ABSTRACT

Metalloporphyrins broadly falls under two catalogs, viz., naturally occurring and synthetically modified metalloporphyrins/porphyrins. Synthetically modified porphyrins and metalloporphyrins are interesting to study because they serve as biological model systems. On the other hand they also exhibit properties permit than to use in the field of medicines (photodynamic therapy of cancer) and also possibilities of using them in the field of material sciences (semi-conductors etc).

Obviously, porphyrin chemistry expands and progresses. This thesis embodies the physico-chemical studies of some vanadyl porphyrins which are not reported in the literature so far. It also incorporated a small chapter on the electrochemistry of some manganese, cadmium and copper porphyrins which are not reported in the literature.

This thesis consists of five chapters. Chapter 1 presents a brief review of the EPR and Cyclic voltammetric studies of some vanadyl porphyrins. Chapter 2 describes different experimental techniques and measurements used in the course of investigation. Chapter 3 presents cyclic voltammetric studies of some vanadyl porphyrins.
Chapter 4 deal with cyclic voltammetric studies of some manganese, cadmium and Copper porphyrins.

Chapter 5 describes EPR of some substituted vanadyl meso-tetraphenyl porphyrins oxidized with SbCl₅

Chapter 1 presents a brief review on vanadyl porphyrins of substituted TPP systems mainly focusing on the electron paramagnetic resonance (EPR) and Cyclic voltammetric (CV) Studies.

Chapter 2 deals with the general experimental techniques and the synthesis of porphyrin and metalloporphyrins, purification of solvents and other reagents used in cyclic voltammetric and ESR studies. \[ T(2,5-(OCH₃)_2)PP \], \[ T(o-NO₂)PP \], \[ T(p-OH)PP \], TPyP and its vanadyl complexes were prepared according to methods described in literature. The crude compound was purified by silica gel column chromatography using dichloromethane. It was conformed by UV spectrophotometer. Vanadyl, manganese, copper and cadmium porphyrins were prepared according to the method as described in the literature. The crude compound was purified by silica gel column chromatography using dichloromethane. It was conformed by UV spectrophotometer

Chapter 3 presents cyclic voltammetric studies of some vanadyl porphyrins. Dichloromethane and tetra-n-butyl ammonium
perchlorate were used as solvent and supporting electrolyte respectively. Cyclic voltammetric studies were done on vanadyl porphyrins viz [VO[T(2,5-(OCH₃)₂)PP], VO[T(o-NO₂)PP], VO[T(p-OH)PP], and VO[TpyP]. All the CV measurements were done with 10⁻³ M solutions of the metalloporphyrins.

The voltammogram of [VO[T(2,5-(OCH₃)₂)PP] indicate the oxidation potentials are slightly higher than that of the VOTPP by about 0.085V and 0.054V respectively. The reason for lowering the oxidation potentials in the case of [VO[T(2,5-(OCH₃)₂)PP] may be because of symmetrical substitution of the phenyl ring which puts it more or less in the similar geometry to that of VOTPP. Although the shifts in the potential either way are small they are quite uniform. This gives us some thoughts to suggest that there are some changes in the geometry of the molecule on substitution which affect the energy levels (HOMO) of the molecule hence shifts in the redox potentials occurs. In fact the voltammogram is of successive one electron transfer of the porphyrin ligand and are reversible. The voltammogram of the VO[T(p-OH)PP] is not a straight forward successive one electron transfer process. The first oxidation potential and its corresponding reduction potential are lower than that of VOTPP, while the second oxidation shows very strong oxidation peak current. The peak current corresponds to more than
one electron transfer. Clearly, the second oxidation involved a process which is irreversible along with the reversible process. This could be due to the formation of secondary oxidation states involving the phenolic groups, leading to oxidative electro polymerizations. On subsequent scanning the peak current decreases leading to film formation at the electrode surface. The electron donating group (-OH) increases the electron density of the macrocycle, making the removal of electron easier. Thus, the oxidation potential decreases. The redox process of VO[T(o-N02)PP], is in line with the redox process of [VO[T(2,5-(OCH3)2)PP] . The first oxidation potential is lower than that of VOTPP. This could be due to the structure factor. The oxidation potentials of VOTpyP are observed to be lower than that of the VOTPP. It is most likely that the lower in oxidation potentials is due to metal dxy porphyrin orbital (a2u) interaction in ruffle distortion and metal dx2-y2 porphyrin orbital (a2u) in saddle distortion.

Chapter 4 deal with cyclic voltammetric studies of some manganese, cadmium and Copper porphyrins. Mn[T(2,5-(OCH3)2)PP], Mn[T(o-N02)PP], Mn[T(p-OH)PP], Mn[TpyP]. Cd[T(2,5-(OCH3)2 )PP], Cd[T(o-N02 )PP], Cu[T(2,5-(OCH3)2 )PP] and Cu[T(o-N02 )PP] All the CV measurements were done with 10^{-3} M solutions of the metalloporphyrins. Manganese porphyrin show
Mn(II) to Mn(III) oxidations. Except Mn[T(p-OH)PP] other three manganese porphyrins exhibit two ligand oxidations. These oxidation potentials are slightly on the lower side. This may be due to structural changes. Mn[T(p-OH)PP] shows polymerization at electrode surface.

In the case Cd and Cu porphyrins, two ligand redox potentials are observed. The redox process involved successive one electron transfer and are reversible. Oxidation potentials are observed to be slightly lower than that of these respective to TPP complexes. This is reversibility due to the distortions in the structure. Further, effect of electron donating and electron withdrawing groups are also reflected on the redox potentials.

Chapter 5 describes EPR of some substituted vanadyl meso-tetraphenyl porphyrins oxidized with SbCl$_5$. Except for the VO[T(p-OH)PP] other three vanadyl porphyrins undergo oxidation with SbCl$_5$ generating radical cations in the same process to that of the oxidation of VOTPP. In case of VO[T(o-NO$_2$)PP]. It clearly undergoes oxidation quite similar to that of the oxidation of VOTPP. VO[T(p-OH)PP] polymerizes an oxidation. Other, Vanadyl porphyrins form triplet state which are observable at room temperature at higher modulation. Pre-oxidizd complexes are also observable at room temperature.