CHAPTER VI

SUMMARY
SUMMARY

The present thesis has basically dealt with the physico-chemical investigations leading to the determination of stability constants and other thermodynamic parameters for simple and mixed ligand metal complex formation with selenite, L-2-aminomercaptopropionic acid (L-cysteine) and sulphur containing Schiff's bases viz. salicylideneorthoaaminobenzenothiol (SOTB-H₂) and salicylideneparaaminothioanisol (SPTA-H) and few diamines. Besides this the isolation and characterization of Schiff's bases and some of their complexes has also been reported.

Chapter I, deals with the brief introduction of the present work. The tendency of complex formation of heavier non metals like sulphur and selenium has been discussed. The literature survey reveals that considerable amount of work is going on in this field but the information on stability of certain simple and mixed ligand metal complexes involving selenite, L-cysteine, salicylideneorthoaaminobenzenothiol (SOTB-H₂), salicylideneparaaminothioanisol (SPTA-H), 2,2'-dipyridyl, ethylenediamine and 1,10-orthophenanthroline is lacking. It has therefore been considered necessary to
evaluate the stability constants of such simple and mixed ligand metal complexes.

In chapter II, the equilibrium studies on the selenite metal complexes of $\text{MA}_n$ type and also mixed ligand complexes of the type $\text{MAA}'$ where $\text{A}$ stands for selenite and $\text{A}'$ represents either L-cysteine, salicylideneoanthroaminobenzo thiol (SOTB-$\text{H}_2$) or salicylideneparaaminothianisole (SPTA-$\text{H}$) have been reported. With the help of stabilities evaluated at three ionic strengths, the thermodynamic stability constants at zero ionic strength were obtained by extrapolation and other thermodynamic parameters like entropy, enthalpy and the free energy changes calculated. On the basis of these studies the following orders of stabilities with metal ions: selenite complexes, simple and metal ions: selenite (SOTB-$\text{H}_2$)/ (L-cysteine)/(SPTA-$\text{H}$) mixed ligand complexes, have been observed.

(i) \textit{Metal ions: selenite complexes, simple system:}

\begin{align*}
\text{Au(III)} & \succ \text{Th(IV)} \succ \text{Pt(IV)} \succ \text{Ge(III)} \succ \text{Zr(IV)} \\
\text{UC}_2(\text{VI}) & \succ \text{Nd(III)} \succ \text{Pr(III)} \succ \text{La(III)} \succ \text{Be(II)}. \\
\end{align*}

(ii) \textit{Metal ions: selenite: (SOTB-$\text{H}_2$)schiff's base mixed ligand complexes.}

\begin{align*}
\text{Au(III)} & \succ \text{Th(IV)} \succ \text{UC}_2(\text{VI}) \succ \text{Nd(III)} \succ \text{Be(II)} \succ \text{Zr(IV)}. \\
\end{align*}
(iii) Metal ion: selenite: L-cysteine mixed ligand complexes.

\[
\text{Au(III)} > \text{UO}_2^{2+} > \text{Be(II)} > \text{Th(IV)} > \text{Nd(III)} > \text{Zr(IV)}.
\]

(iv) Metal ion: selenite: (SPTA-H) schiff's base mixed ligand complexes.

\[
\text{Au(III)} > \text{Be(II)} > \text{Zr(IV)} > \text{Nd(III)} > \text{UO}_2^{2+} > \text{Th(IV)}.
\]

The results obtained on these studies are being given in Table VI-A for comparison. From this table, it has been observed that stepwise stability constants with various secondary ligands i.e. (SOTB-H), (L-cysteine) and (SPTA-H) follows the following decreasing order:

\[
\text{(SOTB-H)} > \text{(SPTA-H)} > \text{(L-cysteine)}.
\]

Chapter III, incorporates the equilibrium studies on L-cysteine metal complexes of \( M_n \) type and mixed ligand metal complexes of \( M_{A}A' \) and \( M_{A}A'' \) type with various metal ions. The thermodynamic stability constants were obtained by extrapolation at zero ionic strength. The results obtained on these studies indicates that the order of step stability
constant values follow the following decreasing order:

(i) **Metal ion : L-cysteine complexes** in a type simple system.

\[
\text{Au(III)} > \text{Pt(IV)} > \text{Th(IV)} > \text{UO}_2\text{(VI)} > \text{Cu(II)} > \text{Co(III)} > \text{Nd(III)} > \text{Pr(III)} > \text{Zr(IV)} > \text{La(III)} > \text{Be(II)} > \text{Co(II)} > \text{Fe(II)}.}
\]

(ii) **Metal ion : 2,2'-dipyridyl : L-cysteine mixed ligand complexes.**

\[
\text{Au(III)} > \text{Th(IV)} > \text{Zr(IV)} > \text{UO}_2\text{(VI)} > \text{Be(II)} > \text{Cu(II)} > \text{Fe(II)} > \text{Nd(III)} > \text{Co(II)}.}
\]

(iii) **Metal ion : ethylenediamine : L-cysteine mixed ligand complexes.**

\[
\text{Au(III)} > \text{Fe(II)} > \text{Th(IV)} > \text{Cu(II)} > \text{Co(II)} > \text{UO}_2\text{(VI)} > \text{Be(II)} > \text{Nd(III)} > \text{Zr(IV)}.}
\]

(iv) **Metal ion : 1,10-orthophenanthroline : L-cysteine mixed ligand complexes.**

\[
\text{Au(III)} > \text{Th(IV)} > \text{UO}_2\text{(VI)} > \text{Be(II)} > \text{Zr(IV)} > \text{Fe(II)} > \text{Co(II)} > \text{Nd(III)} > \text{Cu(II)}.}
\]
In the mixed ligand complexes of the type MA\textsuperscript{A'} studied with various primary ligands like 2,2'-dipyridyl, ethylenediamine and 1,10-orthophenanthroline, the following decreasing order of step stability constant values with respect to ligands was observed:

\[
2,2'-\text{dipyridyl} \succ 1,10\text{-orthophenanthroline} \succ \text{ethylenediamine}.
\]

The results are compared in Table VI-B.

In chapter IV the preparation, composition and structure of some sulphur containing schiff's bases i.e. salicylideneorthoaminobenzothiol (SOTB-H\textsubscript{2}) and salicylidene-paraaminothioanal (SPTA-H) has been discussed. The preparation and characterisation of iron(II), cobalt(II), nickel(II), copper(II) and uranyl(VI) complexes of these schiff's bases has also been described. They appear to be polymeric and their probable structures has been suggested.

Chapter V deals with the equilibrium studies on the sulphur containing schiff's bases (SOTB-H\textsubscript{2}) and (SPTA-H) metal complexes of MA\textsubscript{A} type and mixed ligand metal complexes of the MA\textsubscript{A'} and MA\textsubscript{A}MA\textsubscript{A'} type. In case of MA\textsubscript{A}MA\textsubscript{A'} type, A represents either 2,2'-dipyridyl, ethylenediamine or
1,10-orthophenanthroline and $A'$ represents (SOTB-H$_2$) or (SPTA-H) schiff's bases. The results obtained on these studies are given in Tables VI-C and VI-D, indicates that the stepwise stability constants follow the following decreasing order with various systems:

1. **Metal ion**: (SOTB-H$_2$) / (SPTA-H) schiff's base complexes

   **Simple system.**

   (a) With (SOTB-H$_2$) schiff's base:

   \[
   \text{Au(III)} > \text{UO}_2(\text{VI}) > \text{Fe(II)} > \text{Cu(II)} > \text{Zr(IV)} > \text{Pt(IV)}
   \]

   \[
   \text{Th(IV)} > \text{La(III)} > \text{Be(II)} > \text{Co(III)} > \text{Pr(III)}
   \]

   \[
   \text{Nd(III)} > \text{Co(II)} > \text{Ni(II)} > \text{Mn(II)}
   \]

   (b) With (SPTA-H) schiff's base:

   \[
   \text{Au(III)} > \text{UO}_2(\text{VI}) > \text{Fe(II)} > \text{Zr(IV)} > \text{Cu(II)}
   \]

   \[
   \text{Pt(IV)} > \text{Th(IV)} > \text{La(III)} > \text{Be(II)} > \text{Co(III)}
   \]

   \[
   \text{Pr(III)} > \text{Nd(III)} > \text{Co(II)} > \text{Ni(II)} > \text{Mn(II)}
   \]

2. **Metal ion**: 2,2'-dipyridyl/ethylenediamine/1,10-orthophenanthroline i(SOTB-H$_2$)/(SPTA-H) schiff's base mixed ligand complexes:

   (a) Metal ion: 2,2'-dipyridyl:(SOTB-H$_2$)/(SPTA-H) schiff's base mixed ligand complexes;
(1) With (SOTB-H₂) schiff's base:

**MAA' type**: Fe(II) > Au(III) > Th(IV) > Cu(II) > UO₂(VI) > Zr(IV) > Nd(III) > Be(II) > Co(II) > Mn(II) > Ni(II).

**MA₂A' type**: Fe(II) > Cu(II) > Co(II) > Mn(II) > Ni(II).

(ii) With (SPTA-H) schiff's base:

**MAA' type**: Au(III) > Fe(II) > Th(IV) > Cu(II) > UO₂(VI) > Zr(IV) > Be(II) > Nd(III) > Ni(II) > Co(II) > Mn(II).

**MA₂A' type**: Fe(II) > Cu(II) > Co(II) > Mn(II) > Ni(II).

(b) Metal ions: ethylenediamine {SOTB-H₂}/(SPTA-H) schiff's base mixed ligand complexes.

(i) With (SOTB-H₂) schiff's base:

Au(III) > Th(IV) > UO₂(VI) > Nd(III) > Be(II) > Zr(IV).

(ii) With (SPTA-H) schiff's base:

Au(III) > Th(IV) > UO₂(VI) > Be(II) > Zr(IV) > Nd(III).
(c) Metal ion: 1,10-orthophenanthroline (OTB-H₂)/(SPTA-H)
schiff's base mixed ligand complexes.

(i) With (OTB-H₂) schiff's base:

\[ \text{MA}_{2}A' \text{ type: } - \text{Fe(II)} \rangle \text{Cu(II)} \rangle \text{Co(II)} \rangle \text{Mn(II)} \rangle \text{Ni(II)}. \]

\[ \text{MAA' type: } - \text{Fe(II)} \rangle \text{Au(III)} \rangle \text{Cu(II)} \rangle \text{Th(IV)} \rangle \text{UO}_2(\text{VI}) \rangle \text{Nd(III)} \rangle \text{Be(II)} \rangle \text{Zr(IV)} \rangle \text{Co(II)} \rangle \text{Mn(II)} \rangle \text{Ni(II)}. \]

(ii) With (SPTA-H) schiff's base:

\[ \text{MA}_{2}A' \text{ type: } - \text{Fe(II)} \rangle \text{Cu(II)} \rangle \text{Ni(II)} \rangle \text{Co(II)} \rangle \text{Mn(II)}. \]

\[ \text{MAA' type: } - \text{Fe(II)} \rangle \text{Au(III)} \rangle \text{Th(IV)} \rangle \text{Cu(II)} \rangle \text{Zr(IV)} \rangle \text{Be(II)} \rangle \text{UO}_2(\text{VI}) \rangle \text{Nd(III)} \rangle \text{Ni(II)} \rangle \text{Co(II)} \rangle \text{Mn(II)}. \]

It has been observed that the values obtained on step stability constants of mixed ligand metal chelates (MAA' and MA₂A' type) with various primary ligands were found in the following decreasing order:

\[ \text{2,2'-dipyridyl} \rangle \text{1,10-orthophenanthroline} \rangle \text{ethylenediamine}. \]
The stability constants are closely related to the electronegativity of the central metal ion, as the metal ligand distance and bond strengths depend to a large extent on the electrostatic field of the charged ion. An attempt to correlate the LogK for some simple complexes with the electronegativities of a series of metal ions namely (a) few lanthanide ions and (b) some first row transition metal ions is made as given in figure 65. A perusal of figure indicates that among lanthanide ions, the stabilities more or less remain the same. The exceptional behaviour is exhibited by cerium(III) whose selenite complex is found to have very high stability. Among the first row transition metal ions the stability of (SOTB-H₂) and (SPTA-H) schiff's base complexes increases with the increase in electronegativity, decreases for cobalt (II) and again rises and falls at nickel(II). The exceptionally high value of iron(II) (SOTB-H₂) and (SPTA-H) schiff's base complexes is probably because of operation of resonance stabilization.
energy which has been observed in iron(II) complexes in
the aromatic ring systems (loc.cit.). This fact is further
proved by examining the L-cysteine curve where the stability
constants increases in the Malley and Mellow order: Fe(II)
Co(II) Cu(II).

CORRELATION BETWEEN LOGK OF MIXED LIGAND METAL COMPLEXES
AND pKₙ OF PRIMARY LIGANDS.

The correlation between logK of mixed ligand metal
complexes and pKₙ of primary ligands is given in figure 67.
The correlation has been done with different type of metal
ions namely beryllium(II) (A-class), zirconium(IV) and
neodymium(III) (boarder line), gold(III) (B-class). For
beryllium(II), zirconium(IV) and neodymium(III) the logK is
found to vary regularly with the increase in pKₙ of the
primary ligands. However in case of gold(III) the greater
stability for selenite complex is observed (Fig.67-D).
This fact is probably due to the (B-class behaviour)stronger
binding by selenites involving (Au - Se) bonds.

CORRELATION BETWEEN LOGK OF MIXED LIGAND METAL COMPLEXES
AND pKₙ OF SECONDARY LIGANDS.

The correlation between logK of mixed ligand complexes
and pKₙ of secondary ligands is shown in figure 66; for
beryllium(II) (A-class), zirconium(IV), neodymium(III) (border line) and gold(III) (B-class) metal ions. For beryllium(II) the logK is found to increase with pK of the ligands, excepting beryllium (II), 1,10-orthophenanthroline secondary ligand complexes where slow decrease is observed. The lowering of stability in case of beryllium(II) : 1,10-orthophenanthroline : secondary ligand system is probably due to steric reasons. For neodymium(III) and zirconium(IV) systems, the decrease in the mixed ligand complex formation with the increase in pK of the secondary ligands is observed from salicylideneparaaminothiocinasol to L-cysteine and then there is an increase. The exceptions are zirconium(IV) : 2,2'-dipyridyl mixed ligand system and zirconium(IV) : ethylenediamine mixed ligand systems. These facts indicate that mixed ligand complex formation with L-cysteine is unfavourable in the case of zirconium(IV) and neodymium(III). In case of gold(III) mixed ligand complexes, the logK increases with the increase in pK of the secondary ligands and this change is more predominant for L-cysteine system indicating stronger (S-S) bond in case of L-cysteine as compared to the other schiff's bases i.e. salicylidene-paraaminothiocinasol or salicylideneorthoaminobenzothiol.

TABLES II. ENTHALPY AND ENTROPY CHANGES:

The free energy change of formation of simple and mixed ligand complexes involving selenite, L-cysteine.
2,2'-dipyridyl, ethylenediamine, 1,10-orthophenanthroline, salicylidene-paraaminobenzoic acid (SPTA-H) and salicylidene-orthoaminobenzoic acid (SOTB-H₂) Schiff's base have higher values at higher temperature. All the free energy change values obtained were negative. In general, the enthalpy change for the metal complexes studied is found to be slight and the range is 1.33 to 8.00 kcal/mole whereas for entropy change, higher values and greater range (27.24-97.54 cal/deg/mole) is observed. These facts clearly indicate that the factor affecting stabilities more is the entropy change. In case of metal ion: selenite/L-cysteine/(SPTA-H)/(SOTB-H₂) complexes, simple system, the entropy change values obtained follow the following decreasing order with respect to ligands:

(SOTB-H₂) > (L-cysteine) > (SPTA-H) > selenite.

(i) In case of metal ion: selenite/(SPTA-H)/(L-cysteine)/ (SOTB-H₂) mixed ligand complexes the values of entropy change were found to decrease in the following order:

(SOTB-H₂) > (SPTA-H) > L-cysteine.

(ii) It is quite interesting to mention that in case of metal ion: 2,2'-dipyridyl/ethylenediamine/1,10-orthophenanthroline: (SPTA-H)/L-cysteine/(SOTB-H₂) mixed ligand complexes, the values obtained on entropy change were in the following decreasing order:

2,2'-dipyridyl > 1,10-orthophenanthroline > ethylenediamine.
TABLE VI

Stability constants and the free energy change (ΔF°) values of the selenite metal complexes, simple system and mixed ligand metal complexes with (SOTB–H₂), L-cysteine, and (SPTA–H) at 0.1M ionic strength with respect to KNO₃ at 30°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Cations</th>
<th>Simple system</th>
<th>Mixed ligand systems</th>
<th>Mixed ligand systems</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NA</td>
<td>(SOTB–H₂)</td>
<td>(L-cysteine)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LogK₁</td>
<td>- ΔF° Kcal/mole</td>
<td>LogK₁ Kcal/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Be(II)</td>
<td>7.65</td>
<td>10.60</td>
<td>6.85</td>
</tr>
<tr>
<td>2.</td>
<td>Nd(III)</td>
<td>9.00</td>
<td>12.47</td>
<td>6.70</td>
</tr>
<tr>
<td>3.</td>
<td>Au(III)</td>
<td>13.65</td>
<td>18.91</td>
<td>14.05</td>
</tr>
<tr>
<td>4.</td>
<td>Zr(IV)</td>
<td>9.85</td>
<td>13.65</td>
<td>6.40</td>
</tr>
<tr>
<td>5.</td>
<td>Th(IV)</td>
<td>12.25</td>
<td>16.97</td>
<td>7.95</td>
</tr>
<tr>
<td>6.</td>
<td>UO₂(VI)</td>
<td>9.55</td>
<td>13.23</td>
<td>6.50</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Cations</th>
<th>Simple system</th>
<th>Mixed ligand systems</th>
</tr>
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<tr>
<td></td>
<td>$\Delta F_0$</td>
<td>$\Delta F_0$</td>
</tr>
<tr>
<td></td>
<td>$\log K_1$</td>
<td>$\log K_1$</td>
</tr>
<tr>
<td>1. Fe(II)</td>
<td>$11.00$</td>
<td>$14.62$</td>
</tr>
<tr>
<td>2. Cu(II)</td>
<td>$12.90$</td>
<td>$15.26$</td>
</tr>
<tr>
<td>3. Co(II)</td>
<td>$15.00$</td>
<td>$18.25$</td>
</tr>
</tbody>
</table>

Stability constants and the free energy change values ($\Delta F_0$) of the L-cysteine ethylenediamine and 1,10-orthophenanthroline in different ionic strength by extrapolation at 30°C.
**TABLE VI - C**

Stability constant and the free energy change \((\Delta F^0)\) of the \((SPTA-II)\) Schiff's base complexes simple system and mixed ligand metal complexes with 2,2'-dipyridyl, ethylenediamine and 1,10-orthophenanthroline at 0.10M ionic strength with respect to KNO\(_3\) at 30°C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Cations</th>
<th>(\text{NA} )</th>
<th>(-\Delta F^0) Kcal/mole</th>
<th>(\text{NAA}^\dagger)</th>
<th>(-\Delta F^0) Kcal/mole</th>
<th>(\text{NAA}^\dagger)</th>
<th>(-\Delta F^0) Kcal/mole</th>
<th>(\text{NAA}^\dagger)</th>
<th>(-\Delta F^0) Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Nd(III)</td>
<td>11.90</td>
<td>16.49</td>
<td>8.05</td>
<td>11.15</td>
<td>5.65</td>
<td>7.83</td>
<td>10.60</td>
<td>14.69</td>
</tr>
<tr>
<td>4.</td>
<td>Zr(IV)</td>
<td>14.30</td>
<td>19.81</td>
<td>10.35</td>
<td>14.34</td>
<td>5.70</td>
<td>7.90</td>
<td>11.45</td>
<td>15.86</td>
</tr>
<tr>
<td>5.</td>
<td>Th(IV)</td>
<td>12.90</td>
<td>17.87</td>
<td>12.45</td>
<td>17.25</td>
<td>7.80</td>
<td>10.81</td>
<td>13.15</td>
<td>18.22</td>
</tr>
<tr>
<td>6.</td>
<td>UO(_2)(VI)</td>
<td>15.05</td>
<td>20.85</td>
<td>10.15</td>
<td>14.06</td>
<td>6.80</td>
<td>9.42</td>
<td>11.65</td>
<td>16.14</td>
</tr>
</tbody>
</table>
TABLE I: VI - D

Stability constant and the free energy change (ΔF°) of the (SOTB-H₂)
Schiff's base complexes simple system and mixed ligand metal complexes with
2,2'-dipyridyl, ethylenediamine and 1,10-orthophenanthroline at 0.10M ionic
strength with respect to KNO₃ at 30°C.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Cations</th>
<th>Simple system</th>
<th>Phenanthroline</th>
<th>Ethylenediamine</th>
<th>2,2'-dipyridyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>LogK₁</td>
<td>-ΔF° Kcal/mole</td>
<td>LogK₁</td>
<td>-ΔF° Kcal/mole</td>
</tr>
<tr>
<td>1.</td>
<td>Be(II)</td>
<td>13.45</td>
<td>18.60</td>
<td>11.50</td>
<td>15.93</td>
</tr>
<tr>
<td>2.</td>
<td>Nd(III)</td>
<td>13.15</td>
<td>18.22</td>
<td>11.60</td>
<td>16.07</td>
</tr>
<tr>
<td>3.</td>
<td>Au(III)</td>
<td>16.40</td>
<td>22.73</td>
<td>14.55</td>
<td>20.16</td>
</tr>
<tr>
<td>4.</td>
<td>Zr(IV)</td>
<td>15.55</td>
<td>21.55</td>
<td>10.50</td>
<td>14.55</td>
</tr>
<tr>
<td>5.</td>
<td>Th(IV)</td>
<td>14.15</td>
<td>19.61</td>
<td>14.05</td>
<td>19.47</td>
</tr>
<tr>
<td>6.</td>
<td>UO₂(VI)</td>
<td>16.30</td>
<td>22.59</td>
<td>12.45</td>
<td>17.25</td>
</tr>
</tbody>
</table>
Fig. No. 1. pH-Titration Curves for Metal Ions—SeLEN Simple Systems

C1: Platinum(IV)
C2: Cerium(III)
C3: Thorium(IV)
C4: Gold(III)
C5: Beryllium(II)

Fig. No. B:

C1: Uranyl(VI)
C2: Zirconium(IV)
C3: Gold(III)
C4: Beryllium(II)

Volume of KOH (0.4854 M) ml: 0, 3, 4, 5, 6, 7, 8

Volume of KOH (0.5319 M) ml: 0, 1, 2, 3, 4, 5, 6
FIG. NO. 2. PH-TITRATION CURVES FOR METAL IONS-SELEN-SIMPLE SYSTEMS

VOLUME OF KOH (0.5882 M) ml

PH

C1 LANTHANUM (III)

C2 NEODYMIUM (III)

C2 PRASEODYMIUM (III)

A

B

C
FIG. NO. 3. FORMATION CURVES FOR METAL IONS-[SELEN]-SIMPLE SYSTEMS
Fig. No. 4. pH Titration Curves for Metal Ions- [Se]- [Sb]- [H] Mixed Ligand Systems

- Beryllium (II)
- Uranium (V, I)
- Thorium (IV)
FIG. NO. 5. pH-TITRATION CURVES FOR METAL IONS-[SELEN][SOTB-H] MIXED LIGAND SYSTEMS
FIG. NO. 6: FORMATION CURVES FOR METAL IONS-[SELEN] [SOTB-H] MIXED LIGAND SYSTEMS
Fig. No. 7. pH-Titration Curves for Metal Ions—[Selen][L-Cyst] Mixed Ligand Systems
FIG. 8. pH-TITRATION CURVES FOR METAL IONS-[SELEN] [-CYS]-MIXED LIGANDS
Fig. No. 9. Formation curves for metal ions-[SeLen] (l-Cyst)-mixed ligand system

A. URANYL (VI)
B. THORIUM (IV)
C. ZIRCONIUM (IV)

A. BERYLLIUM (II)
B. NEODYMIUM (III)
C. GOLD (III)
FIG. NO.A

FIG. NO.B

FIG. NO.C

FIG. NO. 10. pH-TITRATION CURVES FOR METAL IONS-[SELEN] [SPTA-H] MIXED LIGAND SYSTEMS
FIG. NO. A. BERYLLIUM (II)
D₁ MA
D₂ MAA'

FIG. NO. B. THORIUM (IV)
D₁ MA
D₂ MAA'

FIG. NO. C. NEODYMIUM (III)
D₁ MA
D₂ MAA'

FIG. NO. 11. pH-TITRATION CURVES FOR METAL IONS-[SELEN][SPTA-H] MIXED LIGAND SYSTEMS

VOL OF KOH (0.0883 M) ml

VOL OF KOH (0.0883 M) ml

VOL OF KOH (0.0883 M) ml
FIG. NO. 12. FORMATION CURVES FOR METAL IONS-[SELEN][SPTA-H] MIXED LIGAND SYSTEMS
Fig. No. 13. Showing $\log K$ values of metal ions-[SeLEN]-Simple system at zero ionic strength by extrapolation.
FIG. NO. 4. FORMATION CURVES FOR PROTON LIGAND SYSTEM.
FIG. NO. A, B, C. pH-TITRATION CURVES FOR METAL IONS-[L-CYST] SIMPLE SYSTEMS

VOL. OF KOH (0.0833 M) ml

C1 THERIUM (IV) C2 NEODYMIUM (III) C3 CERIUM (III) C4 PRASEODYMIUM (III)

C1 ZIRCONIUM C2 LANTHANUM C3 LANTHANUM C4 LANTHANUM

C1 URANYL C2 BERYLLIUM C3 PLATINUM IV

VOL. OF KOH (0.0833 M) ml

PH 1 2 3 4 5 6 7 8 9 10 11
FIG. NO. 23. FORMATION CURVES FOR METAL IONS - [L-CYST]. MIXED LIGAND SYSTEM.

FIG. NO. 17. FORMATION CURVES FOR METAL IONS - [L-CYST]. SIMPLE SYSTEM.
FIG. NO. 18. pH-TITRATION CURVES FOR METAL IONS-[DIPYL][L-CYST] MIXED LIGAND SYSTEMS
FIG. NO. 19. FORMATION CURVES FOR METAL IONS-[DIPYR]-[L-CYST] MIXED LIGAND SYSTEM

FIG. NO. 28. FORMATION CURVES FOR METAL IONS-[PHENAN]-[L-CYST] MIXED LIGAND SYSTEM

IRON (II)
A - MA
B - MA

COBALT (II)
A - MA
B - MA

COPPER (II)
A - MA
B - MA

IRON (II)
A - MA
B - MA

COBALT (II)
A - MA
B - MA

COPPER (II)
A - MA
B - MA

FIG. NO. A
FIG. NO. B
FIG. NO. C

U J

Fie, N0.19. FORMATION CURVES FOR METAL IONS-[DIPYR]-[L-CYST] MIXED LIGAND SYSTEM

FIG. NO. A
FIG. NO. B
FIG. NO. C

U J
FIG NO. 20 - pH-TITRATION CURVES FOR METAL IONS-[DIPYL][L-CYST] MIXED LIGAND SYSTEMS.
FIG. NO. A

- BERYLLIUM II
- NEODYMIUM III
- ZIRCONIUM IV

FIG. NO. B

- URANYL (VI)
- THORIUM (IV)
- GOLD (III)

FIG. NO. 21: FORMATION CURVES FOR METAL IONS-[DIPY] [L-CYST] MIXED LIGAND SYSTEMS
FIG. NO. 22. pH-TITRATION CURVES FOR METAL IONS-[E₇][L-CYST] MIXED LIGAND COMPLEXES.
FIG. NO. 25. FORMATION CURVES FOR METAL IONS \([E_{\eta}][L\cdot\text{CYST}]\) MIXED LIGAND SYSTEMS.
FIG. NO. 26. pH-TITRATION CURVES FOR METAL IONS-[PHENAN] [L-CYST] MIXED LIGAND SYSTEMS.
FIG. NO: A  FIG. NO: B  FIG. NO: C

FIG. NO27. pH-TITRATION CURVES FOR METAL IONS- [PHENAN] [L-CYST] MIXED LIGAND SYSTEMS.
FIG. NO. 29. FORMATION CURVES FOR METAL IONS-[PHENAN][L-CYST] MIXED LIGAND SYSTEMS.
FIG NO. A. SHOWING LOG K VALUES METAL IONS-[CYST]-[DIPYL]/
En]/[PHENAN]-MIXED LIGAND SYSTEM AT ZEPO IONIC STRENGTH BY EXTAPOLATION
FIG. NO. C

FIG. NO. B

FIG. NO. A

FIG. NO. 32

PH TITRATION CURVES FOR METAL IONS - [SPTA-H] SIMPLE SYSTEM
FIG. NO. A

FIG. NO. B

FIG. NO. C

FIG. NO. 33. pH-TITRATION CURVES FOR METAL IONS - [SPTA-H] SIMPLE SYSTEM.
FIG.NO. A

FIG.NO. B

FIG.NO. C

VOLUME OF KOH (0.0769M) ml.

VOLUME OF KOH (0.0769M) ml.

VOLUME OF KOH (0.0769M) ml.

FIG.NO.35. pH-TITRATION CURVES FOR METAL IONS-[DIPYL]-[SPTA-H] MIXED LIGAND SYSTEM.
FIG NO. 36 PH-TITRATION CURVES FOR METAL IONS [DIPYL][SPTA-H] MIXED LIGAND SYSTEM.
FIG. NO. A

FIG. NO. B

FIG. NO. C

FIG. NO. 38. pH TITRATION CURVES FOR METAL IONS-[DIPYL][SPTA-H]-MIXED LIGAND SYSTEM.
FIG. NO. 39. FORMATION CURVES FOR METAL IONS-[DIPYL]-[SPTA-H]- MIXED LIGAND SYSTEM.
FIG. NO. A  
**D₂Uranyl (VI)**  
**D₂Beryllium (II)**

VOLUME OF KOH (0.0769 M) mL.

FIG. NO. B  
**D₁Gold (III)**  
**D₂Zirconium (IV)**

VOLUME OF KOH (0.0769 M) mL.

FIG. NO. C  
**D₁Thorium (IV)**  
**D₂Neodymium (III)**

VOLUME OF KOH (0.0769 M) mL.

FIG. NO. 40. pH-TITRATION CURVES FOR METAL IONS - [Eₙ][SPTA-H] MIXED LIGAND SYSTEM.
Fig. No. A: Formation curves for metal ions - \([E_n]\) [SPTA-H] - mixed ligand system.

- A - UPANYL (VI)
- B - THORIUM (IV)
- C - ZIRCONIUM (IV)

Fig. No. B:

- A - BERYLLIUM (III)
- B - NEODYMIUM (III)
- C - GOLD (III)
FIG. NO. A

FIG. NO. B

FIG. NO. C

VOLUME OF KOH (0.0769M) ml.

VOLUME OF KOH (0.0769M) ml.

VOLUME OF KOH (0.0769M) ml.

D1 - NICKEL (II) A A'
D2 - NICKEL (II) A2A'
D3 - IRON (II) A A'
D4 - IRON (II) A2A'

D1 - MANGANESE (II) A A'
D2 - MANGANESE (II) A2A'

D1 - COPPER (II) A A'
D2 - COPPER (II) A2A'

D1 - COBALT (II) A A'
D2 - COBALT (II) A2A'

FIG.NO.42: pH-TITRATION CURVES FOR METAL IONS-[PHENAN][SPTAH] MIXED LIGAND SYSTEM.
FIG NO.44. pH TITRATION CURVES FOR METAL IONS-[PHENAN]. [SPTA-H]-MIXED LIGAND SYSTEM.

**D_{1}-THORIUM (IV)**

**D_{2}-ZIRCONIUM (IV)**

**D_{1}-URANYL (VI)**

**D_{2}-NEODYMIUM (II)**

**D_{1}-GOLD (III)**

**D_{2}-BERYLLIUM (II)**

**VOLUME OF KOH (0.0769M) ml.**

**PH**
FIG. NO. A

**C_{1} - COPPER (II)**

VOLUME OF KOH SOLUTION (0.0769 M) ml.

FIG. NO. B

**C_{1} - URANYL (VI)**

VOLUME OF KOH SOLUTION (0.0769 M) ml.

**FIG. NO. 47. pH-TITRATION CURVES FOR METAL IONS - [SOTB-H] SIMPLE SYSTEM**
FIG. NO. A

FIG. NO. B

C₁ - MANGANESE (II)
C₂ - COBALT (II)
C₃ - THORIUM (IV)

C₁ - NICKEL (II)
C₂ - IRON (II)

VOLUME OF KOH SOLUTION (0.0775M) ml.

FIG. NO. 49. pH-TITRATION CURVES FOR METAL IONS. [SOTB-H] - SIMPLE SYSTEM
FIG. NO. 50. FORMATION CURES FOR METAL IONS- [SOTB-H] SIMPLE SYSTEM.
FIG. NO. A

FIG. NO. B

FIG. NO. 51. pH-TITRATION CURVES FOR METAL IONS [DIPYL]-[SOTB-H] MIXED LIGAND SYSTEM.
FIG. NO. A

FIG. NO. B

Fig. No. 52. pH-Titrations curves for metal ions [DIPYL]-[SOTB-H] mixed ligand system.
FIG. NO. 53: FORMATION CURVES FOR METAL IONS [DIPYL][SOTB-H]-MIXED LIGAND SYSTEM. MA A'
FIG. NO. A

FIG. NO. B

FIG. NO. C

FIG. 54. PH TITRATION CURVES FOR METAL IONS [DIPYL][SOTB-] MIXED LIGAND SYSTEM.

VOLUME OF KOH (0.0883 M) ml.

PH 7 6 5 4 3 2 1 10 9 8

D1 - NEODYMIUM (III)

D2 - GOLD (II)

D3 - URANYL (VII)
FIG.NO.A  FIG.NO.B  FIG.NO.C

**D₁ - ZIRCONIUM (IV)**

**D₁ - BERYLLIUM (II)**

**D₁ - THORIUM (IV)**

**FIG.NO.55.** PH TITRATION CURVES FOR METAL IONS [DIPYL]-[SOTB-H] MIXED LIGAND SYSTEM.
FIG. NO. A
A - BERYLLIUM (II)
B - NEODYMIUM (II)
C - URANYL (VI)

FIG. NO. B
A - ZIRCONIUM (II)
B - THORIUM (IV)
C - GOLD (III)

FIG. NO. 56. FORMATION CURVES FOR METAL IONS [DIPYL][SOTB-H] MIXED LIGAND SYSTEM.
FIG. NO. A

FIG. NO. B

FIG. NO. C

D<sub>1</sub> - URANYL (VI)

D<sub>1</sub> - GOLD (III)

D<sub>1</sub> - NEODYMIUM (III)

FIG. NO. 57. pH-TITRATION CURVE FOR METAL IONS [E<sub>m</sub>][SOTB-H]- MIXED LIGAND SYSTEM.
FIG. NO. A

FIG. NO. B

FIG. NO. C

D₁ ZIRCONIUM (IV)

D₁ BERYLLIUM (II)

D₁ THORIUM (IV)

FIG. NO. 58. pH-TITRATION CURVES FOR METAL IONS [En][SOTB-H]- MIXED LIGAND SYSTEM.
FIG. NO. A

A - BERYLLIUM (II)
B - ZIRCONIUM (IV)
C - NEODYMIUM (III)

FIG. NO. B

A - URANYL (VI)
B - GOLD (III)
C - THORIUM (IV)

FIG.NO. 59. FORMATION CURVES FOR METAL IONS [En][SOTB-H]- MIXED LIGAND SYSTEM.
FIG. NO. A

FIG. NO. B

FIG. NO. C

FIG. NO. 60. pH-TITRATION CURVES FOR METAL IONS [PHENAN][SO4^2-·H] MIXED LIGAND SYSTEM.
FIG. NO. 6 A: FORMATION CURVES FOR METAL IONS [PHENAN]-[SOTB-H] MIXED LIGAND SYSTEM.

- A - BERYLLIUM (II)
- B - THORIUM (IV)
- C - ZIRCONIUM (IV)

FIG. NO. 6 B:

- A - URANYL (VI)
- B - NEODYMIUM (III)
- C - GOLD (III)
FIG. NO. A
A - COBALT (II)
B - COPPER (II)

FIG. NO. B
A - IRON (II)
B - MANGANESE (II)

FIG. NO. C
A - NICKEL (II)
B - COPPER (II)

FIG. NO. D
A - NICKEL (II)
B - MANGANESE (II)

FIG. NO. E
A - IRON (II)

FIG. NO. F
A - COBALT (II)

FIG. NO. 64. FORMATION CURVES FOR METAL IONS [PHENAN][SOTB-H] MIXED LIGAND SYSTEM.
FIG. NO. 65. CORRELATION BETWEEN LOG K OF SELEN, SPTA-H, L-CYST, SOTB-H METAL COMPLEXES WITH ELECTRONEGATIVITY.
FIG. NO. A

BERYLLIUM (II)
A - [SELEN]
B - [DIPYL]
C - [En]
D - [PHENAN]

LOG K vs PKₐ

FIG. NO. B

NEODYMIUM (III)
A - [SELEN]
B - [DIPYL]
C - [En]
D - [PHENAN]

LOG K vs PKₐ

FIG. NO. C

GOLD (III)
A - [SELEN]
B - [DIPYL]
C - [En]
D - [PHENAN]

LOG K vs PKₐ

FIG. NO. D

ZIRCONIUM (IV)
A - [SELEN]
B - [DIPYL]
C - [En]
D - [PHENAN]

LOG K vs PKₐ

FIG. NO. 66: CORRELATION BETWEEN LOG K OF MIXED LIGAND METAL COMPLEXES AND PKₐ OF SECONDARY LIGANDS.
FIG. NO. A
BERYLLIUM (II)
A - [SOTB-H]
B - [SPTA-H]
C - [L-CYST]

FIG. NO. B
ZIRCONIUM (IV)
A - [SOTB-H]
B - [SPTA-H]
C - [L-CYST]

FIG. NO. C
NEODYMIUM (III)
A - [SOTB-H]
B - [SPTA-H]
C - [L-CYST]

FIG. NO. D
GOLD (III)
A - [SOTB-H]
B - [SPTA-H]
C - [L-CYST]

FIG. NO. 67. CORRELATION BETWEEN LOG K OF MIXED LIGAND METAL COMPLEXES AND PKₙ OF PRIMARY LIGANDS.