CHAPTER V
**Chapter V**

**Discussion**

**Part I**

**Measurements in aqueous medium:**

Complexations of cadmium(II) and lead(II) ions with ligands listed below have been investigated in aqueous medium.

1. Cadmium(II)-thiourea at $\mu = 0.1M(KNO_3)$,
2. Cadmium(II)-nicotinamide at $\mu = 1.0M(NaClO_4)$,
3. Cadmium(II)-nicotinamide at $\mu = 0.5M(KNO_3)$,
4. Cadmium(II)-thioacetamide at $\mu = 0.1M(KNO_3)$,
5. Cadmium(II)-thioacetamide at $\mu = 0.5M(KNO_3)$,
6. Cadmium(II)-2-mercapto ethanol at $\mu = 0.1M(KNO_3)$,
7. Cadmium(II)-2-mercapto ethanol at $\mu = 1.0M(NaClO_4)$,
8. Cadmium(II)-formate at $\mu = 2.0M(NaClO_4)$ and
9. Lead(II)-formate at $\mu = 2.0M(NaClO_4)$.

Discussion of results of these systems follows the same sequence as given above.

The ionic strengths were maintained at 1.0 to 2.0M and 0.1 to 0.5M by the addition of appropriate quantities of sodium perchlorate and potassium nitrate respectively.
The stability constant values at these ionic strengths are not thermodynamic constants as the activity coefficient corrections were not applied. Since the values for several ionic activity coefficients are not available at present, most of the workers in the field of polarography have reported stability constants as the values obtained experimentally.

**Cadmium(II)-thiourea system:**

Thiourea (TU), the thio analog of urea, is a thioamide of carbonic acid. Thiourea has two possible reactive sites, since both nitrogen and sulfur have lone electron pairs. Dipole moment measurements studies (1) show that thiourea is a resonance hybrid with an almost equal contribution from the different canonical forms:

\[ \begin{align*}
S-C & \quad \text{I} \\
\quad \text{II} \\
\quad \text{III}
\end{align*} \]

Analysis of vibrational spectra of thiourea showed, however, the absence of tautomeric modifications and the presence of the thione form I only (2-4). X-ray crystal analysis indicates the coplanarity of the carbon, nitrogen and sulfur atoms (5).
The normal state of thiourea is considered to be that of a zwitterion 'a' (6),

\[ \text{H}_2\text{N} = \text{C} - \text{S}^- + \text{H}^+ \quad \leftrightarrow \quad \text{H}_2\text{N} = \text{C} - \text{S} \text{H} \]

while in the presence of acids, the cation 'b' is derived from zwitterion 'a' (7).

IR absorption spectra of methyl thiourea metal complexes showed that both N and S atoms act as donors for metal atoms (8-12). It was also observed that in the complexation of Cd(II) with thiourea, the coordination takes place through S.

Cd(II)-thiourea system, examined earlier by a number of workers (13-16) in aqueous medium, was re-examined to obtain the experimental values of stability constants under identical experimental conditions. This was essential for making comparison with the results taken in various DMSO-water mixtures used in the present work (Part - II of this chapter).

Four complexes were obtained at 0.1M(KNO₃) ionic strength. Their stability constant values are:

\[ \log \beta_1 = 1.30, \log \beta_2 = 1.77, \log \beta_3 = 1.60 \text{ and } \log \beta_4 = 3.53. \]
A good agreement is found in $\beta$ values obtained in the present investigation and those reported by Lane et al. (13) and Dhuley (16). The difference between $\beta$ values in the present work and those reported by Migal et al. (14, 15), may be attributed to the variation in ionic strength and supporting electrolyte they used.

Exceptionally high value of the stability constant of the last complex may be due to the fact that during the formation of the fourth complex, the coordination number four of Cd(II) is fully satisfied.

**Cadmium(II)-nicotinamide system:**

Nicotinamide (NICO) contains an electron attracting group which is expected to decrease the electron density in the pyridine ring. Murmann and Basolo (17) have studied the effect of substitution in the pyridine ring in silver complexes. They observed that groups in the 4-position tend to pull electrons from Ag(I) ion into the ring i.e. increase the tendency of forming a double bond. It was also noted that the group in 3-position, as found in nicotinamide, cannot contribute to this type of resonance and stabilities of these complexes are expected to largely correlate with the base strength of pyridine.

Literature survey reveals that polarographic study of Cd(II)-nicotinamide system was not done in great detail
except by Zutshi and Chakraborty (13) who examined it in water-formamide mixtures at 0.1M(NaClO₄) ionic strength. They observed the existence of only two very weak complex species.

Investigation of this system both in aqueous as well as in a wide range of alcohol-water mixtures was undertaken. The results in alcohol-water mixtures are discussed in Part-II of this chapter.

The system was examined at two ionic strengths 1.0M and 0.5M maintained with two different inert electrolytes i.e. NaClO₄ and KNO₃ respectively. The results are set out in Table 1. The existence of two weak complex species was revealed in 1.0M(NaClO₄) whereas only one complex was obtained in 0.5M(KNO₃).

Table 1

Stability constants of Cd(II)-nicotinamide system in aqueous medium.

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>log stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0M(NaClO₄)</td>
<td>$\beta_1 = 0.68$</td>
</tr>
<tr>
<td></td>
<td>$\beta_2 = 1.00$</td>
</tr>
<tr>
<td>0.5M(KNO₃)</td>
<td>$\beta_1 = 0.82$</td>
</tr>
<tr>
<td></td>
<td>(obtained by Lingane's method)</td>
</tr>
</tbody>
</table>
Nicotinamide has three possible donor sites: ring nitrogen, carbonyl oxygen and nitrogen of amide group. IR spectral studies and studies of the physical properties of Cd(II)-nicotinamide complexes revealed that the coordination was always through the nitrogen of the pyridine ring (19, 20).

It is expected that the stability constants of Cd(II)-nicotinamide complexes would be lower than those of Cd(II)-pyridine complexes. This was examined by a comparison of the stability constants of Cd(II)-nicotinamide complex determined at \( \mu = 0.5 \text{M KNO}_3 \) ionic strength in the present investigation with the literature value of stability constant of Cd(II)-pyridine complex (21) under identical experimental conditions.

\[
\begin{align*}
\text{Cd(II)-NICO} & \quad \mu = 0.5 \text{M KNO}_3 \quad 25 \pm 0.5^\circ \text{C } \log \beta_1 = 0.82 \\
\text{Cd(II)-Py} & \quad \mu = 0.5 \text{M KNO}_3 \quad 25 \pm 0.5^\circ \text{C } \log \beta_1 = 1.10
\end{align*}
\]

It would be seen from these values that, under identical experimental conditions, the stability constant of Cd(II)-nicotinamide complex is lower than that of Cd(II)-pyridine complex. This can be attributed to the fact that pyridine derives its basicity from the unshared electrons of the nitrogen atom in a trigonal plane \( sp^2 \) orbital. Relative to its basicity, however, it is capable of forming stable
complexes with Cd(II). This is due to the additional
\( \pi \)-bonds \([M \rightarrow L]\) between the completely filled \( d \) orbitals
of Cd(II) and \( \pi \)-electron sextet of pyridine. The
existence of such bonds in Ag(I)-pyridine complex was
observed by Murmann and Basolo (17).

Cadmium(II)-thioacetamide system:

Thioacetamide (TAA) exhibits thione-thiol tautomerism
(22):

\[
\begin{array}{c}
\text{S} \\
\text{CH}_3C\equiv\text{NH}_2 \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{SH} \\
\text{CH}_3C=\text{NH} \\
\end{array}
\]

thione \quad \text{thiol}

Since no sulphhydril vibration has been observed
in the Raman spectrum (23), thioacetamide probably has the
amide structure. The work of Spinner (4) and Truter (24)
shows that the carbon sulfur bond has a negligible single
bond character and the carbon-nitrogen bond has negligible
double bond character so that thioacetamide may not be
having zwitterion character (5). Most of the physical
evidence indicates that acyclic thioamides exist primarily
in the thione form.

Thioacetamide finds its way as a useful reagent in
analytical chemistry and as an important intermediate in
the preparation of other compounds.
Seth and Kapoor (25, 26) undertook the polarographic studies in the complexation of thioacetamide with Cu(I) and Hg(II) in aqueous medium presumably due to the importance of the ligand as a reagent in analytical chemistry. Since there are no published reports on polarographic study of Cd(II)-TAA system, a detailed investigation of the system was made in aqueous and in mixed solvents. The discussion of the system in mixed solvents has been deferred to Part-II of this chapter.

In aqueous medium, two complexes viz. $[\text{Cd(TAA)}]^{2+}$ and $[\text{Cd(TAA)}_2]^{2+}$ were observed at each of the ionic strengths maintained as shown in the Table 2 with stability constant values markedly different at different ionic strengths. The effect of ionic strengths on the stabilities of the complexes in solution is discussed subsequently.

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>log stability constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.1\text{M(KNO}_3)$</td>
<td>$\beta_1 = -0.69$</td>
</tr>
<tr>
<td></td>
<td>$\beta_2 = 1.08$</td>
</tr>
<tr>
<td>$0.5\text{M(KNO}_3)$</td>
<td>$\beta_1 = 0.39$</td>
</tr>
<tr>
<td></td>
<td>$\beta_2 = 1.43$</td>
</tr>
</tbody>
</table>
Effect of ionic strength on $\beta$ values:

In order to understand the effect of ionic strength on stabilities of the complexes, knowledge of both (i) long range interionic forces and (ii) the short range interactions between ions and solvent molecules is necessary. Qualitatively, it can be seen that the net effect of interionic attractions and repulsions is to decrease the free energy of the solute as compared to uncharged particles and hence to decrease the activity coefficient $\gamma$, while the forces between ions and solvent dipoles will tend to hold the solvent in solution with a consequent decrease in solvent vapour pressure from its ideal value and a corresponding increase in activity coefficient of the solute. The short range effect, however, depend approximately linearly on concentration while the inter-ionic effects approach linearity as a function of square root of concentration. The short range effects would be ignored, within the limits of experimental error, below one thousandth molar electrolyte solution.

Robinson and Stokes presented the values of activity coefficients for different electrolytes in water at 25°C (27). It could be seen from these data that:

1) for potassium nitrate, the activity coefficients continuously decreased as the ionic strength changed from 0.1M to 0.5M and so on.
for bivalent electrolytes, like Cd(NO₃)₂, the values first decreased as the concentration changed from 0.1 to 0.4 M and then continuously increased and reached a value 0.573 at 2.5 M.

It is thus evident that short range forces predominate over the long range effects at ionic strengths greater than 0.1 M.

Cadmium(II)-2-mercaptoethanol system:

The thiol group in 2-mercaptoethanol (MEL) is a sulfur analog of the hydroxyl group of alcohol, since the divalent sulfur is attached to both carbon and hydrogen atoms. The hydrogen of the thiol group displays a remarkable reactivity, in contrast to its hydroxyl counterpart, undoubtedly, because of larger atomic size of the sulfur atom resulting in larger atomic bond and smaller binding energy.

Mercapto compounds are found to be useful from the point of view of biological, pharmaceutical and other chemical uses. Purdy and coworkers (28-30) have reported metal complexes of several biologically important compounds. The polarographic behaviour of mercapto compounds viz. thiomalic acid, β-mercapto-propionic acid and ethylthio-glycolate and their metal complexes have been studied by Saxena and coworkers (31-35). However, no polarographic
work seems to have been reported on Cd(II)-2-mercaptoethanol system. This system was, therefore, investigated in an aqueous and in mixed solvents.

In the present work, two complex species $[\text{Cd(MEL)}]^2^+$ and $[\text{Cd(MEL)}_2]^2^+$ were observed with their stability constants $\beta_1 = 1.0$ and $\beta_2 = 23.0$ at $0.1 M$ ionic strength maintained with potassium nitrate.

At higher ionic strength ($1.0 M$) maintained by sodium perchlorate, existence of only 1:1 complex was revealed, its stability constant being $\beta_1 = 15.0$.

Formate systems:

According to the resonance theory, a formate ion is a hybrid of two structures which, having equal stability, contribute equally. Carbon is joined to each oxygen by a "one-and-a half" bond. The negative charge is evenly distributed over both oxygen atoms: $\left\{ -\overset{\text{O}^-}{\text{C}} -\overset{\text{O}^\text{-}}{\text{C}} \right\}$. That the anion is a resonance hybrid is supported by the evidence of bond length. Since formic acid contains a carbon-oxygen single bond, one would expect these bonds to have different lengths. On the other hand, if formate is a resonance hybrid as shown above, sodium or potassium formate should contain two equivalent carbon-oxygen bonds of same length but intermediate
between double bonds and single bonds. X-ray and electron
diffraction studies have shown that formic acid contains
one C=O bond of 1.36 Å (single bond) and another of 1.23 Å
(double bond), and sodium or potassium formate contains
two equivalent carbon-oxygen bonds each 1.27 Å long:

\[
\begin{array}{c}
\text{H}-\text{C} \begin{array}{c}
\cap \\
\cup
\end{array} \\
\begin{array}{c}
\cup \\
\cap
\end{array} \\
\text{O}
\end{array}
\]

\[\text{O}^{-}\text{Na}^{+} \text{ or (K}^{+})\]

Although the complexations of formate with many
metals such as Cd(II), Pb(II), Zn(II), Tl(I) and Cu(II)
have been studied polarographically in aqueous medium by
many workers (36-42), its study in mixed solvent is still
lacking.

The complexation of formate with Cd(II) and Pb(II)
has been investigated in aqueous as well as in mixed solvent
at 2.0M(NaClO₄) ionic strength. The results obtained in
aqueous medium are set out in Table 3.

Table 3.

<table>
<thead>
<tr>
<th>Metal</th>
<th>log stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>(\beta_1 = 0.54), (\beta_2 = 1.47), (\beta_3 = 0.84), (\beta_4 = 1.20)</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>(\beta_1 = 1.30), (\beta_2 = 2.09), (\beta_3 = 1.54), (\beta_4 = 1.46)</td>
</tr>
</tbody>
</table>
From the data in Table 3, it is seen that $\beta_{i_{\text{Pb}}} > \beta_{i_{\text{Cd}}}$ in all the stability values of Cd(II) and Pb(II)-formate systems, where $i$ ranges from 1 to 4. The trend observed here parallels with that of Hershensen et al. (37) and Filipovic et al. (41) but it should be noted that the individual $\beta$ values obtained in the present work did not agree well with the values reported by Hershensen et al. (37).

It is established that the stability constants of the metal complexes increased with increasing electronegativity of the metal ion (43). The electronegativities of Pb(II) and Cd(II) are 1.55 and 1.46 respectively (44). The trend of the stability constants of these metal complexes with the formate can be explained in the light of above argument.

The reactions by which complexes are formed may be represented as under:

\[
\begin{align*}
M^{2+} + (\text{HCOO})^- & \rightleftharpoons [M(\text{HCOO})]^+ \quad \beta_1 \\
M^{2+} + 2(\text{HCOO})^- & \rightleftharpoons [M(\text{HCOO})_2]^- \quad \beta_2 \\
M^{2+} + 3(\text{HCOO})^- & \rightleftharpoons [M(\text{HCOO})_3]^- \quad \beta_3 \\
M^{2+} + 4(\text{HCOO})^- & \rightleftharpoons [M(\text{HCOO})_4]^{2-} \quad \beta_4
\end{align*}
\]

where $M$ is Cd$^{2+}$ or Pb$^{2+}$ ions.
Measurements in mixed solvents:

At the outset, it may be said that the values of stability constants of complexes in mixed solvent media are the "practical" stability constants. This is because it is not possible to get an accurate estimation of $\gamma$ values i.e. activity coefficients in mixed solvents and hence most of the workers in the field of polarography report $\beta$ values simply as those obtained experimentally.

Studies in complexation, in the present work, were carried out in:

i) DMSO-water mixtures,

ii) ethanol-water mixtures,

iii) DMF-water mixture, and

iv) methanol-water mixture.

DMSO-water medium:

DMSO-water medium is used in the polarographic studies of metal complexes by some workers (45-47). DMSO, when mixed with water, evolves heat (48), the magnitude of which depends upon the composition and to a lesser extent upon the temperature of the mixture. The maximum evolution of heat takes
place at approximately 1:2 mole ratio of DMSO to water and this can be explained as follows:

In the solvent mixing process, water-water hydrogen bonds and DMSO-DMSO dipole bonds are broken and water-DMSO bonds are formed with a considerable evolution of heat. This is a clear indication of strength of the newly formed bonds. This is depicted as:

\[ \text{Cadmium(II)-thiourea system:} \]

A systematic survey of literature reveals that Cd(II)-thiourea system was studied polarographically in (i) iso-propylalcohol-water (49), (ii) acetone-water (50), (iii) ethanol-water (14,16), (iv) methanol-water (15) and (v) dioxane-water (51). No work seems to have been reported on the study of this system in DMSO-water and DMF-water media. It was, therefore, decided to study the system in a wide range of DMSO-water mixtures, i.e. 10%, 20%, 30% 40%, 50%, 60% and 70% (v/v) DMSO-water mixtures as well as (v/v) in 20%(v/v) DMF-water and 10%/EtOH-water mixtures.
The stability constants of the system studied in DMSO-water mixture are recorded in Table 4, the first horizontal column giving the volume fraction of DMSO, second, weight percentage of DMSO and third, \( \frac{1}{\varepsilon} \) and the rest giving the \( \beta \) values.

**Table 4.**

Stability constants of Cd(II)-thiourea complexes in DMSO-water mixtures.

\[ \nu = 0.1M(KNO_3) \quad \text{Temp.} = 25 \pm 0.5^\circ C \]

<table>
<thead>
<tr>
<th>Vol. fraction of DMSO, %</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of DMSO, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.99</td>
<td>21.98</td>
<td>32.97</td>
<td>43.96</td>
<td>54.95</td>
<td>65.94</td>
<td>76.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/\varepsilon x 10^3</td>
<td></td>
<td>12.73</td>
<td>12.81</td>
<td>12.90</td>
<td>13.00</td>
<td>13.40</td>
<td>13.70</td>
<td>14.10</td>
</tr>
<tr>
<td>\log \beta_1</td>
<td>1.30</td>
<td>1.60</td>
<td>1.65</td>
<td>1.77</td>
<td>1.69</td>
<td>1.69</td>
<td>2.04</td>
<td>2.17</td>
</tr>
<tr>
<td>\log \beta_2</td>
<td>1.77</td>
<td>2.14</td>
<td>2.49</td>
<td>2.30</td>
<td>2.39</td>
<td>2.39</td>
<td>2.47</td>
<td>2.69</td>
</tr>
<tr>
<td>\log \beta_3</td>
<td>1.60</td>
<td>1.47</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>2.30</td>
<td>2.65</td>
<td>3.30</td>
</tr>
<tr>
<td>\log \beta_4</td>
<td>3.53</td>
<td>3.38</td>
<td>3.68</td>
<td>3.85</td>
<td>3.81</td>
<td>3.69</td>
<td>3.41</td>
<td>3.47</td>
</tr>
</tbody>
</table>

The plots of \( \frac{1}{\varepsilon} \) vs \( \log \beta_i \) are shown in Figs. 5.1 and 5.2.

The observations for individual \( \beta \) values are as follows:

1) \( \beta_1 \) values showed an upward trend up to 30% DMSO-water mixtures, remained constant in the region of 40% to 50% DMSO, and increased further in mixtures with higher percentage of DMSO.
Fig. 5.1

$\text{Cd(II)-thiourea system in DMSO-water mixtures}$

Fig. 5.2

Fig. 5.3

$\text{Cd(II)-nicotinamide system in EtOH-water mixtures}$

Fig. 5.4

$\text{Cd(II)-thioacetamide system in EtOH-water mixtures}$
ii) $\beta_2$ values showed an increase up to 20%, a constant value in the region of 30 to 50% and then a continuous increase in the mixtures having DMSO up to 70%.

iii) $\beta_3$ values dropped slightly in the region of 10% and then showed an upward trend up to 20%, remaining constant thereafter up to 50% and then continuously increased up to 70% DMSO, and

iv) $\beta_4$ values initially dropped a little but increased in the region of 20 to 30% DMSO-water mixture, then again decreased in the region of 30 to 70% DMSO.

$\beta$ values of Cd(II)-TU system in DMSO-water mixtures do not obey linear relationship with $1/\varepsilon$. Such nonlinear relationship was also observed by Tsiplyakova et al. for this system in acetone-water medium (50).

The values of stability constants of Cd(II)-TU complexes in 20% (v/v) DMF-water and 10% (v/v) EtOH-water mixtures are given in Table II.

Ethanol-water medium:

Much work has been done on the stabilities of metal complexes in alcohol-water mixture in the domain of potentiometry, conductometry, and spectrophotometry but comparatively less in the field of polarography (52, 53).
Structure of alcohol-water mixture:

Water is a uniquely structured liquid in the sense that it has three dimensional ice-like framework. Franks and Ives (54) have shown that the addition of the first increments of other organic cosolvent to water leads, at first, not to a reduction of structuredness but actually to an increase in the degree of order of the system. The degree of structuredness must increase until it passes through a maximum. Beyond this composition, the highly ordered solvent structure begins to collapse and the system behaves like an ordinary binary system. Franks and Ives (54) have also reported the structural effects of an ion in water. According to them most ions have one or more shells of completely oriented solvent molecules immediately around them thus creating an order, but at a certain distance from the ion there is a region where the three dimensional structure collapses. One must, therefore, distinguish between the macroscopic dielectric constant of the medium and the dielectric constant of the layer between the metal ion and the ligand.

Relatively small and multivalent ions increase the viscosity of water and these are said to have a net structure making effect (55). Their high electric fields not only polarize, immobilize and electrostrict nearest-neighbour molecules (primary or short range hydration) but they also induce additional order beyond the first water layer (secondary or long range hydration).
The effect of primary solvation is to favour the transfer of ions from water to ethanol–water mixture or to make a negative contribution to free energy changes. Outside the first shell of the solvent molecules, the field of the ion may still be strong enough to cause dielectric saturation, that is to orient the solvent molecules with their negative ends pointing towards the ions. The secondary solvation contributes positively but the primary solvation contributes negatively resulting in the relatively negative values.

Alcohol–water mixtures have been extensively used in the studies of the influence of dielectric constant of the solvent ion, the equilibria and rates of reaction in which charge centres are produced or neutralized. It is evident that the formation of the alcohol–water mixture is a wholesale endothermic destruction of water–water hydrogen bonds, yet, the mixing occurs with evolution of heat and appreciable relative entropy loss. This would denote the establishment of order by the satisfaction of the attractive forces and this indication is reinforced because of the concomitant bond breaking and loss of order involved in the 'depolymerization' of water. It can thus be inferred that rather strong and well organised ethanol–water hydrogen bonds are formed. Since ethanol
is twice as likely to act as a proton acceptor than as a donor, statistically, and since the inductive effect of the alkyl group may promote the same tendency, it is probable that in this mixture "ethanol is more basic than water". In ethanol-water mixture, which is extensively hydrogen bonded, an ethanol molecule induces in a water molecule, adjacent to it and so on over a chain of water molecules, such charge displacements as would make these water molecules also more basic than those in pure water (56). Ethanol is slightly more basic than methanol, so in general, the effect of both when they are mixed with water are nearly the same.

The dielectric constant of the medium strongly affects the stability constants of metal complexes because of the fact that at least one of the constituents is charged and the other is either charged or is a dipole. Specific variation in relative strength of acids and bases, with changing solvents, should be a function of the charge, the radius of ion, and the dielectric constant of the medium. It is extremely difficult to find out separate contribution of individual constituents of mixed solvents, particularly, at higher percentages of organic solvents where it is not known to what extent metal ions and $\text{H}^+$ ions are solvated. An understanding of the influence of the medium on reactivity is, therefore, difficult even at a qualitative level.
It was, therefore, thought that some systems listed below could be investigated in the mixtures of varying proportions of ethanol and water:

1. Cadmium(II)-nicotinamide at $\mu = 1.0M$ (NaClO$_4$),
2. Cadmium(II)-thioacetamide at $\mu = 0.1M$ (KNO$_3$),
3. Cadmium(II)-2-mercaptoethanol at $\mu = 0.1M$ (KNO$_3$),
4. Cadmium(II)-2-mercaptoethanol at $\mu = 1.0M$ (NaClO$_4$),
5. Cadmium(II)-formate at $\mu = 2.0M$ (NaClO$_4$) and
6. Lead(II)-formate at $\mu = 2.0M$ (NaClO$_4$).

**Cadmium(II)-nicotinamide system:**

The system was examined in 10%, 20%, 40% and 50% (v/v) ethanol-water mixtures and in 20% (v/v) methanol-water mixture, with a view to study the effect of dielectric constant and specific chemical effect of the solvents on the complexation of nicotinamide with Cd(II) ion.

Formation of two weak complexes viz $[\text{Cd(NICO)}]^2^+$ and $[\text{Cd(NICO)}_2]^2^+$ was observed in the entire range of ethanol concentration (Table 5).

From the data of $\beta$ values at different percentages of ethanol-water mixtures given in Table 5, it could be concluded that $\beta_1$ and $\beta_2$ did not change measurably with an increase in the percentage of ethanol from 10% to 50%.
Table 5.
Stability constants of Cd(II)-nicotinamide complexes in ethanol-water mixtures.

\[ \mu = 1.0\text{M(NaClO}_4) \quad \text{Temp.} = 25\pm0.5^\circ\text{C} \]

<table>
<thead>
<tr>
<th>Vol. fraction of ethanol</th>
<th>%</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>50</th>
<th>MeOH 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of ethanol</td>
<td>%</td>
<td>7.85</td>
<td>15.70</td>
<td>31.40</td>
<td>39.25</td>
<td>15.83</td>
<td></td>
</tr>
<tr>
<td>(1/\xi \times 10^3)</td>
<td></td>
<td>12.73</td>
<td>13.40</td>
<td>14.20</td>
<td>16.20</td>
<td>17.40</td>
<td>14.30</td>
</tr>
<tr>
<td>(\log \beta_1)</td>
<td></td>
<td>0.68</td>
<td>0.68</td>
<td>0.68</td>
<td>0.68</td>
<td>0.68</td>
<td>0.77</td>
</tr>
<tr>
<td>(\log \beta_2)</td>
<td></td>
<td>1.00</td>
<td>1.25</td>
<td>1.31</td>
<td>1.39</td>
<td>1.32</td>
<td>1.36</td>
</tr>
</tbody>
</table>

It will be seen from the Fig.5.3 that (i) \(\log \beta_1 \) vs \(1/\xi\) is a straight line thus showing a constancy of stability value over the entire range of ethanol-water mixtures and (ii) in the case of \(\log \beta_2 \) vs \(1/\xi\) plot an initial increase is markedly shown near about 10% EtOH concentration and then the values become nearly constant over the entire remaining range.

The observations made above point out that, ethanol as a solvent, is not playing any prominent role in the reaction by which complexation takes place. This is obviously due to the fact that nicotinamide is a stronger base than ethanol.
The log stability constants of Cd(II)-nicotinamide complexes in 20% MeOH-water mixture are given in Table 5.

**Cadmium(II)-thioacetamide system:**

The system was investigated in (i) 10%, 20%, 30%, 40% and 50% (v/v) EtOH-water, (ii) 20% (v/v) MeOH-water, (iii) 20% (v/v) DMF-water and (iv) 20% (v/v) DMSO-water mixtures. The data of stability constants are given in Tables 6 and 7.

**Table 6**

Stability constants of Cd(II)-thioacetamide complexes in ethanol-water mixtures.

\[ \mu = 0.1 M (\text{KNO}_3) \quad \text{Temp.} = 25 \pm 0.5 \, ^\circ\text{C} \]

<table>
<thead>
<tr>
<th>Vol. fraction of ethanol (%)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of ethanol (%)</td>
<td>-</td>
<td>7.85</td>
<td>15.70</td>
<td>23.55</td>
<td>31.40</td>
<td>39.25</td>
</tr>
<tr>
<td>(1/\varepsilon \times 10^3)</td>
<td>12.73</td>
<td>13.40</td>
<td>14.20</td>
<td>15.60</td>
<td>16.20</td>
<td>17.40</td>
</tr>
<tr>
<td>(\log \beta_1)</td>
<td>-0.69</td>
<td>0.00</td>
<td>0.08</td>
<td>0.08</td>
<td>0.20</td>
<td>0.30</td>
</tr>
<tr>
<td>(\log \beta_2)</td>
<td>1.08</td>
<td>1.27</td>
<td>1.30</td>
<td>1.38</td>
<td>1.00</td>
<td>0.74</td>
</tr>
<tr>
<td>(\log \beta_3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.19</td>
<td>1.52</td>
</tr>
</tbody>
</table>
Table 7

Stability constants of Cd(II)-thioacetamide complexes in different organic solvents.

\( \mu = 0.1M(\text{KNO}_3) \) \hspace{1cm} \text{Temp.} = 25\pm0.5^\circ \text{C}

<table>
<thead>
<tr>
<th>Vol. fraction of organic solvent</th>
<th>20% MeOH</th>
<th>20% DMF</th>
<th>20% DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1/\varepsilon \times 10^3 )</td>
<td>14.20</td>
<td>13.52</td>
<td>12.90</td>
</tr>
<tr>
<td>( \log \beta_1 )</td>
<td>0.77</td>
<td>0.50</td>
<td>0.25</td>
</tr>
<tr>
<td>( \log \beta_2 )</td>
<td>0.69</td>
<td>1.00</td>
<td>1.16</td>
</tr>
<tr>
<td>( \log \beta_3 )</td>
<td>1.71</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

From Table 6, it can be seen that the existence of first two weak complexes viz. \([\text{Cd(TAA)}]^{2+}\) and \([\text{Cd(TAA)}_2]^{2+}\) was traced up to 30% (v/v) ethanol concentration. The number of complexes increased to three in 40% and 50% EtOH-water mixtures.

The plots of \( \log \beta_1 \) vs \( 1/\varepsilon \), shown in Fig. 5.4, reveal that (i) \( \beta_1 \) values continuously increase with an increase in ethanol concentration, (ii) \( \beta_2 \) values also increase up to 30% (v/v) ethanol, then register a continuous fall in 40% and 50% (v/v) ethanol-water mixtures.
The data of measurements, taken in 20% (v/v) of different organic solvents, given in Table 7, reveal that in 20% MeOH-water mixture 1:1, 1:2 and 1:3 complex species of Cd(II)-TAA existed while in 20% DMF-water and 20% DMSO-
water mixtures only 1:1 and 1:2 complex species were present.

Cadmium(II)-2-mercaptoethanol system:

The system was studied in 10%, 20%, 30% and 40%(v/v) ethanol-water mixtures at 0.1M(KNO₃) and 1.0M(NaClO₄) ionic strengths.

In all the mixed solvent mixtures, 1:1 and 1:2 complexes were observed at the ionic strengths maintained at 0.1M(KNO₃) and 1.0M(NaClO₄). The log values of the stability constants, at both the ionic strengths, are set out in Table 8 and represented graphically in Figs. 5.5 and 5.6.

Table 8

Stability constants of Cd(II)-2-mercaptoethanol complexes in ethanol-water mixtures.

<table>
<thead>
<tr>
<th>Vol. fraction of ethanol %</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of ethanol %</td>
<td>-</td>
<td>7.85</td>
<td>15.70</td>
<td>23.55</td>
<td>31.40</td>
</tr>
<tr>
<td>1/(\varepsilon) x 10³</td>
<td>12.73</td>
<td>13.40</td>
<td>14.20</td>
<td>15.60</td>
<td>16.20</td>
</tr>
</tbody>
</table>

\[ \mu = 0.1\text{M}(\text{KNO}_3) \]

\[ \log \beta_1 \]

0.00
0.47
0.54
0.47
0.90

\[ \log \beta_2 \]

1.36
1.47
1.62
1.83
2.00

\[ \mu = 1.0\text{M}(\text{NaClO}_4) \]

\[ \log \beta_1 \]

1.17
0.60
0.92
0.97
1.04

\[ \log \beta_2 \]

-1.36
1.36
1.70
1.95
Cd(II)-2 mercaptoethanol system in EtOH-water mixtures

Fig. 5.5 \( \frac{1}{\xi} \) at \( \mu = 0.1 \text{M}(\text{KNO}_3) \)

Fig. 5.6 \( \frac{1}{\xi} \) at \( \mu = 1.0 \text{M}(\text{NaClO}_4) \)

Cd(II)-formate system in EtOH-water mixtures

Fig. 5.7

Fig. 5.8
It is seen from the data recorded in Table 8 and from Figs. 5.5 and 5.6 that:

a) at $\mu = 0.1M(KNO_3)$:

(i) $[\text{Cd(MEL)}]^{2+}$ is absent in aqueous medium but exists in all alcohol-water mixtures. $\log \beta_1$ continuously increased with an increase in $1/\epsilon$ except a value in 30% ethanol (Fig. 5.5) and (ii) $[\text{Cd(MEL)}_2]^{2+}$ species are found in aqueous as well as in aqueous-nonaqueous media. $\log \beta_2$ values are found to bear a linear relationship with $1/\epsilon$ (Fig. 5.5).

b) at $\mu = 1.0M(NaClO_4)$:

(i) There was a decrease in $\log \beta_1$ value on adding the first increment of ethanol. However, the values then continuously increased with an increase in $1/\epsilon$ except the one corresponding to $1/\epsilon = 15.60 \times 10^{-3}$, and (ii) 1:2 complex is absent in aqueous medium but appeared in mixed solvent media. $\log \beta_2$ increased with increase in $1/\epsilon$ (Fig. 5.6).

**Formate systems:**

The complexation of formate with Cd(II) and Pb(II) has been studied in 10%, 20%, 30%, 40% and 50% (v/v) ethanol-water mixtures and also in 20% (v/v) DMF-water mixture at 2.0M(NaClO_4) ionic strength.
Cadmium(II)-formate system:

The stability constant data are given in Table 9.

Table 9.

Stability constants of Cd(II)-formate complexes in ethanol–water mixtures.

\( \mu = 2.0 \text{M}(\text{NaClO}_4) \quad \text{Temp.} = 25 \pm 0.5 \degree \text{C} \)

<table>
<thead>
<tr>
<th>Vol. fraction of ethanol</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of ethanol %</td>
<td>-</td>
<td>7.85</td>
<td>15.70</td>
<td>23.55</td>
<td>31.40</td>
<td>39.25</td>
</tr>
<tr>
<td>( 1/\epsilon \times 10^3 )</td>
<td>12.73</td>
<td>13.40</td>
<td>14.20</td>
<td>15.60</td>
<td>16.20</td>
<td>17.40</td>
</tr>
<tr>
<td>log ( \beta_1 )</td>
<td>0.54</td>
<td>0.69</td>
<td>1.30</td>
<td>1.39</td>
<td>1.54</td>
<td>1.90</td>
</tr>
<tr>
<td>log ( \beta_2 )</td>
<td>1.47</td>
<td>1.66</td>
<td>1.90</td>
<td>2.04</td>
<td>2.39</td>
<td>2.60</td>
</tr>
<tr>
<td>log ( \beta_3 )</td>
<td>0.84</td>
<td>1.57</td>
<td>1.68</td>
<td>1.60</td>
<td>2.38</td>
<td>3.30</td>
</tr>
<tr>
<td>log ( \beta_4 )</td>
<td>1.20</td>
<td>1.43</td>
<td>2.06</td>
<td>2.59</td>
<td>2.84</td>
<td>3.34</td>
</tr>
</tbody>
</table>

It will be seen from the above data that, notwithstanding the percentage of ethanol in the solvent mixture, the species of formate complexes observed always remained four.

The plots of log \( \beta_i \) vs \( 1/\epsilon \) (Figs. 5.7 and 5.8) reveal that (i) in the log \( \beta_1 \) vs \( 1/\epsilon \) plot, a straight line relationship exists with the sole exception of \( \beta_1 \) value corresponding
to \( \frac{1}{\epsilon} = 14.20 \times 10^{-3} \), (ii) a linear relationship exists between \( \log \beta_2 \) and \( \frac{1}{\epsilon} \), (iii) \( \beta_3 \) values increased over the entire range of alcohol-water mixtures with a trend shown in Fig. 5.3, and (iv) in the plot of \( \log \beta_4 \) vs \( \frac{1}{\epsilon} \), all the points fall approximately on a straight line.

In 20% (v/v) DMF-water mixture, four complexes were detected with stability constants as given below:

\[
\log \beta_1 = 1.39, \quad \log \beta_2 = 1.47, \quad \log \beta_3 = 1.47, \quad \text{and} \quad \log \beta_4 = 1.91.
\]

**Lead(II)-formate system:**

As in the case of Cd(II)-formate system, Pb(II) too formed mono-, bis-, tris- and tetrakis-formate complexes in all the ethanol-water mixtures (Table 10).

The data of Table 10 are represented in the plots of \( \log \beta_i \) vs \( \frac{1}{\epsilon} \) (Figs. 5.9 and 5.10). A linear relationship was established for \( \beta_1, \beta_2 \) and \( \beta_4 \). \( \beta_3 \) initially increased in 10% EtOH-water mixture, remained constant thereafter up to 30%, and then showed an upward trend in 40% and 50% ethanol.
Fig. 5.9

Fig. 5.10  Pb(II)-formate system in EtOH-water mixtures
Table 10
Stability constants of Pb(II)-formate complexes in ethanol-water mixtures.

\[ \mu = 2.0 \text{M (NaClO}_4) \] \quad \text{Temp} = 25 \pm 0.5^\circ \text{C} 

<table>
<thead>
<tr>
<th>Vol. fraction of ethanol</th>
<th>% 0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of ethanol</td>
<td>%</td>
<td>7.85</td>
<td>15.70</td>
<td>23.55</td>
<td>31.40</td>
<td>39.25</td>
</tr>
<tr>
<td>(1/\varepsilon \times 10^3)</td>
<td></td>
<td>12.73</td>
<td>13.40</td>
<td>14.20</td>
<td>15.60</td>
<td>16.20</td>
</tr>
<tr>
<td>(\log \beta_1)</td>
<td></td>
<td>1.30</td>
<td>1.60</td>
<td>1.69</td>
<td>2.00</td>
<td>2.30</td>
</tr>
<tr>
<td>(\log \beta_2)</td>
<td></td>
<td>2.09</td>
<td>2.33</td>
<td>2.71</td>
<td>3.16</td>
<td>3.41</td>
</tr>
<tr>
<td>(\log \beta_3)</td>
<td></td>
<td>1.54</td>
<td>2.00</td>
<td>2.06</td>
<td>2.00</td>
<td>3.08</td>
</tr>
<tr>
<td>(\log \beta_4)</td>
<td></td>
<td>1.46</td>
<td>1.84</td>
<td>2.04</td>
<td>2.89</td>
<td>3.19</td>
</tr>
</tbody>
</table>

The values of the stability constants of four complexes present in 20% (v/v) DMF-water mixture: \(\log \beta_1 = 1.30\), \(\log \beta_2 = 2.17\), \(\log \beta_3 = 1.25\) and \(\log \beta_4 = 2.02\).

Stability constants of metal complexes at different aqou-organic solvent mixtures with identical dielectric constant:

The factor that affects the complexation reaction, in addition to dielectric constant of the medium in which the complexation takes place, is the specific chemical role of the solvent. It has been reported that the stabilities of
Cd(II)-thiocyanate complexes in DMF-water mixture and ethanol-water mixture, with identical dielectric constant, are different (16). This was attributed to the different specific chemical role of the two organic solvents (16).

To test the specificity of the chemical role of a solvent, it was necessary to keep the other factor, namely, dielectric constant of the medium constant. The systems Cd(II)-TU, Cd(II)-NICO, Cd(II)-TAA, Cd(II)-formate and Pb(II)-formate were, therefore, investigated in solvent mixtures of DMF-water, ethanol-water, methanol-water and DMSO-water. These are discussed below:

**Cadmium(II)-thiourea system:**

The system was investigated in 20% DMF-water and in nearly 10% ethanol-water mixtures having identical dielectric constants. The system was mainly studied in varying percentages of DMSO-water mixtures (Table 4). From the plots of \( \log \beta_i \) vs \( 1/\epsilon \) (Figs. 5.1 and 5.2) for DMSO-water mixtures, the values of \( \log \beta_1 \), \( \log \beta_2 \), \( \log \beta_3 \) and \( \log \beta_4 \) were obtained at \( 1/\epsilon = 13.50 \times 10^{-3} \) and are given in Table 11. These will be the stability constants in DMSO-water mixtures having the same dielectric constant \( (1/\epsilon = 13.50 \times 10^{-3}) \) as that of 20% DMF-water and 10% EtOH-water mixtures (Table 11).
Table 11.

<table>
<thead>
<tr>
<th>log stability constants</th>
<th>in DMSO-water mixture having $1/\varepsilon = 13.50 \times 10^{-3}$</th>
<th>in 20% DMF-water mixture having $1/\varepsilon = 13.52 \times 10^{-3}$</th>
<th>in 10% EtOH-water mixture having $1/\varepsilon = 13.40 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>1.70</td>
<td>1.69</td>
<td>1.60</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>2.35</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>2.35</td>
<td>2.17</td>
<td>2.00</td>
</tr>
<tr>
<td>$\beta_4$</td>
<td>3.80</td>
<td>3.83</td>
<td>3.65</td>
</tr>
</tbody>
</table>

It is seen from Table 11 that except $\beta_4$, all values in DMSO-water mixture are higher than those in DMF-water mixture. The difference in specific chemical effect of two solvents, despite their identical dielectric constants, is evidently responsible for observed discrepancy. It was observed that free energy of formation of the proton transfer complex between p-nitro phenol and n-butyl amine is $-7.5$ K.cal/mole in DMSO and $-3.9$ K.cal/mole in DMF (57). The $S=O$ group in DMSO is much better proton acceptor than the nitrogen of the DMF. The values in EtOH-water mixture are lower than those in both DMF-water and DMSO-water mixtures. DMF has higher $pK$ and a different structure than ethanol. The discrepancy is observed between $\beta$ values in ethanol-water and DMF-water mixtures. Ethanol can get
hydrogen bonded with thiourea while DMF cannot. The acidities of substituted pyridinium ions and substituted phenols have been studied in DMF and in methanol which have nearly same dielectric constants 36.7 and 32.6 respectively at 25°C (58). The electrostatic force should, therefore, be identical. The observation that picolinium ions are more acidic than phenol and carboxylic acids in DMF than in methanol has been attributed to the stabilization of anionic solutes by hydrogen bonding in methanol. The basicity of ethanol is slightly different than that of methanol and so in general the effect of both, in their water mixture, is expected to be nearly the same.

Cadmium(II)-nicotinamide system:

The values of stability constants of Cd(II)-nicotinamide complexes in 20% methanol-water mixture with $1/\epsilon = 14.20 \times 10^{-3}$, were determined (Table 5). The log $\beta_i$ values corresponding to $1/\epsilon = 14.20 \times 10^{-3}$ for ethanol-water mixture were obtained from the plots of log $\beta_i$ vs $1/\epsilon$ (Fig.5.3). The comparative data are given in Table 12.

<table>
<thead>
<tr>
<th>log stability constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>in 20% methanol-water mixture having $1/\epsilon = 14.20 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\beta_1 = 0.77$</td>
</tr>
<tr>
<td>$\beta_2 = 1.36$</td>
</tr>
</tbody>
</table>
Cadmium(II)-thioacetamide system:

The $1/\varepsilon$ values for 20% methanol-water, 20% DMF-water and 20% DMSO-water mixtures and stability constants of Cd(II)-thioacetamide complexes in these media are listed in Table 7.

The $\beta$ values in ethanol-water mixture, corresponding to $1/\varepsilon = 14.20 \times 10^{-3}$, $13.50 \times 10^{-3}$ and $12.90 \times 10^{-3}$, were read off from the plots of log $\beta_i$ vs $1/\varepsilon$ (Fig. 5.4) and are tabulated in Table 13.

### Table 13.

<table>
<thead>
<tr>
<th>medium</th>
<th>log stability constants</th>
<th>ethanol-water medium ($\beta_i$ obtained from Fig. 5.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% MeOH-water mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>having $1/\varepsilon = 14.20 \times 10^{-3}$</td>
<td>$\beta_1 = 0.77$</td>
<td>$1/\varepsilon = 14.20 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\beta_2 = 0.69$</td>
<td></td>
</tr>
<tr>
<td>20% DMF-water mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>having $1/\varepsilon = 13.52 \times 10^{-3}$</td>
<td>$\beta_1 = 0.50$</td>
<td>$1/\varepsilon = 13.50 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\beta_2 = 1.00$</td>
<td></td>
</tr>
<tr>
<td>20% DMSO-water mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>having $1/\varepsilon = 12.90 \times 10^{-3}$</td>
<td>$\beta_1 = 0.25$</td>
<td>$1/\varepsilon = 12.90 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\beta_2 = 1.16$</td>
<td></td>
</tr>
</tbody>
</table>
Cadmium(II)-formate and lead(II)-formate systems:

Complexation of formate with Cd(II) and Pb(II) was examined in 20% DMF-water mixture. In the first column of the Table 14, are given the $\beta$ values in ethanol-water medium obtained from the plots of $\log \beta_i$ vs $1/\xi$ (Figs. 5.7 - 5.10) following the procedure as given before.

Table 14.

<table>
<thead>
<tr>
<th>log stability constants</th>
<th>in ethanol-water mixture having $1/\xi = 13.50 \times 10^{-3}$ (obtained from Figs. 5.7 - 5.10)</th>
<th>in 20% DMF-water mixture having $1/\xi = 13.52 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cd(II)-formate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_1 = 0.72$</td>
<td>$\beta_1 = 1.39$</td>
<td></td>
</tr>
<tr>
<td>$\beta_2 = 1.65$</td>
<td>$\beta_2 = 1.47$</td>
<td></td>
</tr>
<tr>
<td>$\beta_3 = 1.55$</td>
<td>$\beta_3 = 1.47$</td>
<td></td>
</tr>
<tr>
<td>$\beta_4 = 1.55$</td>
<td>$\beta_4 = 1.91$</td>
<td></td>
</tr>
<tr>
<td><strong>Pb(II)-formate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_1 = 1.55$</td>
<td>$\beta_1 = 1.30$</td>
<td></td>
</tr>
<tr>
<td>$\beta_2 = 2.35$</td>
<td>$\beta_2 = 2.17$</td>
<td></td>
</tr>
<tr>
<td>$\beta_3 = 2.00$</td>
<td>$\beta_3 = 1.25$</td>
<td></td>
</tr>
<tr>
<td>$\beta_4 = 1.85$</td>
<td>$\beta_4 = 2.02$</td>
<td></td>
</tr>
</tbody>
</table>
A close scrutiny of Tables 11, 12, 13 and 14 reveals that the stabilities of metal complexes in different solvent mixtures with the same dielectric constant do not tally with each other. The difference in specific chemical role of different solvents, inspite of identical dielectric constants of their mixture, is probably responsible for the observed discrepancies.

**Van Panthaleon Van Eck equation**

It has been reported (59) that the stepwise constants decrease in a fairly regular manner with increasing coordination number and many systems obey the empirical relation of Van Panthaleon Van Eck (59) viz.

\[ \log K_N = \log K_1 - 2 \gamma (N-1) \]

in which \( \gamma \) is an empirical parameter for each system and \( N \) is the coordination number. This relation was found to hold good for systems in which changes in stereochemistry, in \( \pi \)-bonding, and in the ground state of the central metal ion did not occur. The equation was tested for the systems studied in the present investigation. The stepwise stability constants (\( K \)) were calculated from the overall stability constants (\( \beta \)) using the expression:

\[ \log \beta_i = \log K_1 + \log K_2 + \ldots + \log K_i \]
Cadmium(II)-thiourea system in DMSO-water and 20% DMF-water mixtures.

The plots of log $K_N$ vs $(N-1)$, (Fig. 5.11) show that the linear relationship is not followed by Cd(II)-thiourea complexes but instead large deviations are observed in aqueous as well as in DMSO-water and 20% DMF-water mixtures.

One of the causes for deviation in Van Panhaleon Van Eck equation may be the $\pi$-bond formation between the metal and ligand. A more regular series of $K$ values, without any deviation, would be expected with metal ions with full d orbitals under the valency shell. Zinc(II) and cadmium(II) complexes are normally expected to follow the empirical relationship. The absence of such relationship may be traced to $\pi$-bonding due to the transfer of $\pi$-electron density from the d orbitals of the metal to the ligand.

Cd(II)-formate and Pb(II)-formate systems in EtOH-water and 20% DMF-water mixtures:

Cd(II) and Pb(II) formate complexes in aqueous and in aqueo-nonaqueous media too do not strictly obey linear relationship. The haphazard manner in which the points are situated (Figs. 5.12 and 5.13) indicates the $\pi$-bonding tendency. A similar, but not identical, observation was made by Palaskar (60) and Dhuley (16) in their studies of Cu(II)-phthalate and Cd(II)-thiocyanate systems respectively where they report increased $\pi$-bonding with decreased dielectric properties of the medium.
Fig. 5.11  Cd(II)-thiourea system
Fig. 5.12  (d (1)) - formate system
Fig. 5.13 Pb(II)–formate system
Part - III

Indirect polarographic determination of stability constants.

The stability constants of the metal complexes of the following systems were determined by employing the method of Ringbom and Eriksson (61,62).

1. Zn(II)-nicotinamide,
2. Co(II)-nicotinamide, and
3. Co(II)-thioacetamide.

All these systems have been studied in aqueous medium at 0.5M(KNO₃) ionic strength and at 25±0.5°C, the experimental details for which have been described in Chapter -IV.

The stabilities of these systems were evaluated by Rossotti and Rossotti plots. The essential condition for Rossotti plots was that slope of $\beta_{i-1}$ plots should tally with the intercept for $\beta_i$ plots (equations 4.5 - 4.9, Chapter - IV). The values of stability constants obtained from such plots showed divergence from the Rossotti condition unless the prescribed range values of $n$ (Table I, Chapter-II) were utilized to solve the Rossotti equations.

Zn(II)-nicotinamide system:

Five complexes were observed, with their stability constants as under:

$\beta_1 = 4.0$, $\beta_2 = 60.0$, $\beta_3 = 70.0$, $\beta_4 = 320.0$ and slope = 270.0 = $\beta_5$

(approx.). The $\beta$ values exhibited the trend: $\beta_1 < \beta_2 < \beta_3 < \beta_4 < \beta_5$. 
Co(II)-nicotinamide system:

It was found that four complex species of \([\text{Co(NICO)}]^2+\), \([\text{Co(NICO)}_2]^2+\), \([\text{Co(NICO)}_3]^2+\) and \([\text{Co(NICO)}_4]^2+\) were observed to have the stability constants as evaluated by Rossotti plots as follows:

\[
\beta_1 = 13.0, \quad \beta_2 = 50.0, \quad \beta_3 = 170.0 \text{ and slope } = 418.0 = \beta_4 \text{ (approx.)}
\]

Co(II)-thioacetamide system:

In the study of determination of stability constants of Co(II)-TAA complexes by 'indicator ion method', using Cd(II) as the indicator ion, the plot of \(\bar{n}\) vs \([L]\) (where \([L]\) is free ligand concentration of TAA) indicated the presence of two complexes of Co(II)-TAA. The \(\beta\) values for these complexes are:

\[
\beta_1 = 7.2 \quad \text{and slope } = 4.8 = \beta_2 \text{ (approx.)}
\]

A good agreement between experimental and calculated \(\bar{n}\) values was observed for all systems given above. This led to ascertain the accuracy of \(\beta\) values obtained by Rossotti plots.
REFERENCES


