UV-VISIBLEAND ELECTROCHEMICAL STUDIES ON ACID-BASE EQUILIBRIUM OF $[V^{IV}O(NTA)]^-$ TETRADENTATE COMPLEX ENCAPSULATED IN AQUEOUS SURFACTANT MICELLES

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Abstract: In this paper, we report UV-Visible spectroscopic and electrochemical studies of acid-base equilibrium of nitrilotriacetato oxovanadium(IV) $[V^{IV}O(NTA)]^-$ complex as model complex of non-enzyme vanadium containing metalloenzymes in aqueous surfactant micelles. The observed pKa values and stability of the $[V^{IV}O(NTA)]^-$ complex in aqueous surfactant micelles follow the order: SDS<CTAB. The pH dependent mid-point redox potential of $[V^{IV}O(NTA)]^-$ complex in aqueous surfactant micelles follow the order SDS> TritonX-100 > CTAB.

Keywords: Nitrilotriacetato Oxovanadium(IV) $[V^{IV}O(NTA)]^-$; micelles; redox potential

1. Introduction:

In nature, it is estimated that approximately half of all proteins contain a metal [1]. In another estimate, about one quarter to one third of all proteins are proposed to require metals to carry out their functions [2]. Vanadium can exist in eight oxidation states ranging from -3 to +5, but with the exception of -2. Only the three highest oxidation states i.e. +3, +4 and +5 are important in biological systems. Under ordinary conditions, the +4 and +5 oxidation states are the most stable ones. The majority of V^{IV} compounds contain the VO^{2+} unit (Vanadyl ion). These complexes typically have square planer, pyrimidal or bipyrimidal geometries with an axial oxo ligand. The coordination chemistry of V^V compounds are dominated by oxo complexes, containing VO^{3+} or VO^{2+} [3].Vanadium is a trace element present in almost all living organisms including man. Vanadium is widely recognized as a biological important element [4]. The first two naturally occurring vanadium enzymes are vanadium(V^V)-bromoperoxidase and vanadium-nitrogenase [5]. The vanadium-catalyzed dioxygenase reaction of catechol by activating oxygen was reported via the oxidase product: quinone [6]. In this biomimetic study, we are particularly interested in using nitrogen and oxygen containing V^{IV} complex of tetradentate ligand in aqueous surfactant micelles.

The surfactants used in this work are cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate(SDS) and polyethylene glycol tert-octyl phenyl ether(TritonX-100). The aqueous surfactant micelles are often considered to be biomimetic in that reactions on and within micelles, may mimic reactions at biomembrane interfaces [7,8]. The tetradentate ligand employed in this work is NTA (Nitrilo triacetate). The tetradentate tripodal ligand NTA (Figure 1) has been chosen for the following reasons:

(i) The Lewis acidity of V^{IV} centre is modulated by the tripodal ligand NTA [9]. Presence of nitrogen in the tripodal ligand makes the V^{IV} ion more Lewis acidic and the ligand-metal orbital energy gap diminishes [10].

(ii) The ligand NTA provides reasonable analogues of carboxylate coordination in the non-heme enzymes. Also the ligand NTA is more flexible in chelation to the metal ions than tetradentate Schiff base ligands. The tri-ionic ligand would be expected to favour the V^{IV} oxidation states.

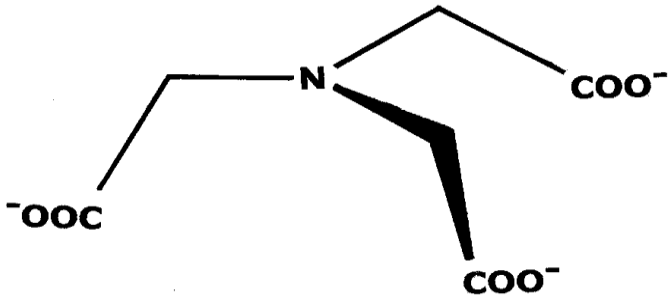


Figure: Structure of tetradentatetripodal ligand NTA.

In this work, we report UV-Visible and electrochemical studies of acid-base equilibria of $[V^{IV}O(NTA)]^-$ complex in aqueous surfactant micelles. The micelle concentrations are 4%, 2% and 3%*w/v* 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 [7,8] and also to make sure that the mid-point redox potential will not change due to any minor fluctuation in the micelle concentration [7,8,11-13]. We expect that UV-Visible and electrochemical studies of acid–base equilibria of $[V^{IV}O(NTA)]^-$ complex in aqueous surfactant micelles would provide considerable amount of understanding about the uptake/release of protons of the axially coordinated ligand of the metallo enzymes.

2. Materials and methods:

Cetyl trimethyl ammonium bromide(CTAB), Sodium dodecyl sulphate(SDS), TritonX-100 were obtained from Sigma Chemicals and used without further purification. Tris-hydroxy methyl aminomethane and Tetra methyl ammonium bromide(TMAB) were obtained from Spectrochem. Sodium nitrate and Sodium acetate were obtained from Loba Chemie. Tetra methyl ammonium bromide was used as counter ions in micelles. Nitrilo triacetic acid (NTA) was obtained from Spectrochem Pvt. Ltd. Bombay, India. The pH measurements were done by Butech Instruments. Electronic spectra were recorded on either Hitachi U-3210 Spectrophotometer or UV-1800 Shimadzu UV-Spectrometer. Infra-red spectra were recorded on IR affinity-1 Shimadzu FT-IR Spectrometer. ^{1}H NMR spectra was recorded on Bruker Ultrashild 300 Instrument Type AV 300N, 300 MHz. Cyclic voltammetric experiments were carried out using BAS 100A Electrochemical Analyzer, Bio-Analytical System, USA. The working electrode was a glassy carbon electrode, platinum wire was an auxillary electrode and Ag-AgCl electrode was used as reference electrode. All the cyclic voltammetric experiments were done in an inert atmosphere by purging the solution with N_2 gas for 15 minutes.

2.1. Synthesis of (Nitrilo triacetato)oxovanadium(IV) $[V^{IV}O(NTA)]^-$:

The complex $[V^{IV}O(NTA)]^-$ was prepared by mixing aqueous solution of vanadyl sulphate [oxovanadium(IV)(sulphate)] and excess of NTA solution in water. In the presence of excess ligand NTA, V^{IV} ion forms vanadium (IV) complex [14].

Infra red spectrum (KBr): The infrared spectrum of $[V^{IV}O(NTA)]^-$ complex shows the $\nu_{C\text{-}N}$is at 1130cm^{-1} (for free NTA $\nu_{C\text{-}N}$ at 1200cm^{-1}), indicating the N-atom of the NTA ligand coordinated with V-atom. The ν_{as}(COOH) at 1728 cm^{-1} of free NTA red shifts to 1636cm^{-1} and the $\nu_s(COO^-)$ at 1331cm^{-1} of free NTA is blue shifted to 1400 cm^{-1}; both confirm that the O^- atom of COO^- groups coordinates the V- atom. The band at 990cm^{-1}can be attributed to the ν(V=O) and ν(V-O-V) vibrations [15].

^{1}HNMR (D_2O/DMSO),δppm: 4.071(s) [16].

3. Results and Discussions:

pH dependent UV-Visible studies of $[V^{IV}O(NTA)]^-$ in aqueous surfactant micelles:

$[V^{IV}O(NTA)]^-$complex was dissolved in aqueous 4% CTAB, 2%SDS, 3% TritonX-100 surfactant micelles. For low pH surfactant micelle, 20mM acetate buffer and for high pH surfactant micelle, 50mM Tris-HCl buffer were used. In aqueous surfactant micelles $[V^{IV}O(NTA)]^-$complex exhibits as aqua

(nitrilotriacetato)oxovanadate(IV) $[V^{IV}O(NTA)(H_2O)]^-$ according to the Equilibrium[14](1). At pH < pKa (below pH 7) in aqueous surfactant micelles, $[V^{IV}O(NTA)(H_2O)]^-$ undrgoes acid-induced disproportionation to oxophilic $[V^{IV}(NTA)(H_2O)]^+$ according to Equilibrium (2) [17].

$$[V^{IV}O(NTA)]^-.micelle + H_2O = [V^{IV}O(NTA)(H_2O)]^-.micelle \quad (1)$$

$$[V^{IV}O(NTA)(H_2O)]^-.micelle+2H^+= [V^{IV}(NTA)H_2O]^+.micelle+H_2O \quad (2)$$

The electronic spectral data of $[V^{IV}(NTA)H_2O]^+$ in aqueous surfactant micelles, present in the Table 1 and Figure 2 shows the electronic spectral changes of $[V^{IV}O(NTA)]^-$ in CTAB micelles with increasing pH. At aqueous surfactant micelles pH > pK_a (above pH 7) the oxophilic cation $[V^{IV}(NTA)H_2O]^+$ coordinated with a hydroxo axial ligand to form hydroxo species $[V^{IV}(NTA)(OH)]^o$ according to the Equilibrium (3).

$$[V^{IV}(NTA)H_2O]^+.micelle + OH^- = [V^{IV}(NTA)(OH)]^o.micelle \quad (3)$$

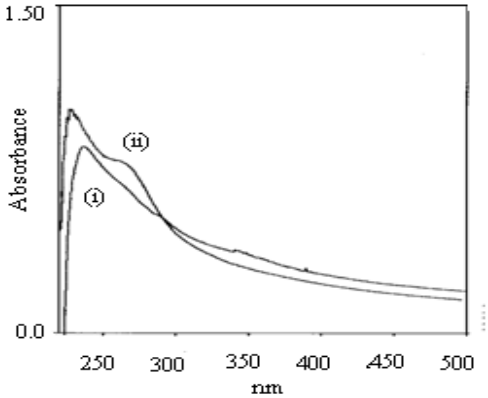


Figure 2: Electronic spectra of 10^{-4} mole dm^{-3}(i) $[V^{IV}(NTA)H_2O]^+$ complex in aqueous CTAB micelle at pH 6.00 (20 mM acetate buffer) and (ii) Hydroxo $[V^{IV}(NTA)(OH)]^o$ complex in aqueous CTAB micelle at pH 9.6 (50mM Tris-HCl buffer).

The pK_a values of the Equilibrium (3) 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 (4).

$$p^k_a = m.p^H - \log \frac{[A^{m-}]}{[AH_m]} \quad (6)$$

where, AH_m and A^{m-} are the acid and conjugated base respectively; and m is the number of protons involved.

$$AH_m \rightleftharpoons A^{m-} + m.\ H^+ \quad \textbf{(5)}$$

For the Equilibrium (3), the plot of absorbance of $[V^{IV}(NTA)H_2O]^+$ as a function of pH in the surfactant micelles (Figure3a and Figure 3b) gave pK_a values for the Equilibrium (3) at 9.44 in CTAB and 9.10 in SDS micelles (Table 1).

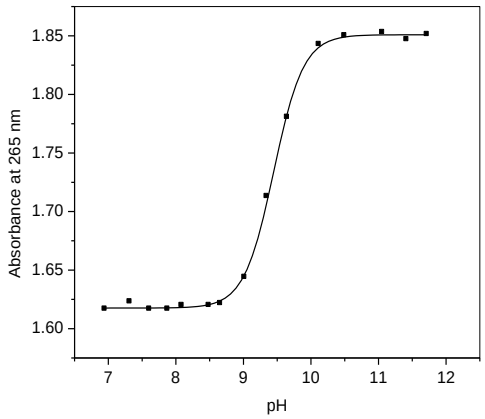


Figure 3a:Change in absorbance of 10^{-4} mole dm^{-3} $[V^{IV}(NTA)]^+$ complex in aqueous CTAB micelle as a function of pH at 229 nm.p^k_a = 9.44 ± 0.01; Temp. 25°C.

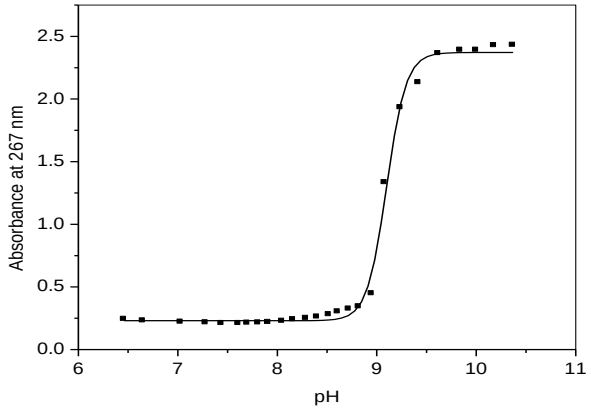


Figure 3b:Change in absorbance of 10^{-4} mole dm^{-3} $[V^{IV}$ (NTA) $]^{+}$ complex in aqueous SDS micelle as a function of pH at 267 nm. p^{k}_{a} = 9.10 ± 0.014; Temp. 25°C.

Table1: pH dependent UV-Vis. spectral changes for $[V^{IV}O(NTA)]^{-}$ complex. Temp. 25°C.

Complex	Aqueous surfactant	pKa (UV-Vis.)
$[V^{IV}O(NTA)]^{-}$	CTAB (at 229 nm) SDS (at 265nm)	9.448 ± 0.010 9.103 ± 0.014

The pK_a values of the aquo-hydroxo equilibrium are dependent on the nature of the surfactant micelles. The pK_a values of $[V^{IV}O(NTA)]^{-}$ complex in CTAB and SDS micelles are higher than $[V^{IV}O(salen)]$ [18] complex in corresponding surfactant micelles. Higher values of pK_a in $[V^{IV}O(NTA)]^{-}$ may be attributed to the Lewis acidity of the V^{IV} centre modulated by the tripodal NTA ligand. In V^{IV} tetradentate complex the proton uptake is the axial ligand, therefore protonation or deprotonation at their site have significant influence on pK_a values. The nature of the surface charge on the micelles and pK_a values of V^{IV} tetradentate complex in micellar solutions have considerable influence on the stability of the aquo or hydroxo V^{IV} tetradentate complex.

The observed pK_a values and stability of the $[V^{IV}O(NTA)(H_2O)]^{-}$ follow the order:

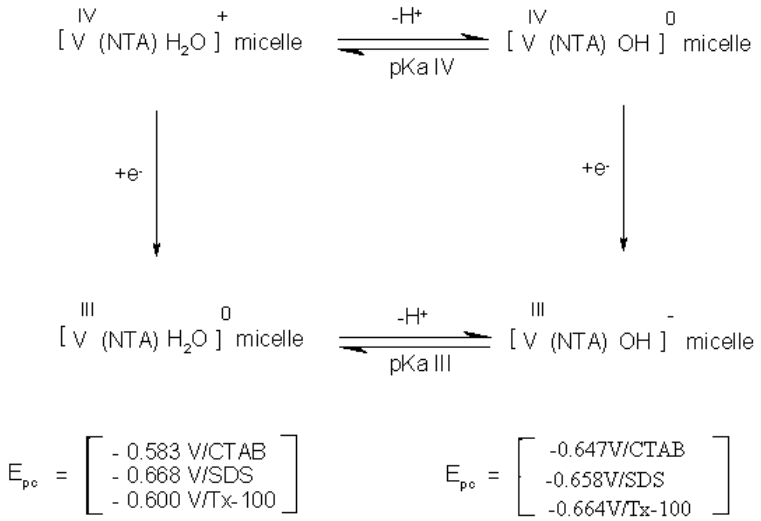
SDS < CTAB.

pH dependent electrochemical studies of $[V^{IV}O(NTA)]^{-}$complex in aqueous surfactant micelles :

At low pH, *ca*. 6.00 (20 mM acetate buffer) the $[V^{IV}(NTA)(H_2O)]^{+}$ species shows only a cathodic peak at -0.583V, -0.668V and -0.600V (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 [19]. At low pH in $[V^{IV}(NTA)(H_2O)]^{+}$ 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 $[V^{IV}(NTA)(H_2O)]^{+}$ at low pH may be explained by the Scheme-I. The positive charged $[V^{IV}(NTA)(H_2O)]^{+}$ species is harder to reduce in negatively charged SDS micellar media, which implies the net stabilization of the $[V^{IV}(NTA)(H_2O)]^{+}$ species in the negative charged SDS micelle is greater than the stabilization of neutral species $[V^{III}(NTA)(H_2O)]^{o}$.



Scheme-I

Inside the microenvironment of the non-ionic TritonX-100 micelle it appears that various forces stabilizing positively charged $[V^{IV}(NTA)(H_2O)]^+$ species and neutral $[V^{III}(NTA)(OH)]^o$ 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 [20-22].

The cyclic voltametric behavior of hydroxo species of $[V^{IV}(NTA)OH]^o$ was investigated in CTAB, SDS and TritonX-100 micelles at pH 10.50 (50 mM Tris-HCl buffer) shows Ep_c at -0.647V, -0.658V and -0.664V respectively at scan rate 0.03V/s (versus Ag-AgCl reference electrode). These process are assumed to be a irreversible [23-26] single-electron oxidation/reduction of the couple $[V^{IV}(NTA)(OH)]^o/[V^{III}(NTA)(OH)]^-$. The redox potential of hydroxo species $[V^{IV}(NTA)OH]^o$ in surfactant micelles vary cathodically in the order:

CTAB < SDS < TritonX-100

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

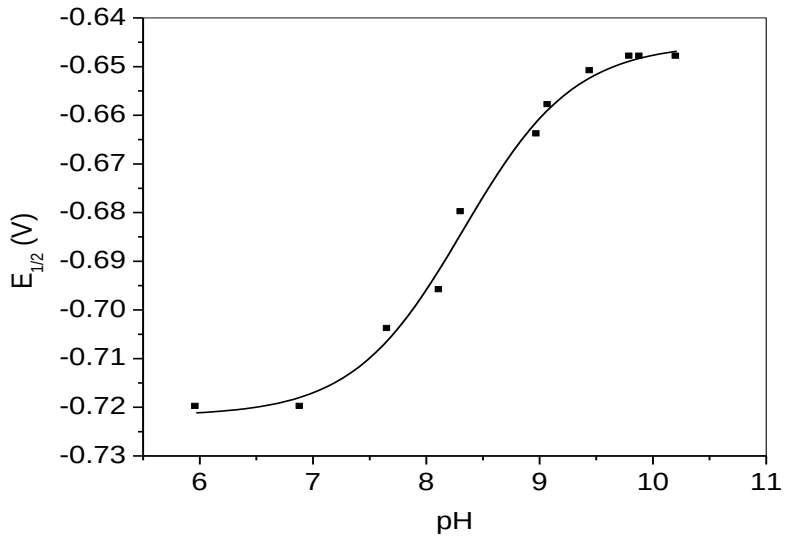


Figure 4a: Change in $E_{1/2}$ of 10^{-3} mole dm^{-3} $[V^{IV}(NTA)(H_2O)]^+$ complex in

aqueous SDS micelle as a function of pH. pKa = 8.33 ± 0.0691; Temp. 25°C.

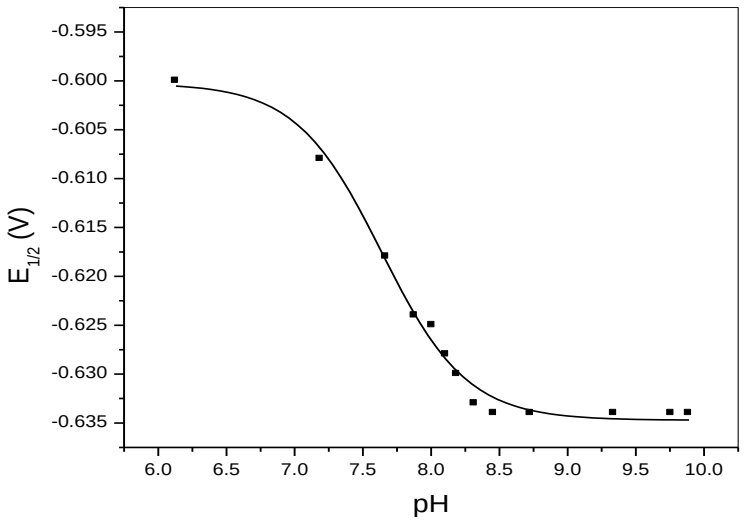


Figure 4b: Change in $E_{1/2}$ of 10^{-3} mole dm^{-3} $[V^{IV}(NTA)(H_2O)]^+$ complex in aqueous TritonX-100 micelle as a function of pH. pKa =7.65 ± 0.044; Temp. 25°C.

The mid-point potential of $[V^{IV}(NTA)(H_2O)]^+$ complex was measured by the cyclic voltametric or OSWV technique as a function of pH shows that the potential shifts cathodically as the pH increases (Figure 4a and Figure 4b).

The pK_a values of the equilibrium from the Scheme-I were obtained by a weighted non-linear least square fit of the potential to a theoretical curve [27-29] described by Equation (6). The best-fitted theoretical curve corresponds to one electron (n≈1) and one proton ionization.

$$E_{1/2} = E_o + \frac{RT}{nF} \ln \frac{p^{k}{}_{a}{}^{III} + [H]^+}{p^{k}{}_{a}{}^{IV} + [H]^+} \quad (6)$$

where pK_a^{IV} and pK_a^{III} are the pK_as of the proton equilibrium in the state of V^{IV} and V^{III} state of V^{IV} complex. The pK_a, pK_a^{IV} and pK_a^{III} values in aqueous SDS, CTAB and TritonX-100 micelles obtained from the curve fitting procedure are presented in the Table 2. The pK_a^{IV} or pK_a^{III} values agree with those obtained from the electronic spectroscopic data.

Table 2: The pHdependent mid-point potentials of $[V^{IV}O(NTA)]^-$ complex in aqueous SDS, CTAB and TritonX-100 micelles. Working electrode: Glassy carbon electrode, Reference electrode: Ag-AgCl electrode. Temp. 25°C.

Solvent	**pK_aIV for V^{IV}**	**pK_aIII for V^{III}**	**pK_a**	**Δ pK_a**	**ΔE/ pH(V)**
SDS	7.65	9.03	8.327±0.069	1.38	-0.054
TX-100	7.40	8.34	7.65 ± 0.044	0.94	-0.054
CTAB	7.10	7.60	7.25 ± 0.060	0.5	-0.053

The pK_a^{IV} and pK_a^{III}values are the pK_as of V^{IV} and V^{III} form of the complexes. They were obtained from the least-square fit of $E_{1/2}$ versus pH using Equation (6);

$$\Delta pK_a = pK_a^{III} - pK_a^{IV}$$

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

4. Conclusions:

The pK_a values of the aquo-hydroxo equilibrium are dependent on the nature of the surfactant micelles.The pKa values of $[V^{IV}O(NTA)]^-$ complex in corresponding surfactant micelles are higher than N,N-bis(Salicylidene)ethylene diamine $V^{IV}O$(Salen) complex [18]. Higher values of pK_a in $[V^{IV}O(NTA)]^-$ may be attributed to the Lewis acidity of the V^{IV} centre modulated by the tripodal NTA ligand. In V^{IV}tetradentate complex the proton uptake is the axial ligand, therefore protonation or deprotonation at the site have significant influence on pKa values. The nature of the surface charge on the micelles and pKa values of $[V^{IV}O(NTA)]^-$ in aqueous surfactant micelles have considerable influence on the stability of the aquo or hydroxo $[V^{IV}O(NTA)]^-$ complex. Aqueous cationic CTAB micelles which have positive charge on the surface stabilizes the negative charged $[V^{IV}O(NTA)]^-$ better than anionic surfactant micelles. Hence, the pKa values and stability of the $[V^{IV}O(NTA)]^-$ follow the order SDS < CTAB. Aqueous surfactant micelles not only solubilises the aquo or hydroxo $[V^{IV}O(NTA)]^-$ complex but also allow spectroscopic studies in a wide range of pH. The hydrophobic environment of the surfactant may influence the Lewis acidity and pKa values of V^{IV} tetradentate ligand complex. The mid-point redox potential of $[V^{IV}O(NTA)]^-$ complex in an aqueous surfactant micelles 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, $[V^{IV}O(NTA)]^-$ complex 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 site of $[V^{IV}O(NTA)]^-$ complex is controlled by uptake/release of proton at the axially coordinated H_2O/OH ligand. Change in mid-point potential per unit change of pH ca.-0.053 to -0.054V indicates proton coupled electron transfer in micelle encapsulated $[V^{IV}O(NTA)]^-$ complex. The pKa values of aquo-hydroxo equilibrium are dependent on the nature of the surfactant. The pKa values of $[V^{IV}O(NTA)]^-$ in CTAB, SDS and TritonX-100 micelles are higher than $V^{IV}O$(Salen) complex in corresponding surfactant micelles [18]. This may be attributed due to the increase the Lewis acidity of the $[V^{IV}O(NTA)]^-$ complex [9].

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