CHAPTER VI

ELECTROCHEMICAL STUDIES ON K[Ru(Salen)Cl₂] AND K[Ru(Saloph)Cl₂]

6.1 Introduction:

In this chapter we report the detailed electrochemical studies on Ru(III) complexes of tetradeutate Schiff-bases (Such as Salen and Salophen) in pure water as well as in aqueous surfactant micelles. Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) are used for these studies. The results in pure water as solvent are compared with those complexes encapsulated in the micelles of surfactant such as SDS, CTAB, TX-100. The complex K[Ru(Salpoh)Cl₂] is sparingly soluble in aqueous medium but it is soluble when the micellar solution is used as the micelles are very good solvent. The proton coupled electron transfer in these system are studied. The mid-point potential of Ru(II)/Ru(III) couple of the complexes are measured by CV and OSWV. The charge transfer is dependent on the environment. We performed these studies in aqueous micellar media as the micelles are an excellent media for electrochemical studies¹. We also determined the diffusion coefficient (D₀) in water and aqueous micellar media.
6.2 Results and Discussion:

In the Table 6.1 we have summarised the results of electrochemical studies of the aquo-hydroxo complexes of Ru(III). The $E_{1/2}$ values reported here corresponds to Ru(III)/Ru(II) redox couple. The influence of the micellar solution on the complex is observed. Detailed discussion of these are given below.

The saloph complexes are in general more stable than the salen complexes. The solvation of Ru(III) Schiff-base complexes implies a displacement of Cl$^-$ ion from the coordination sphere of the metal ion. The solvation effect of the Ru(III) Schiff-base complexes is similar to the flat chelated hemes that are more strongly solvated than the picket fence complexes. Due to the extra stability of the saloph complex it is sparingly soluble in aqueous media, whereas the micelles solubilize the complex very readily.

6.2.1 Cyclic Voltammetry Study:

The cyclic voltammetry study of the Ru(III) complexes have been carried out in water and in micellar solution of the surfactant such as CTAB, SDS, TX-100. The reference electrode used is Ag/AgCl (3M NaCl) electrode and Pt electrode as working electrode. The supporting electrolyte we have used in these studies is NaClO$_4$ and NaCl. The surfactant concentration is taken in all cases at above the cmc determined by UV-Visible spectrophotometric method and described in chapter V. The reason for choosing this concentration of the surfactant is to ensure complete micellization and also to
make sure that the mid-point potential will not change due to any minor fluctuation in surfactant concentration.

6.2.1 [A] Electrochemistry on K[Ru(Salen)Cl₂] :

(i) In water :

The typical cyclic voltammogram in water is shown in Fig.6.1a Vs Ag/AgCl reference and \( E_{1/2} \) is found to be \(-0.407V (\pm 0.005V) \) due to Ru(III)/Ru(II) redox couple. The peak separation \( \Delta E_p = 87mV \) and the ratio of \( i_{Pc} \) and \( i_{Pa} \) is equal to 1.03 at scan rate 20 mVs\(^{-1}\). The mid-point potential measured by OSWV is found to be \(-0.408V (\pm 0.005V) \) under the same experimental conditions. A plot of \( i_{Pc} \) and \( i_{Pa} \) as a function of square root of scan rate is shown in Fig.6.1b. From the behaviour of the plot the system seems to be a quasi-reversible system.

(ii) In SDS :

In the anionic micelle like SDS the mid-point potential shifts towards more negative (cathodic) potential due to combined influence of electrostatic and hydrophobic interaction of the micelles.

The cyclic voltammogram of the complex in SDS is shown in Fig.6.2a Vs Ag/AgCl reference. The \( E_{1/2} \) is found to be \(-0.442V (\pm 0.005V) \). The peak separation \( \Delta E_p \) is equal to 81 mV at the scan rate of 50 mVs\(^{-1}\). The ratio of \( i_{Pc} \) and \( i_{Pa} \) is equal to 1.60. A plot of \( i_{Pc} \) and \( i_{Pa} \) as a function of square root of scan rate is shown in Fig.6.2b.
(iii) In TX-100 :

The cyclic voltammogram of K[Ru(Salen)Cl₂] in a neutral micelle like TX-100 is shown in Fig. 6.3a. The $E_{1/2}$ value of the system is found to be $-0.399V(±0.005V)$ against a Ag/AgCl reference. The peak separation $ΔE_p$ is equal to 80 mV at scan rate 20 mVs⁻¹. The ratio of $i_P$ and $i_P^*$ is found to be 0.876 at scan rate 20 mVs⁻¹. The mid-point potential measured by OSWV is equal to $-0.404V(±0.005V)$ at the same experimental conditions. A plot of $i_P$ and $i_P^*$ as a function of square root of scan rate gives a straight line and it is shown in Fig. 6.3b.

(iv) In CTAB :

The cyclic voltammogram of the complex in a cationic micelle like CTAB is shown in Fig. 6.4a against a Ag/AgCl reference. The $E_{1/2}$ value is found to be $-0.420V(±0.005V)$ and the peak separation $ΔE_p$ is found to be 86 mV at scan rate 20 mVs⁻¹. The ratio of $i_P$ and $i_P^*$ is equal to 0.76 at scan rate 20 mVs⁻¹. The mid-point potential measured by OSWV of the system is found to be $-0.420V(±0.005V)$ under the same experimental conditions. A plot of $i_P$ and $i_P^*$ as a function of square root of scan rate gives a straight line and shown in Fig. 6.4b.

From the above observation it is clear that a cationic or anionic micelle influenced the redox couple Ru(III)/Ru(II) in the K[Ru(Salen)Cl₂] complex in comparison with neutral micelle or pure water. The cationic or anionic micelle influence the complex by
electrostatic interaction together with hydrophobic interaction, whereas in neutral micelle only hydrophobic effect is operating. The net result is that the absolute magnitude of the redox potential of the Ru(III)/Ru(II) couple in the following order -

$$\text{SDS > CTAB > TX-100} \cong \text{H}_2\text{O}$$

(the data given in the Table 6.1)

The similarity of the potential in TX-100 and water indicate that the hydrophobic effect in micelles do not perturb the Ru(III)/Ru(II) couple to a significant extent. The shift is mainly due to electrostatic effect of the charged surfactant molecules, which is maximum for anionic SDS surfactant. We found that the chloride anions readily dissociate from the complex $K[\text{Ru(Salen)}\text{Cl}_2]$. Thus the species in solution is likely to be $[\text{Ru(Salen)}\text{H}_2\text{O}]^2^-$. The cationic complex ion is likely to be stabilised by the anionic SDS micelles, leading to stabilization of the Ru(III) oxidation state, hence giving the largest cathodic shifts in SDS (i.e. Ru(III) is most difficult to reduce).

To identify the diaquo complex ion in micellar solution we prepared (Chapter-V) $[\text{Ru(Salen)}\text{H}_2\text{O}]_2\text{ClO}_4$ by reaction of the dichloro complex with AgClO$_4$. The spectroscopic and electrochemical behaviour of the diaquo complex in water is similar to that of the dichloro complex in aqueous micelles. The species present in the micellar solution of $K[\text{Ru(Salen)}\text{Cl}_2]$ is the diaquo complex ion.
The cyclic voltammogram in pure water of the aquo complex \([\text{Ru(Salen)H}_2\text{O})_2]^+\) is given in Fig. 6.5a. The \(E_{1/2}\) is found to be \(-0.389\text{V}(\pm0.005\text{V})\) versus Ag/AgCl reference and the peak separation \(\Delta E_p\) is equal to 82 mV at the scan rate 20 mVs\(^{-1}\). The ratio of \(i_\text{Pc}\) and \(i_\text{Pa}\) equal to 1.01 at the scan rate 20 mVs\(^{-1}\). The mid-point potential measured by OSWV of the complex is found to be \(-0.394\text{V}(\pm0.005\text{V})\) under the same experimental conditions. A plot of \(i_\text{Pc}\) and \(i_\text{Pa}\) as a function of square root of scan rate gives a straight line and shown in Fig. 6.5b.

6.2.1 [B] Electrochemistry on \(\text{K[Ru(Saloph)Cl}_2]\):

(i) In SDS:

The cyclic voltammogram of the complex in the anionic micelle like SDS is shown in Fig. 6.6a against a Ag/AgCl reference. The \(E_{1/2}\) is found to be \(-0.404\text{V}(\pm0.005\text{V})\) from the cyclic voltammogram. The peak separation \(\Delta E_p\) is equal to 94mV at the scan rate 20mVs\(^{-1}\). The ratio of \(i_\text{Pc}\) and \(i_\text{Pa}\) is found to be 1.024 at the scan rate of 20mVs\(^{-1}\). The mid-point potential measured by OSWV of the complex is equal to \(-0.408\text{V}(\pm0.005\text{V})\) under the same experimental conditions. A plot of \(i_\text{Pc}\) and \(i_\text{Pa}\) as a function of square root of scan rate gives a straight line and shown in Fig. 6.6b.

(ii) In TX-100:

The cyclic voltammogram in a neutral micelle like TX-100 is shown in Fig. 6.7a against a Ag/AgCl reference. The \(E_{1/2}\) is found
to be $-0.422V(\pm0.005V)$ from the cyclic voltammogram. The peak separation $\Delta E_p$ is equal to 93 mV at the scan rate 20 mVs$^{-1}$. The ratio of $i_{Pa}$ and $i_{Pa}$ is equal to 0.79 at the scan rate 20 mVs$^{-1}$. The mid-point potential measured by OSWV is found to be $-0.424V(\pm0.005V)$ under the same experimental conditions. A plot of $i_{Pa}$ and $i_{Pa}$ as a function of square root of scan rate gives a straight line and shown in Fig.6.7b.

(iii) In CTAB:

The cyclic voltammogram in a cationic micelle like CTAB is shown in Fig.6.8a. The $E_{1/2}$ is found to be $-0.436V(\pm0.005V)$ against a Ag/AgCl reference. The peak separation $\Delta E_p$ is equal to 93 mV at the scan rate 20 mVs$^{-1}$. The ratio of the $i_{Pc}$ and $i_{Pa}$ at the same scan rate is equal to 0.76. The mid-point potential measured by OSWV of the complex is found to be $-0.440V(\pm0.005V)$ under the same experimental condition. A plot of $i_{Pc}$ and $i_{Pa}$ as a function of square root of scan rate gives a straight line and shown in Fig.6.8b.

From the above study on the complex K[Ru(Salophen)Cl$_2$] it is observed that the redox potential of Ru(III)/Ru(II) is influenced by the effect of the ionic micelles. Here we could not compare the shift with pure water because the complex is sparingly soluble in water. From the data given in Table 6.1, the order of the $E_{1/2}$ value is as follows-

CTAB $>$ TX-100 $>$ SDS
Here the negatively charged \([\text{Ru}^{III}(\text{Saloph})\text{Cl}_2]^-\) complex anion is stabilized to the maximum extent in cationic CTAB micelles leading to the largest cathodic shift. In anionic SDS micelles the Ru(III) complex is the least stabilized, hence Ru(III) is readily reduced to Ru(II), and a small cathodic shift result.

6.3 Diffusion Co-efficients:

The values of diffusion co-efficients \((D_o)\) are calculated from the plot of peak current as a function of scan rate. The diffusion co-efficient of the Ru(III) complexes in aqueous surfactant micelles are determined (Table 6.1). In aqueous micellar solution the diffusion of the encapsulated electroactive species to the electrode is very low due to high viscosity of the micellar solutions. However, within the micelles the values of diffusion co-efficients can not be given any simple interpretation. The values of \(D_o\) may influence the rate of electron transfer in these complexes.

6.4 Conclusion:

In this chapter we carried out electrochemical studies on the ruthenium (III) complexes of tetradeionate Schiff-bases in aqueous micellar solution which acts as a very good solvent for electrochemistry. The redox potential of Ru(III)/Ru(II) are sensitive to the environment of the solvent. The variation of the mid-point potentials in different micelles indicate the influence of the micellar environment.
The Ru(III) Schiff-base complexes in encapsulated micellar media provides a large macromolecular structure which provide hydrophobic and electrostatic interaction. Since the surfactant micelles are excellent medium for electron transfer\textsuperscript{1} and catalysis\textsuperscript{4,5}, the micelle encapsulated complexes may be employed in homogeneous catalysis.
References:

Table 6.1: Results of the Electrochemical Study of the Ru\textsuperscript{III} Schiff-base Complexes in \(\text{H}_2\text{O}\) and various aqueous micelles

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>pH</th>
<th>(E_{\text{pa}})(V)</th>
<th>(\Delta E_{\text{p}})(mV)</th>
<th>(i_P/i_P^-)</th>
<th>(D_0)(cm(^2)s(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CV</td>
<td>OSWV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K[Ru(Salen)Cl(_2)]</td>
<td>(\text{H}_2\text{O})</td>
<td>2.30</td>
<td>-0.407</td>
<td>-0.408</td>
<td>87</td>
<td>1.03</td>
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<tr>
<td></td>
<td>SDS</td>
<td>2.30</td>
<td>-0.442</td>
<td>-0.448</td>
<td>81</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>TX-100</td>
<td>2.30</td>
<td>-0.399</td>
<td>-0.404</td>
<td>81</td>
<td>0.88</td>
</tr>
<tr>
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<td>CTAB</td>
<td>2.30</td>
<td>-0.420</td>
<td>-0.420</td>
<td>86</td>
<td>0.76</td>
</tr>
<tr>
<td>K[Ru(Saloph)Cl(_2)]</td>
<td>SDS</td>
<td>2.74</td>
<td>-0.404</td>
<td>-0.408</td>
<td>94</td>
<td>1.02</td>
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<td>0.79</td>
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<tr>
<td></td>
<td>CTAB</td>
<td>2.84</td>
<td>-0.436</td>
<td>-0.440</td>
<td>93</td>
<td>0.77</td>
</tr>
<tr>
<td>[Ru(Salen)((\text{H}_2\text{O}))(_2)]\text{ClO}_4</td>
<td>(\text{H}_2\text{O})</td>
<td>2.24</td>
<td>-0.389</td>
<td>-0.394</td>
<td>82</td>
<td>1.01</td>
</tr>
</tbody>
</table>

N.B.: \(\Delta E_{\text{p}}\) at scan rate 20 mVs\(^{-1}\)
6.1a Cyclic voltammogram of $\text{K[Ru(Salen)Cl}_2]$ in $\text{H}_2\text{O}$ Vs $\text{Ag/AgCl}$ ref. S.E. NaCl.

6.1b Plot of $i_{\text{p}}$ and $i_{\text{p}}$ as a function of $\sqrt{v}$ of $\text{K[Ru(Salen)Cl}_2]$ in $\text{H}_2\text{O}$, S.E. NaCl.
6.2a Cyclic voltammogram of K[Ru(Salen)Cl$_2$] in SDS Vs Ag/AgCl ref. S.E. NaCl.

6.2b Plot of $i_{p_c}$ and $i_{p_a}$ as a function of $\sqrt{v}$ of K[Ru(Salen)Cl$_2$] in SDS, S.E. NaCl.
6.3a Cyclic voltammogram of $\text{K[Ru(Salen) Cl}_2\text{]}$ in TX-100 Vs Ag/AgCl ref. S.E. NaCl.

6.3b Plot of $i_{p_o}$ and $i_{p_a}$ as a function of $\sqrt{v}$ of $\text{K[Ru(Salen)Cl}_2\text{]}$ in TX-100. S.E. NaCl
6.4a Cyclic voltammogram of K[Ru(Salen)Cl₂] in CTAB Vs Ag/AgCl ref. S.E. NaCl.

6.4b Plot of \( i_{p_o} \) and \( i_{p_a} \) as a function of \( \sqrt{v} \) of K[Ru(Salen)Cl₂] in CTAB, S.E. NaCl.
6.5a Cyclic voltammogram of $[\text{Ru(Salen)} (\text{H}_2\text{O})_2]\text{ClO}_4$ in $\text{H}_2\text{O}$ Vs Ag/AgCl ref. S.E. Na$_4$Cl.

6.5b Plot of $i_{p_0}$ and $i_{p_a}$ as a function of $\sqrt{v}$ of $[\text{Ru(Salen)} (\text{H}_2\text{O})_2]\text{ClO}_4$ S.E. Na$_4$Cl.
6.6a Cyclic voltammogram of \([\text{Ru (Saloph)}\text{Cl}_2]\) in SDS Vs Ag/AgCl ref. S.E. NaCl.

6.6b Plot of \(i_{\text{pc}}\) and \(i_{\text{pa}}\) as a function of \(\sqrt{v}\) of \(\text{K[Ru(Saloph)Cl}_2]\) in SDS, S.E. NaCl.
6.7a Cyclic voltammogram of [Ru (Saloph)Cl₂] in TX-100 Vs Ag/AgCl ref. S.E. NaCl.

6.7b Plot of \(i_p^c\) and \(i_p^a\) as a function of \(\sqrt{v}\) of K[Ru(Saloph)Cl₂] in TX-100, S.E. NaCl.
6.8a Cyclic voltammogram of [Ru (Saloph)Cl\(_2\)] in CTABVs Ag/AgCl ref. S.E. NaCl.

6.8b Plot of \(i_{p_c}\) and \(i_{p_a}\) as a function of \(\sqrt{v}\) of \([Ru(Saloph)Cl\(_2\)]\) in CTAB S.E. NaCl.