination site[4-5], pH- range of deprotonation, factors like pH dependant behaviour of some molecular moeties, isoelectric points, Zwitterion formation pH, varying electrolyte concentration may give some useful information about higher order complex formation equillibria.

Cation solvo dynamics, symmetry of cation coordination polyhydra, f-shell behaviour are the new dimensions and strong evidences for the formation and stabilization of mixed-ligand complexes which involves the role of astatistical parameters[6-9] like Δ log K, $\Delta\Delta$ log K and % RAS. Offcourse the former requires spectral studies of mixed-ligand complexes. The change in spectral parameters of metal ion and ligand molecule as a result of mixed-ligand complexation depends on or related to $\Delta\Delta$ log K and ligand characteristic. Therefore extrastabilization parameters like Δ log K, $\Delta\Delta$ log K and %RAS which can be calculated by studying the higher order complex formation equillibria in solutions can give some idea about existence and dependence of stability of quaternary complex. We have investigated complex formation equillibria involving simultaneous attachment of three different ligands to

Ln$_{(III)}$ (La$_{(III)}$, Nd$_{(III)}$, Sm$_{(III)}$) at six different concentrations of neutral electrolyte solutions. Formation equillibria at μ = 0.1 moles/dm^3 of KNO$_3$ have been studied at three different temperatures to evaluate thermodynamic parameters in order to support the formation of extrastabilized quaternary complex in solution at this threshold value of electrolyte concentration.

A quantitative evidence for the quaternary complex formation during the course of equillibria have been given by calculating equillibrium constant and constancy is observed in calculated values of formation constant for diprotonated quaternary complex species in working pH-range. This depends on pI values of amino acid ligand (L''). The values are reported in chapter IV (Table 4.2, 4.3, 4.5, 4.7, 4.9, 4.11, 4.13).

Three new parameters Δ log K, $\Delta\Delta$ log K and %RAS which gives the information about involvement of astatistical factor called as extrastabilization factor have been numerically worked out and presented in chapter-IV (Table 4.4, 4.6, 4.8, 4.10, 4.12, 4.14). From the values of stability constant it is clear that 1:1:1:1 quaternary complexation is not favoured over 1:1:1 ternary complexes due to statistical reasons. The order of stabilities of complexes binary 1:1, ternary 1:1:1 and quaternary 1:1:1:1 is observed as

$$\log K^{MLL'}_{MLL'L''}\langle \log K^{ML}_{MLL'} , or \log K^{ML}_{MLL''}\langle \log K^{M}_{ML} , or \log K^{M}_{ML''}$$

To assess the effect of simultaneous addition of three different ligand to Lanthanide (La^{3+}, Nd^{3+}, Sm^{3+}) at different ionic strength of KNO$_3$ (μ = 0.050, 0.070, 0.090, 0.10, 0.125, 0.150, 0.20) have been studied.

Ligand L (NTA, HEDTA, EDTA) forms very stable complex with Lanthanide and exists in the solution in the wide pH-range of 2.50 to $\cong$ 10.5 pH. Ligand L' are dicarboxylic acids (MIA/MAL/GLU) forms stable 1:1 binary complex[10-11] with all

three Rare earth cations and exists in the pH-range approximately 2.40 to $\cong$ 6.30. It is observed that ligand L'' which are PRO/HPRO/TYR forms stable 1:1:1 ternary complex existing in the pH-range of 2.40 to $\cong$ 6.50 as evident from extensive lowering of pH apart from protonation tendencies[12-16].

It is observed that every amino acid used in the present investigation forms stable complex upto their isoelectric points (pI) at different electrolyte concentrations. With increasing electrolyte concentrations of KNO_3, pI value of amino acid decreases which is followed by decrease in pH-range of 1:1:1:1 complex formation.

The values of pK_1 and $\log K_{MLL\,'L''}^{MLL\,'}$ decreases as the ionic concentration of supporting electrolytes increases. The plot of ΣpK_1 + pI of respective amino acid (L'') is plotted against $\sqrt{\mu}$. The values of pI of amino acid are taken into consideration to prove the validity of Bronsted equation which shows the almost linear relationship except the observation at μ = 0.1 moles/dm^3 of KNO_3.

Plot of $\log K_{MLL\,'L''}^{MLL\,'}$ and ΣpK_1 + pI against $\sqrt{\mu}$ in chapter IV (fig. 16, 17, 18, 19, 20, 21) shows that the values constantly decrease with increasing ionic strength except the value at μ = 0.1 moles/dm^3 of KNO_3. The increase in pK_1 values of PRO, HPRO, TYR also increases the value of $\log K_{MLL\,'L''}^{MLL\,'}$ at this electrolyte concentration. After this both values decreases with increase in ionic strength. This reflects on the extrastabilisation of complexes at this fixed ionic strength. It is probably due to much stronger interaction between ligands and $Ln_{(III)}$ ions . The stronger interaction can be predicted from less negative values of Δ log K and high positive values of $\Delta\Delta$ log K[17-18] at μ = 0.1 moles/dm^3 of KNO_3.

The exceptional increase in stability constants of quaternary complexes at $\mu = 0.1$ moles/dm^3 of KNO_3 may be related to polarization of solvent molecule and variation of microscopic and macroscopic dielectric constants[19-20]. It is observed that different electrolyte concentration change the activity coefficient of uncharged electrolytes to different extent [21]. The interaction may reinforce or cancel each other making real understanding difficult. However a qualitative knowledge of ion pair formation change in static dielectric constant[22] values and solvation at various ionic strength are needed to understand the role of neutral electrolyte on dissociation constant and formation constant in solution[23-24]

The formation of mixed-ligand complexes under study is the result of competition between metal ion and protons towards the ligand. At higher pH, the hydroxyl ion competes with the ligand for the metal ion so that hydroxo complexes are present in appreciable concentration. The nature of species present in solution is therefore highly pH-dependent. In the present study the pH-range in which mixed-ligand complex equillibria are studied, the hydroxo complex formation is minimum because in almost all cases the complexation starts at low pH $\cong 2.5$. Appreciable lowering in pH occurs in every individual system and moreover the mixed-ligand complex does not exist after pH $\cong 7$. Therefore it is confirmed that only protonated species are present in the region of calculation. The formation of ternary complex can also be seen on comparison of mixed-ligand titration curve with theoretical composite curve obtained by the graphical addition of the ligand L' and L'' added in the respective systems. The clear difference between them indicates the formation of stable mixed-ligand complexes.

From the experimental results it is inferred that

a) The order of relative stability of all binary, ternary and quaternary complex with respect to metal ion is

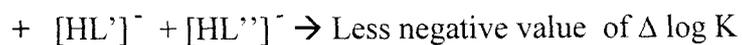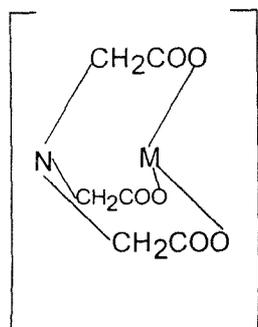$$La_{(III)} < Nd_{(III)} < Sm_{(III)}$$
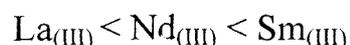
The observed trend of stabilities in binary and mixed ligand chelates may be correlated with decreasing size and increasing ionic potential (change/radius ratio) of the tri-positive Lanthanide ion. This observation is in conformity with the reports published on Lanthanides[25-28].

b) It is very interesting to note that the denticity of the aminopolycarboxylate (L) governs the stability of quaternary chelates. It was expected[29,30] that the quaternary systems with EDTA as first ligand should give a stable chelate after adding a dicarboxylic acid (L') and amino acid (L'') but surprisingly for quaternary systems it is observed that $Ln_{(III)}$ – NTA fascilates the formation of quaternary species obtained by addition of dicarboxylic acids (L') and PRO, HPRO, TYR (L'') rather than $[Ln_{(III)}$ – HEDTA] and $[Ln_{(III)}$ – EDTA]⁻ as observed from formation constant for the respective equillibria studied in solutions in chapter IV (Table 4.2 to 4.13).
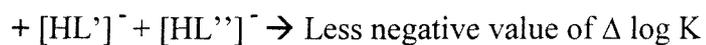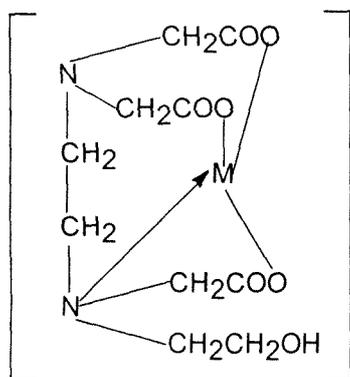
This can be explained on the basis of Coulombic repulsion experienced by incoming oxygen donors having negatively charged coordinating sites (L' and L''). Obviously the neutral $[Ln_{(III)}$ – NTA] will fascilitates the attachment of L' and L'' to the initially existing ML species. This can be further confirmed from variation in astatistical parameters with change in aminopolycarboxylate ions.

Representative Systems: Sm(III) – L - L' - L'' showing variation in astatistical

parameters with aminopolycarboxylate and amino acids.

$$\begin{bmatrix} \begin{array}{c} CH_2COO \\ N \qquad M \\ CH_2COO \\ CH_2COO \end{array} \end{bmatrix}$$

$+$ [HL']$^-$ + [HL'']$^-$ → Less negative value of Δ log K

Neutral

Combination L, L', L''	- Δ log K	+ Δ Δ log K	% RAS
NTA-MIA-PRO	0.07	3.96	- 0.532
NTA-MIA-HPRO	0.23	4.15	- 1.767
NTA-MIA-TYR	0.58	3.98	- 4.599

$$\begin{bmatrix} \begin{array}{c} CH_2COO \\ N \\ CH_2COO \\ CH_2 \qquad M \\ CH_2 \\ N \quad CH_2COO \\ CH_2CH_2OH \end{array} \end{bmatrix}$$

+ [HL']$^-$ + [HL'']$^-$ → Less negative value of Δ log K

Neutral

Combination L, L', L''	- Δ log K	+ Δ Δ log K	% RAS
HEDTA-MIA-PRO	0.19	3.18	- 1.499
HEDTA-MIA-HPRO	0.38	3.31	- 3.037
HEDTA-MIA-TYR	0.58	3.49	- 4.711

$$\left[\begin{array}{c} N\!\!-\!\!CH_2COO \\ \quad CH_2COO \\ CH_2 \\ CH_2 \\ N\!\!-\!\!CH_2COO \\ \quad CH_2COO \end{array} \quad M \right]$$

$+ \ [HL']^- + [HL'']^- \rightarrow$ High negative value of Δ log K
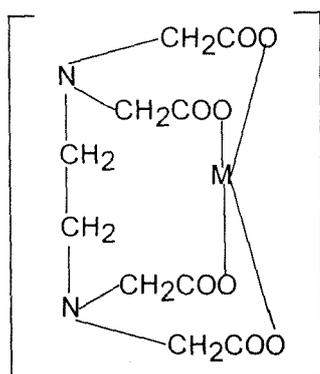
Mononegative

Combination L, L', L''	$- \Delta$ log K	$+ \Delta \Delta$ log K	% RAS
EDTA-MIA-PRO	0.17*	2.54	- 1.391
EDTA-MIA-HPRO	0.52	2.36	- 4.366
EDTA-MIA-TYR	1.09	1.76	- 9.646

* Exceptionally less negative values.

Quaternary 1:1:1:1 complex formation system of $Sm_{(III)}$ with ligands used and the astatistical parameters Δ log K, $\Delta\Delta$ log K, % RAS are cited above for the comparison of extrastability parameters at $\mu = 0.1$ moles/dm^3 of KNO_3.

This shows that negatively charged $[Ln_{(III)}\text{-EDTA}]^-$ species exerts higher coloumbic repulsion on incoming ligand. NTA and HEDTA forms a neutral complex with no electrostatic repulsion from the initially formed $[Ln_{(III)}\text{-NTA}]$ or $[Ln_{(III)}\text{-HEDTA}]$. The lower values of formation constant for HEDTA as compared to NTA may be due to steric factor and presence of one $-CH_2OH$ group in HEDTA.

The order of formation constant with respect to change in primary ligand for the given metal is found to be

NTA > HEDTA > EDTA.

c) The constancy observed in the calculation of formation constants of quaternary species indicates the existence of tri-ligand complex.

The results obtained with respect to change in L are in conformity with the statistical inference[31-35].

For the same reason a rigorous comparison have been made by studying the binary 1:1, ternary 1:1:1 and quaternary 1:1:1:1 titration sets covering all the possibilities of combinations of $La_{(III)}$, $Nd_{(III)}$ and $Sm_{(III)}$ with MIA, MAL, GLU, PRO, HPRO and TYR using $[Ln_{(III)}$-NTA], $[Ln_{(III)}$-HEDTA] and $[Ln_{(III)}$-EDTA]⁻ systems.

Careful observation of stabilities of quaternary complexes for particular metal and primary ligand L shows that the values of stability depends on the amino acid added as L'' and can be correlated with iso-electric point of amino acid (pI). Proline (pI = 7.025) forms stable 1:1:1:1 complex as compared to quaternary systems with Hydroxyproline (pI = 6.22) and Tyrosine (pI = 5.67). Iso-elctric point dependent existence and stabilities of quaternary systems are reported for the first time.

The stabilities of 1:1:1:1 complexes can be explained on the basis of existence of positively charged protonated amino group and Zwitterion in the lower pH-range.

This can be further confirmed from disproportionation of 1:1:1:1 species after crossing the pI value of respective amino acid because after iso-electric pH the amino acid takes anionic form and hence experiences the repulsive force from initially formed $[M-LL']^{-1}$ ternary species. A correlation between stability constants of $\Sigma\ pk_1 + pI$ against $\sqrt{\mu}$ have been attempted to support the observation. A linear relationship is observed with positive slope except at ionic strength $\mu = 0.1$ moles/dm³ of KNO_3.

This observation confirms the involvement of PRO, HPRO and TYR in the quaternary complex formation only upto their iso-electric point under the given set of experimental conditions. It is observed that higher the value pI higher is the stability and existing pH-range of 1:1:1:1 species.

The disproportionation pH of 1:1:1:1 quaternary complex at $\mu = 0.1$ moles/dm^3 of KNO$_3$ is given in table.

Amino Acid	PRO	HPRO	TYR
Iso-electric Point (pI)	7.025	6.22	5.67
1:1:1:1 pH-range	6.92	6.20	5.70

* ± 0.1 pH unit

It may be suggested that at pH = pI two equillibria simultaneously exists in solution and the Zwitterion retaining equillibria is more predominant as compared to quaternary complex formation. This can be justified on the basis of more stability of neutral Zwitterion in solution.

Offcourse basicity of these α-amino acids, their structure and other factors are also equally important in deciding the stability of quaternary complex species.

Δ log K values are negative in all cases which should be primarily due to electrostatic repulsion induced and less number of coordination sites available on ML complex. It is observed that the Δ log K values are less negative when L in ML is NTA. NTA acts as tetradentate ligand and forms a neutral ML-complex. Therefore second and third ligand experiences less repulsion from [ML] species and there quaternary complex formation is favoured. HEDTA acts as pentadentate ligand but the resulting [ML] complex is neutral and thus attachment of L' and L'' takes place more easily as compared to EDTA. EDTA being hexadentate occupies more coordination

sites on $Ln_{(III)}$ and the resulting Metal-EDTA species is mononegative due to which the added ligand L' and L'' experiences more electrostatic repulsion forming less stable quaternary complexes[17,36].

The stability of quaternary complex formed decreases with addition of L'' in the order.

PRO > HPRO > TYR

With change in L' the order of stability observed is

MIA > MAL > GLU

The observed decrease in stabilities of quaternary chelates formed with respect to change in L' may be attributed to the nature of dicarboxylic acids used in the present investigation. MIA is a dicarboxylic acid with π-bonding between carbon atom whereas MAL and GLU are saturated dicarboxylic acids with increase in length of carbon chain[37].

Calculated parameters of Δ log K, $\Delta\Delta$ log K and %RAS may find to be useful to explain the observed trends in stabilities with change in L' and L'' in the present investigations.

It is observed that for a particular Metal ion (M) and aminopolycarboxylate (L) the nature of L' (MIA/MAL/GLU) and L'' (PRO/HPRO/TYR), the stability of 1:1:1 ternary complex depends on ligand L' and that of 1:1:1:1 quaternary complex is governed by combination of L' and L''. The observed trend in stabilities are as follows.

ML-MIA-PRO > ML-MAL-PRO > ML-GLU-PRO

ML-MIA-HPRO > ML-MAL-HPRO > ML-GLU-HPRO

ML-MIA-TYR > ML-MAL-TYR > ML-GLU-TYR

The order of stabilities of 1:1:1:1 quaternary complex can be justified on the basis of presence of OH group in Hydroxyproline and presence of aromatic ring in Tyrosine molecule[38,39].

The relative order of stability of ternary and quaternary complexes with respect to secondary and tertiary ligand can be explained on the basis of decrease in basicity order of the carboxylic acid proton involved in complex formation in pH-range in which calculation have been made. The numerical values of Δ log K, $\Delta\Delta$ log K and % RAS may find useful in supporting and explaining the formation of stable quaternary complexes inspite of statistical unfavourableness[40-42].

The negative Δ log K values reveals that the formation of ternary and quaternary complexes is not favoured over that of binary complexes due to electrostatic repulsion between L' and L'' in $[M_{(III)}\text{-NTA}]$ neutral complex species and increased electrostatic repulsion between $[Ln_{(III)}\text{-EDTA}]^-$ mononegative complex species and between the L' and L''.

Positive value of $\Delta\Delta$ log K indicates intramolecular hydrophobic interaction. Significantly positive values of $\Delta\Delta$ log K in all quaternary complexes may be regarded as an evidence of hydrophobic interaction responsible for stabilization of mixed-ligand quaternary complexes[43-45]. Ligand-ligand cooperative effect between all the ligands participating in the formation of 1:1:1:1 quaternary species may be inferred from numerically high values of percentage relative astatisticality (%RAS) and thus involvement of astatistical factors such as electrostatic effect, steric effect, size of chelate rings, asymmetry of ligand field plays an important role in formation of quaternary complexes of Lanthanide ions ($La_{(III)}$, $Nd_{(III)}$ and $Sm_{(III)}$) with dicarboxylic acids and amino acids.

In order to see the effect of temperature on stabilities of binary, ternary and quaternary complexes the proton-ligand and metal-ligand formation equillibria are studied at different temperature. The stability constant of the chelates decreases with increase in temperature indicates that the formation of equillibria are exothermic and spontaneous in nature. The enthalpy and free energy favours the formation of binary, ternary and quaternary complexes.

The more negative Δ log K indicates less stability for the 5 and 7 membered chelates due to steric effect.

The stability constant of mixed-ligand complexes are characterized by Δ log K and $\Delta\Delta$ log K and their values are in accordance with statistically expected values. The binding of ligand L' and L'' to the ML does not allow the concentration of electron density on metal ion to increase significantly and therefore electron repulsion is reduced to minimum due to Metal-ligand interaction[32]. This facilitates stronger interaction between ML and added ligand L', L''. Another explaination was extended by Griesser and Sigel[43] in terms of Pearson's hard and soft acid base rule. As the result of back donation of electron from metal ion orbital, the metal ion becomes harder acid and this favours coordination with oxygen donors. The system having more negative values of Δ log K particularly in EDTA is due to negatively charged $[ML]^{-1}$, and ligand L' and L'' which carries negative charge, lowers the interaction of ligands with $[ML]^{-1}$. In such complexes the π-interaction is restricted due to repulsion experienced by L' and L''.

A direct correlation of complex stabilities however could not be made since the ligand basicities of these ligands are not in same order. The base strength is a measure of σ-bonding ability of ligand with metal ion. Therefore a direct comparison of the

stabilities would not throw any light on factors like π-bonding, sterric and chelate effect. The stability per unit base strength (SUBS)[46] gives rational explaination to overcome such difficulties.

It can be seen that binary complexes are more stable than ternary complexes resulting a negative Δ log K value in all mixed-ligand system. Such lowering of stabilities of mixed-ligand chelates may be due to the greater destabilization effect caused by the ligand repulsion in mixed-ligand system coupled with lesser number of coordination sites for second and third ligand on the primary complex ML as compared to free $[M^{3+}_{(aq)}]$ ion. This point towards the fact that various factors such as statistical, astatistical, electrostatic and other operative factors are involved during formation of mixed-ligand higher order complexes. The combine effect of all factors on stabilities is termed as 'total effect'[33].

It is observed that Δ log K becomes less negative when L' is MIA and L'' is PRO and becomes more negative when L'' are HPRO and TYR. This may be due to decreasing ligand-ligand interaction between dicarboxylic acid and amino acid (HPRO, TYR) having –OH group in HPRO and a noncoordinated hydroxyphenyl groups respectively.

Recently studies on mixed-ligand complexes of Lanthanides involving histidine and some amino acids have been studied[14] and electronic spectral parameters such as oscillator strength (p), Judd-ofelt parameter (τ_λ), changes in inter-electronic repulsion (δE^k) and nephelauxetic effect ($\delta E^3/\delta E$) are calculated to give spectral evidence for occurrence of intra-molecular inter-ligand interaction and consequent changes in spectral parameter are correlated with $\Delta\Delta$ log K called as extrastabilization parameter. This was our attempt to evidence and support the existence of 1:1:1:1 quaternary

complexes by investigating some new parameters, ligand characteristic and the factors which governs the 1:1:1:1 complex formation equillibria. Offcourse it is very necessary to support the observation by studying some more systems with spectroscopic studies before reaching to some solid conclusion.

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