CHAPTER VIII

Summary and conclusions

The thesis involves detailed EPR studies on some paramagnetic metalloporphyrins. A brief review on the impact of metalloporphyrins in chemistry, biology, and physics has been presented in the first chapter. Two aspects of the paramagnetic metalloporphyrins have been highlighted in this work. (i) The static spin Hamiltonian parameters for structural elucidation. (ii) Dynamic aspects reflected by the study of relaxation times. The static Hamiltonian parameters have been investigated for the one-electron oxidation product of Ni(II) porphyrins (Chapter IV). The EPR spectra obtained for the one-electron oxidation product of Ni(II) porphyrins have been reported to be very much dependent on the oxidant and solvent. We have attempted a detail study on the EPR measurements on the oxidation of a few Ni(II) porphyrins with bromine, iodine, I$_2$/AgClO$_4$, boron-trifluoride and trifluoro-acetic acid. EPR spectra were recorded at room temperature and liquid nitrogen temperatures. Three distinct species were identified from our studies.

1) A Ni(II)TPP radical cation (Ni(II)TPP$^+$) having a broad line epr spectrum.

2) A radical cation having a very sharp line epr spectrum.

3) Ni(III) porphyrin having anisotropic peak with $g_\parallel < g_\perp$.

The second part of the thesis involves the study of relaxation times by the method of continuous wave saturation recovery method. The relaxation behaviour of Cu(II) porphyrins have been investigated as function of added π electron acceptors. Both diamagnetic and paramagnetic π-acceptors has been included. A method has been developed for the determination of the stoichiometry of donor-acceptor complex by CW
saturation recovery method. An order of magnitude estimation of equilibrium constant has also been attempted.

The following systems have been investigated by CW saturation method

Complexes formed between

1) Cu(II)TPP and Trinitrobenzene (TNB).

2) Cu(II)TPP and 1,2-dichloro3,4-dicyano5,6-benzoquinone (DDQ).

This study is presented in Chapter V. It has been observed that the parameter $\gamma^2 T_1 T_2$ depends on the ratio of the concentration of Cu(II)TPP and the $\pi$-acceptor (TNB or DDQ). The quantity, $P_{1/2} = K_0 (\gamma^2 T_1 T_2)^{-1}$ was obtained from the saturation profiles of Cu(II)TPP in the presence of various concentration of acceptor. A plot of $P_{1/2}$ versus various concentration of the acceptor yields the stoichiometry of the complex.

It has been observed that in the presence of the $\pi$-acceptor, the EPR lineshapes of frozen solution of Cu(II)TPP are dominated by homogeneous broadening. The changes in the parameter $P_{1/2}$ as a function of acceptor concentration could be directly correlated to the changes in the spin-lattice relaxation times of Cu(II) centre.

A different set of complex involving Cu(II) and Fe(III) or Mn(III) porphyrin have been taken up for EPR studies. These studies are reported in Chapters VI and VII. In Chapter VI, the studies on the complexes formed between Cu(II)TPP and Fe(III) porphyrins have been reported. One of the porphyrins has strong electronegative substituents in the periphery, and hence it behaves like a $\pi$-acceptor. The following combinations have been investigated.

1) Cu(II)TPP and Fe(III)TPPC(N)₄Cl.

2) Cu(II)TPP and Fe(III)TPPC(N)₂Cl.
3) Cu(II)TPP(CN)$_4$ and Fe(III)OEP Cl.

From the $P_{1/2}$ values obtained for a fixed concentration of Cu(II)TPP against varying concentrations of iron porphyrins, the stoichiometry and a rough estimation of equilibrium constant have been obtained. It has been noticed that the saturation profiles of Cu(II)TPP are dominated by inhomogeneous broadening, which obviously arises from the dipolar interactions between the Cu(II) and Fe(III) centres.

In Chapter VII, a similar study is presented on the interaction between Cu(II)TPP and Mn(III) porphyrins brought together by charge transfer interactions. The following combinations have been investigated.

1) Cu(II)TPP and Mn(III)TPP(CN)$_4$Cl.

2) Cu(II)TPP and Mn(III)TPP(CN)$_3$Cl.

The stoichiometry and the equilibrium constants have been obtained wherever possible.

The following generalities have been observed in the presence of Mn(III) or Fe(III) porphyrins. In some cases complex formation has been indicated by the plots of $P_{1/2}$ versus concentration of Mn(III) or Fe(III) porphyrins. In all these cases the general trend observed for $T_1$ and $T_2$ are $T_1 < T_2 < (\gamma B_1)^{1}$. It has been observed uniformly that the ratio of $T_1$ for the uncomplexed Cu(II) porphyrin to that in the complexed state is very nearly equal to the inverse ratio of the corresponding $P_{1/2}$ values.

\[
\frac{T_1 \text{(Cu(II)TPP)}}{T_1 \text{(Cu(II)-Fe(III) complex)}} = \frac{P_{1/2} \text{(complex)}}{P_{1/2} \text{(Cu(II)TPP)}}
\]

The same trend has been noted for Cu(II)TPP-TNB and Cu(II)TPP-DDQ systems.

Hence it appears that the changes in the saturation characteristics of Cu(II) centre are entirely arising from the changes in $T_1$ values, which in turn may be directly correlated to the spin-spin interactions between Cu(II) centre and Fe(III) or Mn(III) centres.