STUDY OF ELECTROCHEMICAL BEHAVIOR OF OXO-VANADIUM(IV) COMPLEXES WITH TETRADENTATE AND BIDENTATE LIGANDS BY CYCLIC VOLTAMETRIC METHOD

Dr Prem Yadav
Assistant Professor
Department of Chemistry
S.G.N. Government P.G. College, Muhammadabad Gohna Mau, UP 276403 India

Abstract:

The electrochemical behaviour of tetradentate Schiff base complex with oxovanadium(IV), VO(salen) **1**, (salen = N,N'-ethylene bis-(salicylaldiminato) dianion), bidentate Schiff base complex with oxovanadium(IV) complex $VO(sal\text{-}anl)_2$ **2** (sal-anl= Salicylaldehyde-aniline) and $VO(bipy)_2^{2+}$ **3** (bipy=2,2'-bipyridine) have been examined in DMSO with 0.1M TBAP using cyclic voltammetry at a Pt working electrode. The behaviour of tetradentate and bidentate Schiff base ligands are observed in different scan rate and found that reversible and irreversible both peaks are obtained in tetradentate Schiff base Oxovanadium (IV) complex while in bidentate mostly irreversible peaks are obtained. Complex 1 showed two irreversible anodic waves at Epa1 = +0.68 V and Epa2 = +1.06 V vs SCE and also two irreversible cathodic peaks at Epc1/ = -0.90 V and Epc2 = -1.325 V vs SCE followed by an irreversible anodic peak Epa21 = -0.42 V. Complex 2 and 3, irreversibly oxidized ($VO^{2+/3+}$) in the positive potential region with Epa_1 = +1.05 – 1.12V vs SCE at 200 mVs^{-1}. The initial reduction of this complex revealed two irreversible cathodic peaks in the more negative potential region with Epc_1 = -0.96 to –1.13 V and Epc_2 = -1.17 to -1.30 V vs SCE. This potential depends upon the Inductive effect and electron donating and withdrawing group.

Index Terms - Cyclic Voltammetry, Schiff Base, Electrochemical, Oxovanadium

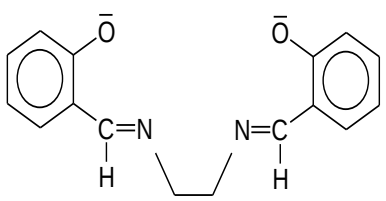
I. INTRODUCTION

The coordination chemistry of oxovanadium (IV) complexes has growing applications in catalysis, therapeutics, and biological activity [1-3]. Vanadium containing compounds have their utility as insulin mimetic and antiamoebic agent [4]. Vanadium dependent enzymes, mainly nitrogenases and haloperoxidases are still a subject for intensive biochemical investigation $V^{5+/4+}$ and $V^{4+/3+}$ redox systems are very significant from reactivity view point. Vanadium compounds have been utilized in various homogeneous/heterogeneous catalytic processes [5], where they exhibited good synthetic potential. Oxovanadium complexes are coordination compounds containing vanadium in its oxo form (VO^{2+}), widely studied for their structural diversity, catalytic activity, and biological relevance. They are particularly important in oxidation reactions, enzyme mimicking, and potential therapeutic applications [5,6]. Vanadium coordination chemistry has recently attracted increasing interest due to the model character of many of its complexes for the biological function in catalysis and material chemistry and potential applications such as the treatment of diabetes [2-4].

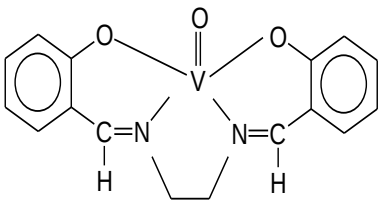
II EXPERIMENT

The details of the electrochemical measurements are already described in our earlier papers [7-8]. Pt was used as a working electrode. The saturated calomel electrode (SCE) was used as reference electrode (E^0=+242mV vs NHE). The potentials reported here are uncorrected for junction potentials. All experiments were performed at 25±1^{0}C in dimethylsulfoxide (DMSO) and dimethylformamide (DMF). containing 0.1M Tetrabutyl ammonium perchlorate (TBAP). Analytical grade chemicals were used without any further purification. TBAP (Fluka), $VOSO_4.2H_2O$, 2, 2'-bipyridyl, 1, 10-phenanthroline, DMF and DMSO (E. Merck) were procured different commercial sources and were used as such without further

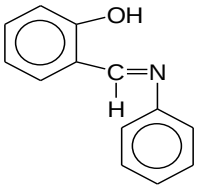
purification. The Schiff bases and their complexes with vanadium (IV) were prepared according to literature procedures [11].



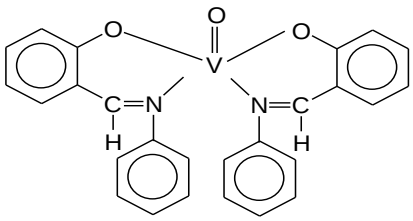
salen = N,N' - ethylenebis (salicylaldiminato) dianion



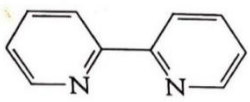
VO (salen) **1** (green)



sal-anl = salicylaldehyde-aniline



VO (sal-anl)$_2$ **1** (green)



2, 2' - bipyridine (bipy)

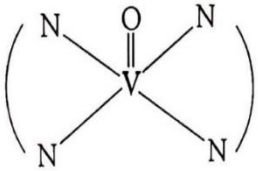


Figure: Structure of ligands and their compounds

III RESULT AND DISCUSSION

The electrochemical behaviour of tetradentate Schiff base complex with oxovanadium(IV), VO(salen) 1, (salen = N,N'-ethylene bis-(salicylaldiminato) dianion), bidentate Schiff base complex with oxovanadium(IV) complex VO(sal-anl)$_2$ 2 (sal-anl= Salicylaldehyde-aniline) and VO(bipy)$_2^{2+}$ 3 (bipy=2,2'-bipyridine) have been examined in DMSO with 0.1M TBAP using cyclic voltammetry at a Pt working electrode. A representative scan of cyclic voltammogram of 4mM VO (salen) 1 in 0.1 M TBAP/DMSO at a scan rate of 200 mVs^{-1} is displayed in Figure and the CV results are presented in Table 1. A positive scan initiated at -0.25 V in the potential range from + 1.0 to -1.75 V vs SCE revealed an oxidation peak (a_1) at + 0.45 V, while the reverse scan produced a reduction peak (c_1) at +0.36 V, in addition to a large irreversible cathodic wave (c_2) at -1.65 V over a range of scan rates studied. Switching at -1.75 V and scanning anodically, an irreversible small anodic peak (a'_2) appeared at -0.125 V in the second cycle (Table 1). The lack of associated anodic wave of the first reduction (c_2) for this complex is due to the formation of a V^{III}-oxo complex species that is likely to be very unstable. The dependence of anodic wave (a'_2) on the reduction peak, c_2 further supports that the first reduction process (c_2) follows the ECE mechanism [6]. The electrochemical and EPR studies of some oxovanadium (IV) complexes with ONO donor Schiff base ligands have very recently been reported by Prasad et al [7]. The redox process in these complexes also follows ECE mechanism. The oxidation of 1 is both chemically and electrochemically reversible with the cathodic-to-anodic peak current ratio, (Ipc_1/Ipa_1) equal to unity and peak potential separation, $\Delta Ep \approx 60$ mV. Scan rate dependence studies (25-300 mVs^{-1}) show that all of the peak currents scale with the square root of the scan rate ($\nu^{1/2}$) as expected for diffusion [8] of the electroactive species to the electrode surface, this indicates that within this potential range and at these scan rates, the electroactive species remains in solution. Schiff base ligands assure a constant coordination geometry and an electronically flexible environment to the metal. The vacant coordinate site(s) may be occupied by coordinating solvent molecules particularly in mononuclear vanadium complexes in solution. These results are reasonably represented by equations (1) to (4):

$$\overset{E^r}{\rightleftharpoons}$$

$$[V^{IV}O\ (salen)\mathbf{S}] \qquad [V^{V}O\ (salen)\mathbf{S}]^{+} + \bar{e} \quad a_1/c_1 \qquad (1)$$

$$[V^{IV}O\ (salen)\mathbf{S}] + \bar{e} \xrightarrow{E^{irr}} [V^{III}O\ (salen)\mathbf{S}]^{-} \qquad c_2 \qquad (2)$$

$$[V^{III}O\ (salen)\mathbf{S}]^{-} + 2H^{+} \xrightarrow[CHEM]{Fast} [V^{III}\ (salen)\mathbf{S}_2]^{+} + H_2O \qquad (3)$$

$$[V^{III}\ (salen)\mathbf{S}_2]^{+} \xrightarrow{E^{irr}} [V^{IV}\ (salen)\mathbf{S}_2]^{2+} + \bar{e} \qquad a'_2 \qquad (4)$$

where, S is a solvent molecule.

It should be mentioned that the peak potentials (Epa_1, Epc_1 and Epc_2) of VO(salen) are more positive in the present study as compared to those reported previously [9] in a given solvent. In fact in earlier studies TEAP was used as the supporting electrolyte. The difference in peak potentials may to be due to the effect of electrolytes. The electrochemical behaviour of complex **2** showed two irreversible anodic waves at Epa_1 = +0.68 V and Epa_2 = +1.06 V vs SCE and also two irreversible cathodic peaks at Epc_1' = -0.90 V and Epc_2 = -1.325 V vs SCE followed by an irreversible anodic peak Epa_2^1 = -0.42 V. On the basis of CV results, (table 2) it is concluded that in complex **2**, the redox processes a_1 and c_2 are metal-based corresponding to:

$$[VO^{IV}(sal\text{-}anl)_2] \xrightarrow{E^{ir}} [VO^{V}(sal\text{-}anl)_2]^{+} + \bar{e} \quad \text{and}$$

$$[VO^{IV}(sal\text{-}anl)_2] + 2H^{+} + \bar{e} \xrightarrow{E^{ir}} [V^{III}(sal\text{-}anl)_2S_2]^{+} + H_2O$$

On the otherhand, the redox processes a_2 and c_1' seem to be ligand-based.

A cyclic voltammogram of VO $(bipy)_2^{2+}$ complex **3** in 1:10 VO^{2+}-bipy system in DMSO/0.1M TBAP at a Pt working electrode at 200 mVs^{-1} is shown in Figure. A positive scan initiated at 0.0V in the potential range from +1.25 to -1.50 V vs SCE reveals an irreversible oxidation peak (a_1) at +1.05V in the forward scan and scan reversal at +1.25V does not show its associated cathodic peak. However, three partly overlapped irreversible cathodic waves (marked as c'_1, c_1 and c_2) are observed at -0.93, -1.13 and -1.27V, respectively (Table 1). It is noteworthy that a potential scan initiated in the negative direction at 0.0V with potential range -1.5 to +1.25V shows only two irreversible cathodic peaks c_1 and c_2 in the forward cycle and two irreversible anodic peaks Epa'_1 and Epa''_1 at -0.50 and +0.62 V, respectively, in addition to anodic peak a_1. It is evident from the voltammograms (Figure) that the cathodic peak c'_1 is dependent on the anodic peak a_1 and the anodic peaks a'_1 and a''_1 are dependent on the cathodic process c_1. It must be mentioned that solutions containing 1mM bipy in DMSO containing 0.1M TBAP do not show any electrochemistry (no redox process) in the potential range studied. On the basis of these results, the anodic process (a_1) may be attributed to the irreversible single - electron oxidation of the complex, $[VO(bpy)_2]^{2+}$ to $[VO(bipy)_2]^{3+}$, which is unstable under the experimental conditions and that the electron transfer reaction is coupled with a fast chemical reaction [10,11].

$$[VO(bipy)_2]^{2+} \xrightarrow{\bar{e}} [VO(bipy)_2]^{3+} \qquad a_1$$

$$[VO(bipy)_2]^{3+} \xrightarrow{CHEM} \Pr oduct\,(P)$$

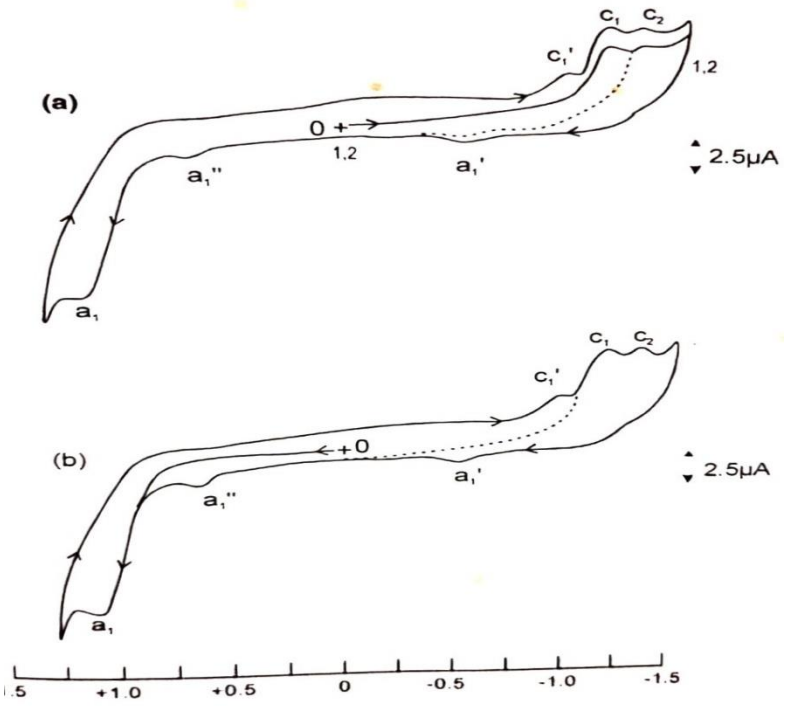


Figure: Cyclic Voltammograms for 1:10 VO^{2+}-bipy system in DMSO/ 0.1M TBAP

Thus, the redox process (c'_1) may be assigned to irreversible reduction of the complex species (P) into some lower oxidation state. On the otherhand, cathodic processes c_1 and c_2 may possibly be due to the reduction of oxovanadium(IV)-bipy complex, $[VO(bipy)_2]^{2+}$ into lower valent non-oxovanadium tris-(bipy) complex species, $V(bipy)_3^{n+}$ ($n \leq 3$). In fact lack of coulometric results at hand prohibit us to assign the correct oxidation state of the metal in the various electrochemically generated complex species.

Table 1-Cyclic voltammetric data for 4mM VO(salen) in dimethylsulfoxide (DMSO) containing 0.1M TBAP

Scan rate / $mV\,s^{-1}$	Epa_1/mV	Epc_1/mV	Ipa_1/μA	Ipc_1/μA	E^0/mV	△Ep/mV	Ipc_1/Ipa_1	Epc_2/V	Ipc_2/μA	*Epa'_2/mV
25	+360	+300	2.4	2.0	+330	60	0.83	-1.65	3.5	-600
50	+360	+300	3.2	2.6	+330	60	0.81	-1.68	5.0	-590
100	+360	+300	4.4	3.6	+330	60	0.82	-1.70	6.5	-590
150	+370	+300	5.6	4.2	+335	70	0.75	-1.71	7.8	-580
200	+370	+300	6.4	4.8	+335	70	0.75	-1.73	8.5	-580
250	+370	+290	7.2	5.6	+330	80	0.78	-1.74	9.3	-570
300	+380	+290	8.0	6.0	+335	90	0.75	-1.75	10.2	-560

*Ipa_2' not measurable

Table 2-Cyclic voltammetric data for 4mM VO(sal-anl)$_2$ in dimethylsulfoxide (DMSO) containing 0.1M TBAP

Scan rate / mV s^{-1}	Epa_1/mV	Epa_2/V	Ipa_1/μA	Ipa_2/μA	Epc'_1/mV	Epc_2/V	Ipc'_1/μA	Ipc_2/μA	Epa'_2/mV	Ipa'_2/μA
25	+650	+1.04	1.3	5.0	-880	-1.275	0.5	11.2	-520	0.5
50	+660	+1.05	1.8	5.4	-890	-1.300	0.7	13.8	-490	0.6
100	+680	+1.06	2.7	7.0	-900	-1.325	1.5	18.5	-420	0.8
150	+710	+1.07	3.0	9.0	-920	-1.350	2.2	21.0	-390	1.0
200	+730	+1.07	3.5	10.5	-930	-1.350	3.0	23.5	-370	1.5
250	+750	+1.08	4.0	11.7	-940	-1.375	4.5	26.0	-360	1.7

Table 3-Cyclic Voltammetric Data for 1:10 VO^{2+}-bipy system in DMSO/ 0.1M TBAP $VOSO_4.2H_2O$=2mm

Scan rate /mV s^{-1}	Epa_1/V	Epc'_1/V	Ipa_1/μA	Ipc'_1/μA	Epc_1/V	*Epc_2/V	Ipc_1/μA	Epa'_1/V	Epa''_1/V	Ipa'_1/μA	Ipa''_1/μA
25	+0.95	NA	3.0	---	-1.10	-1.22	2.25	NA	NA	--	-
50	+0.97	-0.90	4.2	1.00	-1.12	-1.25	3.00	NA	NA	--	-
100	+1.00	-0.92	6.0	1.25	-1.13	-1.27	4.50	-0.50	+0.60	0.50	0.50
200	+1.05	-0.93	8.2	1.75	-1.14	-1.30	6.00	-0.50	+0.62	0.75	0.65
300	+1.07	-0.95	10.0	2.25	-1.15	-1.31	7.50	-0.50	+0.63	1.00	0.75

*Ipc_2 is not measurable; NA; not appeared.

It should be noted that the anodic peak(a_1) potentials for the oxidation process $VO^{2+/3+}$ are shifted to more positive values in the sequence: VO(salen) (+370mV) → VO(sal-anl)$_2$ (+730mV) → VO(bipy)$_2$ (+1050mV) , indicating that the oxidation of complex **3** is most difficult while complex **2** is easily oxidizable .In principle, the elctronic effects(σ-donation and π-backdonation) in combination with steric factors of the ligands and solution factors affect the redox potentials of the complexes [12-13].

IV REFERENCES

1. (a) H. Schmidt, M. Bashirpoor and D. Rehder, J. Chem. Soc. Dalton Trans, 1996, 3865; (b) E. Tsuchida, K. Yamamoto and K. Oyaizu, J. Am. Chem. Soc. 1996, **118**, 12665; (c) E. Tsuchida, K. Oyaizu, E. L. Dewi, T. Imai and F. C. Anson, Inorg. Chem., 1996, **38**, 3704.
2. (a)C. Orvig, K. H. Thompson, M. Battell and J. H. McNeill, in Metal Ions in Biological Systems : Vanadium and Its Role in Life, H. Sigel and A. Sigel (Eds.), Marcel Dekker, New York, 1995, Vol. 31, p. 575; (b). K.H. Thompson, V. G. Yuen, J. McNeill and C. Orvig, in Vanadium Compounds : Chemistry, Biochemistry and Therapeutic Applications, A. S. Tracey

ad D. C. Crans. (Eds.), Oxford University Press, New York, 1998, pp. 329-343.(c)R. Wever and K. Kustin, in Advances in Inorganic Chemistry : Vanadium, A Biologically Relevant Element, A. G. Sykes (Ed.), Academic Press, New York, 1990, Vol. 35, p. 81-110.(d) A. Butler and C. J. Carrano, Coord. Chem. Rev., **109**, 61-105 (1991).

3. a) A. Butler, Coord. Chem. Rev., 1999, **187**, 17; (b) M. R. Maurya, S. Khurana, C. Schulzke and D. Rehder, Eur. J. Inorg. Chem., 2001, 779; (c) M. R. Maurya, S. Khurana, Shailendra, A. Azam, W. Zhang and D. Rehder, Eur. J. Inorg. Chem., 2003,1966; (d) A.G.J. Ligtenbarg, R. Hage and B. L. Feringa, Coord. Chem. Rev., 2003, **237**, 89.
4. V. Conte, F. Di Funa and G. Licini, Appl. Catal. A General, 1995, **157**, 335.
5. (a) R. K. Narla, Y. Dong, O.J. D'Cruz, C. Navara and F.M. Uckun, Clin. Cancer Res., 2000, **6**, 1546; (b) V. K. Wuthrich, Helvetica, Chimica Acta, 1965, **48,** 779.
6. Yadav P, Srivastava K & Prasad J, J Indian Chem Soc,83,14-17, 2005.
7. a. Vlček A A, Electrochim Acta,13 (1968) 1063; b. Tait A M, Lovecchio F V & Busch D H, Inorg Chem 16 (1977) 2206; c. Averill D F & Broman R F, Inorg Chem, 17 (1978) 3389.
8. Sakurai H, Tamura A, Fugono J, Yasui H & Kiss T, Coord Chem Rev 245 (2003).
9. Maurya M R, Coord Chem Rev, 237 (2003) 163; c. Xing Y H, Aoki K & Bai F Y, J Coord Chem, 57 (2004) 157.
10. (a)T. Saji and S. Aoyagui, Chemistry letters, 1974, 203-206; (b) E. Reisenhofer and G. Costa, Inorg. Chim. Acta, 1981, **49,** 121-124; (c) A. Kapturkiewicz and B. Behr, Inorg. Chim. Acta, 1983, **69**, 247.
11. (a) K. B. Pandeya, D. Khare, J. Prasad and K. Srivastava, Microchem. Journal, 1994, **50**, 136; (b) K. Srivastava, D. Srivastava, M. Kumari, S. Khare and J. Prasad, J. Indian. Chem. Soc., 2005, **82**, (c) Prem Yadav, K. Srivastava and J. Prasad, J. Indian Chem. Soc.,83,56-62.
12. A. J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamentals and Applications", John Wiley and Sons, Inc., USA, Chapt.11, 1980,. p. 429.
13. (a)A. Kapturkiewicz, Inorg. Chim. Acta, 1981, **53**, L77; (b) R. Seangprasertkij and T. L. Riechel, Inorg. Chem., 1986, **25**, 3121; (c) J.A. Bonadies, W.M. Butler, V.L. Pecoraro and C.J. Carrano, Inorg. Chem., 1987, **26,** 1218; (d) Z. Liu and F.C. Anson, Inorg. Chem., 2000, **39,** 274; (e) J. J. Steggerda, J. A. Cras, J. Willemse, Recl. Trav. Chim. Pays-Bas, 1981, **100** (2), 41.