CHAPTER I

INTRODUCTION

1.1 Introduction :

This thesis deals with spectroscopic and electrochemical study on iron (III) Schiff-base complexes derived from salicylaldehyde and L-amino acids as well as ruthenium (III) complexes of tetradeutete Schiff-bases in aqueous solutions of surfactant micelles. The iron (III) complexes were earlier proposed as a model for tyrosinate proteins\textsuperscript{1-7}. A brief overview of the Fe-phenolate and Ru-phenolate complexes are given in sec(1.2). Recently it was shown that surfactant micelles are excellent medium for solubilization of sparingly soluble metal complexes in aqueous solution. Iron porphyrins encapsulated in micelles was found to be a good model for hemo-proteins. Moreover, it is known that the micelles are also good medium for catalytic reactions. A discussion on this is given in sec (1.3). The scope and objectives of this study is discussed in sec (1.5).

Models of iron-tyrosinate proteins essentially deal with phenolate-iron coordination since tyrosine, which is an amino acid containing a phenol group, is bound to the metal at the active site\textsuperscript{3}. The dependence of the phenolate-iron charge transfer on the electrostatic and hydrophobic interactions in a protein may be simulated by surfactant micelles. Both the series of complexes studied here contain phenolate-metal co-ordination.
1.2 Metal(III)-Phenolate (M=Fe,Ru) Complexes :

The iron tyrosinate proteins are a heterogeneous group of non-heme iron proteins including Catechol dioxygenase and purple acid phosphoges. In spite of their diverse functions, these proteins display, as a common spectral feature, a moderately intense absorption band in the range 400-600 nm which dominates the visible spectrum. This originates from a tyrosinate to iron(III) charge-transfer transition. The position and intensity of this band are sensitive to the ligand environment of iron(III). Hence the importance of model studies that can provide useful data to improve our understanding and spectra-structure correlations for the protein metal site.

In an attempt to study iron(III) tyrosinate models, a series of iron (III) complexes of L-amino-acids has been prepared. The phenolate co-ordination of tyrosine give rise to a ligand-to-metal charge transfer interaction which is characteristic of these proteins. Tyrosine-iron (III) charge transfer is well known and may be compared with a wide range of iron (III) complexes containing \( \text{O}_2\text{N}_2 \) type chromophore. The phenolate moieties of the Schiff-bases mimic the two tyrosine (Tyr) coordination, while the imine functionalities and coordinated imidazoles provide some correspondence to the histidine coordination in a protein (Fig.1.1). Therefore the studies on iron complexes of quadridantate Schiff-bases would be of considerable significance in designing proper synthetic models for the non-heme iron (III) proteins.

A considerable amount of work has been carried out on the tetradeinate Schiff - base complexes of the type \( \text{Fe}^{III}(\text{salen})\text{L} \) and
Fe^{II}(Salophen)L [where, Salen = 1,2 - bis (2-hydroxybenzylidineamino) ethane and salophen = 1,2 - bis (2-hydroxybenzylidine amino) benzene]. A series of Fe(salen)X and Fe(salophen)X complexes (where X = catechol or phenolate) has been synthesized and their physical properties have been studied. The catecholate complex formation of Fe(Salophen)^+ in solution has been reported. The Salophen analogue, [(salophen)Fe(cat)]^- contains a bidentate Cat^2- ligand. Dimerization of Fe(salophen)^+ to give the μ-oxo species takes place in solution quite readily.

The non-heme iron proteins such as catechol Dioxygenase are involved in redox reactions such as oxidation of catechol. A suitable model for such proteins are likely to be interesting for catalytic oxidation of organic substrates. Though several iron complexes of salen and salophen ligands are proposed as models of enzyme Dioxygenase, none of them are found to be good functional model for the proteins. Since ruthenium complexes are important in homogeneous catalysis, we have undertaken a study of the Ru-analogues of the iron Schiff-bases as models for dioxygenase.

Several ruthenium(III) Schiff-base complexes of the composition [Ru(L)(X)(Y)] (where L=Schiff-base, viz. bis-(salicylaldehyde) ethylenediamine(salen), bis-(salicylaldehyde)-o-phenylene diamine (salophen), X=Chloro (Cl), Y=Chloro (Cl), imidazole) were synthesized and characterised by various physical methods. These complexes are low-spin Ru(III) unlike the iron analogues which are high-spin. The ruthenium (III) Schiff-base complexes with variation of donor sites has been synthesised by Taqui Khan et al. Binding of CO and O_2 to these complexes exhibit some discrimination though the electronic effects of the axial and equatorial ligands are about the same. The lower stability
stability of ruthenium (III) Carbonyls seems to be due to a weak dπ-
pπ backbonding to CO in these complexes. In the ruthenium (III) carbonyls studied, the CO is reversibly bonded and is displaced by bubbling N₂ through the solution in contrast to the irreversible binding of CO in Fe(II) porphyrins. The Ru(III) Chloro-complexes have shown the displacement of the axial Cl⁻ group in the Schiff-base complexes by a solvent or CO. The polarity of the solvent play an important role in binding substrates. The lability of the chloro group is very important for catalysis of the complexes in carbonylation reaction. The complexes with equatorial substitution are in general more stable than the unsubstituted aldehydes and show greater affinity for O₂ binding compared to CO. The formation of Ru(IV) superoxo complexes was confirmed by IR spectra of the complexes. All these reported work were in organic solvents. In aqueous solutions the study of the Ru(III) and Ru(IV) compounds are restricted because of the tendency of the complexes to undergo hydrolysis.

1.3 (a) Solubilization and micellization:

Surfactants solubilize sparingly soluble substances in water. The surfactants form micelles which encapsulate the substance. There are several sites in the micelles for solubilization, for example, near the micellar surface and between the head groups in nonionic surfactants in the palisade layer, and in the core or interior of the micelle. Depending upon the nature of the solubilizate and the surfactant different types of compounds (Polar and nonpolar) are solubilized at the various possible sites of the micelle. The lesser the polarity of the solubilizate more it is likely to penetrate deeper into the micellar interior.
1.3 : (b) Micellization of the complexes:

The surfactants used in these works are:

(i) Cationic - Cetyl Trimethyl Ammonium Bromide (CTAB);
\[ \text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}((\text{CH}_3)_3'^\text{Br}^-] \\
(ii) Neutral - Ethoxy Poly Ethanol (Triton X-100);
\[ (\text{CH}_3)_3\text{CCH}_2\text{C(CH}_3)_2\text{-O}((\text{CH}_2\text{CH}_2\text{O})_{12}\text{-H} \\
(iii) Anionic - Sodium Dodecyl sulphate (SDS);
\[ \text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SO}_4\text{Na}^+ \\

The reason for using these surfactant is because the resultant micelles are known to biomimic the protein pocket of heme proteins. Above the critical micellar concentration (cmc) the surfactant molecules aggregate to form nearly macromolecular structure which encapsulate the iron porphyrins. A sketch of the encapsulated complex is shown in Fig.1.2. Since the model complex is entrapped in a macromolecular structure further reaction (i.e. hydrolysis) which may lead to the decomposition of the complex, do not take place. The interior of the micelle is hydrophobic (i.e. nonpolar) whereas the surface charges on the outside make the entire molecule soluble in polar solvent such as water (Fig.1.3).

1.3(c) Critical Micellar Concentration and Aggregation Number:

The critical micellar concentration (cmc) is a narrow range of concentration of the surfactant below which there is virtually no aggregation and above which concentration there is no unassociated surfactant ion or molecule in solution present in detectable concentration. The aggregation number of a micelle is the number of
monomeric surfactant units forming the micelle. The aggregation number (like \( \text{cmc} \)) is in a close range rather than being an exact number. Most of the observable parameters (such as absorbance, conductance), if plotted against the concentration of the surfactant appear to change at a different rate above and below the \( \text{cmc} \) may be represented as in the Fig.1.4. The critical micellar concentration and aggregation numbers of various surfactant is given below\(^{27}\).

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>( \text{cmc} )</th>
<th>Aggregation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB</td>
<td>(9.2 \times 10^{-4} \text{M} )</td>
<td>61</td>
</tr>
<tr>
<td>TX-100</td>
<td>(4.0 \times 10^{-3} \text{M} )</td>
<td>139</td>
</tr>
<tr>
<td>SDS</td>
<td>(8.3 \times 10^{-3} \text{M} )</td>
<td>131</td>
</tr>
</tbody>
</table>

Various factors determine the critical micellar concentration and aggregation number of surfactants\(^{20}\). These are -

(i) the length and structure of the hydrocarbon chain
(ii) the head group
(iii) the electrolytic activities &
(iv) the temperature.

1.4 Electrochemistry in Aqueous Micellar Solution:

The surfactant solution in comparison to ordinary aqueous solution is that compounds that are ordinarily insoluble or sparingly soluble in aqueous media get solubilized in the surfactant solutions\(^{20,27,28}\). The aqueous solutions of added surfactants offer a convenient system for electrochemical analysis over ordinary aqueous system. This has been established by some recent studies\(^{29-31}\). In the presence of micelles
the aqueous solution acquire a much wider window of potential scan in the electrochemical experiment towards the cathodic and anodic side as compared to ordinary water\textsuperscript{29}. This window has been subject to a thorough testing in the required range of interest, supporting electrolytes and working electrodes of interest\textsuperscript{29-31}.

1.5 Objective of the present study:

The major aim of the present work is to study the spectroscopic and electrochemical behaviour of iron and ruthenium Schiff-base complexes encapsulated in aqueous surfactant micelles. Due to the presence of a hydrocarbon core and surface charges, the hydrophobic and electrostatic interaction in micellar solutions are expected to give rise to interesting property. For example, solubilization of sparingly soluble substances, stabilization of the complexes (with respect to hydrolysis and dimerization) and modification of electrochemical behaviour are possible.

The study was undertaken keeping in mind the interesting redox behaviour of non-heme iron proteins\textsuperscript{1-4}. Hence the complexes chosen for this study are the proposed models for Iron tyrosinate proteins\textsuperscript{3,6,12}; the common features in the models is the phenolate-metal bond (Fig.1.5). Encapsulation in the micelle is likely to solubilize the complexes in aqueous media under conditions similar to those in proteins. Moreover, the micelle encapsulation would provide the electrostatic and hydrophobic interactions present in metalloproteins.

We also wish to investigate the possibility of using aqueous surfactant solution for electrochemical study. The effect of surfactant
on the redox potential of the metal should be of considerable significance.

Lastly, it is known that surfactant micelles promote catalysis since the micelles provide an ordered surface in aqueous solutions. Encapsulations of potential catalysts, such as the ruthenium complexes, may be the first step towards designing more efficient systems for homogeneous catalysis.
REFERENCES:


(b) M. Nozaki; Top curr. Chem. 1979, 78, 145-186.


(b) L. Que, Jr., R.M. Epstein; Biochemistry. 1977, 16, 2545.


(10) (a) P. Pfeiffer, E. Breith, E. Lubbs, T. Tsumaki; Annalen. 1933, 504, 84.
(b) H. Thielert, P. Pfeiffer; Chem. Ber. 1938, 71, 1399


1.1 Proposed structure of Catechol-1,2-Dioxygenase.
1.2 Sketch of micelle encapsulated complex.
1.3 Representative structure of a micellar interior.
1.4 Physical properties of aqueous solutions with surfactant core.

(not drawn to scale)
1.5 Structure of the complexes synthesised.