CONCLUSION

Our major aim in the current work is our progress towards understanding the various structural aspects of the Galactose Oxidase enzyme and Co-enzyme B\textsubscript{12} by preparing novel Copper Schiff base or bis-phenolato complexes as model compounds of copper proteins and cobaloximes and their methyl derivatives as models of vitamin B\textsubscript{12} and then study their spectroscopic and electrochemical behaviour in various aqueous surfactant micellar solutions. The model compounds of galactose oxidase such as copper schiff base complexes in aqueous solutions of surfactant micelles closely mimic the natural copper protein. Thus cobalt complexes encapsulated in micelles are likely to be good functional models for vitamin B\textsubscript{12}. This shows that further studies on these systems are likely to provide valuable information on the redox chemistry of cyanocobalamin and methylcobalamin.

Surfactant micelles provide the typical hydrophobic environment in aqueous solutions around the metal complexes at the active site of metalloproteins under certain physiological pH. Micelle encapsulation leads to mono-dispersion of the complex and the effective concentration of the monomers in solutions increases and hence the molar extinction coefficient values are larger. The surface charges on the surfactant micellar solutions give rise to interesting property. The sparingly soluble complexes can be solubilized in surfactant micelles above a threshold concentration of the surfactant. Surfactant micelles promote catalysis since the micelles provide an ordered surface in aqueous solution.
The complexes of the type Cu(Salen) are dimeric in nature in the solid state and are sparingly soluble in water or aqueous solution. Cu(SalenS) is highly soluble in water and Cu(salicyldehyde)$_2$ is sparingly soluble in water and Cu(Sal1,3pn) monomeric in the solid state is soluble in water and in aqueous solutions of surfactant media. The solubility of the complexes increases in aqueous surfactant micellar solutions. The copper complex in a micelle interacts with the surfactant and hence the micelle encapsulated complex show interesting changes in the spectral and electrochemical results on increasing the pH of the aqueous solutions. The results are pH dependent. They show interesting color changes with a structural change between a four coordinated flattened tetrahedron to a five coordinated square pyramidal structure on increasing the pH of the aqueous solutions. At low pH (2.0-4.0) the complexes are four coordinated while at high pH (4.0-7.0) the predominant form is five coordinated. Increasing absorbance at 375nm relative to that at 326nm is taken as evidence of a new charge transfer process arising from solvation to the metal. At pH less than 4.0 the four coordinated violet coloured complex is the major species, while at pH values more than 4.0 the green colour five coordinated aqua complex is the major one.

Aqueous micellar solution is an excellent media for electrochemical studies of Copper(II) Schiff base complexes. Schiff base complexes are very sensitive to the hydrophobic environment of surfactants in micelles. The protonation or deprotonation of a ligand also influence the potential. The midpoint potential of the complex increases with increasing concentration of surfactants beyond which
the potential changes less rapidly or remain constant. The threshold concentration beyond which the midpoint potential tends to attain a constant value is the critical micellar concentration (cmc) of the surfactant. The hydrophobic environment of micelles induces a positive shift of the midpoint potential of the complex as compared to that in water.

The oxidation potentials found in Cu(Schiff base) complexes are compared with that of Zn(Schiff base) complexes in micellar solution by electrochemical techniques. The Zn$^{2+}$ and Cu$^{2+}$ complexes show their midpoint potential values ($E_{1/2}$) in the range +200 to +400mV in SDS and CTAB micellar solution which may be attributed to the oxidation of the coordinated phenolate anion in the schiff base ligand. The potential at the negative side found in the complexes is assigned to the Cu$^{II}$/Cu$^{I}$ couple which is absent in Zinc(II) complexes. The observed oxidation of the phenol-phenoxy radical couple in p-cresol is very similar to the one observed in the copper and zinc schiff base complexes. Oxidation of copper and zinc schiff base complexes by ammonium ceric nitrate in aqueous micellar as well as organic solvents also indicate ligand oxidation to a phenoxy radical. Micellar solution of the complexes on treatment with (NH$_4$)$_2$[Ce(NO$_3$)$_6$] results in a color change. A new optical absorption band at around $\lambda_{max} = 440$nm indicates the generation of $M^{II}$-phenolate radical similar to those generated for galactose oxidase. Electrochemically generated $M^{II}$-phenolate radical species are confirmed by uv-visible spectra and also by electron paramagnetic resonance technique.
It is also demonstrated that an aqueous surfactant solution of a copper phenolate complex in the presence of air at room temperature catalyse the oxidation of primary alcohols (such as n-propanol, n-butanol, benzyl alcohol and galactose) to their corresponding aldehydes. The Cu$^{1+}$ complex is soluble and stable in aqueous micelles. In the presence of alcohol the Cu$^{1+}$ complex rapidly reacts with O$_2$ or air. From the spectroscopic and electrochemical studies it appears that the oxidized product, is more stable at lower pH(<5).

In addition to examining the feasibility of redox mechanisms of Cu(Salen) complex under various environments, the stabilization of an oxidation state of the complex may be justified from the variation of redox potential in salen and other metal complexes. The redox potentials of copper complex with reference to additional protonation at the phenolate group such as the transition of [Cu(Salen)] to [Cu(Salen)H$^+$] produces some changes in the shifting of electron from the ligand after protonation at phenolate group. It has been found that the oxidation potential obtained from electrochemical studies are not exactly equal to the computed values for [Cu(Salen)H$^+$] (except for the reduction potential of HF/STO-3G).

Use of modern spectroscopic and electrochemical techniques have shown further insight into the nature of the oxidation state of cobalt atom in vitamin B$_{12}$ and its model compounds. The solvent dielectric in micellar medium and hydrophobic environment of surfactants around the metal complexes and vitamin
$\text{B}_{12}$ has shown a considerable influence on the visible absorption bands and the redox potentials. Ligands also show a considerable influence on the UV-visible absorption bands. The model complexes are very sensitive to pH and solvents.