CHAPTER III

METAL-VITAMIN/AMINO ACID-2,2'-DIPYRIDYL/ETHYLENEDIAMINE MIXED LIGAND SYSTEMS—POTENTIOMETRIC STUDY
Mixed ligand complexes, in which metal ion is bound to two or more different complexing species; are usually formed when a solution of metal ion contains more than one kind of complexing ligands. The simplest example of mixed ligand formation has been considered when only two ligands are coordinated to the central metal ion (M). For undertaking such studies, ligands which form quite stable (1:1) chelates with metal ions have been selected as primary ligands (A) and the tendency of these primary complexes (MA) to combine with a second ligand (L) called as secondary ligand has been measured potentiometrically (by pH metric method). For the successful study of the mixed ligand systems, it is essential that (i) the formation of the primary complex i.e. (MA) from primary ligand (A) and the metal (M) should take place at low pH and (ii) the primary complex formed at low pH should remain stable even up to higher pH values, where the combination of the secondary ligand with the primary complex (MA) takes place.

The formation and the stabilities of mixed ligand complexes have been studied extensively in recent years (1,2) because of their importance in analytical (3) and biological
systems (4,5). One of the useful analytical application is the spectroscopic determination of fluoride ions, separation of bis-dimethylglyoximes of cobalt (II) and nickel (II). The separation of palladium (II) from nickel(II) has been achieved by coordinating insoluble bis-dimethylglyoxime palladium (II) complex with hydroxide ion to form a soluble anionic mixed ligand complex, which separates from the insoluble nickel (II) dimethylglyoxime complex. Most of the catalytic and enzymatic reactions are found to proceed through the formation of mixed ligand complexes.

The present chapter deals with the physico-chemical studies on mixed ligand complexes of various metal ions, such as manganese (II), iron (II), cobalt (II), nickel (II), copper (II), beryllium (II), zirconium (IV) and uranium(VI). One of the ligands is either ascorbic acid or glutamic acid and the other is either 2,2'-dipyridyl or ethylenediamine. The titrations have been carried out employing Bjerrum-Calvin's titration technique as modified by Irving and Rossotti at a fixed temperature of 25°C and a constant ionic strength of 0.1M (KNO₃) in an atmosphere of nitrogen gas. The formation constants of the resulting complexes have been evaluated by the modified form of Irving and Rossotti's titration technique (6-9).
Materials

The details regarding the materials used, the methods of preparation of standard solutions along with experimental set up and instrumentation have already been mentioned in the previous chapter. However, some more details are described below:

(a) **Potassium hydroxide solution**: (0.2M) carbon dioxide free potassium hydroxide solution was prepared by dissolving the requisite amount of (AR, BDH) alkali in redistilled water in a well corked pyrex measuring flask. The solution was then standardized by titrating it against standard solution of oxalic acid, using phenolphthalein as an indicator. A fresh solution of potassium hydroxide was always used in all the experiments.

(b) **Nitric acid solution**: (0.1M) solution of the acid was prepared by diluting a required volume of (AR, BDH) quality in redistilled water in a 500 ml measuring flask. The exact concentration of the solution was determined by titrating it against a standard solution of potassium hydroxide.

(c) **Potassium nitrate solution**: Potassium nitrate (1.0M) was prepared by dissolving the required quantity in redistilled water.
(d) Metal ion solution: (0.01M) solutions of various metal ions used in the present investigation were freshly prepared from the analytical grade reagents and were standardized by conventional methods (10).

(e) Ligand solutions: The ligands were obtained from various chemical companies i.e.

(i) Ascorbic acid (99.7%, Sarabhai M.Chems.).
(ii) Ethylenediamine (99.0%, Sarabhai M.Chems.).
(iii) Glutamic acid (99.0%, E. Merck, India).
(iv) 2,2'-dipyridyl (99.5%, E. Merck, Germany).

(0.01M) ligand solutions of glutamic acid and 2,2'-dipyridyl were prepared by taking the requisite amount of respective ligand in redistilled water. Solution of ascorbic acid was always prepared just at the time of titration in redistilled water through which nitrogen gas was previously passed for thirty minutes and the resultant solution was kept saturated with the gas in a well stoppered corning flask. Further, ethylenediamine solution was made by diluting the required volume of redistilled sample of ethylenediamine of known calculated concentration in redistilled water.

As already mentioned, the solvent used throughout the experiments was redistilled water, free from carbon
dioxide and prepared by redistillation of distilled water containing alkali permanganate. The pH of this water was found to be about 6.8.

Instruments, including pH meter, titration cell, thermostatic arrangements and other accessories as well as the methods of operation employed were the same as already described in the chapter second.

Method and calculations

A set of reaction mixtures including one containing a metal ion-vitamin/amino acid and other ligand (2,2'-dipyridyl and ethylenediamine) in the ratio of (1:1:1) has been prepared. The total volume in all the cases was raised to 50.0 ml with redistilled water. Each solution was then separately titrated against a standard solution of carbonate free potassium hydroxide at a temperature of 25°C in presence of nitrogen gas and changes in pH recorded. The reaction mixtures prepared were as under:

A, 5.0 ml KNO₃ (1M) + 10.0 ml HNO₃ (0.1M).
B, 5.0 ml KNO₃ (1M) + 10.0 ml HNO₃ (0.1M) + 10.0 ml secondary ligand (0.01M).
C, 5.0 ml KNO₃ (1M) + 10.0 ml HNO₃ (0.1M) + 10.0 ml primary ligand (0.01M) + 10.0 ml metal ion solution (0.01M); 1:1.
V. 5.0 ml KNO₃ (1M) + 10.0 ml HNO₃ (0.1M) + 10.0 ml primary ligand (0.01M) + 10.0 ml metal ion solution (0.01M) + 10.0 ml secondary ligand (0.01M) : 1:1:1.

Potassium nitrate solution was added to the solutions to maintain the ionic strength constant. In these mixed ligand complexes, 2,2'-dipyridyl is considered to be the primary ligand, whereas ethylenediamine is taken as the secondary ligand. The 2,2'-dipyridyl has been found to be neutral towards protons at low pH, whereas ethylenediamine gets protonated in acidic solutions. Consequently, the titration of the reaction mixture containing primary ligand and the metal ion in the ratio of (1:1) has not been conducted in the systems where 2,2'-dipyridyl is taken as the primary ligand, e.g. in the case of metal-2,2'-dipyridyl-ascorbic acid and metal-2,2'-dipyridyl-glutamic acid systems.

The plots of pH against volume of potassium hydroxide solution added were drawn (Figs. 24-34) and the curves so obtained were referred to as:

A, Acid titration curve.
B, Secondary ligand titration curve.
C, Primary complex titration curve.
D, Mixed ligand complex titration curve.

The stability constants of the mixed ligand complexes
Log $K_{MAL}^{MA}$, where M is the metal, L the secondary ligand and A the primary ligand have been evaluated using Irving-Rossott's pH titration technique and modified method employed by Bhattacharya coworkers (11). The formation of a mixed ligand complex can be represented as:

$$\text{MA} + \text{L} \rightleftharpoons \text{MAL} \quad \ldots \quad (\text{III.1})$$

$$K_{MAL}^{MA} = \frac{[\text{MAL}]}{[\text{MA}] [\text{L}]} \quad \ldots \quad (\text{III.2})$$

However, the possible reaction taking place in the above case can occur in the following five ways:

1. Both the ligands can combine simultaneously with the metal ion to form a mixed ligand complex in a single step.

$$\text{M} + \text{A} + \text{L} \rightleftharpoons \text{MAL} \quad \ldots \quad (\text{III.3})$$

II. Due to slight differences in the affinities of the ligands for the metal ion, a mixed ligand complex can result by two overlapping steps.

$$\text{M} + \text{A} + \text{L} \rightleftharpoons \text{MA} + \text{L} \rightleftharpoons \text{MAL} \quad \ldots \quad (\text{III.4})$$

III. Due to wide differences in the affinities of the ligands for the metal ion, the mixed ligand complex formation can take place in distinct separate steps.

$$\text{M} + \text{A} + \text{L} \rightleftharpoons \text{MA} + \text{L} \rightleftharpoons \text{MAL} \quad \ldots \quad (\text{III.5})$$
IV. A mixture of two simple chelate compounds may be formed instead of a mixed ligand complex. The chelates will be containing different ligands bound to the same metal ion.

\[ 2M + nA + nL \rightleftharpoons MA_n + ML_n \] ... (III.6)

V. Instead of forming a mixed ligand complex, a simple complex is formed between one ligand and the metal ion, while the other ligand remains unbound in the solution.

\[ M + A + L \rightleftharpoons MA + L \] ... (III.7)

It has been reported that presence of large number of vacant coordination sites in the metal ion results in the formation of hydroxy metal chelates i.e. \([MA(OH)_n]\) in the simple systems. But in the present case, after the formation of primary complex (MA), the coordination sites remaining vacant on the metal ions are further filled up by the secondary ligands. Thus, the hydrolysis of the primary complex is suppressed. The suppression of hydrolysis of metal ions through the mixed ligand complex formation has been shown by Martell (12) who studied the formation of several mixed ligand chelates of zirconium (IV) (13), thorium (IV) (14) and uranium (VI) (15) in solution. He has reported that such complexes are much more resistant to hydrolysis, olation and polymerization reactions than (1:1) simple metal chelates.
The values of $\bar{n}_H$ i.e. average number of protons attached to the secondary ligands have been calculated by measuring the horizontal distance accurately between the acid titration curves A and the secondary ligand titration curves B at the corresponding pH values employing the Irving-Rossotti's technique in the Equation:

$$\bar{n}_H = \frac{Y T_{CL_0} - \frac{(N+\text{E}^0)(V_2-V_1)}{(V_0+V_1)}}{T_{CL_0}} \ldots (III.8)$$

Where

$\bar{n}_H$ = Average number of protons attached per ligand ion.

$Y$ = Total number of replaceable/dissociable protons attached per ligand molecule.

$N$ = Total concentration of alkali.

$\text{E}^0$ = Initial concentration of the free acid.

$V_1$ and $V_2$ = Volumes of alkali needed to reach the same value of pH in the titration of acid and secondary ligand, respectively.

$V_0$ = The total volume of reaction mixtures.

$T_{CL_0}$ = The total concentration of the ligands.

By plotting experimentally calculated values of $\bar{n}_H$ against pH, proton-ligand formation curves have been
prepared from which the values of proton-ligand stability constants have been evaluated by Bjerrum's half \( \bar{n} \) method and graphical methods (Table 6). These constants are employed for further calculations of \( \bar{n} \) values i.e. average number of secondary ligands bound to the primary complex. In case of metal-ascorbic acid-ethylenediamine and metal-glutamic acid-ethylenediamine systems, \( \bar{n} \) values have been calculated by measuring accurately the horizontal distances \( (V_3) \) between the secondary ligand titration curves \( B \) and the mixed-ligand complex titration curves \( D \) and subtracting from them the horizontal distances \( (V_2) \) between the primary complex titration curves \( C \) and acid titration curves \( A \) at the corresponding pH values. From the point, primary complex titration curve \( C \) diverges to \( C' \) (called composite curve), the calculations have been done on the basis of differences between \( C' \) and \( A \). Thus, the difference \( (V_3 - V_2) \) gives the amount of extra alkali required for the formation of a mixed ligand complex at the corresponding pH values and is a measure of ternary complex formation. In the titration curves \( B \), the release of protons may be due to self dissociation of secondary ligands, whereas \( (V_3 - V_2) \) will give the amount of alkali required for the neutralization of protons released due to mixed ligand complex formation only.

Further, in case of metal-2,2'-dipyridyl-ascorbic acid and metal-2,2'-dipyridyl-glutamic acid systems, the
Table 6

Proton-ligand stability constants of secondary ligands at 25°C and $\mu = 0.1\text{M (KNO}_3\text{)}$

<table>
<thead>
<tr>
<th></th>
<th>Log $K^H_1$</th>
<th>Log $K^H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid</td>
<td>11.80</td>
<td>4.20</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>9.20</td>
<td>4.15</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>10.00</td>
<td>7.00</td>
</tr>
</tbody>
</table>
horizontal distances \( (V_2) \) between acid titration curves A and secondary ligand titration curves B have been measured and subtracted from the horizontal distances \( V_2 \) between mixed ligand complex titration curves D and acid titration curves A at a series of corresponding pH values. Thus, the differences between B and D i.e. \( (V_3 - V_2) \) giving the amount of alkali required for the formation of mixed ligand complexes have been obtained. With the help of experimentally determined values of \( (V_3 - V_2) \) at various pH values, \( \bar{n} \) values i.e. average number of vitamin or amino acid molecules bound to the primary complex can be obtained from the original Equation (II.9):

\[
\bar{n} = \frac{(N + E^0)(V_3 - V_2)}{(V_0 + V_1) \times \bar{n}_H \times T_{CMA_0}} \quad ... (II.9)
\]

Since, the dissociation of primary complex (MA) does not take place in the range of combination of secondary ligand, it has been considered that the secondary ligand combines with the primary complex (MA) just as it does with \([M(aq)]^{n+}\) in simple systems and hence the concentration of primary complex (MA) will be equal to initial concentration of the metal ions under investigation. Thus, \( T_{CMA_0} \) can be taken equal to initial concentration of metal ions (\( T_{CM_0} \))
as it is assumed that all the metal ions have reacted with the primary ligand and are existing as the complex (MA). \( N, E^0 \), and other values have the usual significance as mentioned in the equation employed for the calculation of \( n_H \) values. The third and the last formation function known as free ligand exponent, \( pL \), has been evaluated from the same Equation (II.3) as employed for the binary systems in the previous chapter of this thesis.

**Results and discussion**

Irving–Rossotti's technique as modified by Bhattacharya and coworkers has been used to study the mixed ligand complex systems such as:

- **A**, Metal-2,2'-dipyridyl-ascorbic acid.
- **B**, Metal-2,2'-dipyridyl-glutamic acid.
- **C**, Metal-2,2'-ascorbic acid-ethylenediamine.
- **D**, Metal-glutamic acid-ethylenediamine.

The metal ions chosen for such studies are manganese (II), iron (II), cobalt (II), nickel (II), copper(II), beryllium (II), zirconium (IV) and uranium (VI). In case of these complexes, two types of systems were taken, the first is the metal-2,2'-dipyridyl-ligand system (where ligand is either ascorbic acid or glutamic acid). In this system
2,2'-dipyridyl acts as a primary ligand, because the 2,2'-dipyridyl-metal complexation is complete even at very low pH, and can be shown by the Equation:

\[
M^{x+} + H_2N \cdot C_6H_5 \cdot C_6H_5 \cdot NH_2 \rightarrow [M \cdot NH_2 \cdot C_6H_5 \cdot C_6H_5 \cdot NH_2]^{x+} \quad \text{(III.10)}
\]

where \( M^{x+} \) is metal ion with charge \( x^+ \). The increase in the pH of the metal-2,2'-dipyridyl-AsH_2/GlH_2 systems leads to gradual ionization of the secondary ligand which is either ascorbic acid or glutamic acid.

\[
H_y (\text{Ligand}) \quad \leftrightarrow \quad yH^+ \quad (\text{Ligand})^{y^-} \quad \quad \text{... (III.11)}
\]

\( y \) being the number of protons attached to the secondary ligand. The ionized secondary ligands then enter into complex formation with (1:1) metal-2,2'-dipyridyl complex to form the mixed ligand complex, i.e.

\[
[M \cdot NH_2 \cdot C_6H_5 \cdot C_6H_5 \cdot NH_2]^{x+} + (\text{Ligand})^{y^-} \leftrightarrow [M \cdot NH_2 \cdot C_6H_5 \cdot C_6H_5 \cdot H_2N \cdot (\text{Ligand})^{(x-y)^+} \quad \quad \text{... (III.12)}
\]

On further increase of pH, the mixed ligand complex undergoes hydrolysis due to increase in the hydroxide ion concentration in the solution and thus, leads to the precipitation of metal hydroxides.
The second type involves metal-ligand-ethylenediamine system (ligands being similarly ascorbic acid or glutamic acid), where ethylenediamine acts as a secondary ligand as its deprotonation takes place at higher pH. In such systems at low pH, ascorbic acid and glutamic acid remain undissociated and ethylenediamine exists as a completely protonated species (en H\textsuperscript{+}).

The titration of the (vitamin/glutamic acid-en-H\textsuperscript{+}) system by an alkali at first leads to first dissociation of the vitamin/glutamic acid, which practically completes between pH 4-5 (pK\textsubscript{2} for ascorbic acid = 4.20 and for glutamic acid its value is 4.15, chapter II Equations (II.10), and (II.16), respectively). Practically all the anionic species combine with metal ion to form metal-vitamin or metal-amino acid complexes. Thus, the primary complexation is complete around pH 5.0 as given below:

\[
[M^{x+} + (\text{Ligand})^{y-} \rightarrow [M \cdot \text{Ligand}]^{(x-y)+} \quad \text{(III.14)}]
\]

On further titration of the system by alkali the species (en H\textsubscript{2})\textsuperscript{2+} is gradually deprotonated according to Equation:
The gradual increase in ethylenediamine concentration leads to the mixed ligand complex formation by attachment of ethylenediamine with metal primary ligand complex i.e.

\[(\text{en} \, H_2)^{2+} \rightleftharpoons (\text{en}) + 2H^+ \quad (pK_1 = 10.0 \text{ and } pK_2 = 7.0) \ldots (III.15)\]

On further titration, the concentration of hydroxyl ions becomes quite large, which ultimately leads to gradual hydrolysis of the metal-ligand mixed complex.

**Metal-2,2'-dipyridyl-ascorbic acid system:**

Figs. 24 and 25 contain the typical titration curves i.e. acid A, secondary ligand B and the mixed ligand complex D, \( D_1 \), respectively. The complex curves D and \( D_1 \) have been found to coincide with the secondary ligand titration curves up to volume of alkali \( a = 2.5 \text{ ml (0.203 M)} \) in most of the metal ions under investigation. However, the displacement of the mixed ligand complex titration curve D from the curve B varies from metal to metal i.e. a buffer region exists from the pH range 3.0 to 7.0 with these metal ions. Thus, these are the regions where the coordination of the secondary ligand (ascorbic acid) with the primary
complex (metal-2,2'-dipyridyl) is considered to get initiated. Such statement can be represented by the Equation:-

\[
\begin{align*}
M^{x+} + A & \rightleftharpoons [MA]^{x+} \quad \ldots \quad (\text{III}.17) \\
MA^{x+} + L^{-} & \rightleftharpoons [MAL]^{(x-y)+} \quad \ldots \quad (\text{III}.18)
\end{align*}
\]

Where A is the primary neutral ligand (2,2'-dipyridyl),\( L^{-} \) is the secondary ligand ion (ascorbate ion ) and \( x^{+} \) is the charge or valency of the metal ions M. It has been assumed that the secondary ligand combines with the primary complex i.e. \([M(dipyridyl)]^{x+}\), just as it does with \([M(aq)]^{x+}\) species in simple systems. As such, the horizontal distances between curves B and D have been measured and used for the calculations of \( \bar{n} \) values. The values of \( \bar{n} \) were always found below one, indicating that one ascorbic acid molecule has combined with each \([M(dipyridyl)]^{x+}\). \( \bar{n} \) and \( pL \) values were calculated at different points in the pH ranges 3.0 to 6.0 in case of complexes of beryllium(II), zirconium (IV) and uranium(VI), whereas these values were calculated between pH ranges of 6.0 to 8.0 in the case of rest of the mixed ligand complexes i.e. iron (II), manganese(II), cobalt(II), nickel(II) and copper(II), respectively. Further, the colour changes have been considered to be due to the complex formation. Thus, the
deep red colour in case of iron complex gets intensified as the pH increases. However, in case of beryllium (II) and zirconium (IV) - 2,2'-dipyridyl - ascorbic acid complexes, white precipitate appeared at pH 6.0 and 4.6, respectively. The calculations for the $\bar{n}$ and $pL$ were done below the pH of formation of metal hydroxides. In case of uranium (VI) complex, the colourless solution changed from pale yellow to brown and finally a precipitate was obtained at pH 6.0. Rest of the complexes were found to be stable up to pH 9.0, though their colours got intensified with increase in pH. Beyond pH 9.0, a slight turbidity was observed in case of manganese (II) and nickel (II) - 2,2'-dipyridyl-ascorbic acid complexes.

From the $n$ - $pL$ data, as given in the formation curves (Fig. 35), $\log K_{MAL}$ were evaluated by reading the $pL$ values at half $\bar{n}$ and are given in Table 7. The order of the formation constants is found to be greater than the simple (metal-ascorbic acid) systems. The effect of the basicity of the ligand and its ring size on the stabilities of the mixed ligand complexes
<table>
<thead>
<tr>
<th>System</th>
<th>Constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>Manganese(II)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>5.80</td>
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<tr>
<td>Iron(II)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>8.12</td>
</tr>
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<td>Cobalt(II)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>6.10</td>
</tr>
<tr>
<td>Nickel(II)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>5.95</td>
</tr>
<tr>
<td>Copper(II)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>8.35</td>
</tr>
<tr>
<td>Beryllium(II)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>9.70</td>
</tr>
<tr>
<td>Zirconium(IV)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>11.20</td>
</tr>
<tr>
<td>Uranium(VI)-Dipy-(AsH₂)</td>
<td>Log Kₐₚy</td>
<td>10.25</td>
</tr>
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</table>
is explained by Sharma et al., (16). The Log $K_{MAL}$ values of the present system were found greater than the Log $K_{ML}$ values of the simple metal-ascorbic acid systems. The increase in the stabilities of iron (II) and copper (II) systems is prominent. In case of copper, the presence of 2,2'-dipyridyl as primary ligand stabilises the (+2) oxidation state and it is possible to evaluate the stability constants of the mixed ligand complexes.

**Metal-2,2'-dipyridyl-glutamic acid system:**

The potentiometric titration curves i.e. acid A, secondary ligand B and mixed ligand D, $D_1$, $D_2$ and $D_3$, respectively, are represented in the Fig. 26. The nature of the curves is almost the same as that of metal-2,2'-dipyridyl-ascorbic acid systems. An inspection of the various curves reveals that the curves $D$, $D_1$ and $D_2$ etc., are displaced from the secondary ligand (curves B) differently with various metal ions and the displacement is proportional to the amount of the complex formed. However, in general, for the systems studied these curves start diverging from the secondary ligand curve in the pH range $\approx 3.0 - 5.0$. At lower pH the curves overlap each other indicating absence of complexation reaction with the primary complex.
The existence of the mixed ligand complexes has further been supported by the fact that solutions undergo marked changes in colours with the complex formation. Thus, the colourless solutions of mixed ligand complexes D containing manganese (II) and uranium (VI) were found to change to dark yellow and yellow colours as a result of mixed ligand complex formation, respectively. In solutions of the ligands containing iron (II), cobalt (II) and copper (II), changes from red to intense red, light pink to dark brown and light blue to intense blue colours appeared, respectively. Slight yellow precipitates in case of manganese (II) and uranium (VI) at pH 6.0 and 4.8, and white precipitates in case of beryllium (II) and zirconium(IV) appeared at pH 3.2 and 4.5, respectively. In all cases the $\bar{n}$ and $pL$ calculations were carried out below the pH of formation of precipitates. The plot of $\bar{n}$ against $pL$ is given in Fig. 36.

The stability constants of the metal-2,2'-dipyridyl-glutamic acid complexes have been evaluated by Bjerrum's half $\bar{n}$ method. The values have been summarized in Table 8. A perusal of the table shows that the values of $\log K_{MAL}$ are slightly less than the $\log ML$ values of the simple metal-glutamic acid complexes already studied and presented in the previous chapter of this thesis. This decrease in
<table>
<thead>
<tr>
<th>System</th>
<th>Constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>Iron(II)-AsH₂-(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>6.30</td>
</tr>
<tr>
<td>Cobalt(II)-AsH₂-(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>5.75</td>
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<td>Nickel(II)-AsH₂-(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>7.05</td>
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<tr>
<td>Copper (II)-AsH₂-(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>7.60</td>
</tr>
<tr>
<td>Beryllium(II)-AsH₂(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>6.62</td>
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<tr>
<td>Zirconium(IV)-AsH₂-(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>5.20</td>
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<tr>
<td>Uranium(VI)-AsH₂-(en)</td>
<td>Log K_{AsH₂}^{MAL}</td>
<td>8.55</td>
</tr>
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stability constants of mixed ligand complexes is in good agreement with the results obtained by most of the workers. However, the decrease in the values of stability constants is small, which can be attributed to the fact that 2,2' -dipyridyl molecule with a bigger size should be expected to produce a greater steric hindrance and decrease Log $K_{\text{MAL}}$. 2,2'-dipyridyl molecule has been found to play a special role i.e. it is bound to the metal ion not only by metal nitrogen sigma bond; but it also forms a pi-bond by the back donation of electrons from the d $\pi$ -orbital of the metal ion to the nitrogen p $\pi$ -orbital on the ligand molecule (17). This d $\pi$ -p $\pi$ interaction does not allow the concentration of electrons on the metal ions to increase significantly. In other words, the effective positive charge on the metal ion in $[\text{M(dipyridyl)}]^x+$ is almost the same as in $[\text{M(aq)}]^x+$. As such the the tendency of the ligand to combine with $[\text{M(dipyridyl)}]^x+$ is almost the same as its tendency to combine with $[\text{M(aq)}]^x+$. This explains why Log $K_{\text{MAL}}$ is approximately equal to Log $K_{\text{ML}}$(18). Thus, it can be concluded that the d $\pi$ -p $\pi$ interaction varies, when the secondary ligand is replaced by other secondary ligand as a result of which the stabilities either increase or decrease in the mixed ligand complex formation as compared to simple systems.
Metal-ascorbic acid-ethylenediamine system

The potentiometric titration curves dealing with the metal-ascorbic acid-ethylenediamine systems are given in the Figs. 27-30. The secondary ligand i.e. ethylenediamine which gets protonated in acidic medium is gradually deprotonated with the titration of the reaction mixture by the alkali (curve B). The primary complex curves C show an inflection at about pH ≈ 6-9 (volume of alkali i.e. a = 4.5-5.0 ml) in almost all the cases. After this these curves drift below, indicating the gradual hydrolysis of primary metal complexes. From the points of inflection corresponding to neutralization of the free acid present in the reaction mixtures C, extensions parallel to the curves A have been constructed on the curves C. The extensions have been denoted as composite curves C' broken lines) (see page 75). The mixed ligand complex titration curves D show buffer regions at higher pH values than the primary complex curves C, indicating the formation of such mixed ligand complexes. In most of the cases the colour of the solutions D change in the pH ranges of the formation of mixed ligand complexes which further confirms the formation of such complexes. It was noted that solutions containing (1:1) primary complexes of various metal ions remain faintly coloured, whereas in the mixed ligand complex systems; solutions were found to assume intensified colours i.e. iron (II) giving dark brown colour,
cobalt (II) dark pink, uranium (VI) yellow colour and in case of beryllium (II), nickel (II) and zirconium (IV) solutions, no change in colour was observed. The solutions of the mixed ligand complexes were stable towards hydrolysis up to pH 9.0 beyond which however, a slight turbidity was detected. In case of (1:1) primary complexes of different metal ions, precipitates appeared at pH ≈ 9.5 in manganese (II), 7.0 in iron (II), 9.5 in case of cobalt (II), 9.0 in nickel (II), 4.0 in copper (II), 9.0 in beryllium (II), 4.2 in zirconium (IV) and 5.4 in case of uranium (VI). The $n_\text{a}$ and $pL$ values were calculated below the range at which the precipitates were observed. From the $n_\text{a}$ - $pL$ data formation curves (Fig. 37) were prepared and $pL$ values at $n_\text{a} = 0.5$ were taken equal to $\log K_{MAL}$. The values have been given in Table 9.

**Metal-glutamic acid-ethylenediamine system:**

The pH titrations were done as in case of metal-ascorbic acid-ethylenediamine systems and the curves A, B, C, C' and D were prepared accordingly (see page 89). The formation curves dealing with metal-glutamic acid-ethylenediamine system are given in the Fig. 38. The pH ranges for the formation of metal-glutamic acid-ethylenediamine complexes for different metal ions as observed in Figs. 31-34 are given below:-
Table 9

Stability constants of metal-glutamic acid mixed ligand complexes with 2,2'-dipyridyl at 25°C and \( \mu = 0.1 \text{M} (\text{KNO}_3) \)

<table>
<thead>
<tr>
<th>System</th>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese(II)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>3.25</td>
</tr>
<tr>
<td>Iron(II)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>7.10</td>
</tr>
<tr>
<td>Cobalt(II)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>3.57</td>
</tr>
<tr>
<td>Nickel(II)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>4.65</td>
</tr>
<tr>
<td>Copper (II)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>6.95</td>
</tr>
<tr>
<td>Beryllium(II)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>7.00</td>
</tr>
<tr>
<td>Zirconium(IV)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>8.35</td>
</tr>
<tr>
<td>Uranium(VI)-Dipy-(Glx2)</td>
<td>Log ( K ) Dipy MAL</td>
<td>8.15</td>
</tr>
</tbody>
</table>
### pH ranges for complex formation

<table>
<thead>
<tr>
<th>Element</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese(II)</td>
<td>8.25-9.50</td>
</tr>
<tr>
<td>Iron(II)</td>
<td>6.50-7.50</td>
</tr>
<tr>
<td>Cobalt(II)</td>
<td>6.25-7.50</td>
</tr>
<tr>
<td>Nickel(II)</td>
<td>5.75-7.25</td>
</tr>
<tr>
<td>Copper(II)</td>
<td>4.00-7.00</td>
</tr>
<tr>
<td>Beryllium(II)</td>
<td>6.00-8.00</td>
</tr>
<tr>
<td>Zirconium(IV)</td>
<td>5.25-8.00</td>
</tr>
<tr>
<td>Uranium(VI)</td>
<td>4.00-4.75</td>
</tr>
</tbody>
</table>

The values of stability constants are given in Table 10. A comparison of the stability constants for the mixed ligand complexes i.e. metal-ascorbic acid and metal-glutamic acid with ethylenediamine systems studied (Tables 9 and 10) with the Log $K_1$ and Log $K_2$ values for the simple metal chelates (Tables 2 and 5) shows that these values are greater in comparison to both Log $K_1$ and Log $K_2$ values in case of cobalt (II), nickel (II), complexes of ascorbic acid, and cobalt (II), nickel (II), copper (II) and uranium (VI) complexes of glutamic acid. However, the values of stability constants of mixed ligand complexes show a decrease as compared to those of Log KML values of simple systems i.e. beryllium (II), iron (II) and manganese (II), iron (II), zirconium (IV) for ascorbic acid and glutamic acid systems, respectively. This may be due to the fact that
Table 10

Stability constants of metal-glutamic acid mixed ligand complexes with ethylenediamine at 25°C and $\mu = 0.1$ M ($\text{KNO}_3$)

<table>
<thead>
<tr>
<th>System</th>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese(II)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>3.47</td>
</tr>
<tr>
<td>Iron(II)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>5.75</td>
</tr>
<tr>
<td>Cobalt(II)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>5.70</td>
</tr>
<tr>
<td>Nickel(II)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>6.90</td>
</tr>
<tr>
<td>Copper(II)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>9.50</td>
</tr>
<tr>
<td>Beryllium(II)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>6.41</td>
</tr>
<tr>
<td>Zirconium(IV)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>5.13</td>
</tr>
<tr>
<td>Uranium (VI)-GlH$_2$-(en)</td>
<td>$\text{Log } K_{\text{Mal}}$ GlH$_2$</td>
<td>11.00</td>
</tr>
</tbody>
</table>
in the formation of mixed ligand complexes no charge neutralization is involved. The increase in stability constants of nickel (II), copper (II) and uranium (VI) complexes is prominent.
REFERENCES


