CHAPTER-III

3.1 INTRODUCTION:

In this chapter, we report a UV-Visible spectroscopic study on acid–base equilibria of $V^{IV}$O(Salen), $[V^{IV}$O(NTA)]$^-$ and Ru$^{III}$NTA tetradentate ligand complexes in aqueous surfactant micelles. The micelle concentrations are 4%, 2% and 3% for CTAB, SDS and TritonX-100, respectively, for all the studies reported here. The concentrations are much above the critical micellar concentration. The reason for choosing these concentrations of the surfactants is to ensure complete micellization$^{1-2}$ and also to make sure that the mid-point redox potential will not change due to any minor fluctuation in the micelle concentration$^{1-6}$.

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

3.2 RESULTS AND DISCUSSION:

Aqueous solution of the complexes in the surfactants is prepared according to the procedure described in CHAPTER-II. Low pH (pH 4.0-6.50) aqueous surfactant micellar solutions are prepared in 20 mM acetate buffer and high pH (pH 6.50-11) aqueous surfactant micellar solutions are prepared in 50 mM Tris-HCl buffer. For acid-base equilibrium titrations of complexes in aqueous surfactants, the desired pH was adjusted by using NaOH solution. At pH < $pK_a$ (below pH 7) in aqueous surfactant micelles, $V^{IV}$O(Salen) undergoes acid-induced disproportionation to oxophilic $[V^{IV}(salen)]^{2+}$ according to Equilibrium reaction$^7$ (1).

\[
V^{IV}\text{O(Salen)} + 2H^+ = [V^{IV}(salen)]^{2+} + H_2O = [V^{IV}(salen)(H_2O)]^{2+} \quad (1)
\]

In the aqueous surfactant micelles the oxophilic $[V^{IV}(salen)]^{2+}$ is axially coordinated with an aquo group to form $[V^{IV}(salen)(H_2O)]^{2+}$. At pH > $pK_a$ (above pH 7) the aquo species $[V^{IV}(salen)(H_2O)]^{2+}$ deprotonates to form the hydroxo species $[V^{IV}(salen)OH]^+$. The equilibrium may be represented as,

\[
[V^{IV}(salen)H_2O]^{2+}. \text{micelle} + OH^- = [V^{IV}(Salen)OH]^+. \text{micelle} + H_2O \quad (2)
\]
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The electronic spectrum of aquo species \([\text{V}^{IV}(\text{salen})(\text{H}_2\text{O})]^{2+}\) and hydroxo species \([\text{V}^{IV}(\text{Salen})(\text{OH})]^+\) are shown in the Figure-3.1a, Figure-3.1b, Figure-3.1c and Figure-3.1d.

**Figure 3.1a** Electronic spectrum of \(10^{-5}\) mole dm\(^{-3}\) (i) aquo \([\text{V}^{IV}(\text{salen})(\text{H}_2\text{O})]^{2+}\) complex in aqueous CTAB micelle at pH 4.18 (20 mM acetate buffer) and (ii) hydroxo \([\text{V}^{IV}(\text{salen})\text{OH}]^+\) complex in aqueous CTAB micelle at pH 9.89 (50mM Tris-HCl buffer).

**Figure 3.1b** Electronic spectrum of \(10^{-4}\) mole dm\(^{-3}\) aquo \([\text{V}^{IV}(\text{salen})(\text{H}_2\text{O})]^{2+}\) complex in aqueous SDS micelle at pH 4.53 (20 mM acetate buffer).
Figure 3.1c Electronic spectrum of $10^{-4}$ mole dm$^{-3}$ hydroxo [$V^{IV}$\text(salen)$\text{OH}^+$ complex in aqueous SDS micelle at pH 9.17 (50 mM Tris-HCl buffer).

Figure 3.1d Electronic spectrum of $10^{-5}$ mole dm$^{-3}$ (i) aquo [$V^{IV}$\text(salen)$\text{(H}_2\text{O)}^2+$ complex in aqueous TritonX-100 micelle at pH 5.58 (20 mM acetate buffer) and (ii) hydroxo [$V^{IV}$\text(salen)$\text{OH}^+$ complex in aqueous TritonX-100 micelle at pH 9.80 (50 mM Tris-HCl buffer).
Thus the nature of $V^{IV}\text{O(salen)}$ complex depend on the pH of the aqueous surfactant micelles. At high pH (when the operating pH $> \text{pK}_a$) the cationic hydroxo species $[V^{IV}(\text{salen})\text{OH}]^+$ is predominant in micellar solution, Equilibrium (2). Figure-3.2a and Figure-3.2b shows the electronic spectral changes of $V^{IV}\text{O(Salen)}$ complex in SDS and TritonX-100 micelles with increasing pH. The electronic spectrum of $V^{IV}\text{O(salen)}$ complex (Figure-3.2a and Figure-3.2b) shows isosbestic points at 347 nm in SDS and 346 nm in TrironX-100 micelles clearly indicating the presence of two absorbing species $[V^{IV}(\text{salen})(\text{H}_2\text{O})]^2+$ and $[V^{IV}(\text{salen})(\text{OH})]^+$, Equilibrium (2).

Figure-3.2a Electronic spectral variations of $10^{-4}$ mole dm$^{-3}$ $[V^{IV}(\text{Salen})\text{H}_2\text{O}]^{2+}$ complex in aqueous SDS micelle as a function of measured pH range (1) pH = 4.53 to (8) pH=9.17.
Figure-3.2b Electronic spectral variations of $10^{-5}$ mole dm$^{-3}$ [V$^{IV}$(Salen)H$_2$O]$^{2+}$ Complex aqueous TritonX-100 micelle as a function of measured pH range (1) pH = 5.58 to (10) pH = 9.80.

Depending on the nature of the surfactants the electronic spectrum of V$^{IV}$O(salen) complex exhibit bands in the region 255 to 326 nm at pH < pK$_a$ and another in the region 230 to 394 nm at pH > pK$_a$ (Table-3.1).
In aqueous surfactant micelles (nitrilotriacetato)oxovanadate(IV) \([\text{V}^{IV}\text{O(NTA)}]\) complex exhibits as aqua(nitrilotriacetato)oxovanadate(IV) \([\text{V}^{IV}\text{O(NTA)}(\text{H}_2\text{O})]\) according to the Equilibrium\(^8\) (3). At pH < pK\(_a\) (below pH 7) aqueous surfactant micelles \([\text{V}^{IV}\text{O(NTA)}(\text{H}_2\text{O})]\) may undergo acid-induced disproportionation to oxophilic cation \([\text{V}^{IV}\text{(NTA)}\text{H}_2\text{O}]^+\) according to the Equilibrium\(^7\) (4).

\[\text{[V}^{IV}\text{O(NTA)}]\cdot \text{micelle} + \text{H}_2\text{O} = \text{[V}^{IV}\text{O(NTA)(H}_2\text{O)}_2]\cdot \text{micelle} \quad (3)\]

\[\text{[V}^{IV}\text{O(NTA)(H}_2\text{O)}_2]\cdot \text{micelle} + 2\text{H}^+ = \text{[V}^{IV}\text{(NTA)}\text{H}_2\text{O}]^+. \text{micelle} + \text{H}_2\text{O} \quad (4)\]

The electronic spectral data of \([\text{V}^{IV}\text{(NTA)}]^+\) in aqueous surfactant micelles, present in the Table-3.1 and Figure-3.3 shows the electronic spectral changes of \([\text{V}^{IV}\text{O(NTA)}]^-\) in CTAB micelles with increasing pH. At aqueous surfactant micelles pH > pK\(_a\) (above pH 7)
the oxophilic cation \([\text{V}^{\text{IV}}(\text{NTA})]^+\) coordinated with a hydroxo axial ligand to form hydroxo species \([\text{V}^{\text{IV}}(\text{NTA})(\text{OH})]\) according to the \textbf{Equilibrium (5)}.

\[
[\text{V}^{\text{IV}}(\text{NTA})\text{H}_2\text{O}].\text{micelle} + \text{OH}^- = [\text{V}^{\text{IV}}(\text{NTA})(\text{OH})].\text{micelle}
\]  \hspace{1cm} (5)

\textbf{Figure-3.3} Electronic spectra of 10\textsuperscript{-4} mole dm\textsuperscript{-3} (i) \([\text{V}^{\text{IV}}(\text{NTA})]^+\) complex in aqueous CTAB micelle at pH 6.00 (20 mM acetate buffer) and (ii) Hydroxo \([\text{V}^{\text{IV}}(\text{NTA})(\text{OH})]\) complex in aqueous CTAB micelle at pH 9.6 (50mM Tris-HCl buffer).

In aqueous surfactant micelles (nitrilotriacetato) ruthenium(III) \([\text{Ru(III)(NTA)}]\) complex exhibits as diaqua(nitrilotriacetato) ruthenium(III), \([\text{Ru}^{\text{III}}(\text{NTA})(\text{H}_2\text{O})_2]\) according to the following \textbf{Equilibrium\textsuperscript{6}(6)}:

\[
[\text{Ru}^{\text{III}}(\text{NTA})].\text{micelle} + 2\text{H}_2\text{O} = [\text{Ru}^{\text{III}}(\text{NTA})(\text{H}_2\text{O})_2].\text{micelle}
\]  \hspace{1cm} (6)

At pH > pK\textsubscript{a} the \([\text{Ru}^{\text{III}}(\text{NTA})(\text{H}_2\text{O})_2]\) deprotonates to form aquo- hydroxo species. The aquo-hydroxo equilibrium may be represented as;

\[
[\text{Ru}^{\text{III}}(\text{NTA})(\text{H}_2\text{O})_2].\text{micelle} + \text{OH}^- = [\text{Ru}^{\text{III}}(\text{NTA})(\text{H}_2\text{O})(\text{OH})].\text{micelle} + \text{H}_2\text{O}
\]  \hspace{1cm} (7)
The electronic spectral data of [Ru\textsuperscript{III}(NTA)] in aqueous surfactant micelles are presented in the Table-3.1.

The pK\textsubscript{a} values of the Equilibrium (2), (5) and (7) in surfactant micelles were analyzed by a weighted non-linear least-square fit from the plot of absorbance as a function of pH to the Henderson-Hesselback Equation (8).

\[ p_{k_a} = m.p^H - \log\frac{[A_{m-}]}{[AH_m]} \quad (8) \]

Where, AH\textsubscript{m} and A\textsuperscript{m-} are the acid and conjugated base respectively; and m is the number of protons involved.

\[ AH_m \rightarrow A^{m-} + m. H^+ \quad (9) \]

For V\textsuperscript{IV}O(Salen) complex, the plot of absorbance as a function of pH in the CTAB, SDS and TritonX-100 surfactant micelles are shown in the Figure-3.4a, Figure-3.4b and Figure-3.4c. The pK\textsubscript{a} values for the Equilibrium (2) was calculated using Equation (8) and are found at 7.47 in CTAB, 8.34 in SDS and 8.10 in TritonX-100 micelles (Table-3.2). Similarly, for the Equilibrium (5), the plot of absorbance of V\textsuperscript{IV}O(NTA) as a function of pH in the surfactant micelles (Figure-3.5a and Figure-3.5b) gave pK\textsubscript{a} values for the Equilibrium (5) at 9.44 in CTAB and 9.10 in SDS micelles (Table-3.2).
Figure-3.4a  Change in absorbance of 10^{-5} mole dm^{-3} [V^{IV}(Salen)H_2O]^{2+} complex in aqueous CTAB micelle as a function of pH at 383 nm. p_{K_a} = 7.47 \pm 0.037; Temp. 25^\circ C

Figure-3.4b  Change in absorption of 10^{-5} mole dm^{-3} [V^{IV}(Salen)H_2O]^{2+} complex in aqueous SDS micelle as a function pH at 323nm. p_{K_a} = 8.34 \pm 0.034; Temp. 25^\circ C.
**Figure-3.4c** Change in absorbance of \(10^{-5}\) mole dm\(^{-3}\) \(\text{[V}^\text{IV}(\text{Salen})\text{H}_2\text{O}]^{2+}\) complex in aqueous TritonX-100 micelle as a function of pH at 377nm. \(p_{\text{Ka}} = 8.10 \pm 0.026;\) Temp. 25°C.

**Figure-3.5a** Change in absorbance of \(10^{-4}\) mole dm\(^{-3}\) \(\text{[V}^\text{IV}(\text{NTA})\text{]}^+\) complex in aqueous CTAB micelle as a function of pH at 229 nm. \(p_{\text{Ka}} = 9.44 \pm 0.01;\) Temp. 25°C.
Figure-3.5b  Change in absorbance of $10^{-4}$ mole dm$^{-3}$ [ V$^{IV}$ (NTA) ]$^+$ complex in aqueous SDS micelle as a function of pH at 267 nm. $pK_a = 9.10 \pm 0.014$; Temp. 25°C.

Similarly for the Equilibrium (7), the plot of absorbance of Ru$^{III}$(NTA) complex as a function of pH in the surfactant micelles (Figure-3.6) gave $pK_a$ values for the Equilibrium (7) at 7.64 in CTAB and 6.89 in SDS surfactant micelles (Table-3.2).

Figure-3.6  Change in absorbance of $10^{-4}$ mole dm$^{-3}$ [ Ru$^{III}$(NTA)(H$_2$O)$_2$]$^+$ complex in aqueous SDS micelle as a function of pH at 288 nm. $pK_a = 6.89 \pm 0.004$; Temp. 25°C.
3.3 CONCLUSION:

The pKₐ values of the aquo-hydroxo equilibrium are dependent on the nature of the surfactant micelles. The pKₐ values of \([\text{V}^{IV}\text{O}(\text{NTA})]^−\) complex in CTAB and SDS micelles are higher than \([\text{V}^{IV}\text{O(salen)}]\) and \([\text{Ru}^{III}(\text{NTA})]\) complex in corresponding surfactant micelles. Higher values of pKₐ in \([\text{V}^{IV}\text{O}(\text{NTA})]\) may be attributed to the Lewis acidity of the \(\text{V}^{IV}\) centre modulated by the tripodal NTA ligand. In \(\text{V}^{IV}\) and \(\text{Ru}^{III}\) tetradeptate complexes the proton uptake is the axial ligand, therefore protonation or deprotonation at their site have significant influence on pKₐ values. The nature of the surface charge on the micelles and pKₐ values of \(\text{V}^{IV}\) and \(\text{Ru}^{III}\) tetradeptate complexes in micellar solutions have considerable influence on the stability of the aquo or hydroxo \(\text{V}^{IV}\) and \(\text{Ru}^{III}\) tetradeptate complexes.
Aqueous anionic SDS micelle which have negative charge on the surface stabilizes the positive charged aquo species \([V^{IV}(Salen)(H_2O)]^{2+}\) better than cationic or non-ionic TritonX-100 micelles. Hence, the observed pKₐ values and stability of the \([V^{IV}O(NTA)(H_2O)]^-\) follow the order

\[SDS < CTAB.\]

Similarly, the pKₐ value and net stabilization of negatively charged aquo-hydroxo species, \([Ru^{III}(H_2O)(OH)]^-\) is greater in aqueous CTAB micelle than in aqueous SDS micelle.

\[SDS < CTAB\]

Aqueous surfactant micelles not only solubilizes the aquo or hydroxo \(V^{IV}\) and \(Ru^{III}\) tetradentate ligand complexes but also allow spectroscopic studies in wide range of pH. The hydrophobic environment of the surfactant may influence the Lewis acidity and pKₐ values of \(V^{IV}\) and \(Ru^{III}\) tetradentate ligand complexes.
REFERENCES: