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PART III
CHAPTER 1
NON-AQUEOUS TITRIMETRY
SECTION A
INTRODUCTION

Heterocyclic compounds have acquired immense industrial importance due to versatility in their use. Particularly, they are widely used in pharmaceutical industry for the manufacture of a large variety of common drugs such as antipyretics, analgesics, antimalerials, anti-inflammatory, sedatives, tranquillizers, anaesthetics, antidiabetics, antifungal, antiviral, antiulcer, hypnotics etc. Due to varied applications, their structural, physicochemical, physiological and related studies have been undertaken in recent years.

Since the compounds reported in Part I and II of the thesis have got significance in pharmaceutical and analytical chemistry where they are used in micro or semimicro quantity, it was thought of interest to try some of the methods for their determination on semimicro scale. Since the compounds are insoluble in water, use of non-aqueous solvent became essential. Conant and Hall\(^1\) have reported determination of both acidic as well as basic compounds in non-aqueous solvent.

There are some problems with the use of non-aqueous solvents because of their following properties,

i. rapid evaporation of these solvents.

ii. the coefficient of expansion is generally more than water.
iii. solubility of carbondioxide is higher.
iv. viscosity and surface tension are low.
v. they possess low dielectric constant.
vi. presence of even traces of water interferes seriously in the results, and
vii. some of the non-aqueous solvents are highly corrosive and toxic; they are also very costly.

Therefore proper precautions must be taken during non-aqueous titrimetry.
The information on titrations in non-aqueous media is available in literature\textsuperscript{2-4} and should be consulted for experimental details. Inspite of these difficulties non aqueous titrimetry has acquired popularity because -
i. many compounds insoluble in water can be determined by using non-aqueous solvent in which they are fairly soluble.

ii. acidic or basic nature of the solute can be enhanced by selecting proper basic or acidic solvent respectively.

However, it should be noted that there is no specific rule for their choice. Hence the solvent has to be selected by trial and error method. Choice of titrant is also one of the important factors for reproducibility and accuracy of the results in non-aqueous solvents. In the determination of very weak acids, use of basic solvents and a very strong basic titrant is made, while for very weak basic compounds, acidic solvent like acetic acid is recommended and very strong acidic titrant like perchloric acid is used. Recently, the use of non-aqueous solvents in the determination of both acidic as well as basic compounds has been investigated in detail\textsuperscript{5-11}.
Titrations in non-aqueous solvents are widely used in the analysis of tobacco for alkaloid content, determination of organic compounds, very weak acids and bases and their multicomponent mixtures of salts. The determination of very weakly acidic compounds using basic solvents and strong basic titrants like alc. KOH and tetra-n-butyl ammonium hydroxide has been carried out employing enthalpimetric, conductometric and potentiometric methods.

In petroleum products, the titration of hydrogen sulphide and mercaptans, either singly or in combination, is carried out in a 1:1 mixture of methanol-benzene with a methanolic solution of silver nitrate using silver calomel electrode system. There are several methods for the determination of acidic compounds which are used as drugs. The simplest method for the determination of the end point in non-aqueous titrimetry is 'Visual titration'. Agrawal has titrated about fifteen pharmaceutical compounds with tetra-n-butyl ammonium hydroxide using o-nitroaniline as indicator and methanol and DMF as solvents. Konupcik et al. have titrated ascorbic acid in chloroform with sodium methoxide using phenolphthalein indicator. Vaughan and Swithenbank have used acetone as a solvent for titrations of phenols. Greenhow and Spencer have used thermometric indicator like acrylonitrile or methyl acrylate for different solvents and have titrated barbiturates and other weak acids. The applications of thermometric titrations in non-aqueous media have also been reported.

The conductometric and high frequency titrations have been used for determination of pharmaceutical compounds. These methods have been discussed and reviewed by Kreshkov and co-workers. 2-Methoxy ethanol has been used by Schwartz and Barker as a solvent for conductometric titration of weak acids. Conductometric titrations in dimethyl sulphoxide medium for barbiturates and other
weak acids have been carried out by Lemahieu-Hode and Lemahien. The conductometric titrations of benzoic acid and alkaloid salts in dimethylsulphoxide medium using tetra-n-butyl ammonium hydroxide as a titrant have also been reported.

The potentiometric titrations in non-aqueous media are widely used for the determination of many pharmaceutical compounds. These have been reported by Blesova and co-workers. The most commonly used electrode system is of glass and calomel. Dimethylformamide has been used as a solvent for the determination of barbiturates, sulphonamides, phenols, and chalcone oxime. Acetone has been used as a solvent for the determination of saccharin, ascorbic acid, aspirin, paracetomol (4'-hydroxyacetamide) etc. using conductometric, enthalpimetric and potentiometric techniques.

In recent years, electrometric titrations in non-aqueous solvents have been widely used for the determination of organic acids and bases, alone or in mixtures. Some of the difficulties associated with alkalimetric titrations of dilute solutions of weak acids are removed, when weak acids are potentiometrically titrated with alkali employing glass-calomel electrodes. Wadhwa et al. have reported the determination of some organic acids by iodometric and acid-base potentiometric titrations in ethanol-water mixture. Similarly, many workers have reported the determination of acids in non-aqueous media.

Agrawal and Shukla have reported the determination of β-diketones and their derivatives by visual and potentiometric titrations in methanol using tetra-n-butyl ammonium hydroxide as a titrant. β-Diketones behave as weak acids and their pKₐ values lie between 6 to 9. For visual titrations crystal violet was used as
an indicator and it was reported that potentiometric titrations gave more precise and accurate results. Bork et al have determined ketones and mixture of ketones with aldehydes by quantitative oxolation of \( \text{NH}_2\text{OH.HCl} \) using 0.1 M pyridine in isopropanol as solvent. However, only small amount of ketones (5 to 20 mgs) was accurately determined. For larger amounts percentage errors were found to be appreciable. Vyas and Kharat have titrated saccharin in non-aqueous medium by enthalpimetric, conductometric and potentiometric methods. Sabde has reported the determination of chalcone oximes by instrumental methods using acetone as a solvent and tetra-n-butyl ammonium hydroxide, potassium hydroxide and potassium tertiary butoxide in isopropyl alcohol as titrants. Alcoholic KOH was was found to be the most suitable titrant. The interaction of Fe(III) with various substituted chalcones has been investigated potentiometrically by Chincholkar and co-workers. Gholse and Kharat have reported the rapid extraction and spectrophotometric determination of vanadium with 2-hydroxy-4-methoxy-5-methyl chalcone oxime. Verma et al have carriedout potentiometric titrations of mercaptans in non-aqueous solvent. Tembhare et al have carriedout determination study of 2-hydroxy-5-methyldibenzoylmethane in nonaqueous medium by enthalpimetric, conductometric and potentiometric methods. It has been revealed that potentiometric method gives the best results. Raju et al have reported an accurate and convenient spectrophotometric titration method for the determination of microgram amounts of thiazine dyes employing iron (II) as a reductant in buffer medium in the presence of sodium oxalate. Tembhare et al have carriedout determination studies of hydroxy chalcones and diketones in non-aqueous media by enthalpimetric, conductometric and potentiometric methods and reported that alcoholic KOH gave more accurate results than tetra-n-butyl ammonium hydroxide. Babu K. Suresh et al has reported titrimetric determination of reductants like ascorbic acid in \( \text{H}_3\text{PO}_4 \) medium, KI and hydroquinone with Mn(IV) using sodium diphenyl sulfonate as an indicator.
Bhattacharyya et al. have described an electrothermal atomic absorption spectrometric method for the determination of manganese with dissolved monothioxo-β-diketone as chelating ion exchanger.

**PRESENT WORK**

The compounds like chalcones, β-diketones, isoxazolines and pyrazolines have acquired very much industrial importance due to variety of their applications, some of these compounds have also been used as analytical reagents. However, from the literature survey, it appears that much less work has been done on their determination in non-aqueous medium by instrumental methods. It was therefore thought interesting to carry out the determination studies of some of the newly synthesised compounds by enthalpimetric, conductometric and potentiometric titration methods in nonaqueous medium. The present work describes the determination of newly synthesised chalcone, β-diketone, isoxazoline and pyrazoline by above mentioned methods in non-aqueous medium.

The following compounds were selected for the determination study.

1. 2'-Hydroxy-5'-chloro-4-dimethylamino chalcone (HCDMAC) (Mol. wt. 301.5).
2. 1-(2-Hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanedione (HCPPPDP) (Mol. wt. 274.5).
3. 3-(2-Hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl)-Δ²-pyrazoline (HCPDMAPP) (Mol. wt. 315.5).
4. 3-(2-Hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl) isoxazoline (HCPDMAPI) (Mol. wt. 316.5).

The structural details of these compounds have been discussed in Part I of the thesis.
Experimental

Chemicals:

In the present work, determination of the compounds was carried out by three different methods viz. potentiometry, conductometry and enthalpimetry in acetone. Alcoholic KOH was used as a titrant. All the chemicals used were of A.R. grade. Following solutions were prepared for the titrations:

i. **Benzoic acid solution**:

0.1 M benzoic acid solution was prepared by dissolving accurately weighed 1.22 gms of dried benzoic acid in 100 ml of purified acetone. This solution was used for standardisation of basic titrant by different methods.

ii. **Potassium hydroxide solution (titrant)**:

About 0.58 gm of solid potassium hydroxide was dissolved in 100 ml of anhydrous isopropyl alcohol. The solution was kept overnight and filtered through sintered glass just before use. It was standardised with benzoic acid solution.

iii-vi. **Solutions of compounds (titrands)**:

Stock solutions of compounds (containing HCDMAC, 3.01 mg/ml, HCPPPD, 2.75 mg/ml, HCPDMAPI, 3.17 mg/ml and HCPDMAPP, 3.16 mg/ml) were prepared by dissolving requisite quantity in 50 ml of solvent (acetone). Different volumes of these solutions were diluted to 25 ml with acetone to get the solutions of different concentrations and titrated separately with alc. KOH.
Method:

i. Potentiometric titrations:

Direct reading digital potentiometer (Equip-Tronics model EQ-601) was employed for potentiometric titrations. Glass electrode gives reduced response to hydrogen ions due to dehydration of the glass membrane and is not therefore suitable in such titrations. Sabde and Kharat\(^6\) have reported the use of aluminium electrode as an indicator electrode. Greenhow and Al-Mudarris\(^6\) after studying various metal and metalloid electrodes reported that aluminium electrode was most suitable for potentiometric titrations of weak acids. Roberts and Fenwick\(^6\) have used antimony/antimony oxide indicator electrode and found reproducible potentials and correct end points. Therefore, in the present work also antimony and glass were chosen as indicator and reference electrodes respectively. It was found that the above electrode system gave better results. The electrode reaction maybe given as,

\[
\text{Sb}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Sb} + 3\text{H}_2\text{O}
\]

A review of theory and procedures of many non-aqueous titrations have been carried out by Fritz and Lisicky\(^6\) and also by other workers\(^6\).

Required volume of the solution of the compound was diluted to 25 ml and the electrodes were dipped in it keeping minimum distance between them (0.5 to 1.0 cm). The titrant was added in lots of 0.1 ml and potential developed across the two electrodes was measured after each addition. The solution was stirred by a magnetic stirrer and some time interval was allowed so as to get the potential stabilised. At the end point 0.02 ml titrant was added and continued till there was no appreciable increase in emf value. The end point was determined from the graph drawn between potential developed and volume of titrant added. If necessary end point was determined from the graph of $\Delta E/\Delta V$ against $V$. 

ii. **Conductometric titrations**:

Direct reading digital (Century model CC-601) conductometer with glass conductivity cells (cell constant 1.13 cm⁻¹) was used for conductometric titrations. The cell was conditioned by keeping it in anhydrous acetone for twenty four hours before titration. These titrations were carried out at a constant temperature and the volume of titrand solution was always kept constant (25 ml). The titrant was added from a 5 ml microburette equipped with a guard tube containing solid KOH to prevent absorption of moisture and carbon dioxide.

Required volume of the solution of a compound was diluted to 25 ml with acetone and conductance of the solution was measured. Temperature of the solution was maintained constant and the titrant (Alc. KOH) was added in lots of 0.1 ml at a time. Solution was stirred by a magnetic stirrer and conductance was measured after each addition. Titration was continued till slight excess (about 0.5 ml) of the titrant was added. End point was determined from the graph drawn between conductance and volume of titrant added.

iii. **Enthalpimetric titrations**:

The apparatus employed by Greenhow and Spencer²¹ was modified and used for enthalpimetric titrations throughout the experiments. Titrations were carried out in a 50 ml beaker provided with a lose cover through which a thermometer (least count 0.1 °C) and the tip of a microburette were passed. The solution in the beaker was stirred by a magnetic stirrer. The microburette was provided with a guard tube containing solid potassium hydroxide to protect the titrant from atmospheric moisture and carbon dioxide. A slow and steady stream of dry nitrogen gas was bubbled through the contents of the beaker. Nitrogen was rendered free
from traces of moisture and carbon dioxide by passing it over solid potassium hydroxide.

A 0.01 M solution of a compound was prepared by dissolving appropriate quantity of given compound in 50 ml of acetone. Different volumes of this solution were pipetted out in 50 ml beaker. The volume was made up to 25 ml with solvent. The beaker was thermally insulated and the temperature of the solution was recorded. A slow stream of dry nitrogen gas, free from carbon dioxide, was bubbled through the solution to keep solution free from carbon dioxide. The titrant (aq. KOH) was continuously added at a rate of 0.5 ml per minute with constant stirring, the temperature was recorded for the addition of every 0.2 ml titrant. The rate of addition of titrant was made slow near the end point and temperature was recorded for every 0.2 ml addition. The addition of titrant was continued till about 0.2 to 0.4 ml excess of titrant was added. A graph was then plotted between temperature and volume of titrant added. The end point was determined from the graph by extrapolation. End point for standard benzoic acid and the titrant were determined in the same way. In thermometric titrations, sudden rise in temperature at the equivalence point is taken as an end point. Whenever acetone is used as a solvent for non-aqueous titrations, there is no need of adding another monomer as indicator. When a slight excess of basic titrant is added acetone undergoes dimerisation. Vaughan and Swithenbenk suggested a novel use of secondary temperature rise for determination of end point. This secondary polymerisation process is exothermic and produces a sharp increase in temperature. The reaction of acetone with a base proceeds in three stages as -

\[
\begin{align*}
\text{CH}_3\text{-CO-CH}_2 + \text{OH} & \rightleftharpoons \text{CH}_3\text{-CO-CH}_2^- + \text{H}_2\text{O} \\
\text{CH}_3\text{-CO-CH}_2 + \text{CH}_3\text{-CO-CH}_2 & \rightleftharpoons \text{CH}_3\text{-CO-CH}_2^- \cdot \text{C(OH)} \cdot \text{(CH}_3)_2 \\
\text{CH}_3\text{-CO-CH}_2^- \cdot \text{C(OH)} \cdot \text{(CH}_3)_2 + \text{H}_2 & \rightleftharpoons \text{CH}_3\text{-CO-CH}_2^- \cdot \text{C(OH)} \cdot \text{(CH}_3)_2 + \text{OH}
\end{align*}
\]
In the present work acetone was found to be the most suitable solvent and therefore all the titrations were performed in it.

Discussion of the Results:

Determination of compounds:

This part deals with the discussion of the results, obtained in the quantitative determination of compounds by potentiometry, conductometry and enthalpimetric methods using anhydrous acetone as a solvent and alcoholic KOH solution as a titrant. Accuracy of every method has been evaluated in order to know the most suitable method for such type of estimations.

i. Potentiometric titrations:

2.0 ml solution of given compound was diluted to 25 ml with acetone and potentiometric titrations were carried out employing antimony rod as indicator and glass as reference electrode. Alcoholic KOH was used as a titrant and the end point was determined graphically (Fig. 1). The procedure was repeated for different concentrations of compounds. The results are given in Table 1.1 to 1.4.

ii. Conductometric titrations:

2.0 ml solution of a compound was diluted to 25 ml with acetone and conductometric titrations were carried out employing glass conductivity cell. Alcoholic KOH was used as a titrant and the end point was determined from a graph drawn between conductance and volume of titrant added. The similar procedure was repeated for different concentrations of compounds (Fig. 2). The results are shown in Table 1.1 to 1.4.
FIG. 1: Potentiometric titrations of compounds

A - HCDMAC
B - HCPPPD
C - HCPDMAPP
D - HCPDMAPI
FIG. 2: Conductometric titrations of compounds

A - HCDMAC
B - HCPPPD
C - HCPDMAPP
D - HCPDMAPI
iii. Enthalpimetric titrations

From the stock solution of a compound, 2.0 ml solution was pipetted out in a beaker and volume was made up to 25 ml with solvent, acetone. The titrant was added continuously at a rate of 0.5 ml per minute with constant stirring. The temperature was recorded for the addition of every 0.2 ml titrant. The addition of titrant was continued till about 0.2 ml to 0.3 ml excess of titrant was added. A graph was then plotted between temperature and volume of titrant and the end point was determined by extrapolation (Fig. 3). The similar procedure was repeated for different concentrations of compounds. The results are given in Table 1.1 to 1.4.

Table 1.1: Determination of HCDMAC

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<thead>
<tr>
<th>Weight titrated (mg)</th>
<th>Potentiometry</th>
<th>Conductometry</th>
<th>Enthalpimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>weight found</td>
<td>% Error</td>
<td>weight found</td>
</tr>
<tr>
<td>3.01</td>
<td>2.99</td>
<td>-0.66</td>
<td>2.98</td>
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<tr>
<td>6.02</td>
<td>6.00</td>
<td>-0.33</td>
<td>6.08</td>
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<tr>
<td>9.03</td>
<td>9.05</td>
<td>+0.22</td>
<td>8.90</td>
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<tr>
<td>12.04</td>
<td>12.01</td>
<td>-0.25</td>
<td>11.79</td>
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<td>15.05</td>
<td>14.83</td>
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<td>14.72</td>
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<td>18.06</td>
<td>17.79</td>
<td>-1.50</td>
<td>17.52</td>
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</table>
FIG. 3: Enthalpimetric titrations of compounds

A - HCDMAC
B - HCPPPD
C - HCPDMAPP
D - HCPDMAPI
Table 1.2: Determination of HCPPPD

<table>
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<th>Weight titrated (mg)</th>
<th>Potentiometry weight found</th>
<th>% Error</th>
<th>Conductometry weight found</th>
<th>% Error</th>
<th>Enthalpimetry weight found</th>
<th>% Error</th>
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<td>2.75</td>
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Table 1.3: Determination of HCPDMAPP

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<th>% Error</th>
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<th>% Error</th>
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Table 1.4. Determination of HCPDMAPI

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<th>% Error</th>
<th>Enthalpimetry weight found</th>
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</table>

From the data shown in the Tables 1.1 to 1.4, it follows that out of these three methods, potentiometric titrations give the most accurate results. It could accurately estimate the amount of compounds from 2.75 mg to 22.00 mg with little error. The detection of end point was comparatively easier due to sharp change in the potential values during potentiometric titrations. It has also been observed that the best results are obtained at lower concentrations of compounds. At higher concentrations percent error became appreciable. Similarly, the percent error appeared to have increased with increase in the molecular weights of the compounds. The amounts of HCDMAC and HCPPPD could be estimated accurately in case of most of the samples in the concentration range of 2.75 mg to 18.06 mg with percent error less than ±2%. For HCPDMAPP and HCPDMAPI, accurate results were obtained in the concentration range of 3 mg to 13 mg and above this range percent error seemed to have increased appreciably.
Conductometry also gave reasonably good results, particularly at lower concentrations. At higher concentrations percent error seemed to be quite higher. Thus, the amounts of HCDMAC and HCPPPD could be estimated satisfactorily in the concentration range of 2.75 mg to 16.00 mg involving percent error less than \( \pm 2.5\% \). However above this range, percent error increased considerably. For HCPDMAPP and HCPDMAPI, satisfactory results were obtained for a limited concentration range from 3 mg to 12.64 mg and above this range percent error was more than \( \pm 2.5\% \).

Enthalpimetry was found to be the most easy method for nonaqueous titrations. It is easier to perform and record the observations. However, difficulty arises as regards location of correct end point. The end point is indicated by sudden break in the curve accompanied by sharp rise in temperature. Therefore the end points were obtained by extrapolation of straight curves. Results obtained from enthalpimetric titrations show that the method works better at lower concentrations and percent error increases considerably at higher concentrations. For HCDMAC and HCPPPD, this method gave reasonably good results in the concentration range of 2 mg to 15 mg involving percent error lesser than \( \pm 3\% \). However in the cases of HCPDMAPP and HCPDMAPI, the concentration range of 3 mg to 9.5 mg gave satisfactory results with percent error lesser than \( \pm 3\% \).

Thus, it can be concluded that potentiometry gives the best results amongst all the three methods. The results obtained by this method, show more accuracy with percent error remaining below \( \pm 3.52\% \) for all the samples of the compounds involving concentration range from 2.75 mg to 22.20 mg. Therefore, this method can be safely employed in the quantitative estimation of compounds on micro scale where conventional methods do not give desired results.
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39. Idem ibid, 52(1980), 151R.
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CHAPTER 2
THERMAL ANALYSIS OF COMPOUNDS

SECTION A
INTRODUCTION

The thermal methods of analysis can be defined as the experimental methods for characterising a system (element or compound) by measuring changes in physicochemical properties as a function of increasing temperature with time. Thermal analysis includes a group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme. Some of the common thermal analysis techniques are Thermogravimetry (TG), Derivative Thermogravimetry (DTG), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Dynamic Refractance Spectroscopy (DRC), Evolved Gas Detection (EGD), Thermomechanical Analysis or Dilatometry (TMA), Emonation Thermal Analysis (ETA) etc.

Since the past few years, the methods of thermal analysis have been widely accepted in analytical chemistry\(^1-3\). Also the flash vacuum pyrolysis has played an increasingly important role in preparative organic chemistry\(^4\). Thermogravimetric analysis either alone or combined with differential thermal analysis has been the chief diagnostic tool used in the study of the thermal decomposition of organic compounds.

The thermal degradation study of organic compounds like chalcones, \(\beta\)-diketones and pyrazolines which are widely used as ligands in metal complexes and also employed for medical purpose has become a subject of active interest.
Systematic study of the thermal behaviour of these compounds in vacuum or in an inert atmosphere gives information about the nature of the degradation products produced at various temperatures. Wendtandt has presented a relationship between thermal stability of metal chelates and structure of chelating agents. Duval has made a comprehensive compilation of the use of thermogravimetry. According to Nikolaev et al. water eliminated below 150°C can be considered as the crystal water, and that eliminated above 150°C may be due to its co-ordination to the metal atom present in chelates. Bhave and Kharat have studied the thermal properties of metal complexes of some chalcone oximes, isodithiobiurets etc. and found that decomposition of the complexes took place in a single step and suggested the order of thermal stability of these complexes. Huff et al. have reported the thermolysis highly halogenated Δ²-pyrazolines. Their pyrolysis gave cyclopropanes and rearranged olefins. Monozova et al. have studied the thermal decomposition of Ruthenium β-diketones. Their thermal stability was studied in inert, oxidising and reducing atmosphere by DTA and comparison was made. In an inert atmosphere and in oxygen, RuO₂ and sometimes Ruthenium were obtained whereas in a hydrogen atmosphere Ruthenium was obtained as the final product of thermal decomposition.

Iyer et al. has described the study of kinetic parameters of some polymeric chelates of pseudothiohydantoin with Ni, Co and Cu with the help of isothermal and non-isothermal TG pattern. The polychelates of Mn, Fe, Co, Ni and Cu with 4,4'-dihydro-3,3'-diacetylbiphenyl dithioxamide have been prepared and stability order viz. Ni > Fe > Co > Mn > Cu was reported by Aswar.

Tembhare has carried out thermal study of chalcones, β-diketones and pyrazolines and explained thermal stability, possible mode of decomposition and kinetic parameters of thermal decomposition reaction of these compounds. Levai
has reported synthesis and thermal decomposition of 3-aryloyl-4-aryl-2-pyrazolines. These compounds on thermal denitrogenation gave β-methyl-α,β-unsaturated ketones. An extensive thermal study on Mn, Fe, Ca, Ni and Cu chelates with polyschiff base ligands has been carried out by Aswar et al. Various thermodynamic parameters such as ΔS, Δf, S* and Z for the polychelates have been evaluated by using thermal data. Activation energy and order of reaction of these polychelates were calculated by using Freeman-Carroll and Sharp-Wentworth method.

PRESENT WORK:

The thermal analysis of organic compounds is one of the least studied aspects of organic chemistry. There are stray references in literature on the thermal analysis of organic compounds. However, there are some important applications of thermogravimetry as it can provide (1) The determination of the purity and thermal stability of both primary and secondary standards. (2) the investigation of correct drying temperatures and the suitability of various weighing forms for gravimetric analysis. (3) Direct application to analytical problems (automatic thermogravimetric analysis). (4) The determination of the composition of complex mixtures. The thermal analysis of compounds like chalcones, isoxazolines, pyrazolines and thiazines helps in the understanding of thermal stability and other kinetic parameters of these compounds which may be of practical significance.

In the present work, some of the synthesised compounds, as mentioned above, were subjected to thermal analysis. From the thermogravimetric data, attempt has been made, to explain decomposition pattern of these compounds with increase in temperature. Further various kinetic parameters viz, percent weight loss at different temperatures activation energy of thermal decomposition, order of decomposition reaction etc. of these compounds have been evaluated using Broido's method. The summary of the work done can be given as follows.
The seven compounds were subjected to thermogravimetric analysis as representative cases. They are -

1. 4-Methoxychalcone (MCHA) \((\text{C}_{16}\text{H}_{14}\text{O}_{3})\)
2. 3,5-Diphenylisoxazoline (DPIS) \((\text{C}_{13}\text{H}_{13}\text{ON})\)
3. 3-Phenyl-5-(4-methoxyphenyl)-\(\Delta^2\)-pyrazoline (PMPP) \((\text{C}_{16}\text{H}_{16}\text{ON})\)
4. 4,6-Diphenyl-2-imino-6H-2,3-dihydro-1,3-thiazine (DPIDT) \((\text{C}_{16}\text{H}_{14}\text{N}_{2}\text{S})\)
5. 1-Carboxamido-3-(2-hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl)-\(\Delta^2\)-pyrazoline (CHCPDMAPP) \((\text{C}_{16}\text{H}_{19}\text{O}_{2}\text{N}_{4}\text{Cl})\).
6. 3-(2-Hydroxy-5-chlorophenyl)-4-benzoyl-5-(4-dimethylaminophenyl) isoxazoline (HCPBDMAPIS) \((\text{C}_{24}\text{H}_{20}\text{O}_{3}\text{N}_{2}\text{Cl})\)
7. 4-(2-Hydroxy-5-chlorophenyl)-5-benzoyl-6-(4-dimethylaminophenyl)-2-imino-6H-2,3-dihydro-1,3-thiazine (HCPBDMAPIDT) \((\text{C}_{25}\text{H}_{22}\text{O}_{2}\text{N}_{3}\text{Cl})\). Their structural details have been discussed in Part I of the thesis.

From the TG data of these compounds, various kinetic parameters were determined using Broido's Method. The results are given in the Table 2.1.
Table 2.1  
Thermogravimetric Analysis of Compounds.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>Half decomp. temp. (°C)</th>
<th>Temperature in °C and % Weight loss</th>
<th>Decomposition temperature range in °C</th>
<th>Activation Energy (E*) of thermal decomp. in</th>
<th>Order of decomp. reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MCHA</td>
<td>293.5</td>
<td>225 270 285 300 315 330 345 360 375</td>
<td>225 to 420</td>
<td>23.6692</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.46 14.62 30.25 69.90 92.85 95.15 96.84 98.14 98.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>DPIS</td>
<td>246.0</td>
<td>210 225 240 255 270 285 300 315 330</td>
<td>210 to 410</td>
<td>12.9159</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.63 7.05 42.85 71.25 89.75 92.50 93.95 95.15 96.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PMPP</td>
<td>303.0</td>
<td>150 180 240 270 300 330 360 420 480</td>
<td>150 to 510</td>
<td>6.3232</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.85 5.60 15.62 26.10 45.75 71.55 81.58 87.85 96.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>DPIDT</td>
<td>406.5</td>
<td>180 210 270 330 390 450 510 525 540</td>
<td>165 to 555</td>
<td>12.2382</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.60 2.85 7.25 20.55 37.50 77.90 84.65 87.50 93.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CHCPDMAPP</td>
<td>287.0</td>
<td>210 230 250 270 290 330 370 490 510</td>
<td>210 to 510</td>
<td>10.8951</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.70 12.75 20.60 34.65 53.05 69.85 75.65 82.95 83.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>HCPBDMAPIS</td>
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<td>186 210 240 260 280 310 330 350 490</td>
<td>186 to 490</td>
<td>9.8056</td>
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<tr>
<td>7</td>
<td>HCPBDMAPDT</td>
<td>256.0</td>
<td>150 200 220 240 260 290 310 330 -</td>
<td>150 to 350</td>
<td>7.6237</td>
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<tr>
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<td></td>
<td>1.05 2.90 9.30 25.40 59.75 98.20 98.90 99.10</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
Thermogravimetry is one of the most important techniques in which a change in the weight of a substance is recorded as a function of temperature or time. The significance of this technique lies in the fact that TG curve is quantitative and hence calculations on compound stoichiometry can be made at any given temperature.

Although there is lot of work on thermal analysis of coordination compounds comparatively less work has been done on organic compounds, particularly on heterocyclic compounds. Thermal study of chalcones, β-diketones and pyrazolines has been carried out by Tembhare and thermal decomposition of these compounds has been explained with TG data. Other kinetic parameters like activation energy of thermal decomposition, order of decomposition reaction have also been determined.

The work presented here deals with the thermal study of some of the synthesized compounds like chalcone, isoxazolines, pyrazolines and thiazines. An attempt has been made to explain thermal behaviour of these compounds from TG data. Various kinetic parameters like percent weight loss at different temperatures, activation energy of thermal decomposition order of decomposition reaction etc. have been determined using Broido’s method.

**Experimental Technique:**

Thermogravimetric analysis (TG) was carried out on Perkin-Elmer Thermogravimetric analyzer System Model TGS-2 at RSIC, Nagpur University, Nagpur. The sample was placed in a Platinum crucible, heated in an electric furnace.
and the weight of the sample was recorded on semimicrobalance continuously as a function of temperature. Temperature of the furnace was calibrated by magnetic transition temperature of different alloys (supplied with the instrument). The following conditions were used and maintained during all experiments.

i. Heating rate : 5°C min\(^{-1}\)

ii. Sample holder : Platinum crucible and

iii. Atmosphere : Dry nitrogen at a flow rate of 30 cm\(^3\)min\(^{-1}\)

**Determination of Kinetic Parameters**:

Pyrolysis of many organic compounds gives the TG curve which is almost sigmoidal in shape. In such a case, the weight of the sample decreases slowly in the beginning of the reaction, which is followed by a sharp decrease indicating comparatively more rapid weight loss. A TG curve may be presented as a measure of the loss in mass of a sample as a function of temperature. The shape of a TG curve depends primarily on the following kinetic parameters involved in the reaction rate (i) order of decomposition reaction (n) (ii) Frequency factor (A) (iii) Activation energy (E\(^*\)). The values of these parameters can be of vital importance in the illustration of mechanism involved in the chemical reaction. These data are analysed to estimate various kinetic parameters of the degradation reaction by several methods. In the present work, Broido's method has been used which is discussed below.

**Evaluation of Kinetic Parameters from TG data by Broido's Method**:

Broido\(^{19}\) showed that the weight of the sample (W\(_t\)) subjected to thermal analysis at time t is related to the fraction of the number of initial molecules not yet decomposed, Y by the equation as given below,

\[
Y = \frac{N}{N_0} = \frac{W_t - W_0}{W_0 - W_0} = \frac{W_t - W_0}{W_0 - W_0}
\]
where \( W_t \) = The active weight of the material at any time \( t \).

\( W_0 \) = The weight of the material at the end of pyrolysis.

\( W_o \) = The weight of the material taken initially.

\( N \) = The number of molecules at the end of pyrolysis.

\( N_0 \) = The number of molecules initially present.

Its simplified equation for 1st order is

\[
\ln \left( \frac{1}{Y} \right) = \frac{-E^*}{R} \left( \frac{1}{T} \right) + \text{constant} \quad \text{------- (2)}
\]

For 2nd order reaction (\( n = 2 \)), equation (3) has been proposed.

\[
\ln \left( \frac{1-Y}{Y} \right) = \frac{-E^*}{R} \left( \frac{1}{T} \right) + \text{constant} \quad \text{------- (3)}
\]

Therefore, the slope of plots of \( \ln \left( \frac{1}{Y} \right) \) and \( \ln \left( \frac{1-Y}{Y} \right) \) vs \( \frac{1000}{T} \) for \( n = 1 \) and \( n = 2 \) respectively should give the energy of activation of thermal decomposition.

Following the calculations of Broido's method\(^{10}\), plots of \( \ln \left( \frac{1}{Y} \right) \) vs \( \frac{1000}{T} \) for \( n = 1 \) were drawn. As the plot for \( n = 1 \) was found to be a straight line. These results showed that the order of thermal decomposition reaction (\( n \)) for all the compounds under study is one. The slope of the plots gave the energy of activation (\( E^* \)).

The work presented here describes the thermal analysis (TG, DTG) of 4-methoxychalcone (MCHA) and 3,5-diphenylioxazoline (DPIS) and thermogravimetric analysis (TG) of 3-phenyl-5-(4-methoxyphenyl)-\( \Delta^2 \)-pyrazoline (PMPP), 4,6-diphenyl-
2-imino-6H-2,3-dihydro-1,3-thiazine (DPIDT), 1-Carboxamido-3-(2-hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl)-Δ²-pyrazoline (CHCPDMAPP), 3-(2-hydroxy-5-chlorophenyl)-4-benzoyl-5-(4-dimethylaminophenyl) isoxazole (HCPBDMAPIS) and 4-(2-hydroxy-5-chlorophenyl)-5-benzoyl-6-(4-dimethylaminophenyl)-2-imino-6H-2,3-dihydro-1,3-thiazine (HCPBDMAPIDT). The thermograms were analysed to obtain information about percent weight loss at different temperatures. From these thermal data, kinetic plots were drawn and various kinetic parameters of these compounds were determined.

1. 4-Methoxychalcone (MCHA):

The TG and DTG curves obtained for 4-methoxychalcone are shown in figure (1). From the figure it follows that in the beginning decomposition of MCHA was rather slow which started at 498°K. The initial weight loss can be attributed to loss of moisture. The decomposition was hundred percent at 693°K which corresponded to its complete thermal oxidation. The TG curve shows that MCHA is thermally stable up to 493°K. On the basis of DTG, it can be said that the actual thermal degradation of the compound started at 498°K with to 648°K. It can also be noted that the rate of thermal decomposition of MCHA was much higher in the temperature range from 528°K to 588°K corresponding to the percent mass loss from 7.50% to 92.85%. The activation energy \( E^* \) of thermal degradation has been calculated from kinetic plot (fig.2) by applying the Broido's method. The values of kinetic parameters are summarised in Table 2. For MCHA, \( E^* \) was found to be 23.6692 K.Cal/mol and order of thermal decomposition reaction was one.
Fig. 1: MCHA

TG

DTG

TEMP (°C)

WEIGHT %
Fig. 2: Kinetic plot of MCHA

slope = 5.1724

$E^* = 2.56692 \text{ kcal/mol}$
Table 2.2
Evaluation of Kinetic Parameters of MCHA
Initial Weight of the sample (Wo) = 100 mg.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Temp. °K</th>
<th>$10^3 (°K^{-1})$</th>
<th>Mass Loss %</th>
<th>Residual Weight (Wt) in mg</th>
<th>$Y = \frac{W_t}{W_o}$</th>
<th>$\frac{1}{Y}$</th>
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</thead>
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<td>225</td>
<td>498</td>
<td>2.008</td>
<td>2.46</td>
<td>97.54</td>
<td>0.9754</td>
<td>0.0107</td>
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<td>4.12</td>
<td>95.88</td>
<td>0.9588</td>
<td>0.0183</td>
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<td>92.50</td>
<td>0.9250</td>
<td>0.0338</td>
</tr>
<tr>
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<td>543</td>
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<td>0.8538</td>
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</tr>
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<td>550.5</td>
<td>1.816</td>
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<td>0.7860</td>
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<tr>
<td>285</td>
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<td>92.85</td>
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</tr>
</tbody>
</table>

2. 3,5-Diphenylisoxazoline (DPIS):

The thermal decomposition of 3,5-diphenylisoxazoline (DPIS) has been studied with TG and DTG and is shown in Figure 3. The T.G. curve shows that DPIS is thermally stable upto 477°K. The actual thermal degradation of DPIS started from 483°K and nearly completed at 683°K corresponding to the mass loss from
1.63% to 98.15%. It follows from the TG curve (Fig.3) that the decomposition of DPIS was slow in the beginning and the total decomposition corresponded to thermal oxidation. It can be noted that the rate of thermal degradation was much higher in the temperature range from 498°K to 543°K corresponding to percent weight loss from 7.05 to 89.75%. The activation energy \((E^*)\) of thermal decomposition has been calculated from the kinetic plot (Fig.4) by following the Broido's method. The values of kinetic parameters are given in Table 2.3. For DPIS, \(E^*\) was found to be 12.9159 K.Cal/mole and order of thermal decomposition reaction was one.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Temp. °K</th>
<th>(10^3/\text{T}°(\text{K}^{-1}))</th>
<th>Mass Loss %</th>
<th>Residual Weight (Wt) in mg</th>
<th>(Y = \frac{Wt}{Wo})</th>
<th>(\log \frac{1}{Y})</th>
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<td>683</td>
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</table>
Fig. 4: Kinetic plot of DP1S

slope = 2.8 ± 2.5
$E^* = 12.9159 \text{ kcal/mol}$
3-Phenyl-5-(4-methoxyphenyl)-α-pyrazoline (PMPP):

The T.G. curve of PMPP (Fig. 5) shows that it is thermally stable up to 398°K. In the beginning, it appears that the thermal decomposition is slow. The actual thermal degradation starts from 423°K and is complete at 783°K, corresponding to its thermal oxidation. The rate of thermal degradation is much higher in the temperature range 513°K to 633°K with the corresponding percent mass loss from 15.62 to 81.58%. However, after 633°K up to 723°K the rate of thermal degradation slows down with a percent mass loss from 81.58% to 90.63%. This may be attributed to various redox reactions taking place in the compound at the above mentioned temperatures. From kinetic plot (Fig. 6), activation energy of thermal decomposition ($E^*$) has been calculated by following Broido's method. The kinetic parameters are given in Table 2.4. For PMPP, $E^*$ was found to be 6.3232 K.Cal/mol and the order of thermal decomposition reaction was one.

### Table 2.4
Evaluation of Kinetic Parameters of PMPP
Initial Weight of the sample (W₀) = 100 mg.

<table>
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<th>Temp. °C</th>
<th>Temp. °K</th>
<th>$\frac{10^3}{T}$ (°K⁻¹)</th>
<th>Mass Loss (%)</th>
<th>Residual Weight (Wt) in mg</th>
<th>$Y = \frac{Wt}{W₀}$</th>
<th>$\log \frac{1}{Y}$</th>
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Fig 5: PMPP

![Graph showing weight change with temperature (TG)](image)
Fig. 6: Kinetic plot of PMPP

slope = 1.3818

$E^* = 6.3232$ kcal/mol.
4. **4,6-Diphenyl-2-imino-6\(\text{H}\)-2,3-dihydro-1,3-thiazine (DPIDT):**

From the TG curve of DPIDT (Fig. 7), it follows that compound is thermally stable up to 433\(^\circ\)K. The actual thermal decomposition began from 438\(^\circ\)K with a percent mass loss of 1.35\% and completed at 828\(^\circ\)K. Initially the decomposition of the compound was slow. However, the rate of thermal decomposition was much higher in the temperature range from 543\(^\circ\)K to 723\(^\circ\)K corresponding to percent mass loss of 7.25\% to 77.90\%. The decomposition rate again lowered for a temperature range from 738\(^\circ\)K to 783\(^\circ\)K followed by rapid increase till the complete weight loss.

The activation energy (\(E^*\)) of thermal decomposition was calculated from kinetic plot (Fig. 8) by following Broido's method. The values of kinetic parameters are given in Table 2.5. For DPIDT \(E^*\) was found to be 12.2382 K Cal/mol and the order of thermal decomposition reaction was one.

**Table 2.5**

Evaluation of Kinetic Parameters of DPIDT

<table>
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<tr>
<th>( \text{Temp.} ) (^\circ)C</th>
<th>( \text{Temp.} ) (^\circ)K</th>
<th>( \frac{10^3}{T} ) ({\text{K}^{-1}})</th>
<th>Mass Loss (%)</th>
<th>Residual Weight (Wt) in mg</th>
<th>( Y = \frac{Wt}{W_0} )</th>
<th>( \log \frac{1}{Y} )</th>
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</table>
Fig. 8: Kinetic plot of DPIDT

slope = 2.6744
E' = 12.2382 kcal/mole
5. 1-Carboxamido-3-(2-hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl)-\(\Delta^2\)-pyrazoline (CHCPDMAPP):

The TG curve of CHCPDMAPP (Fig. 9) shows that it is thermally stable up to 478°K. The thermal decomposition was slow in the beginning. The actual thermal degradation started from 483°K with a percent mass loss of 2.70% and showed 83.90% mass loss at 783°K with a residual weight of 16.10 mg. The rate of thermal degradation is much higher in the temperature range from 483°K to 603°K corresponding to 2.70% to 69.85% weight loss respectively. It is observed that the compound didn't undergo complete thermal decomposition at a given temperature range of 210 to 510°C (Residual weight at 510°C = 16.10 mg).

From the kinetic plot (Fig. 10) and by following Broido's method, Activation Energy of thermal decomposition of CHCPDMAPP was found to be 10.895 K.Cal/mol and the order of thermal decomposition reaction was one. The kinetic parameters of CHCPDMAPP are shown in Table 2.6. It also follows that CHCPDMAPP has more thermal stability than PMPP. This may be due to the presence of Hydrogen bonding in the former which is absent in the latter.
Fig. 10: Kinetic plot of CHCPDMAPP

slope = 2.3809
$E' = 10.891\text{ K-cal/mol}$
6. 3-(2-Hydroxy-5-chlorophenyl)-4-benzoyl-5-(4-dimethylaminophenyl) isoxazoline (HCPBDMAPIS):

From the TG curve of (HCPBDMAPIS) (Fig. 11), it follows that the compound is thermally stable up to 443°C. The thermal decomposition was slow in the beginning and it actually started from 459°C with a percent mass loss of 1.85% and almost completed at 763°C with the percent mass loss of 96.35% (Residual weight = 3.65 mg). It is observed that the rate of thermal degradation is much higher in the
Fig.12: Kinetic plot of HCPBDMAPIS

\[
\text{slope} = 2.1428 \\
E^* = 9.8056 \text{ Kcal/mol}
\]
temperature range from 473°K to 553°K corresponding to 3.70% to 88.10% mass loss respectively.

From the kinetic plot (Fig. 12), activation energy of thermal degradation was calculated by following the Broido's method. The kinetic parameters of HCPBDMAPIS are given in Table 2.7. For HCPBDMAPIS, activation energy of thermal degradation (E*) was found to be 9.8056 K.Cal/mol and the order of thermal decomposition was one. It comparison is made between DPIS and HCPBDMAPIS, it follows that the former (E* = 12.9159) is more stable than the latter. This can be explained due to the fact that involvement of large bulky groups in the latter renders it less stable and hence lesser the thermal stability than DPIS. This is also supported by TG curves which show that DPIS is thermally stable upto 477°K whereas HCPBDMAPIS is stable upto 443°K.

Table 2.7
Evaluation of Kinetic Parameters of CHCPDMAPP
Initial Weight of the sample (Wo) = 100 mg.

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<th>Temp. °C</th>
<th>Temp. °K</th>
<th>$10^3 \frac{1}{T}$ (°K$^{-1}$)</th>
<th>Mass Loss %</th>
<th>Residual Weight (Wt) in mg</th>
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7. 4-(2-Hydroxy-5-chlorophenyl)-5-benzoyl-6-(4-dimethylaminophenyl)-2-imino-6H-2,3-dihydro-1,3-thiazine (HCPBDMAPIDT):

The TG curve of HCPBDMAPIDT (Fig. 13) shows that it is thermally stable up to 393°K. In the beginning the thermal decomposition was also and it actually started from 423°K with a percent mass loss of 1.05% and completed at 603°K (99.10% mass loss). It is observed that the rate of thermal decomposition was comparatively higher in the temperature range from 483°K to 543°K corresponding to 5.15% to 94.75% mass loss respectively.

Following the Broido's method, activation energy of thermal degradation was calculated from the kinetic plot (Fig. 14) of HCPBDMAPIDT. The kinetic parameters are given in Table 2.8. For HCPBDMAPIDT, \( E^* \) was found to be 7.6237 K.Cal/mol and the order of thermal decomposition reaction was one. From the TG curves, it follows that DPIDT (\( E^* = 12.2382 \) K.Cal/mol) is more stable than HCPBDMAPIDT, which is due to the fact that involvement of large bulky groups in the latter makes it less stable and hence lesser the thermal stability. This is also supported by the fact that DPIDT was thermally stable up to 433°K whereas HCPBDMAPIDT was thermally stable up to 393°K.
Fig. 14: Kinetic plot of HCPBDMAp!DT

slope = 1.666

$E^* = 7.6237 \text{ kcal/mol}$
Table 2.8
Evaluation of Kinetic Parameters of HCPBDMAPIIDT
Initial Weight of the sample (Wo) = 100 mg.

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<th>Temp °C</th>
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<th>Residual Weight (Wt) in mg</th>
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REFERENCES


CHAPTER 3

P^H METRIC STUDY OF BINARY COMPLEXES OF SOME TRANSITION METAL IONS

SECTION A

INTRODUCTION

A considerable amount of work on the evaluation of the stability constants of binary complexes involving readily available ligands has been reported in literature. However, the studies on the formation of the complexes involving heterocyclic compounds as ligands have not been done with the same interest. But since the last decade, more attention was drawn on the study of binary complexes involving heterocyclic compounds as ligands.

Potentiometric method involving the use of pH metric titration technique has been proved to be one of the most reliable and useful methods. The stepwise attachment of the ligands to the central metal ion gives stepwise binary complexes, the stability constants of which may be conveniently evaluated by Bjerrum-Calvin titration technique using the method of Irving and Rossotti.

Formation of metal complex can be considered due to the displacement of a proton from the ligand causing a drop in the pH values of the solution. Martell has carried out potentiometric study of metal complexes of a large variety of polycarboxylic acids, oximes, phenols etc.
The stability of complexes also depends upon the size and number of chelating rings. The size of the chelating ring and number of rings formed on chelation are determined by the structure of chelating agent. Hence both the factors govern the stability of chelates. Pfeiffer\textsuperscript{4} reported that the five-membered ring is more stable when the ring is entirely saturated but when one or more double bonds are present the six-membered ring is favoured. Schwarzenbach et al.\textsuperscript{5} have observed that there is a decrease in chelate stability with the increase in the ring size. Chelation as well as stability is governed by the nature of metal. Nature of metal ion also plays an important role in chelation and stability of complexes. The stability order of metal complexes of transition metal ions was found by Irving and Williams\textsuperscript{6} by comparing the ionic radius and second ionisation potentials of the metal ions which is also valid for most nitrogen and oxygen donor ligands. The stability order was given as Mn$^{2+} <$ Fe$^{2+} <$ Ni$^{2+} <$ Cu$^{2+} >$ Zn$^{2+}$.

Heterocyclics such as isoxazolines, pyrazolines, thiazines etc. have been reported as important drugs apart from their other applications by number of workers. A great deal of work has been done since the last two decades on the physical as well as chemical study of these heterocyclics. The rate of passage of a drug through a membrane is dependent upon the pH and the dissociation constant (pK) of the drug\textsuperscript{7}. Biological activities of the drugs are dependent on their chemical structure as well as physical properties. Physical properties play an important role in the absorption, pharmacological transport-mechanism and excretion of drugs\textsuperscript{8}. Dissociation constants as well as stability constants determine the physiological activity of the drug. Dissociation constant of the drug not only gives the idea about the transport of the drug across cell membrane but also decides whether the drug will act in ionised or un-ionised form\textsuperscript{9,10}. 
The formation of metal-complex imparts some important characteristics to the drug, which are helpful in its biological activity e.g. low dissociation constants, special redox potential, electron distribution and solubility. These characteristics have marked effect on the solubilities of drugs in the lipid and their transfer through the cell membrane. Complexation with metals also help in the natural process of bond formation and bond cleavage and the group transfer reactions. Metal complexation not only polarise electrons from the ligands towards metal but also brings the reacting molecules together to give an activated complex. The values of formation constants and free energy changes indicate the relation between stability and basicity of ligands. Bulkier groups increase the basicity as well as stability of the molecule.

Correlation between the basicity of the ligand and the stability of complexes:

Generally, the complex formation is a complexation between metal ions and protons. It is, therefore, expected that there is some correlation between the stability constant of the complex and the acidic dissociation constant of the conjugate acid of the ligand. Larsson found a linear relationship between the corresponding constants for the complexes of Silver(I) with organic amines. Subsequently similar correlation were found in many complex systems. The ligand may affect the chelating tendency in two possible ways.

i. It may influence the basicity of the donor groups by inductive and resonance effects and/or

ii. the addition of groups on the ligand may be purely statistical. Sterical effects prevent the ligand ions or molecules from acquiring the orientation about the central
metal ion most favourable for chelation. In certain cases a linear correlation was found between the Hammett's constants for the functional groups in ligand and the logarithms of the stability constants of the complexes. May and Jones\textsuperscript{11} have applied Hammett's equation to the complexes of substituted benzoic acids. Irving and Desilva\textsuperscript{12} introduced a stability factor 'S\textsubscript{f}' which is a measure of the stabilization due to bonding.

The determination of pK or log K values at various percentages of dioxane-water or methanol-water mixtures has been carried out by number of workers\textsuperscript{13}. Ohtaki\textsuperscript{14} showed the solvent effect on the dissociation of ammonium and pyridinium ions. Palaskar\textsuperscript{15} has shown the effect of dielectric constant on Cu(II) complexes of phthalic acids in various percentages of dioxane-water mixture and observed d\pi-\pi interaction with increase in dioxane percentage. Alekseevskii et al\textsuperscript{16} studied the effect of C\textsubscript{6}H\textsubscript{4}, DMF on stability constants of Cu and Ni-bisacetylacetonates, bidibenzoyl methanates and Cu-dibenzoylmethane complex.

Binary complexes of transition metals, lanthanides and uranyl ion with 5-sulphosalicylic acid have been studied by Jahagirdar and Khanolkar\textsuperscript{16a}. Narwade\textsuperscript{17} studied the pK and logK values in dioxane-water and methanol-water mixtures. Metal chelates of 3-(2-hydroxyphenyl)-5-phenylisoxazoline with Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and dioxouranium (IV) have been investigated by Khadilkar et al\textsuperscript{17a}. Steric influence of the ligands like \(\beta\)-diketones and their tetramethyl analogs has been studied by Fukuda et al\textsuperscript{18}. Saha and Sinha\textsuperscript{19} reported increase in the value of formation constant with the change of alkyl group from methyl to n-butyl in \(R_2\)-Sn (IV) possibly due to increase in the electrophilic character of tin with increase in the length of alkyl chain. Gudadhe et al\textsuperscript{20} reported potentiometric studies of thorium (IV) complexes with some substituted pyrazolines at 0.1 M ionic strength.
Aihara et al. carried out a potentiometric study of copper(II) complexes with β-diketones in micellar solution using a copper(II) ion-selective electrode. The complexes of some bivalent metal ions such as Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) with 4-amino-3-thio-6-methyl 2,3,4,5 tetrahydro 1,2,4 triazine have been investigated by Sing et al. Similarly, the derivatives of triazines formed complexes with Ni(II), Pd(II) and Pt(II) metal ions. Sawalakhe has studied metal-ligand complexes with some substituted β-diketones, 3,5-diarylpyrazoles and pyrazolines. Gudadhe has carried out potentiometric studies on proton-ligand stability constants with some substituted pyrazolines in 70% dioxane-water mixture. Rajput has also determined proton-ligand stability constants of substituted pyrazoline, pyrazole, isoaxazole and isoxazole by potentiometry. Sawalakhe and Narwade have investigated the metal-ligand stability constants of Fe(III), Cr(III) and Al(III) metal ion complexes with some substituted pyrazoles and pyrazolines. Raghuwanshi et al. have shown 1:1 and 1:2 complex formation of Cu(II), Ni(II) with some substituted chalcones and isoaxazolines potentiometrically and spectrophotometrically. Spectrophotometric investigation of Fe(III) complexes with substituted thiazines and phenylthiazines have shown 1:1 and 1:2 complex formation at pH 3.0 and 5.00 respectively. Mandakmare has reported metal ligand stability constants of complexes of some substituted coumarins, triazines and thiazolines (dihydrothiazoles) with Co(II), Ni(II), Cu(II), Fe(III), Al(III), Cr(III), UO2(II) and Th(IV) ions by potentiometric technique at 28°C in 70% dioxane-water medium. Raghuwanshi et al. carried out spectrophotometric investigation on Cu(II) complexes with substituted chalcone, isoaxazole, pyrazoline and thiazine and showed 1:1 complex formation at about pH 3.0. Venugopalan and Krishnanenkutty has reported chelation of Co(II), Ni(II) and Cu(II) complexes with some 5-aryl-1-phenyl-4-pentene-1,3-diones in 50% (v/v) aqueous-dioxane medium.
Potentiometric Method for the Determination of Stability Constants:

Formation of metal complex can be considered to be due to the displacement of a proton from the ligand causing a decrease in the pH value of the solution. Irving and Rossotti have given a method for calculation of stability constants of complexes by potentiometry. A general technique followed is due to Calvin and Bjerrum. Martell has carried out potentiometric study of metal complexes of a large variety of polycarboxylic acids, oximes, phenols etc. Number of methods are employed in the study of complex equilibria of chelates such as potentiometry, spectrophotometry, polarography, optical activity, ion-exchange, magnetic measurements, X-ray measurements, gas chromatography etc.

The stepwise formation of the mononuclear binary complexes can be represented by a set of equilibrium constants. The concentration changes caused by a complex formation are reflected in the potential of well-chosen electrodes. The potentiometric measurements are, therefore, very frequently applied in the study of complex equilibria. For the potentiometric measurements an electrode must be selected, the potential of which is a well defined function of the concentration of the ion to be determined and also a reference electrode.

The formation of complex $ML_n$ is in general a stepwise process involving a series of equilibria of the type,

\[
\begin{align*}
M + L &\rightleftharpoons ML &\quad 1(a) \\
ML + L &\rightleftharpoons ML_2 &\quad 1(b) \\
ML_2 + L &\rightleftharpoons ML_3 &\quad 1(c) \\
ML_{n-1} + L &\rightleftharpoons ML_n &\quad 1(d)
\end{align*}
\]

(The charges on a metal ion are omitted)
The corresponding stepwise formation constants are then given by -

\[ K_1 = \frac{ML}{M'\text{L}} \]
\[ K_2 = \frac{ML_2}{M'\text{L}} \]
\[ K_3 = \frac{ML_3}{M'\text{L}} \]
\[ K_n = \frac{ML_n}{M'\text{L}_{n-1}} \] .......................... (1e)

The stability constant \( \beta_n \) for the overall equilibrium process,

\[ M + n\text{L} = \text{ML}_n \] .......................... (2)

is the product of various stepwise formation constants and can be given as:

\[ \beta_n = K_1 \times K_2 \times K_3 \ldots \ldots K_n = \frac{\text{M}^n\text{L}_n}{\text{M}^n\text{L}} \] .......................... (3)

Similarly, the equations 1(a) to 1(d) for ligand equilibria can be written in the following generalised form:

\[ ^1\text{H}_{l-1} + \text{H} = \text{LH}_i \] .......................... (4)

where \( \text{LH}_i \) is the ligand acid. The proton-ligand stability constant for such a reaction is given by:

\[ K_i^{H} = \frac{\text{LH}_i}{\text{LH}_{l-1}\text{H}} \] .......................... (5)

where, \( K_i^{H} \) is called the ith thermodynamic proton-ligand stability constant and is the reciprocal of thermodynamic dissociation constant of the acid \( \text{LH}_i \) dissociating as:

\[ \text{LH}_i = \text{LH}_{l-1} + \text{H} \] .......................... (6)
The pKi value is given by -

\[ pKi = \frac{a_{LH_{n+1}}a_H}{a_{LH_1}} \] ................................. (7)

For monobasic ligand pK_iH = pK_i in magnitude.

For polybasic acids (HnA),

\[ pK_i = p^{ka_i}, p^{k_2} = pK_{h-1}, p^{ka} = pK_H \]

The degree of formation or ligand number \( \bar{n} \) is expressed by Bjerrum as:

\[ \bar{n} = \frac{\sum_{i=0}^{N} i[MLi]}{\sum_{i=0}^{N} [MLi]} \] ................................. (8)

Substituting for the values of MLi from equation 1(e) applied to equilibria 1(a) to 1(d) and eliminating M, eqn. can be given as:

\[ \bar{n} = \frac{K_1[Li] + 2K_1K_2[Li]^2 + nK_1K_2n}{1 + K_1[Li] + K_2[Li]^2 + K_1K_2} \] ................................. (9)

which can also be written using eqn (3) as -

\[ \bar{n} = \frac{\sum_{i=0}^{N} bi[Li]^2}{\sum_{i=0}^{N} bi[Li]^2} (\beta_o - 1) \] ................................. (10)
A similar function for proton-ligand constant is given by,

\[ \bar{n}_n = \frac{\sum_{i=0}^{N_i} i \beta_i [H]^i}{\sum \beta_i [H]^i} \times (\beta_o^n - 1) \quad (11) \]

where \( \bar{n}_n \) is the mean number of protons bound per noncomplex bound ligand molecule. The total concentration \( T_M \) of the metal ion \( M \), is the sum of concentrations of the different species containing it,

\[ T_M = [M] + [ML] + \ldots + [ML_n] \quad (12) \]

Similarly, the total concentration of ligand is the weighed sum of concentrations of the species containing it,

\[ T_L = [L] + [ML] + 2[L_2] + \ldots + n[L_n] \quad (13) \]

The total concentrations of \( T_M \) and \( T_L \) are given by the expression -

\[ T_M = [M] \sum_{i=0}^{N_i} i \beta_i [L]^i \quad (14) \]

\[ T_L = [L] + [M] \sum_{i=1}^{N_i} i \beta_i [L]^i \quad (15) \]
The extent of complex formation is characterised by the ligand number $\bar{n}$, given as,

$$\bar{n} = \frac{[ML] + 2[ML_2] + \ldots \ldots M[ML_n]}{[M] + [ML] + [ML_2] + \ldots \ldots [ML_n]}$$  \hspace{1cm} (16)$$

$$\bar{n} = \frac{T_L - [L]}{T_M}$$  \hspace{1cm} (17)$$

where $T_L$ is the concentration of ligand in all forms, $[L]$ is the concentration of free chelating species and $T_M$ is the total concentration of metal ion-bound or free.

**Determination of stability constants:**

The determination of the stability constants from the experimental data involves the following three steps.

1. The construction of the formation curve of the system expressed as a plot of $\bar{n}$ against $p^L = \log 1/[L]$
2. The calculation of $K_1$, $K_2$ values by solving the formation function of the system.
3. The conversion of the stoichiometric constants into the thermodynamic functions.

The experimental procedure involves the titrations of

i) Acid (A).

ii) Acid + Ligand (A + L)

iii) Acid + Ligand + Metal salt (A + L + M)

with standard solution of alkali. The ionic strength of each solution is kept constant generally at 0.1 M by the addition of KNO₃.
**Calculation of $\bar{n}_A$, $\bar{n}$ and $p^+$**:

The experimental data obtained from the titration curves helps in the calculation of $\bar{n}_A$ and $\bar{n}$. Proton-ligand formation number, $\bar{n}_A$ for different pH values can be obtained from the following equation,

$$
\bar{n}_A = Y - \frac{(N + E^o)(V_2 - V_1)}{T_L^o(V^o + V_1)} \quad (18)
$$

where $Y =$ Number of replaceable protons in ligand

$N =$ Normality of alkali

$E^o =$ Strength of acid in system

$V^o =$ Initial volume of the system

$V_1$ & $V_2 =$ Volumes of alkali required in the acid and ligand titrations respectively at same pH.

$T_L^o =$ Total concentration of ligand in system.

Similarly, the metal ligand formation number $\bar{n}$ can be calculated from the equation,

$$
\bar{n} = \frac{(N + E^o)(V_3 - V_2)}{\bar{n}_A T_M^o (V^o + V_2)} \quad (19)
$$

where $V_3 =$ volume of alkali required for the titration of acid + ligand + metal solution to obtain the same pH

$T_M^o =$ Total concentration of metal ion in system.
The pL values are calculated at the corresponding n values, using the same equation as in original paper of Irving and Rossotti.

\[
p^L = \log \frac{1 + \beta_1[H^+] + \beta_2[H^+]^2 + \ldots + \beta_n[H^+]^n}{T_L - \mathbb{T}_M^n} \quad \ldots \quad (20)
\]

where \( \beta_1, \beta_2 \) and \( \beta_n \) are the gross stability constants and \( p^L \) and \( \mathbb{n} \) have their usual meaning.

This equation expresses \( \mathbb{n} \) as a function of \( p^L \) which is represented as formation curve for metal-ligand stability constant. It can be obtained by plotting \( \mathbb{n} \) against \( p^L \). The number of complexes formed in the reaction can be deduced from the formation curve and the values of stability constants can be determined as,

\[
\begin{align*}
\log K_1 &= pL \text{ at } \mathbb{n} = 0.5 \\
\log K_2 &= pL \text{ at } \mathbb{n} = 1.5 \\
\log K_3 &= pL \text{ at } \mathbb{n} = 2.5
\end{align*}
\]

**PRESENT WORK**

The metal-ligand stability constants of the complexes involving hydroxy and amino-hydroxy phenols, naphtols and sulphonlic acids as ligands have been reported by many workers. It has been tried to observe the effect of solute-solvent interaction on protonation equilibria of organic acids and chelation equilibria of their transition metal ion complexes. Gudadhe et al. have studied proton-ligand and metal-ligand stability constants of Th(IV) complexes with some substituted pyrazolines at 0.1 Mionic strength in 70% Dioxane-water mixture. Sawalakhe and Narwade have investigated the metal-ligand stability constants of Fe(III), Cr(III) and Al(III) metal
ion complexes with some substituted pyrazoles and pyrazolines. Transition metals, lanthanides and uranyl complexes of 5-sulphosalicylic acids have been studied by Jahagirdar and Khanolkar. Recently, Raghuwanshi et al have reported 1:1 and 1:2 complex formation of Cu(II) and Ni(II) with some substituted chalcones and isoxazolines by potentiometry and spectrophotometry. However, potentiometric studies on the formation of metal complexes involving the heterocyclics like pyrazolines, isoxazolines and thiazines as ligands have not been undertaken on wider scale. Some of these compounds have been successfully tested as indicators due to their complex forming ability. These compounds therefore have analytical applications.

It was therefore thought of interest to study the metal-ligand stability constants of Co(II), Ni(II) and Cu(II) with the newly synthesised heterocyclics like substituted pyrazolines, isoxazolines and thiazine. Attempt has been made to correlate the stability constant of a complex and the nature of substituent groups present on the ligand.

The following ligands were used in the present work. (Their structural details have been discussed in Part I of the thesis).

1. 3-(2-Hydroxy-5-methylphenyl)-5-(4-dimethylaminophenyl)-Δ²-pyrazoline (HMDMAP).
2. 3-(2-Hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl)-Δ²-pyrazoline (HCDMAP).
3. 3-(2-Hydroxy-5-methylphenyl)-5-(4-dimethylaminophenyl)-isoxazoline (HMDMAI).
4. 3-(2-Hydroxy-5-chlorophenyl)-5-(4-dimethylaminophenyl)-isoxazoline (HCDMAI).
5. 4-(2-Hydroxy-5-chlorophenyl)-6-(4-dimethylaminophenyl)-2-imino-6H-2,3-dihydro-1,3-thiazine (HCDMAT).
SECTION B
EXPERIMENTAL AND DISCUSSION OF THE RESULTS

Experimental:

In the present work Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti has been employed as the ligands used are weakly acidic in nature. Since the ligands are insoluble in double distilled water, their solutions were prepared in purified dioxane. All the experiments were carried out at a fixed ionic strength. The experimental details are as follows.

Materials:

1. Water: CO₂ free double distilled water was used. It was obtained by redistilling the distilled water over alkaline KMnO₄. The pH of this water was about 6.9.

2. Sodium hydroxide solution: CO₂ free NaOH solution was prepared following the detailed procedure given in 'Inorganic Quantitative Analysis' by A.I. Vogel.

   The prepared solution was standardized by titrating it potentiometrically against a standard potassium hydrogen phthalate solution. The concentration of NaOH was checked from time to time.

3. Potassium nitrate: Desired amount of KNO₃ (A.R.) was dissolved in double distilled water, so as to prepare a stock solution of 1.0 M.

4. Nitric Acid: The required stock solution (0.1 M) was prepared by diluting a suitable quantity of original A.R. acid.
The strength of acid was estimated by titrating against NaOH potentiometrically. The concentration of stock solution was checked from time to time during its use.

5. Metal solutions: The 0.01 M stock solutions of Co(NO$_3$)$_2$.6H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O and Cu(NO$_3$)$_2$.3H$_2$O were prepared by weighing requisite amounts and dissolving in a calculated quantity of nitric acid solution in order to avoid hydrolysis of metal ions.

6. Ligand solutions: The 0.01 M stock solutions of ligands (ligand 1-6) were prepared in purified dioxane since they are insoluble in double distilled water. The purity of the compounds was checked by TLC.

All the reagents used during the work were of A.R. grade.

Instrument: pH meter:

The digital pH meter (Systronics model-335) having glass calomel electrode assembly was employed for pH measurements.

The electrode system contained a reference electrode (calomel electrode) and an indicator electrode (glass electrode). In order to prevent the formation of chloro complex, the calomel electrode was not dipped directly into the experimental vessel but it was kept in saturated solution of KCl, in a beaker and then was connected to the titrating vessel through a salt bridge, prepared by setting a mixture of saturated KNO$_3$ and agar-agar (3%).

The pH indicator scale was calibrated in the acidic range by using 0.05 M potassium hydrogen phthalate solution and in the alkaline range by 0.01 M solution
of Borax. Before calibration of the pH indicator scale, the temperature compensation knob on the pH meter was kept at a temperature at which the actual experiments were to be carried out. The buffer solutions were also allowed to attain the same temperature.

All the experiments were carried out at a constant temperature of 27°C. The oxygen free nitrogen was continuously bubbled through the reaction mixture to avoid the oxidation of ligands. All weights were taken using an electronically operated one pan balance (Model DHONA).

DISCUSSION OF THE RESULTS:

For the determination of proton ligand and metal ligand stability constants, three mixtures were prepared and titrated against standard NaOH using pH-meter. In all these cases, the final volume of systems was kept constant by making total volume 100 ml, so that the concentration of acid i.e. HNO₃ remained constant for all the systems.

The concentration of all the common ingredients were kept identical in different cases, maintaining an ionic strength of 0.1 M (m = 0.1 M of KNO₃). The ratio of metal to ligand (in system no III) was kept 1:5.

A graph was then plotted between pH meter reading and volume of NaOH added. The nature of graph is shown in Figs. 1 to 15.

The details of the final concentration of all the reactants and various constants used in the calculation of $\bar{n}_A$, $\bar{n}$ and pL values are summarised in Table 3.1.
Table 3.1 Details of various parameters used in the calculations (at μ = 0.1 M of KNO₃)

<table>
<thead>
<tr>
<th>No</th>
<th>Ligand</th>
<th>Y</th>
<th>N</th>
<th>E</th>
<th>T₉₀</th>
<th>T₉₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HMDMAP</td>
<td>1</td>
<td>1.11</td>
<td>1.0 x 10⁻²</td>
<td>4.0 x 10⁻³</td>
<td>8.0 x 10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>HCDMAP</td>
<td>1</td>
<td>1.11</td>
<td>1.0 x 10⁻²</td>
<td>4.0 x 10⁻³</td>
<td>8.0 x 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>HMDMAI</td>
<td>1</td>
<td>1.11</td>
<td>1.0 x 10⁻²</td>
<td>4.0 x 10⁻³</td>
<td>8.0 x 10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>HCDMAI</td>
<td>1</td>
<td>1.11</td>
<td>1.0 x 10⁻²</td>
<td>4.0 x 10⁻³</td>
<td>8.0 x 10⁻⁴</td>
</tr>
<tr>
<td>5</td>
<td>HCDMAT</td>
<td>1</td>
<td>1.11</td>
<td>1.0 x 10⁻²</td>
<td>4.0 x 10⁻³</td>
<td>8.0 x 10⁻⁴</td>
</tr>
</tbody>
</table>

Practical Proton Ligand Stability Constants of Ligands:

The plots of volume of alkali against pH meter reading Figs. (1), (4), (7), (10) and (13) were used to evaluate proton ligand stability constants of various ligands.

The horizontal distance (V₂-V₁) measured accurately between acid curve (I) and acid + ligand curve (II) was used to calculate the formation function T₉. The values of log K₉ were then read from the graph of T₉ Vs pH.

Since the ligands involved in the present study contain a phenolic -OH group, they can be considered as monobasic acids having only one dissociable H⁺ ion and therefore, can be represented as HL. The dissociation of ligand may be represented as:

\[ \text{HL} \rightleftharpoons \text{H}^{+} + \text{L} \]
By the law of mass action, we have,

$$K = \frac{[H^+] [\bar{L}]}{[HL]}$$

where the quantities in brackets denote the concentrations of the species at equilibrium.

The formation curves, $\bar{n}_A$ against pH for the proton ligand systems of all the five ligands (HMDMAP, HCDMAP, HMDMAI, HCDMAI and HCDMAT) at 27°C and at a fixed ionic strength ($\mu = 0.1$ M) are shown in Fig. 16. In the calculations of $\bar{n}_A$, the value of $Y$ is assumed to be 1 since all the ligands contain only one replaceable H$^+$ ion. The pK values obtained by interpolation at half $\bar{n}_A$ values are given in Table 3.2.

From the formation curves (which extended between 0 to 1), it appears that dissociation of these ligands occurred at higher pH. All the ligands showed their dissociation in the pH range of 9.30 to 10.50. HMDMAP with its pK value of 10.49 seemed to have dissociated at comparatively higher pH whereas HCDMAT showed the lowest pK value of 9.38.

Table 3.2. Practical Proton-ligand stability constants (pK) of ligands at $t = 27^\circ$C and $\mu = 0.1$ M (KNO$_3$).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand</th>
<th>Constant (pK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HMDMAP</td>
<td>10.49</td>
</tr>
<tr>
<td>1</td>
<td>HCDMAP</td>
<td>10.21</td>
</tr>
<tr>
<td>1</td>
<td>HMDMAI</td>
<td>9.63</td>
</tr>
<tr>
<td>1</td>
<td>HCDMAI</td>
<td>9.57</td>
</tr>
<tr>
<td>1</td>
<td>HCDMAT</td>
<td>9.38</td>
</tr>
</tbody>
</table>
From the above values and dissociation of HMDMAP, HCDMAP, HMDMAI, HCDMAI and HCDMAT, it can be assumed that these ligands act as monodentate in the formation of binary complexes with Co\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) metal ions.

**Metal-ligand Stability Constants of Binary Complexes:**

The complex formation between \(M = \text{Co(II), Ni(II), Cu(II)}\) and the ligands, \(L = \text{HMDMAP, HCDMAP, HMDMAI, HCDMAI and HCDMAT}\) was studied by keeping the ratio of \(M:L\) as 1:5. An observation of these systems shows that the metal complex curves diverge from the ligand titration curves in the pH range of 3 to 4 indicating that the formation of metal complex \((M:L)\) took place at low pH.

The suitable method for the calculation of metal-ligand stability constants for any system is decided by (i) the symmetry of the corresponding formation curve about its midpoint (ii) the stability constant values for 1:1 and 1:2 complexes, which can be obtained from the midpoint slope of the formation curve (\(\bar{n}\) vs \(pL\)) and (iii) the availability of \(\bar{n}\) values in the low (L) region. The formation curves differ from each other considerably in symmetry and other characteristics and therefore no uniform method of calculations can be employed.

In the present investigation, the metal-ligand stability constants were calculated by interpolation at half \(\bar{n}\) values by employing Irving and Rossott's expressions (equations 19,20).

The accuracy of function, \(\bar{n}\) depends upon how accurately the values of \(V_1\) and \(V_2\) are read. Thus, the titration curves were plotted on expanded scale for
determining the accurate values of \( V_3 - V_2 \), which is the difference in the volume of alkali required to reach the same pH in the titration of acid + ligand + metal salt and acid + ligand titration. The values of \( \bar{n} \) were calculated at different pH values. The values of pL were calculated by using the original equation at different pH and the formation curves for M(II)-L were drawn between \( \bar{n} \) and pL (Fig. 17 to 21). The values of \( \log K_1 \) and \( \log K_2 \) have been read from the formation curves (\( \bar{n} \) vs pL) at \( \bar{n} = 0.5 \) and 1.5 respectively.

**Metal-ligand Stability Constants of Binary Complexes of Co\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) metal ions**

i) Co\(^{2+}\)-HMDMAP:

The displacement between the titration curve B and C (Fig. 1) shows that the complexation occurs at a lower pH (3.0). The \( \bar{n} \) values (Fig. 17) extends from 0.1 to 1.9. The formation of the complex was also indicated due to sharp change in colour from orange red to pale yellow. The values of stability constants obtained from the plot between \( \bar{n} \) vs pL, by interpolation of \( \bar{n} \) at 0.5 and 1.5 are as follows.

\[
\log K_1 = 9.41 \\
\log K_2 = 6.88
\]

ii) Ni\(^{2+}\)-HMDMAP:

The titration curves (Fig. 2), B and C of Ni(II)-HMDMAP system, start deviation at about pH 3.0. The \( \bar{n} \) value (Fig. 17) extends from 0.3 to 1.95. During the titration the colour of the solution changed from red to lemon yellow. The values obtained from the plot between \( \bar{n} \) vs pL by interpolation of \( \bar{n} \) at 0.5 and 1.5 are as follows.

\[
\log K_1 = 9.43 \\
\log K_2 = 7.48
\]
iii) Cu\(^{2+}\)-HMDMAP:

The titration curves (Fig. 3), B and C for the system Cu(II)-HMDMAP start deviating from pH 3. The formation of the complex was indicated due to sharp change in colour from orange red to bluish green during the titration. The \( n \) value extended from 0.45 to 1.95 and showed that the complex is more stable than those of Co\(^{2+}\)-HMDMAP and Ni\(^{2+}\)-HMDMAP. This is also consistent with the observation\(^{34}\) that the stabilities increase with the increasing atomic number up to the end of transition series and then fall at Zinc. Mellor and Malley\(^{15}\) have also obtained the following order of relative stabilities of complexes of bivalent metal ions,

\[
\text{Pd} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}
\]

Irving and Rossotti\(^{36}\) have reported that irrespective of the nature of ligand, stability of metal complexes always follow the following order whether the steric hinderance occurs or not.

\[
\text{Mg} < \text{Zn} < \text{Ni} < \text{UO}_2 < \text{Cu}
\]

The values obtained for Cu\(^{2+}\)-HMDMAP binary complex from the plot between \( n \) vs \( pL \), by interpolation of \( n \) at 0.5 and 1.5 are given below.

\[
\log K_1 = 9.92 \\
\log K_2 = 7.87
\]

Thus, the stability order of Co\(^{2+}\), Ni\(^{2+}\), and Cu\(^{2+}\) metal ions can be given as Co(II) < Ni(II) < Cu(II). The greater stability of Cu\(^{2+}\)-HMDMAP complex can be attributed to the fact that smaller the size of the metal ion stronger will be the attractive force between metal ion and the ligand and hence more stable will be the complex formed.
iv) Co\(^{2+}\)-HCDMAP (V) Ni\(^{2+}\)-HCDMAP and (VI) Cu\(^{2+}\)-HCDMAP:

The titration curves for Co(II)-HCDMAP, Ni(II)-HCDMAP and Cu(II)-HCDMAP are shown in figures 4, 5 and 6. The displacement between the titration curve B and C shows that the complexation occurred at about pH 3.4. The $\bar{n}$ values extended from 0.1 to 1.84, 0.3 to 1.99 and 0.4 to 1.88 respectively for Co(II)-HCDMAP, Ni(II)-HCDMAP and Cu(II)-HCDMAP. The values obtained from the plots between $\bar{n}$ vs $p_L$, by interpolation of $\bar{n}$ at 0.5 and 1.5 are as follows,

\[
\begin{align*}
\text{Co}^{2+}\text{-HCDMAP:} & \quad \log K_1 = 8.69; \quad \text{Ni}^{2+}\text{-HCDMAP} \quad \log K_1 = 9.12 \\
& \quad \log K_2 = 6.86 \quad \log K_2 = 7.42 \\
\text{Cu}^{2+}\text{-HCDMAP:} & \quad \log K_1 = 9.20 \\
& \quad \log K_2 = 7.84
\end{align*}
\]

From the above values, it follows that as compared to Co\(^{2+}\)-HDMMP, Ni\(^{2+}\)-HMDMP and Cu\(^{2+}\)-HMDMAP, the stability of above complexes has decreased. This decrease in the values of stability constants can be attributed to the presence of -Cl in HCDMAP which acts as an electron withdrawing group and thus opposes the donation of electrons to the metal ions. On the other hand, in Co\(^{2+}\)-HCDMAP, Ni\(^{2+}\)-HCDMAP and Cu\(^{2+}\)-HCDMAP, the ligand HMDMP, in addition to -N(CH\(_3\))\(_2\) contains methyl group (instead of -Cl) which favours the donation of electrons to the metal ions and thus increase in the stability of those complexes.

VII) Co\(^{2+}\)-HCDMAI (VIII), Ni\(^{2+}\)-HCDMAI and (IX) Cu\(^{2+}\)-HCDMAI:

The titration curves for above systems are shown in figures 7,8,9. The ligand titration curves (B) and ligand + metal complex titration curves (C) deviate from about pH 3.4 $\bar{n}$ values for these systems seemed to have extended between 0.4
The values obtained from the plots between $n$ vs $pL$ by interpolation of $n$ at 0.5 and 1.5 are as follows,

$Co^{2+}$-HCDMAI: $\log K_1 = 8.53$; $Ni^{2+}$-HCDMAI $\log K_1 = 8.55$

$\log K_2 = 6.48$ $\log K_2 = 6.97$

$Cu^{2+}$-HCDMAI: $\log K_1 = 8.63$

$\log K_2 = 7.11$

X) $Co^{3+}$-HCDMAI (XI), $Ni^{3+}$-HCDMAI and (XII) $Cu^{3+}$-HCDMAI:

The titration curves for above systems are shown in figures 10, 11, and 12. The ligand + metal complex titration curves (C) start deviating from those of ligand titration curves (B) at a slightly higher pH (3.6), which shows that the complexation occurs at a slightly higher pH value. The $n$ values for these complexes extended between 0.3 to 2.0. The values obtained from the plots between $n$ vs $pL$, by interpolation of $n$ at 0.5 and 1.5 are given below.

$Co^{3+}$-HCDMAI: $\log K_1 = 7.44$; $Ni^{3+}$-HCDMAI $\log K_1 = 8.05$

$\log K_2 = 6.11$ $\log K_2 = 6.39$

$Cu^{3+}$-HCDMAI: $\log K_1 = 8.21$

$\log K_2 = 6.57$

It can be observed that the stability of above complexes has decreased from those of $Co^{3+}$-HMDMAI, $Ni^{3+}$-HMDMAI and $Cu^{3+}$-HMDMAI. This can be explained due to the fact that the complexes shown at serial number VII, VIII and IX contain the ligand having electron releasing group (-CH$_3$), favouring the process of donation of electrons to metal ions and hence stronger the interaction between the ligand and the metal ions. On the other hand, the above mentioned complexes (S.Nos.
X, XI and XII) contain the ligand having electron with drawing group (-Cl) instead of -CH\textsubscript{3} which opposes the donation of electrons to the metal ions and hence poor the interaction between the ligand and the metal ion.

However, the above complex shown at serial numbers VII, VIII, IX and X, XI, XII are still less stable than those mentioned at serial numbers I to VI. This decrease in the stability may be attributed to the fact that the presence of more electronegative oxygen atom on the heterocyclic ring of the ligand disfavours the donation of electrons to the metal ion and thus lesser the stability of these complexes.

XIII) Co\textsuperscript{3+}-HCDMAT (XIV), Ni\textsuperscript{2+}-HCDMAT and (XV) Cu\textsuperscript{2+}-HCDMAT:

The titration curves (figs. 13,14, and 15) of above systems shows that the complexation occurs at a slightly higher pH (3.8). The $\bar{n}$ values for these system extended between 0.2 to 2.00. The plots of $\bar{n}$ vs pL gave the log $K_1$ and log $K_2$ values by interpolation of $\bar{n}$ at 0.5 and 1.5 and are given below.

\begin{align*}
\text{Co}^{3+}-\text{HCDMAT}: \log K_1 &= 7.26; \quad \text{Ni}^{2+}-\text{HCDMAT} \quad \log K_1 &= 7.55 \\
\log K_2 &= 5.32 \quad \log K_2 &= 5.71 \\
\text{Cu}^{2+}-\text{HCDMAT}: \log K_1 &= 7.86 \\
\log K_2 &= 5.95
\end{align*}

The lowest values stability constants for above complexes can be explained due to the fact that the ligand involved in the formation of above complexes is rather bulky containing six membered heterocyclic ring which may cause steric hinderance and secondly, the electron withdrawing -Cl group opposes the electron donation to the metal ions and hence lowest the stability of these complexes.
The values of metal-ligand stability constants of binary complexes of Co(II), Ni(II) and Cu(II) with HMDMAP, HCDMAP, HMDMAI, HCDMAI and HCDMAT are summarised below in Table 3.3.

Table 3.3 Metal-ligand stability constants of binary complexes of Co(II), Ni(II) and Cu(II).

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Stability constant</th>
<th>L</th>
<th>I</th>
<th>G</th>
<th>A</th>
<th>N</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HMDMAP</td>
<td>HCDMAP</td>
<td>HMDMAI</td>
<td>HCDMAI</td>
<td>HCDMAT</td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>log$K_1$</td>
<td>9.41</td>
<td>8.69</td>
<td>8.53</td>
<td>7.44</td>
<td>7.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>log$K_2$</td>
<td>6.88</td>
<td>6.86</td>
<td>6.48</td>
<td>6.11</td>
<td>5.32</td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>log$K_1$</td>
<td>9.43</td>
<td>9.12</td>
<td>8.55</td>
<td>8.05</td>
<td>7.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>log$K_2$</td>
<td>7.48</td>
<td>7.42</td>
<td>6.97</td>
<td>6.39</td>
<td>5.71</td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>log$K_1$</td>
<td>9.92</td>
<td>9.20</td>
<td>8.63</td>
<td>8.21</td>
<td>7.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>log$K_2$</td>
<td>7.87</td>
<td>7.84</td>
<td>7.11</td>
<td>6.57</td>
<td>5.95</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions:

From the Table, the trend in the stability order of metal ions can be given as Co(II)<Ni(II)<Cu(II). Similarly, the trend in the stabilities of binary complexes of these metal ions with respect to change in ligand can be given as,

HCDMAT < HCDMAI < HMDMAI < HCDMAP < HMDMAP
Both the above trends are justified on the grounds that (i) smaller the size of a cation, stronger will be its interaction with the ligand and consequently higher will be the stability of a complex formed. ii) The complex formed from a ligand containing electron releasing groups like -CH₃ will be more stable than those containing electron withdrawing groups like -Cl. iii) the pk values of the above mentioned ligands also follow the same order from HCDMAT to HMDMAP and IV) The ligands involving five membered heterocyclic ring containing nitrogen atoms may form more stable complexes than that containing bulkier six membered ring.
Fig. 1: Co-HMD MAP

Vol. of NaOH (ml) →

A
B
C

pH
0.25 0.5 0.75 1.0 1.25 1.50
Fig. 3: Cu-HMDMAP
Fig. 4: Co-HCDMAP

Vol. of NaOH (mL)
Fig. 5: Ni-HCDMAP.
Fig. 6: Cu-HCDMAP

Vol. of NaOH (ml)
Fig. 7: Co-HMDMA1

Vol. of NaOH (ml)
Fig. 8: Ni-HMDMA1
Fig. 10: Co-HCDMA1

Vol. of NaOH (ml)

Vol. of NaOH (ml)
Fig. 11: Ni-HCDMA1

Vol of NaOH (ml)

A B C
Fig. 13: Co-HCDMAT

Vol. of NaOH (mL)
Fig. 14: Ni-HCDMAT

Vol. of NaOH (ml) →

Vol. of NaOH (ml) →
Fig. 15: Cu-HCDMAT

Vol. of NaOH (ml) →

A

B

C
Fig. 17: $\tilde{n} \times pL$

1: Co-HMDMAP
2: Ni-HMDMAP
3: Cu-HMDMAP;
Fig. 18: $\bar{n} \times pL$

4: Co-HCDMAP
5: Ni-HCDMAP
6: Cu-HCDMAP
Fig. 19: $\bar{n} \times pL$

- 7: Co-HMDMAI
- 8: Ni-HMDMAI
- 9: Cu-HMDMAI

$\bar{n}$ and $pL$ are plotted on the graph.
Fig. 20: $\bar{n} \times p_L$

10: Co-HCDMAI
11: Ni-HCDMAI
12: Cu-HCDMAI
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