

SUMMARY AND CONCLUSIONS

The detailed survey of literature revealed that **Schiff Bases (also known as Azomethines)** behave as monodentate, bidentate and polydentate ligands towards many metal ions in the formation of complexes. The characterization of metal-schiff base complexes synthesized electrochemically has also been reported in the literature. Studies of Metal-Azomethine complexes in solution have been carried out by several authors. Metal-to-ligand ratio and stability constants for the complexes were computed using P^H metric and Potentiometric, Spectrophotometric and Conductometric techniques. Polarographic technique has also been employed by various authors in the study of Metal-Azomethine complexes to determine coordination number, stability constants, kinetic parameters and stereochemical behaviour in solution for reversible and irreversible electrode systems. The most characteristic aspect of the compounds containing the **>C=N-** group which show basic properties lies in the formation of complexes with metals. These complexes provide some very characteristic series of coordination compounds. The basic strength of the **>C=N** group is inadequate by itself to permit the formation of stable complexes by simple coordination of the lone pair of electrons to a metal ion. Therefore, in order that stable compounds to be formed it is necessary that there should also be present in the molecule a functional group with a replacable hydrogen atom, preferably a hydroxyl group near enough to the **> C=N-** group to permit the formation of a five or six membered ring by chelation to the metal atom.

The **>C=N-** group is present in many organic molecules of fundamental importance. They have got extensive applications in biological and industrial fields. Schiff bases with potential pharmaceutical use were synthesized. Azomethines were also used as starting material and intermediates in the preparation of herbicides. It is found that schiff bases have been employed as growth regulators and useful as plant growth regulators. Some azomethine compounds used as growth stimulants were also reported in the literature.

The use of organic reagents in inorganic analysis is a major field of interest. The various organic compounds usually employed in chemical analysis are oximes, oxines, Schiff bases, semicarbazones, thiosemicarbazones, hydrazones, xanthates, dithiols, dithiocarbamates etc. Of the $>C=N-$ group containing reagents Schiff bases (also termed as Azomethines) are said to possess many important applications in the fields of greater interest like medicine, pharmacy, agriculture, photography, catalysis, polymer technology, paints and pigments and industries such as textiles glass, automobile, electroplating, perfumes, filament etc., Organic compounds of varied nature are widely employed as analytical reagents. Schiff bases of aldehydes and ketones occupy an important place amongst other organic compounds like oximes, semicarbazones and thiosemicarbazones as complexing agents. The contributing factor of the importance of azomethines lies in their readiness to form coordination compounds with metals. This fact has been well established for many years by several authors.

The complex forming ability of Schiff bases is attributed to the presence of basic site i.e., $>C=N-$. The more ease with which it donates lone pair of electrons, more will be the stability of the complex. This depends on the presence of substituent groups in the compound. Literature survey revealed that Schiff bases behaved as monodentate, bidentate, tridentate, tetradentate etc. If an $-OH$ group is present at ortho position, it is capable of forming chelate rings which in turn enhances the stability of the complex. It is quite evident that complexes containing six membered rings are more stable than that of five membered rings.

2-Amino-2-Methyl-1-Propanol, $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$ (shortly termed as AMP) is one of the important compounds of unique series of alkanolamines of aliphatic hydroxyl amines. Perusal of literature revealed that not much work has been carried out in establishing the complexing ability of 2-amino-2-methyl-1-propanol, towards metal ions. Even the available few references on metal complexes of AMP not fully established the coordinating ability of AMP towards metals, but only emphasized the applications of those complexes in biological fields. The Schiff bases derived from AMP also finds significant applications in the field of medicine and industry.

In view of the these facts in a view, the author in the present investigation has prepared five new Schiff bases using 2-Amino-2-Methyl-1-Propanol (AMP) as common amine with a hope that some of them as such or in the form of metal complexes may finds a place in any of the above mentioned fields. In the present research investigation new Azomethines (Schiff Bases) derived from AMP and substituted aromatic aldehydes.

In the present research study, The author has prepared the five new Schiff bases and studied their Polarographic behavior in presence of Cadmium metal ion. In addition, Voltammetric Studies of newly synthesized Schiff Bases have been reported in this research investigation. Electrochemical behaviour of Cadmium-New Azomethine Complexes has been discussed in detail. Keeping the significant importance of electrochemical studies of Schiff Bases and its metal complexes in a view, Polarographic method has been employed in the present investigation for detailed study of metal – new azomethine complexes.

The research programme embodied in the present investigation consists of seven chapters and literature citations are exclusively given. The important aspects, synthesis, characterization, experimental research, structural elucidation and biological evaluation are described in the part of the thesis. Further, detailed electrochemical behaviour of newly synthesized five Schiff Bases have been discussed and electrochemical investigations has been carried out by Polarography and Cyclic Voltammetric studies. Every chapter has been divided into different sections. The work carried out in the present research investigation has been discussed in the seven chapters.

CHAPTER – I is concerned with Theoretical principles of Polarography. It is further subdivided into three sections.

Section (i) includes General principles of polarography

Section (ii) represents methods for Reversible electrode reactions of complexes at D.M.E.

Section (iii) represents methods for Irreversible electrode reactions of complexes at DME

CHAPTER – II deals with detailed **Literature survey of Schiff bases**. It is subdivided into three sections

Section (i) includes Chemistry of Schiff bases

Section (ii) represents the Applications of Schiff Bases and their metal complexes

Section (iii) Illustrates the chemistry of AMP

CHAPTER – III describes Scope of the study, Synthesis and Characterization of the following five Schiff Bases derived from 2-Amino-2-Methyl-1-Propanol (AMP) and substituted aromatic aldehydes.

In the present research investigation author Synthesized five novel Schiff bases (Azomethines) by the condensation of 2-Amino-2-Methyl-1-Propanol with 2-Hydroxy-3-MethoxyBenzaldehyde(O-Vanillin),4-Hydroxy-3-Methoxy-Benzaldehyde (P-Vanillin),4-Hydroxy-3,5DimethoxyBenzaldehyde (Syringaldehyde), 3,4-Dimethoxy Benzaldehyde (Veratraldehyde) and 3, 4, 5-Trimethoxy Benzaldehyde (TMB).

- i) **2-hydroxy-3-methoxy bezaldehyde-AMP(O-VAMP)**
- ii) **4-hydroxy-3-methoxy bezaldehyde-AMP(P-VAMP)**
- iii) **4-hydroxy-3,5-Dimethoxy bezaldehyde-AMP(SYN-AMP)**
- iv) **3,4-Dimethoxy bezaldehyde-AMP(VER-AMP)**
- v) **3,4,5-Trimethoxy bezaldehyde-AMP(TMB-AMP)**

Synthesis and characterization of five new Schiff bases have been reported in Chapter 3 . Elemental analysis and IR data confirmed the formation of >C=N- group. Synthesized Schiff Bases have been characterized by employing IR, UV techniques and its structures were established by Infrared, Ultraviolet techniques and elemental analysis.

CHAPTER –IV Is devoted to study the complexing ability of the synthesized Schiff bases towards Cadmium metal ion. This chapter is further sub-divided into four sections.

Section (i) describes the **Effect of hydrogen ion concentration** on Cadmium-Schiff base complexes

Section (ii) furnishes the **Effect of ligand concentration** on wave height.

Section (iii) elucidates the experimental results pertaining to the **Effect of height of mercury column.**

Section (iv) explains the **Effect of metal ion concentration**

In order to establish the complexing ability of newly prepared Schiff bases (**O-VAMP,P-VAMP,SYN-AMP,VER-AMP and TMB-AMP**) Cadmium metal ion has been selected for detailed electrochemical investigation. The electrochemical studies include effect of pH, effect of ligand concentration, effect of height of mercury column and effect of metal ion concentration [**CHAPTER-IV; Section (i) - (iv)**]. The results revealed that electrode reactions of metal complexes were diffusion controlled. In all the systems, the diffusion current decreased and half-wave potential shifted towards more negative value suggesting the complex formation.

CHAPTER – V illustrates the experimental data obtained for the determination of ligand number and stepwise formation constants of Cadmium complexes with five new azomethines using standard methods. It is clearly evident that electrode reactions at d.m.e can broadly be divided into two categories, namely reversible and irreversible processes. Reversible processes are so rapid that thermodynamic equilibrium is very nearly attained at every instant the life of a drop at any potential. These reactions are of much help in determining the metal-to-ligand ratio and the stability constants of complex species that are undergoing reduction in solution. From the slope of the logarithmic analyses, which are very close to the theoretical value of the reversible two-electron reduction step viz. 0.03 V vs SCE, it is observed that Cadmium is reduced reversibly at d.m.e in presence of Schiff bases.

From the preliminary studies (**Chapter IV-Section i-iv**), it was observed that Cadmium formed complexes with all new Schiff bases under consideration over the concentration studies. The reduction of these complexes at d.m.e was diffusion controlled and reversible with two electrons participating in the electrode reaction. The presence of more than one complex species in equilibrium in all the systems was evidenced from the smooth curves obtained when plots (Chapter V-Figs.1,5,9 and 15) were drawn between $E_{1/2}$ and $-\log [X]$. Hence DeFord and Hume method was employed to calculate the metal-to-ligand ratio and stepwise formation constants for each system. The obtained data (**Chapter V-Tables 1-4**) indicates that **Cadmium formed 1:2 complexes with OVAMP and PVAMP systems and 1:4 complexes with VERAMP AND TMBAMP systems.**

It is well known fact that Schiff bases are weakly basic compounds. The basicity which is attributed to the presence of lone pair of electrons on the nitrogen atom of $>C=N-$ group is responsible for complex formation with metal ions. They can also form five or six membered stable chelates with metals if a functional group with a replaceable hydrogen atom, preferably an hydroxyl group, is present at ortho position to the $>C=N-$ group. The basicity of the imino group is influenced by variation of substituents present either in the aldehyde moiety or in the amine moiety. Also each substituent varies the basicity more or less with respect to its position. In the present investigation, as the Schiff bases were prepared from a common aliphatic hydroxyl amine and various aldehydes, the basicity of the Schiff bases was affected by different substituents present in the aldehyde component. The complexing ability of these Schiff bases with Cadmium, which depends on the basicity of the $>C=N-$ group, has been understood on the basis of inductive, mesomeric and steric effects of the substituents. **From the stability constant values (Chapter V-Table 5), it is clearly noticed that Cd-OVMP complexes were more stable than Cd-PVMP complexes and on the other hand, Cd-VERAMP complexes were more stable than Cd-TMBAMP complexes.**

CHAPTER – VI describes the detailed Voltammetric Studies of newly prepared Schiff bases derived from AMP and substituted aromatic aldehydes. This chapter has been divided into three sections.

Section i – Materials and Methods involved in Voltammetric Studies

Section ii – Polarographic studies of Schiff Bases derived from AMP

Section iii – Cyclic Voltammetric studies of Schiff Bases derived from AMP

In this chapter, The Polarographic and Cyclic Voltammetric studies of Schiff bases have been discussed in detail towards understanding detailed aspects of electrochemical behavior of azomethines. The electrochemical studies includes the Effect of pH, Effect of height of mercury column, Effect of concentration of substrate and Evaluation of Kinetic Parameters. The Electrochemical studies of Schiff bases were carried out in Britton-Robinson Buffer Solutions of pH 4.1 and 8.1 and effect of mercury column height was carried out at pH 4.1.

Millicoulometric analysis was carried out for all Schiff bases to know the number of electron in the redox behavior of different functional groups present in the Schiff bases. The Polarographic reduction waves noticed in the Schiff bases was attributed to the reduction of the exo-cyclic Azomethine group. From the preliminary studies, it was observed that half-wave potential increases with pH and diffusion current values decreases with increase in pH values. For irreversible systems, Kinetic parameters have been evaluated. The number of polarographic reduction wave in DC Polarography and number of cathodic peaks in Cyclic Voltammetric studies are one and the same. The additional anodic peak noticed for all Schiff bases under experimental conditions and the anodic peak attributed to two electron oxidation of primary alcohol group to aldehyde. The reduction process in Polarographic studies and simultaneous oxidation and reduction process in Cyclic Voltammetric studies clearly examined.. The reduction potential of Cadmium metal is different from the reduction potential of $>C=N-$ group, therefore the reduction of $>C=N-$ group will not interfere the actual reduction of metal ion while studying the complexing ability of Schiff bases. This chapter significantly describes the redox behavior of Schiff bases derived from AMP and aromatic substituted aldehydes.

CHAPTER – VII describes the detailed **Biological evaluation** of newly prepared Schiff bases derived from AMP and also deals with anti-bacterial studies of Cadmium-New Azomethine metal complexes. On perusal of literature survey revealed that the Schiff bases have got extensive applications in Biological and Pharmaceutical fields. Complexes with bidentate Schiff bases were reported to possess biocide activity against bacteria and fungi. 2-Amino-2-Methyl-1-Propanol (AMP) and its metal complex derivatives were used as inflammatory inhibitors, Antipyretic, analgesic, antitumor, antiviral, antifungal and antibacterial agents and they also found wide applications in immuno-pharmacology. Keeping all these facts in a view in the present investigations the author studied the **antibacterial Activity of some novel Schiff bases derived from AMP and O-vanillin. P-Vanillin. Syringaldehyde, Veratraldehyde and Trimethoxy benzaldehyde.**

The antibacterial studies were carried out using the chloramphenicol and ketocanazole as reference standards. The results pertaining to antibacterial activity of Schiff bases against gram positive and gram negative bacteria was presented in the (**Chapter VII Table 1**) and the zone of inhibition of Schiff bases was demonstrated in **Plate-1 and Plate-2**. The experimental results on antibacterial studies revealed that all Schiff bases under present investigations exhibit moderate to good antibacterial activity. The order of Schiff base activity is **TMB-AMP>VER-AMP>SYN-AMP>O-VAMP>P-VAMP**. This is in accordance with electronic parameters of the Schiff bases.

It may be concluded that the preparation of new Schiff bases, will be a new addition to the already well existing Schiff base chemistry. The present studies may contribute immensely to the none to existing literature on the polarographic studies of Metal Schiff base complexes. It may, therefore, well be claimed as a novel attempt, as far as Polarography of Metal-Schiff base complexes is concerned.. The detailed electro chemical investigation of Cd (II)-New Schiff Base complex systems may add new dimensions to coordination chemistry of metal complexes. Studies pertaining to reversible and irreversible electrode reactions and thereby determination of Metal-to-ligand ratio, stability constants, rate constants are perhaps the most noteworthy feature of this investigation. Further, Polarographic and Cyclic :Volatammetric Studies of Schiff Bases will enrich subject knowledge on the redox behavior of Schiff bases in different conditions. Biological evaluation of new Schiff bases finds significant applications and the detailed electrochemical investigation may add new dimensions to Coordination Chemistry of metal complexes.
