CHAPTER VI

DISCUSSION OF THE RESULTS OF MIXED LIGAND COMPLEXES.

Mixed ligand complexes are those in which more than one kind of ligand, other than solvent molecule, are present in the innermost coordination sphere of central metal ion. Their synthesis, kinetic behaviour and isomerism are treated in many papers and monographs (1-5). The formation of mixed ligand complexes is responsible for some catalytic effects in redox reactions (6) and plays an important role in the action of enzyme models (7). They are vital in analytical methods and help to understand the behaviour of pollutants in natural waters (8). Owing to these and other properties of mixed ligand complexes, many chemists developed interest in the determination of nature and stabilities of mixed ligand complex species in solution state with the help of a variety of techniques such as potentiometry (9), spectrophotometry (10) and liquid-liquid extraction (11). In recent years polarographic technique, in the determination of the nature of mixed ligand complexes, has been receiving an increasing attention especially after the researches in the field by Schaap and McMasters (12).

Survey of literature in the field revealed that few mixed ligand systems have been studied so far (13-22).
The present work was undertaken to investigate some mixed ligand systems with a view to elucidate the composition and stability constants of the mixed ligand complexes. The mixed ligand systems studied are:

1. Cd(II)-oxalate-phthalate,
2. Cd(II)-oxalate-adipate,
3. Cd(II)-oxalate-thiocyanate,
4. Cd(II)-oxalate-sulphosalicylate,
5. Cd(II)-succinate-salicylate, and
6. Pb(II)-succinate-salicylate.

The polarographic investigation on simple systems of Cd(II)-oxalate (12,13), Cd(II)-phthalate (23), Cd(II)-adipate (24), Cd(II)-thiocyanate (25-27), Cd(II)-sulphosalicylate (28), Cd(II)-salicylate (29), Cd(II)-succinate (13,24), Pb(II)-succinate (30) and Pb(II)-salicylate (31) was already made by many workers. However, these systems were reinvestigated in the present work with the intention of obtaining their stabilities under identical experimental conditions maintained for the respective mixed ligand systems.

A consolidated data of stability constants of the simple systems are listed in Table 54 of Chapter - IV. These stability constant values are in satisfactory agreement with those reported by various workers (12,13,23-31) considering the different experimental set up.
Mixed ligand systems:

The log values of the stability constants of the mixed ligand complexes are given in the Table 1.

Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>log stability constants</th>
<th>log D = log $\beta_{30}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta_{11}$</td>
<td>$\beta_{12}$</td>
</tr>
<tr>
<td>Cd(II)-OX-PHLT</td>
<td>3.75</td>
<td>3.89</td>
</tr>
<tr>
<td>Cd(II)-OX-ADPT</td>
<td>3.81</td>
<td>4.71</td>
</tr>
<tr>
<td>Cd(II)-OX-SCN</td>
<td>-ve</td>
<td>3.90</td>
</tr>
<tr>
<td>Cd(II)-OX-SSA</td>
<td>3.38</td>
<td>3.63</td>
</tr>
<tr>
<td>Cd(II)-SUCG-SA</td>
<td>2.35</td>
<td>-ve</td>
</tr>
<tr>
<td>Pb(II)-SUCG-SA</td>
<td>3.69</td>
<td>-ve</td>
</tr>
</tbody>
</table>

It should be noted that the negative values of the stability constants of some mixed ligand complexes indicate the absence of the respective species in the solution.

The results of the systems are discussed in the same order as given in Table 1.
Cd(II)-oxalate-phthalate system:

It was observed that Cd(II) ion formed hexacoordinate complexes with oxalate (OX) and phthalate (PHLT) ions individually. The stability constants for these systems are given below:

<table>
<thead>
<tr>
<th>Equilibria</th>
<th>log stability constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cd}^{2+} + \text{(OX)}^{2-}$</td>
<td>$\left[ \text{Cd(OX)} \right]$</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 2\text{(OX)}^{2-}$</td>
<td>$\left[ \text{Cd(OX)}_2 \right]^{2-}$</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 3\text{(OX)}^{2-}$</td>
<td>$\left[ \text{Cd(OX)}_3 \right]^{4-}$</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + \text{(PHLT)}^{2-}$</td>
<td>$\left[ \text{Cd(PHLT)} \right]$</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 2\text{(PHLT)}^{2-}$</td>
<td>$\left[ \text{Cd(PHLT)}_2 \right]^{2-}$</td>
</tr>
<tr>
<td>$\text{Cd}^{2+} + 3\text{(PHLT)}^{2-}$</td>
<td>$\left[ \text{Cd(PHLT)}_3 \right]^{4-}$</td>
</tr>
</tbody>
</table>

The concentration of (PHLT) was kept constant at 0.08 and 0.16M because, at these concentrations, 1:1 and 1:2 complexes respectively were in predominant quantities for Cd(II)-PHLT simple system. The oxalate concentration was then continuously varied from 0.02 to 0.50M. The ionic strength was maintained constant at 1.0M with potassium nitrate.

In the presence of the mixture of oxalate and phthalate ions, the possibility of formation of three mixed ligand
complex species would be \([\text{Cd(OX)}(\text{PHLT})]^2^-\), \([\text{Cd(OX)}(\text{PHLT})_2]^4^-\) and \([\text{Cd(OX)}_2(\text{PHLT})]^4^-\), the total number of ligand being limited to three due to the bidentate nature of the ligands. The existence of these species has been indeed observed and their respective stability constants are:

\[
\begin{align*}
[\text{Cd(OX)}(\text{PHLT})]^2^- & \quad \log \beta_{11} = 3.75 \\
[\text{Cd(OX)}(\text{PHLT})_2]^4^- & \quad \log \beta_{12} = 3.89 \\
[\text{Cd(OX)}_2(\text{PHLT})]^4^- & \quad \log \beta_{21} = 5.02
\end{align*}
\]

The values of the stability constants of mixed ligand complexes are, as expected, greater than those of parent simple complexes.

The determination of composition and the evaluation of the stability constants of mixed ligand complexes showed that in the phthalate complexes of cadmium, the replacement of phthalate by oxalate takes place as was evident from the nature of the plots of \(F_{10}\) vs \(G_L\) (Figs. 54.b and 54.c, Chapter- IV). Such replacement was confirmed by the fact that the mean value of coefficient \(D\) coincided exactly with the stability constant of \([\text{Cd(OX)}_3]^4^-\) i.e. \(\beta_{30}\). The mean \(\log D\) value is equal to 5.17 which agreed well with \(\log \beta_{30} = 5.14\), the stability constant of \([\text{Cd(OX)}_3]^4^-\) complex.
Cd(II)-oxalate-adipate system:

Here both the ligands are bidentate aliphatic acids. The log stability constants at 1.0M ionic strength for the simple systems are listed in Table 54, Chapter - IV.

Concentration of adipate (ADPT) was kept constant at two values of 0.08 and 0.20M and oxalate (OX) concentration was varied from 0.02 to 0.50M.

It was found that three mixed species viz $[\text{Cd(OX)}(\text{ADPT})]^{2-}$, $[\text{Cd(OX)}(\text{ADPT})]^{4-}$, and $[\text{Cd(OX)}_{2}(\text{ADPT})]^{4-}$ were present in the solution with their respective complexation constants as $\log \beta_{11} = 3.81$, $\log \beta_{12} = 4.71$ and $\log \beta_{21} = 5.11$.

A complete replacement of adipate by oxalate was indicated by the mean value of $\log D = 5.15$ which happens to be equal to $\log \beta_{30}$ of $[\text{Cd(OX)}]^{4-}$. This was also proved by the plots of $F_{10}$ vs $C_L$ (Figs. 55.a and 55.b).

Cd(II)-oxalate-thiocyanate system:

This system involves bidentate and monodentate complexing agents like oxalate and thiocyanate respectively to form mixed complexes with Cd(II) ion. Thiocyanate is an ambident anion. It behaves as if the negative charge resides on both sulfur and nitrogen. It is reported that the thiocyanate ion possesses two different donor atoms viz. the sulfur 'S' preferred by soft acids such as Cd$^{2+}$.
Cu⁺, Ag⁺, etc. and the harder 'N' preferred by hard acids such as Fe³⁺, Co³⁺, UO₂⁺, etc. (32). It can, therefore, be inferred that cadmium-thiocyanate binding occurs through 'S'. There is no ligand field stabilization in the Cd(II) ion because of its completed 'd' shells. Thus the stereochemistry of the compounds is determined solely by consideration of size, electrostatic forces and covalent binding forces.

The stability constants of simple complexes of oxalate and thiocyanate with Cd(II) are given in Table 54, Chapter IV.

Thiocyanate (SCN⁻) concentration was kept constant at 0.16 and 0.40M and oxalate (OX⁻) concentration was varied.

The stabilities of the mixed ligand complexes were evaluated by following the usual procedure. They are:

\[
\begin{align*}
[Cd(OX)(SCN)_2]^{2-} & \quad \log \beta_{12} = 3.90 \\
[Cd(OX)_2(SCN)]^{3-} & \quad \log \beta_{21} = 4.80
\end{align*}
\]

The negative value of \(\beta_{11}\) reveals the absence of \([Cd(OX)(SCN)]^{-}\) complex species in solution. The mean value of \(\log D = 5.10\), coincided well with \(\log \beta_{30} = 5.14\), the stability of \([Cd(OX)_3]^{4-}\) complex.
Cd(II)-oxalate-sulphosalicylate system:

The nature of mixed ligand chelates of Cd(II) with bidentate ligands like oxalate and salicylate ions has been determined earlier in this laboratory (33). The mixed chelates were found to possess higher stabilities than would be predicted on strict statistical calculations. The enhancement of the complexation constants of mixed ligand chelates such as $[\text{Cd(OX)}(\text{SA})]^{-}$ and $[\text{Cd(OX)}_{2}(\text{SA})]^{3-}$ was explained on the basis of statistical factors and was attributed to the possibility of simultaneous $\pi$-bonding between Cd(II) and both the ligands (33).

In the present study, instead of salicylic acid, sulphosalicylic acid (SSA) was chosen as a ligand in combination with oxalic acid, keeping the metal ion the same. The concentration of (SSA) was kept constant at two values of 0.16M and 0.60M.

At pH $\approx 7$, dipotassium salt of (SSA) would dissociate into potassium ions and the ionic ligand can be represented as (SSA)$^{2-}$, pK values of $-\text{SO}_{3}\text{H}$, $-\text{COOH}$ and $-\text{OH}$ being 0.69(34), 2.49 and 12.00 (35) respectively.

The existence of three species $[\text{Cd(OX)}(\text{SSA})]^{2-}$, $[\text{Cd(OX)}(\text{SSA})_{2}]^{4-}$ and $[\text{Cd(OX)}_{2}(\text{SSA})]^{4-}$ was established with their respective stability constants as under:

$log \beta_{11} = 3.38$, $log \beta_{12} = 3.63$ and $log \beta_{21} = 4.91$. 
The mean log $D = 5.17$, equal to log $\beta_{30} = 5.14$, showed that the formation of tris- complex of Cd(II)-OX is favoured by replacement of SSA ions by oxalate ions.

**Cd(II)-succinate-salicylate systems:**

In the study of simple systems, it was observed that Cd(II) formed three complexes with succinate and two with salicylate (Table 54, Chapter- IV).

Salicylate concentrations were kept constant at 0.15 and 0.55M while succinate concentration was varied from 0.02 to 0.60 M.

Salicylic acid (SA) is present in the form of $(SA)^{-}$ at pH=7.0 as the pK values of the -COOH and -OH groups are 3.13 and 13.30 respectively (36).

The mixed ligand complexes observed with their stability constants are:

\[
\begin{align*}
[Cd(SUCC)(SA)]^{-} & \quad \log \beta_{11} = 2.35 \\
[Cd(SUCC)_{2}(SA)]^{3-} & \quad \log \beta_{21} = 3.19 \\
[Cd(SUCC)(SA)_{2}]^{2-} & \quad \beta_{12} = -\text{ve}
\end{align*}
\]

The negative value of $\beta_{12}$ indicates that $[Cd(SUCC)(SA)_{2}]^{2-}$ complex is absent.

In this case too, a mean log $D = 3.14$ coincided well with log $\beta_{30} = 3.14$, the stability constant of $[Cd(SUCC)_{3}]^{4-}$. 
Pb(II)-succinate-salicylate system:

It was observed that Pb(II) forms complexes with succinate and salicylate ions (Table 54, Chapter IV).

Polarographic investigation of the Pb(II)-succinate-salicylate system revealed the presence of $[\text{Pb(SUCC)}(\text{SA})]^{-}$, and $[\text{Pb(SUCC)}_2(\text{SA})]^{3-}$ complex species in the solution. Their stability constants are respectively $\log \beta_{11} = 3.69$ and $\log \beta_{21} = 3.45$. The complex $[\text{Pb(SUCC)}(\text{SA})]^{2-}$ should be taken as nonexistent in the solution since its stability constant value comes out to be negative.

A good agreement between the values of $\log \beta$ and the complexation constant of $[\text{Pb(SUCC)}_3]^{4-}$ was observed.

Prediction of $\beta$ values from statistical factors

Cd(II)-oxalate-phthalate system:

The observed complexation constant can be compared with the values which one might predict from those of the simple complexes by following the statistical procedure suggested by Watters (37). The gross statistical effect is absent in a saturated complex since all the available positions in an aquo ion are occupied by the same number of ligands. However, there is a statistical factor in the stability constant of mixed complex species. In the present case,
with equal concentrations of oxalate and phthalate, the probability that the first bonded ligand will be oxalate is $\frac{1}{2}$. The probability that successive oxalate ions will be bound to Cd(II) to form $[\text{Cd(OX)}_3]^{4-}$ is $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ i.e. $1/8$. The same argument will hold good for $[\text{Cd(PHLT)}_3]^{4-}$. The remaining 6/8 probabilities will be equally divided between $[\text{Cd(OX)}_2(\text{PHLT})]^{4-}$ and $[\text{Cd(OX)}(\text{PHLT})_2]^{4-}$. The predicted values for complexation constants then will be i) $3 \times \beta_{20}^{2/3} \beta_{03}^{1/3} = 10^{4.36}$ as compared to $10^{5.02}$ observed for $[\text{Cd(OX)}_2(\text{PHLT})]^{4-}$ and ii) $3 \times \beta_{30}^{1/3} \beta_{02}^{2/3} = 10^{3.69}$ as compared to $10^{3.89}$ observed for $[\text{Cd(OX)}(\text{PHLT})_2]^{4-}$. The enhancement values come out to be $10^{+0.67}$ and $10^{+0.20}$ respectively.

The statistical factor favouring the mixed complex $[\text{Cd(OX)(PHLT)}]^{2-}$ is two. In this case, however, the term $\beta_N^{\frac{1}{2}}$ also contains a gross statistical factor of $3/2$, since there are only two ligands in the complex whereas Cd(II) ion has a capacity of three ligands. Thus the ligand factor becomes $(2/3)^{\frac{1}{2}} \beta_N^{\frac{1}{2}}$. The observed value $10^{3.75}$ is greater than the calculated $2 \times \beta_{20}^{\frac{1}{2}} \beta_{02}^{\frac{1}{2}} = 10^{3.46}$ by $10^{+0.29}$. The results of the enhancement values thus obtained are given in Table 2.
Table 2

<table>
<thead>
<tr>
<th>Complex species</th>
<th>Stability constant</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td>Calculated</td>
<td>enhancement</td>
</tr>
<tr>
<td>$[\text{Cd(OX)(PHLT)}]^2-$</td>
<td>$\beta_{11}$</td>
<td>$10^{3.75}$</td>
<td>$10^{3.46}$</td>
</tr>
<tr>
<td>$[\text{Cd(OX)(PHLT)}^2]^4-$</td>
<td>$\beta_{12}$</td>
<td>$10^{3.89}$</td>
<td>$10^{3.69}$</td>
</tr>
<tr>
<td>$[\text{Cd(OX)}_2(\text{PHLT})]^4-$</td>
<td>$\beta_{21}$</td>
<td>$10^{5.02}$</td>
<td>$10^{4.35}$</td>
</tr>
</tbody>
</table>

The enhancement values for the remaining mixed ligand systems like Cd(II)-OX-ADPT, Cd(II)-OX-SCN, Cd(II)-OX-SSA, Cd(II)-SUCG-SA and Pb(II)-SUCG-SA, were calculated in a similar manner as described above. The data are summarised in Table 3.

Table 3

<table>
<thead>
<tr>
<th>System</th>
<th>$\beta_{11}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)-OX-ADPT</td>
<td>$10^{+0.51}$</td>
<td>$10^{+1.20}$</td>
<td>$10^{+0.83}$</td>
</tr>
<tr>
<td>Cd(II)-OX-SCN</td>
<td>-</td>
<td>$10^{+0.57}$</td>
<td>$10^{+1.27}$</td>
</tr>
<tr>
<td>Cd(II)-OX-SSA</td>
<td>$10^{+0.63}$</td>
<td>$10^{+0.91}$</td>
<td>$10^{+1.37}$</td>
</tr>
<tr>
<td>Cd(II)-SUCG-SA</td>
<td>$10^{+0.20}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb(II)-SUCG-SA</td>
<td>$10^{+1.31}$</td>
<td>-</td>
<td>$10^{+0.52}$</td>
</tr>
</tbody>
</table>
It was not possible to evaluate theoretical value of $\beta_{21}$ for Cd(II)-SUCG-SA system because $\beta_{03}$ was absent in the simple Cd(II)-salicylate system. The enhancement values could not be calculated for the species $[\text{Cd(OX)(SCN)}]^{-}$ and $[\text{Cd(SUCG)(SA)}]^{2-}$ due to negative values of $\beta_{11}$ and $\beta_{12}$ of these species which showed that the species are absent in solution.

The observed enhancement, in the stability constants of mixed ligand complexes of all the above mixed ligand systems investigated in the present work, may be probably due to (i) a possibility of simultaneous $\pi$-bonding between metal ion and the ligands, and (ii) the possibility of some extra weak bonding between unlike bound ligands.
REFERENCES


SUMMARY AND CONCLUSIONS

CHAPTER - I

This chapter begins by giving salient points of polarographic technique used in the studies of metal complexes. A brief description of the development in coordination chemistry is given with special reference to Werner's work and Valence Bond, Crystal Field, Ligand Field and Molecular Orbital theories. The chapter also deals with different methods used in the studies of metal complexes, putting special emphasis on polarographic technique used in the present work.

CHAPTER - II

The principles of polarography, with necessary theoretical background, are elaborated in this chapter. The methods of Lingane, DeFord and Hume, Schaap and McMasters, Ringbom and Eriksson etc. used for the determination of complexation constants of metal complexes are discussed here.

CHAPTER - III

Instrumentation and details regarding materials, their purity, and conditions maintained in the present investigation have been given in this chapter.
CHAPTER - IV

This chapter is divided into four parts.

Part - I: Measurements in aqueous medium:

Thiourea (TU), nicotinamide (NICO), thioacetamide (TAA),
2-mercaptoethanol (MEL) and formate complexes with Cd(II)
and Pb(II) have been investigated.

The experimental procedure for Cd(II)-TU, as a representa-
tive system, has been given in detail. The stability
constants of all the systems are evaluated by employing
either (i) Lingane or (ii) DeFord and Hume method.

Part - II: Measurements in mixed solvents:

The mixed solvents used are (i) varying percentages of
DMSO-water mixtures, (ii) various percentages of EtOH-water
mixtures, and (iii) MeOH-water, DMF-water, DMSO-water mixtures.
The investigation in mixed solvents is made on the complexes
of TU, NICO, TAA and MEL with Cd(II) and formate complexes
with Cd(II) and Pb(II).

Part - III: Indirect polarographic determination
of stability constants.

Zn(II)-NICO, Co(II)-NICO and Co(II)-TAA systems are
investigated by Ringbom and Eriksson's 'indicator ion'
method.
Part - IV: *Mixed ligand systems:

The stability constants of mixed complexes of Cd(II)-oxalate-phthalate, Cd(II)-oxalate-adipate, Cd(II)-oxalate-thiocyanate, Cd(II)-oxalate-sulphosalicylate, Cd(II)-succinate-salicylate and Pb(II)-succinate-salicylate are determined by following the procedure of Schaap and McMasters.

CHAPTER - V

DISCUSSION

In this chapter, the results of Cd(II) complexes with TU, NICO, TAA, MEL and formate and Pb(II) complexes of formate in aqueous as also in mixed solvents are discussed in Part I and Part II respectively. Part III consists of the discussion of systems studied by 'Indicator ion method'.

Part - I: *Measurements in aqueous medium:

A study of TU, NICO, TAA, MEL and formate complexes revealed following results:

a) $\beta$ values of Cd(II)-TU complexes follow the order $\beta_1 < \beta_2 > \beta_3 < \beta_4$. Exceptionally high value of $\beta_4$ as compared to $\beta_1$, $\beta_2$ and $\beta_3$ has been attributed to the
observation that during the formation of the fourth complex, the coordination number of Cd(II) is fully satisfied.

b) In Cd(II)-NICO system, 1:1 and 1:2 complex species are detected at 1.0M(NaClO₄) while only 1:1 complex is established at 0.5M ionic strength maintained by KNO₃.

Under identical experimental conditions, a comparison of $\beta_1$ value of Cd(II)-NICO complex at $\mu = 0.5M$ (KNO₃) with the literature value of $\beta_1$ of Cd(II)-pyridine complex brought out that the stability of Cd(II)-NICO complex is, as expected, lower than that of pyridine complex. This is attributed to the stronger $\pi$-bonding in Cd(II)-pyridine complex relative to Cd(II)-NICO complex.

c) $\beta$ values of Cd(II)-TAA complexes are higher at 0.5M (KNO₃) ionic strength than that at 0.1M (KNO₃).

d) The system of Cd(II)-MEL is studied at 0.1M(KNO₃) and 1.0M(NaClO₄) ionic strengths. Two complex species of Cd(II)-MEL complexes existed at 0.1M(KNO₃). However, at higher ionic strength of 1.0M(NaClO₄), only 1:1 complex species is observed.

e) Formate formed mono, bis-, tris- and tetrakis-complexes with Cd(II) and Pb(II). It is seen that $\beta_{i_{\text{Pb}}} > \beta_{i_{\text{Cd}}}$ (where $i = 1$ to 4). This trend is explained in the light of electronegativity of metal ion; the electronegativity of Pb(II) being higher than that of Cd(II). The stability
constant of metal complex increases with an increase in electronegativity.

Part - II: Measurements in mixed solvents:

The systems examined in various aquo-nonaqueous media are Cd(II)-TU, Cd(II)-NICO, Cd(II)-TAA, Cd(II)-MEL, Cd(II)-formate and Pb(II)-formate.

The important features of this investigation were as follows:

a) For Cd(II)-TU system in DMSO-water mixtures, it is observed that $\beta$ values do not obey a linear relationship with $1/\xi$.

b) The observation made in the Cd(II)-NICO system studied in EtOH-water mixtures revealed that the $\beta$ values remain nearly constant over the entire range of EtOH-water mixtures. This leads to the conclusion that solvent ethanol as such is not playing any prominent role in the reaction by which complexation occurs.

c) In the study of Cd(II)-TAA system, in varying percentages of EtOH-water mixtures, $\beta_1$ values continuously increased with increase in ethanol concentration, whereas $\beta_2$ values tended to increase up to 30% EtOH and then decreased continuously in 40% and 50% EtOH-water mixtures.

d) Cd(II)-MEL system, at 0.1M(KNO$_3$) and 1.0M(NaClO$_4$) ionic strengths, is investigated in EtOH-water mixtures:
(i) at ionic strength of 0.1M(KNO₃), β₁, which was absent in aqueous medium existed in EtOH, and was found to increase with an increase in 1/ε. β₂ values obeyed a linear relationship with decrease in dielectric constant of the medium, (ii) at 1.0M(NaClO₄) ionic strength, β₁ values, though initially decreased was found to increase with increasing percentage of EtOH. 1:2 complex was absent in aqueous medium but appeared in all ethanol-water mixtures.

e) In both the Cd(II)- and Pb(II)-formate systems, it was found that β₁, β₂ and β₄ bore a linear relation with 1/ε, however, in case of β₃ such relationship was not observed.

The stability constants of Cd(II)-TU system in DMSO-water mixtures having 1/ε = 13.50 x 10⁻³ are different from those obtained in 20% DMF-water and 10% EtOH-water mixtures which have nearly identical dielectric constant i.e. 1/ε = 13.50 x 10⁻³. This argument holds good for other systems of Cd(II)-NICO, Cd(II)-TAA, Cd(II)-formate and Pb(II)-formate investigated in different aquo-organo solvent mixtures with almost identical dielectric constants. This implies that, in addition to dielectric constant, a specific chemical role of solvent may be an important factor which also affects the complexation reaction.

The Van Panthaleon Van Eck equation was applied to Cd(II)-TU, Cd(II)-formate and Pb(II)-formate systems. The plots of log Kₐ vs N-1 are discussed in the light of π-bonding between the metal ion and the ligand.
Part - III: *Indicator ion method*

Zn(II)-NICO, Co(II)-NICO and Co(II)-TAA systems have been investigated by Ringbom and Eriksson's indicator ion method. Cd(II) was used as an indicator ion. The data are given and are discussed in brief.

**CHAPTER - VI**

Discussion of the results of mixed ligand systems:

The stability constants of Cd(II)-oxalate-phthalate, Cd(II)-oxalate-adipate, Cd(II)-oxalate-thiocyanate, Cd(II)-oxalate-sulphosalicylate, Cd(II)-succinate-salicylate and Pb(II)-succinate-salicylate systems are determined in aqueous medium. The $\beta$ values of mixed complexes are, as expected, greater than those of parent complexes. The prediction of $\beta$ values of mixed complexes from statistical considerations, shows that the observed $\beta$ values are greater than those calculated. The observed enhancements were attributed to the possibility of (i) simultaneous $\pi$-bonding between the metal ion and the ligand and (ii) some extra weak bonding between unlike bound ligands.