4.1 INTRODUCTION:

In this chapter we report the potentials of V\textsuperscript{IV}/V\textsuperscript{III} and Ru\textsuperscript{III}/Ru\textsuperscript{II} redox couples of V\textsuperscript{IV}O(Salen), [V\textsuperscript{IV}O(NTA)]\textsuperscript{-} and Ru\textsuperscript{III}(NTA) complexes as a function of pH in aqueous surfactant solutions. The micelle concentrations are 4%, 2% and 3% for CTAB, SDS and TritonX-100 respectively, in all the studies reported here. The concentrations of the surfactant are much above the critical micellar concentration. The reason for choosing these concentrations of the surfactants is to ensure complete micellization\textsuperscript{1,2} and also to make sure that the mid-point redox potential will not change due to any minor fluctuation in the micelle concentration.

We believe that electrochemical study on acid-base equilibria of V\textsuperscript{IV}O(Salen), [V\textsuperscript{IV}O(NTA)]\textsuperscript{-} and Ru\textsuperscript{III}(NTA) tetradentate ligand complexes would provide considerable amount of understanding of the uptake/release of protons of the axially coordinated ligand.

4.2 RESULTS AND DISCUSSION:

4.2.1 ELECTROCHEMICAL STUDIES OF V\textsuperscript{IV}O(Salen) IN AQUEOUS SURFACTANT MICELLES:

In aqueous surfactant micelles pH < pK\textsubscript{a} (i.e. below pH 7) V\textsuperscript{IV}O(Salen) undergoes disproportion to oxophilic [V\textsuperscript{IV}(Salen)]\textsuperscript{2+} according to the reaction\textsuperscript{3}

\[ \text{V}^{\text{IV}}\text{O(salen)}\text{. micelle} + 2\text{H}^+ = \text{[V}^{\text{IV}}\text{(Salen)H}_2\text{O]}^{2+}\text{. micelle} \] (1)

At low pH ca. 6.00 (20 mM acetate buffer) the aquo [V\textsuperscript{IV}(Salen)H\textsubscript{2}O]\textsuperscript{2+} species shows only a cathodic peak at -0.448 V, -0.586 V and -0.476 V (versus Ag-AgCl electrode at scan rate 0.03V/s ) in CTAB, SDS and TritonX-100 micelles, respectively. The data of Table-4.1 shows that the redox potential of V\textsuperscript{IV}/V\textsuperscript{III} couple is strongly dependent on the nature of the surfactant micelles and on the pH of the solution\textsuperscript{4,5}. The mid-point potential increases cathodically in the order.

CTAB < TritonX-100 < SDS
The potential of dipositive aquo $[\text{V}^{IV}(\text{Salen}) \text{H}_2\text{O}]^{2+}$ species is more cathodic (-ve) in SDS micelles with respect to CTAB and TritonX-100 micelles. The reduction of aquo $[\text{V}^{IV}(\text{Salen})\text{H}_2\text{O}]^{2+}$ may be explained by the **Scheme-I**

\[ \text{IV}^{2+} + \text{H}^+ \xrightarrow{\text{pK}_a \text{IV}} \text{IV}^{+} \]

\[ \text{III}^{0} + \text{H}^+ \xrightarrow{\text{pK}_a \text{III}} \text{III}^{+} \]

\[ E_{p\theta} = \begin{bmatrix} -0.448 \text{ V/CTAB} \\ -0.586 \text{ V/SDS} \\ -0.476 \text{ V/Tx-100} \end{bmatrix} \quad E_{p\theta} = \begin{bmatrix} -0.574 \text{ V/CTAB} \\ -0.625 \text{ V/SDS} \\ -0.554 \text{ V/Tx-100} \end{bmatrix} \]

**Scheme - I**

The dipositive charged aquo $[\text{V}^{IV}(\text{Salen})\text{H}_2\text{O}]^{2+}$ is harder to reduce in negatively charged SDS micellar media, which implies the net stabilization of the dipositive $[\text{V}^{IV}(\text{Salen})\text{H}_2\text{O}]^{2+}$ species in the negatively charged SDS micelle is greater than the mono positive $[\text{V}^{III}(\text{Salen})\text{H}_2\text{O}]^{+}$ species.
Table-4.1 Electrochemical results for $[V^{IV}\text{O(Salen)}]$ , $[V^{IV}\text{O(NTA)}]^{-}$ and $[\text{Ru}^{III}\text{(NTA)}]$ complexes in aqueous surfactant micelles at pH 6.00 (20 mM acetate buffer) and 10.50 (50mM Tris-HCl buffer). Working electrode: Glassy carbon electrode; Reference electrode: Ag-AgCl electrode; Temp. 25°C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Surfactant</th>
<th>pH</th>
<th>$E_{pc}$ (V) from C.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[V^{IV}\text{(Salen)H}_2\text{O}]^{2+}$</td>
<td>CTAB</td>
<td>6.00</td>
<td>$E_{pc} = -0.432$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>6.00</td>
<td>$E_{pc} = -0.580$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>TritonX-100</td>
<td>6.00</td>
<td>$E_{pc} = -0.436$ (at 0.03 V/s)</td>
</tr>
<tr>
<td>$[V^{IV}\text{(Salen)OH}]^{+}$</td>
<td>CTAB</td>
<td>10.50</td>
<td>$E_{pc} = -0.574$ (at 0.05 V/s)</td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>10.50</td>
<td>$E_{pc} = -0.625$ (at 0.05 V/s)</td>
</tr>
<tr>
<td></td>
<td>TritonX-100</td>
<td>10.50</td>
<td>$E_{pc} = -0.554$ (at 0.03 V/s)</td>
</tr>
<tr>
<td>$[V^{IV}\text{(NTA)H}_2\text{O}]^{+}$</td>
<td>CTAB</td>
<td>6.00</td>
<td>$E_{pc} = -0.583$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>6.00</td>
<td>$E_{pc} = -0.668$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>TritonX-100</td>
<td>6.00</td>
<td>$E_{pc} = -0.600$ (at 0.03 V/s)</td>
</tr>
<tr>
<td>$[V^{IV}\text{(NTA)OH}]^{n}$</td>
<td>CTAB</td>
<td>10.50</td>
<td>$E_{pc} = -0.647V$, (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>10.50</td>
<td>$E_{pc} = -0.658V$, (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>TritonX-100</td>
<td>10.50</td>
<td>$E_{pc} = -0.664V$, (at 0.03 V/s)</td>
</tr>
<tr>
<td>$[\text{Ru}^{III}\text{(NTA)(H}_2\text{O)}_2]^{n}$</td>
<td>CTAB</td>
<td>6.00</td>
<td>$E_{pc} = -0.640$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>6.00</td>
<td>$E_{pc} = -0.685$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>TritonX-100</td>
<td>6.00</td>
<td>$E_{pc} = -0.728$ (at 0.03 V/s)</td>
</tr>
<tr>
<td>$[\text{Ru}^{III}\text{(NTA)(H}_2\text{O)}\text{OH}]^{-}$</td>
<td>CTAB</td>
<td>10.50</td>
<td>$E_{pc} = -0.591$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>10.50</td>
<td>$E_{pc} = -0.559$ (at 0.03 V/s)</td>
</tr>
<tr>
<td></td>
<td>TritonX-100</td>
<td>10.50</td>
<td>$E_{pc} = -0.562V$ (at 0.03 V/s)</td>
</tr>
</tbody>
</table>
The cyclic voltammogram of hydroxo species of [V$^{IV}$ (Salen)OH]$^+$ in CTAB, SDS and TritonX-100 micelles at pH 10.50 (50 mM Tris-HCl buffer) shows only a cathodic peak at -0.574 V (at scan rate 0.03V/s) and -0.625 V (at 0.03V/s) and -0.554 V (at scan rate 0.03V/s (versus Ag-AgCl reference electrode, working electrode glass carbon electrode) respectively. The presence of only cathodic peak indicates an irreversible system in surfactant micelle. The voltammograms are shown in the Figure- 4.1a and Figure-4.1b. The data of Table-4.1 shows that the cathodic peak potential is strongly dependent on the nature of the surfactant micelles and on the pH of the solution. The mid-point potential increases cathodically in the order:

TritonX-100 < CTAB < SDS

The potential of hydroxo species [V$^{IV}$ (Salen) (OH)]$^+$ is more cathodic (-ve) in SDS micelles with respect to CTAB and TritonX-100 micelles. The reduction of the hydroxo electroactive species [V$^{IV}$ (Salen)(OH)]$^+$ may be explained by Scheme-I. The positive charged hydroxo species is harder to reduce in negatively charged SDS micellar media, which implies the net stabilization of the [V$^{IV}$ (Salen)(OH)]$^+$ species in the negatively SDS miceller is greater than the stabilization of the neutral hydroxo electroactive species [V$^{III}$ (Salen)(OH)]$^0$. 


**Figure-4.1a** Cyclic voltammogram for $10^{-3}$ mole dm$^{-3}$ V$^{IV}$O(Salen) complex in aqueous SDS micelle at pH 10.50 (50 mM Tris-HCl buffer). Scan rate 0.05V/s.

**Figure-4.1b** Cyclic voltammogram for $10^{-3}$ mole dm$^{-3}$ V$^{IV}$O(Salen) complex in aqueous TritonX-100 micelle at pH 10.50 (50 mM Tris-HCl buffer) Scan rate 0.05V/s.
4.2.2 ELECTROCHEMICAL STUDIES OF [V^{IV}O(NTA)]^{+} IN AQUEOUS SURFACTANT MICELLES:

In aqueous surfactant micelles nitrolotriacetato oxovanadium(IV) [V^{IV}O(NTA)]^{+} complex exhibits as aqua(nitrolotriacetato) oxovanadium(IV) [V^{IV}O(NTA)(H_{2}O)]^{+} according to the Equilibrium\(^6\) (2).

\[
[V^{IV}O(NTA)]^{+}\text{. micelle} + H_{2}O = [V^{IV}O(NTA)(H_{2}O)]^{+}\text{. micelle}
\]  

(2)

In aqueous surfactant micelles pH < pK\(_a\) (i.e. below pH 7) [V^{IV}O(NTA)(H_{2}O)]^{-} undergoes disproportion to the oxophilic cation [V^{IV}(NTA)(H_{2}O)]^{+} according to the equilibrium\(^3\) (3)

\[
[V^{IV}O(NTA)(H_{2}O)]^{-}\text{.micelle} + 2H^{+} = [V^{IV}(NTA)(H_{2}O)]^{+}\text{.micelle}
\]  

(3)

At aqueous surfactant micelles pH > pK\(_a\) (i.e. above pH 7) in the oxophilic cation [V^{IV}(NTA)(H_{2}O)]^{+} the aquo ligand deprotonates to hydroxo axial ligand to form neutral hydroxo species [V^{IV}(NTA)(OH)]^{0} according to the Equilibrium (4).

\[
[V^{IV}(NTA)(H_{2}O)]^{+}\text{.micelle} + OH^{-} = [V^{IV}(NTA)OH]^{0}\text{. micelle}
\]  

(4)

In three surfactant micelles at low pH (when the operating pH < pK\(_a\) ) the [V^{IV}(NTA(H_{2}O))]^{+} species is predominant in the micellar solutions. At low pH, ca. 6.00 (20 mM acetate buffer) the [V^{IV}(NTA(H_{2}O))]^{+} species shows only a cathodic peak at -0.583 V, -0.668 V and -0.600 V (versus Ag-AgCl reference electrode, scan rate 0.03V/s in CTAB, SDS and TritonX-100 micelles respectively. At low pH the cathodic peak potential increases in the order:

CTAB < TritonX-100 < SDS

This trend is similar to one found in micellar solution of hemin\(^7\). At low pH in [V^{IV}(NTA(H_{2}O))]^{+} complex the potential is more cathodic (-ve) in SDS with respect to CTAB, while the potential in Triton X-100 micelle is not as consistant. The reduction of species [V^{IV}(NTA(H_{2}O))]^{+} at low pH may be explained by the Scheme-II. The positive charged [V^{IV}(NTA(H_{2}O))]^{+} species is harder to reduce in negatively charged SDS micellar
media, which implies the net stabilization of the $[\text{V}^{IV}(\text{NTA})(\text{H}_2\text{O})]^+$ species in the negative charged SDS micelle is greater than the stabilization of neutral species $[\text{V}^{III}(\text{NTA})(\text{H}_2\text{O})]^0$.

Inside the microenvironment of the non-ionic TritonX-100 micelle it appears that various forces stabilizing positively charged $[\text{V}^{IV}(\text{NTA})(\text{H}_2\text{O})]^+$ species and neutral $[\text{V}^{III}(\text{NTA})(\text{OH})]^0$ electroactive species are approximately balanced, and small change in the nature of the complex can alter this balance. The cathodic peak potential in the non-ionic TritonX-100 micelle is essentially due to its the hydrophobic effect of surfactant\textsuperscript{8,9,10}.

The cyclic voltametric behavior of hydroxo species of $[\text{V}^{IV}(\text{NTA})\text{OH}]^0$ was investigated in CTAB, SDS and TritonX-100 micelles at pH 10.50 (50 mM Tris-HCl buffer) shows $E_{pc}$ at -0.647 V, -0.658 V and -0.664 V respectively at scan rate 0.03 V/s (versus Ag-AgCl reference electrode). These process are assumed to be a
irreversible\textsuperscript{11,12,13,14} single-electron oxidation/reduction of the couple \([V^{IV}(NTA)(OH)]^0/\ [V^{III}(NTA)(OH)]^+\) (Figure-4.2.a, Figure- 4.2.b and Figure-4.2.c). The redox potential of hydroxo species \([V^{IV}(NTA)OH]^0\) in surfactant micelles vary cathodically in the order:

\[ \text{CTAB} < \text{SDS} < \text{TritonX-100} \]

The reduction of the hydroxo species may be explained by the Scheme-II.

\textbf{Figure-4.2a} Cyclic voltammogram for 10\textsuperscript{-3} mole dm\textsuperscript{-3} \([V^{IV}O(NTA)OH]^0\) in aqueous CTAB micelle at pH 10.50 (50 mM Tris-HCl buffer). Scan rate 0.030 V/s
Figure-4.2b Cyclic voltammogram for $10^{-3}$ mole dm$^{-3}$ $[\text{V}^{IV}\text{O(NTA)OH}]^0$ in aqueous SDS micelle at pH 10.50 (50 mM Tris-HCl buffer). Scan rate 0.030 V/s.

Figure-4.2c Cyclic voltammogram for $10^{-3}$ mole dm$^{-3}$ $[\text{V}^{IV}\text{O(NTA)OH}]^0$ in aqueous TritonX-100 micelle at pH 10.50 (50 mM Tris-HCl buffer).
4.2.3 ELECTROCHEMICAL STUDIES OF Ru$^{III}$ (NTA) IN AQUEOUS SURFACANT MICELLES:

At low pH (when the operating pH < pK$_a$ [Ru$^{III}$ (NTA)(H$_2$O)$_2$]$^+$ is predominant in the micellar solutions. At low pH, ca. 6.00 (20mM acetate buffer) the Ru$^{III}$ (NTA)(H$_2$O)$_2$]$^+$ species shows only a cathodic peak at -0.640 V, -0.685 V and -0.728 V (versus Ag-AgCl reference electrode, scan rate 0.03 V/s) in CTAB, SDS and TritonX-100 micelles respectively. Table-4.1 shows that the cathodic peak potential of Ru$^{III}$ (NTA)(H$_2$O)$_2$]$^+$ in surfactant micelles vary cathodically in the order:

CTAB < SDS < TritonX-100

The reduction of Ru$^{III}$ (NTA)(H$_2$O)$_2$]$^+$ may be explained by the Scheme-III

\[
\begin{align*}
\text{III} & \quad \text{[Ru (NTA)(H$_2$O)$_2$] micelle} \\
\text{II} & \quad \text{[Ru (NTA)(H$_2$O)$_2$] micelle} \\
\text{I} & \quad \text{[Ru (NTA)(H$_2$O)$_2$] micelle}
\end{align*}
\]

\[
E_{pc} = \begin{bmatrix}
-0.640 \\
-0.685 \\
-0.728 \\
\end{bmatrix}_{\text{CTAB}} \quad E_{pc} = \begin{bmatrix}
-0.591 \\
-0.559 \\
-0.362 \\
\end{bmatrix}_{\text{TX-100}}
\]

Scheme-III
The cyclic voltammogram of aquo-hydroxo species [Ru\textsuperscript{III}(NTA)(H\textsubscript{2}O)OH]\textsuperscript{-} in CTAB, SDS and TritonX-100 micelles at pH 10.50 (50mM Tris-HCl buffer) shows only a cathodic peak at -0.591 V, -0.559 V and -0.562 V respectively, at scan rate 0.03 V/s (versus Ag-AgCl reference electrode) (Figure-4.3a, Figure-4.3b). The redox potential of [Ru\textsuperscript{III}(NTA)(H\textsubscript{2}O)OH]\textsuperscript{-} measured by OSWV was found at -0.560 V (versus Ag-AgCl reference electrode) at pH 10.50 (50 mM Tris-HCl buffer) (Figure- 4.3c).

![Cyclic voltammogram for 10\textsuperscript{-3} mole dm\textsuperscript{-3} [Ru\textsuperscript{III}(NTA)(H\textsubscript{2}O)OH]\textsuperscript{-} complex in aqueous SDS micelle at pH 10.50 (50 mM Tris-HCl buffer). Scan rate 0.030 V/s.](image)

**Figure-4.3a** Cyclic voltammogram for 10\textsuperscript{-3} mole dm\textsuperscript{-3} [Ru\textsuperscript{III}(NTA)(H\textsubscript{2}O)OH]\textsuperscript{-} complex in aqueous SDS micelle at pH 10.50 (50 mM Tris-HCl buffer). Scan rate 0.030 V/s.
Figure-4.3b Cyclic voltammogram for $10^{-3}$ mole dm$^{-3}$ [Ru$^{III}$(NTA)(H$_2$O)OH]$^-$ complex in aqueous TritonX-100 micelle at pH 10.50 (50 mM Tris-HCl buffer) Scan rate 0.030 V/s.

Figure-4.3c Osteryoung Square-Wave voltammogram for $10^{-3}$ mole dm$^{-3}$ [Ru$^{III}$(NTA)(H$_2$O)OH]$^-$ complex in aqueous TritonX-100 micelle at pH 10.50 (50 mM Tris-HCl buffer). Scan rate 0.030 V/s.
The mid-point potential increases cathodically in the order:

$$\text{SDS < Triton-100 < CTAB}$$

In aquo-hydroxo electropositive species $[\text{Ru}^\text{III}(\text{NTA})(\text{H}_2\text{O})\text{OH}]^-$ the cathodic peak potential is more cathodic (-ve) in CTAB micelle with respect to SDS micelle, while the potential in TritonX-100 micelle is not as consistent. The reduction of the aquo-hydroxo species $[\text{Ru}^\text{III}(\text{NTA})(\text{H}_2\text{O})\text{OH}]^-$ may be explained by the Scheme-III. The negative charged aquo-hydroxo species is harder to reduce in positively charged CTAB miceller media, which implies the net stabilization of electroactive $[\text{Ru}^\text{III}(\text{NTA})(\text{H}_2\text{O})\text{OH}]^-$ species in positively charged CTAB micelle is greater than negatively charged SDS species.

Inside the microenvironment of the non-ionic TritonX-100 micelle, it appears that the various forces stabilizing the negatively charged aquo-hydroxo electroactive species $[\text{Ru}^\text{III}(\text{NTA})(\text{H}_2\text{O})\text{OH}]^-$ species and dinegative $[\text{Ru}^\text{II}(\text{NTA})(\text{H}_2\text{O})\text{OH}]^2^-$ are approximately balanced and small change in the nature of the complex can alter this balance. The cathodic peak potential in the non-ionic TritonX-100 micelle is essentially due to the hydrophobic effect of surfactant$^{10}$.

4.2.4 DEPENDENCE OF MID-POINT POTENTIALS ON pH:

The mid-point potential of $V^{IV}(L)X$ or $\text{Ru}^{III}(L)X$ complexes were measured by the cyclic voltametric or OSWV technique as a function of pH show that the potential shifts cathodically as the pH increases. Figure-4.4a, Figure-4.4b, Figure-4.5a, Figure-4.5b, Figure-4.5c, and Figure-4.6. The $pK_a$ values of the equilibrium from the Scheme-I-III were obtained by a weighted non-linear least square fit of the potential to a theoretical curve$^{15-17}$ describe by Equation (5). The best-fitted theoretical curve corresponds to one electron ($n\approx1$) and one proton ionization.

$$E_{1/2} = E_o + \frac{RT}{nF} \ln \frac{p_{K_a}^{IV} + [H]^+}{p_{K_a}^{III} + [H]^+}$$

(5)

Where $pK_a^{IV}$ and $pK_a^{III}$ are the $pK_a$s of the proton equilibrium in the state of $V^{IV}$ (or $\text{Ru}^{III}$) and $V^{III}$ (or $\text{Ru}^{II}$) state of $V^{IV}(L)$ or $\text{Ru}^{III}(L)$ complexes. The $pK_a$, $pK_a^{IV}$ (or $pK_a^{III}$) and $pK_a^{III}$
(or $pK_a^{II}$) values in aqueous SDS, CTAB and TritonX-100 micelles obtained from the curve fitting procedure are presented in the Table-4.2. The $pK_a^{IV}$ or $pK_a^{III}$ values agree with those obtained from the electronic spectroscopic data.

![Graph of pH vs. $E_{1/2}$](image)

**Figure-4.4a** Change in $E_{1/2}$ of $10^{-3}$ mole dm$^{-3}$ [V$^{IV}$ (Salen)(H$_2$O)]$^{2+}$ complex in aqueous SDS micelle as a function of pH. $pK_a = 7.57 \pm 0.026$; Temp.25°C.
Figure 4.4b Change in $E_{1/2}$ of $10^{-3}$ mole dm$^{-3}$ $[\text{V}^{IV}(\text{Salen})(\text{H}_2\text{O})]^{2+}$ complex in aqueous TritonX-100 micelle as a function of pH. $pK_a = 7.28 \pm 0.020$; Temp. 25°C.

Figure 4.5a Change in $E_{1/2}$ of $10^{-3}$ mole dm$^{-3}$ $[\text{V}^{IV}(\text{NTA})(\text{H}_2\text{O})]^{+}$ complex in aqueous CTAB micelle as a function of pH. $pK_a = 9.85 \pm 0.047$; Temp. 25°C.
Figure-4.5b Change in $E_{1/2}$ of $10^{-3}$ mole dm$^{-3}$ $[V^{IV}(NTA)(H_2O)]^+$ complex in aqueous SDS micelle as a function of pH. $pK_a = 8.33 \pm 0.0691$; Temp. $25^\circ$C.

Figure-4.5c Change in $E_{1/2}$ of $10^{-3}$ mole dm$^{-3}$ $[V^{IV}(NTA)(H_2O)]^+$ complex in aqueous TritonX-100 micelle as a function of pH. $pK_a = 7.65 \pm 0.044$; Temp. $25^\circ$C.
Figure 4.6 Change in $E_{1/2}$ of $10^{-3}$ mole dm$^{-3}$ [Ru$^{III}$(NTA)(H$_2$O)$_2$]$^0$ complex in aqueous TritonX-100 micelle as a function of pH. pKa = 7.2 ± 0.039; Temp. 25°C.
Table 4.2 The pH dependent of mid-point potentials of $V^{IV}$O(Salen), $[V^{IV}$O(NTA)]$^{-}$ and $Ru^{III}$(NTA) complexes. Working electrode: Glassy carbon electrode, Reference electrode: Ag-AgCl electrode. Temp. 25°C.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$pK_{a,IV}$ for $V^{IV}$</th>
<th>$pK_{a,III}$ for $V^{III}$</th>
<th>$pK_{a,II}$ for $Ru^{II}$</th>
<th>$pK_{a}$</th>
<th>$\Delta pK_{a}$</th>
<th>$\Delta E$/pH(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{IV}$O(Salen)</td>
<td>CTAB</td>
<td>6.85</td>
<td>7.34</td>
<td>7.098 ± 0.050</td>
<td>0.49</td>
<td>-0.055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SDS</td>
<td>7.31</td>
<td>7.83</td>
<td>7.57 ± 0.026</td>
<td>0.52</td>
<td>-0.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TX-100</td>
<td>7.24</td>
<td>7.32</td>
<td>7.28 ± 0.020</td>
<td>0.08</td>
<td>-0.055</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CTAB</td>
<td>9.60</td>
<td>10.10</td>
<td>9.85 ± 0.047</td>
<td>0.5</td>
<td>-0.053</td>
<td></td>
</tr>
<tr>
<td>$[V^{IV}$O(NTA)]$^{-}$</td>
<td>SDS</td>
<td>7.65</td>
<td>9.03</td>
<td>8.327 ± 0.069</td>
<td>1.38</td>
<td>-0.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TX-100</td>
<td>7.40</td>
<td>8.34</td>
<td>7.65 ± 0.044</td>
<td>0.94</td>
<td>-0.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CTAB</td>
<td>7.10</td>
<td>7.60</td>
<td>7.25 ± 0.060</td>
<td>0.5</td>
<td>-0.053</td>
<td></td>
</tr>
<tr>
<td>$Ru^{III}$(NTA)</td>
<td>SDS</td>
<td>6.84</td>
<td>7.50</td>
<td>7.18 ± 0.032</td>
<td>0.65</td>
<td>-0.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TX-100</td>
<td>6.849</td>
<td>7.515</td>
<td>7.2 ± 0.039</td>
<td>0.66</td>
<td>-0.055</td>
<td></td>
</tr>
</tbody>
</table>
The pK_a IV (pK_a III for Ru^{III}) and pK_a III (pK_a II for Ru^{II}) values are the pK_a s of V^{IV} or Ru^{III} and V^{III} and or Ru^{II} form of the complexes. They were obtained from the least-square fit of $E_{1/2}$ versus pH using Equation (5);

$$\Delta pK_a = pK_a\text{III}(or\ pK_a\text{II for Ru}^{II}) - pK_a\text{IV} (or pK_a\text{III for Ru}^{III})$$

The uptake and release of protons on reduction of V^{IV}(L) or Ru^{III}(L) tetradeutate ligand complexes may be explained by the Scheme-I-III. When the operating pH is in between pK_a IV (or pK_a III) and pK_a III (or pK_a II) i.e. in the range pK_a IV (or for Ru^{III} pK_a III) < pH < pK_a III (or for Ru^{II} pK_a II) the electron proton coupling takes place in the redox equilibrium. Between pK_a IV (or for Ru^{III} pK_a III) and pK_a III (or for Ru^{II} pK_a II) the change in the potential per unit change in the pH($\Delta E/\Delta pH$) was -0.055 V indicating one proton dissociation per electron transferred from the complex. Thus for the range pK_a IV (or for Ru^{III} pK_a III) < pH < pK_a III (or for Ru^{II} pK_a II) proton coupling to electron uptake occurs. Since pK_a IV (or for Ru^{III} pK_a III) is substantially below and the pK_a III (or for Ru^{II} pK_a II) above the operating pH, the reduction of the V^{IV}(L) or Ru^{III} tetradeutate ligand complex is accompanied by the uptake of a proton.

4.3 CONCLUSION:

The mid-point redox potential of V^{IV}(L) or Ru^{III}(L) tetradeutate ligand complexes in an aqueous surfactant micelles solution is dependent on the state of the axially coordinated H_2O/OH ligand. There are several metal dioxygen enzymes where uptake/release of protons of axially coordinated ligands controls the redox potential of the metal dioxygenase enzymes. Thus, V^{IV}(L) or Ru^{III}(L) complexes in aqueous surfactant micelles may be good model with which to study proton coupled electron transfer in metal dioxygenase enzymes. The electron transfer at vanadium or ruthenium site of V^{IV}(Salen), [V^{IV}O(NTA)]^- and Ru^{III}(NTA) complexes are controlled by uptake/release of proton at the axially coordinated H_2O/OH ligand. A change in the mid-point potential permit change of pH ca. -0.053 to -0.055 V indicates proton coupled electron transfer in micelle encapsulated V^{IV}(Salen), [V^{IV}O(NTA)]^- and Ru^{III}(NTA) complexes. The pK_a values of aquo-hydroxo
equilibrium are dependent on the nature of the surfactant. The pKₐ values of [V⁴⁺O(NTA)]⁻ in CTAB, SDS and TritonX-100 micelles are higher than V⁴⁺(Salen), Ru³⁺(NTA) complexes in corresponding surfactant micelles. This may be attributed due to the increase the Lewis acidity of the [V⁴⁺O(NTA)]⁻ complex.¹⁸
REFERENCES:


