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EFFECT OF DIFFERENT NONAQUEOUS SOLVENTS ON ELECTROCHEMICAL BEHAVIOR OF OXOVANADIUM(IV) COMPLEXES WITH BI- AND TETRADENTATE LIGAND

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Abstract: The electrochemical behaviour of VO (salen), **1** and VO(sal-anl)$_2$ **2** has been studied in DMSO, DMF, AN, THF, DCM and DCE containing 0.1 M TBAP as the supporting electrolyte at a Pt working electrode. The CV results obtained for VO (salen) in DMSO, DMF, AN and CH_2Cl_2 are qualitatively very similar. A representative scan of cyclic voltammogram of 4mM VO (salen) in 0.1 M TBAP/DMF at a scan rate of 200 mVs^{-1} show 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**.** The values of the formal potentials, E$^{0/}$ for **1** in different solvents are shifted to more positive values in the sequence: DMSO (+335mV) → DMF (+405mV) → AN (+460mV) →CH_2Cl_2 (+615 mV), indicating that the oxidation of this complex is easiest in DMSO and most difficult in CH_2Cl_2. It is interesting that ease of oxidation increases with increasing donor number of the solvent.

Index Terms **-** oxovanadium (IV) complexes, cyclic voltammogram, Oxidation, Redox

I. INTRODUCTION

The coordination chemistry of oxovanadium (IV) complexes has growing applications in catalysis[**1**], therapeutics[**2**], and biological activity[**3**]. Vanadium containing compounds have their utility as insulin mimetic[**4**] and antiamoebic[**5**] agent. Vanadium dependent enzymes, mainly nitrogenases and haloperoxidases are still a subject for intensive biochemical investigation. It is found in the active sites of metalloenzymes[**4-6**] conferring specific functions and controlling their catalytic reactivity. Vanadium is associated with a number of activities, e.g. enzyme inhibitory, mitogenic, antitumorigenic, and insulinomimetic[**7**]. Studies showed that V^{V} and V^{IV} are the two important oxidation states in biological media[**8**]. Vanadium^{IV} has two common coordination numbers-five and six and because of its hard nature it has good affinity towards N, O donor ligands. Schiff bases, their derivatives and their metal complexes have been found to have potential application[**9**] in industry and biology; as pigments and dyes, thermoresistant, polymers, potential catalysts, insecticide, biomimetic synthetic models and as a vehicle for the delivery of metals to the sites in biological systems.

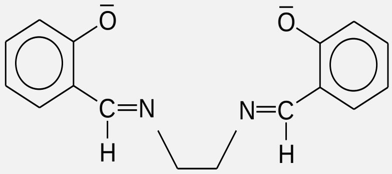
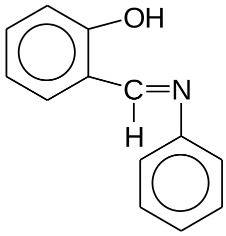
Keeping in view the above points we have study the redox chemistry and the electrochemical behaviour of Oxovanadium (IV) complexes in different nonaqueous solvents.

EXPERIMENTAL SECTION

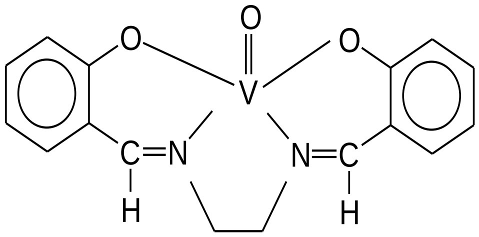
In the study of electrochemical behavior, the cyclic voltammetry was carried out with a BAS model CV-IB (Indiana West Lafayette, USA) instrument having an electrochemical cell with a three-electrode system. Saturated calomel electrode (SCE) was used as a reference electrode (E^0 = + 0.242 V vs NHE). The working electrode was a platinum microelectrode (MF-2013), Platinum wire was used as an auxiliary electrode. The cyclic voltammograms were recorded on an X-Y recorder. All the cyclic voltammetry experiments were done in an inert atmosphere achieved by purging the cell solution with nitrogen for about 20 minutes. An inert atmosphere of nitrogen was also maintained over the cell solution during recording of the voltammograms. All experiments were performed at 25± 1^0C. The potentials reported here are uncorrected for liquid-junction potential.

Spectroscopic grade dimethylformamide (DMF), dichloromethane (DCM), dichloroethane (DCE) and acetonitrite (AN, 99.7%) supplied by S.D. fine Chem. Ltd. and dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF, 99%) by E. Merck were used as such without further purification. Tetrabutyl ammonium perchlorate (TBAP > 98%) was obtained from Fluka Chemika, Switzerland and was used as the supporting electrolyte in the present electrochemical studies. All of the solvents were deoxygenated before use. Glasswares were rinsed with methanol and dried at 110-120°C before use.

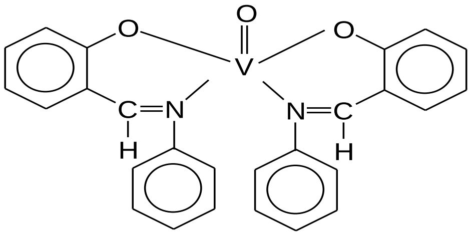
The complexes were prepared according to methods described earlier[10]. Ethanolic solution of the respective ligand and the aqueous solution of $VOSO_4.2H_2O$ were missed together in 1:1 or 1:2 molar ratio. The coloured complex separated out instantaneously. It was filtered, washed with water and 50% ethanol and dried over P_2O_5 in vaccum desiccator. The purity of the complexes was checked by elemental analyses. The structures of the tetradentate Schiff base dianionic ligands and their oxovanadium (IV) complexes are shown below:

S.No	*Name of Ligand*	*Structure of Ligand*
01	N,N'-ethylene bis(salicyladiminato) dianionic = salen	
02	Salicylaldehyde-aniline= sal-anl	

The study of complexes which form in solution by adding metal and ligand in ratio1:1 and 1:2. The structure of complexes is proposed as-



VO (salen) **Complex-1**



VO(sal-anl)$_2$ **Complex-2**

RESULT AND DISCUSSION

The VO (salen) was characterized[10,] by EPR, potentiometry, UV-visible, and IR ($\nu_{v\text{-}0}$ = 981 cm^{-1} (KBr disc), 953 cm^{-1} (DMSO). The coordination geometry was octahedral in DMSO but square pyramidal in the solid. Pandeya and Khare have reported[11] that complexes 1, 2, and 3 dissolved in DMF exhibited isotropic eight line epr pattern typical of VO^{2+} complexes (S=1/2, I(^{51}V)=7/2). Ligand superhyperfine splittings have not been observed, suggesting that the unpaired electron is in the b_2g (dxy) orbital localized on the metal, thus excluding any possibility of its direct interaction with the ligand. Forzen solution spectra are anisotropic and two sets of resonance components. $g_{||}$ and $g_{\perp}$ are observed.

The electrochemical behaviour of VO (salen), **1** and VO(sal-anl)$_2$ **2** has been studied in DMSO, DMF, AN, THF, DCM and DCE containing 0.1 M TBAP as the supporting electrolyte at a Pt working electrode. The CV results obtained for VO (salen) in DMSO, DMF, AN and CH_2Cl_2 are qualitatively very similar. A representative scan of cyclic voltammogram of 4mM VO (salen) in 0.1 M TBAP/DMF at a scan rate of 200 mVs^{-1} is displayed in Figure 1 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 (Figure 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[12-14]. 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**.** 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 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. It should be noted that the values of the formal potentials, $E^{0/}$ for **1** in different solvents are shifted to more positive values in the sequence: DMSO (+335mV) → DMF (+405mV) → AN (+460mV) →CH_2Cl_2 (+615 mV), (Table-1), indicating that the oxidation of this complex is easiest in DMSO and most difficult in CH_2Cl_2. It is interesting that ease of oxidation increases with increasing donor number of the solvent. Solvent effects on the redox potentials of transition metal complexes have earlier been widely studied[15]

Table 1- Cyclic voltammetric data for 4mM VO(salen) in DMF, DMSO, Acetonitrile, Dichloromethane containing 0.1M TBAP

Scan rate/ mVs^{-1}	DMF		Acetonitrile (AN)		DMSO		Dichloromethane	
	Epa_1/mV	Epc_1/mV	Epa_1/mV	Epc_1/mV	Epa_1/mV	Epc_1/mV	Epa_1/mV	Epc_1/mV
25	+430	+370	+490	+430	+360	+300	+650	+575
50	+440	+370	+490	+430	+360	+300	+650	+575
100	+440	+370	+500	+430	+360	+300	+660	+570
150	+440	+370	+500	+420	+370	+300	+670	+560
200	+450	+360	+510	+420	+370	+300	+675	+550
250	+450	+360	+510	+410	+370	+290	+675	+550
300	+450	+360	+510	+410	+380	+290	+680	+550

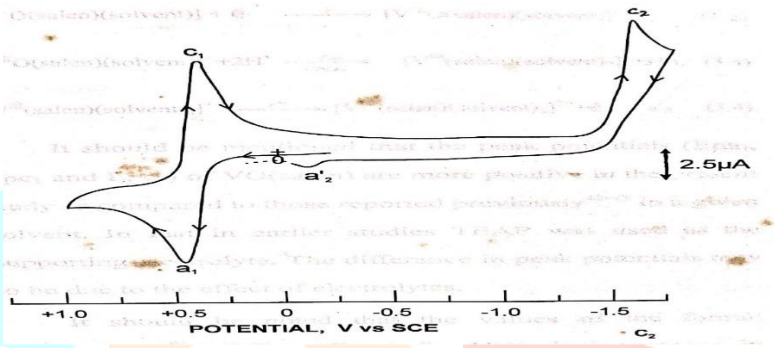


Figure 1: Cyclic Voltammogram of Complex 1 [VO(salen)]

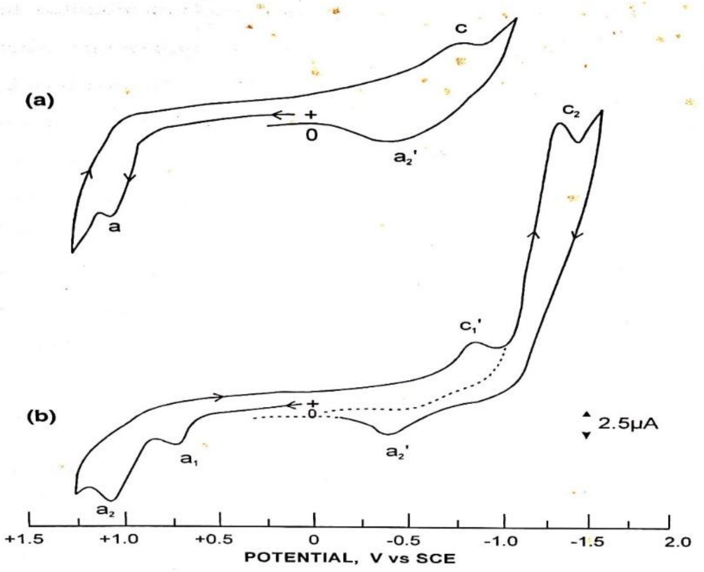


Figure 2: Cyclic Voltammogram of Complex 2 [$VO(sal-anl)_2$)]

On the other hand, the electrochemical behaviour of $VO(sal-anl)_2$ **2** has been studied in DMSO, DMF, AN, THF, DCM and DCE containing 0.1 M TBAP as the supporting electrolyte at a Pt working electrode. The CV results obtained for $VO(sal-anl)_2$ **2** in DMSO, DMF, AN and CH_2Cl_2 are qualitatively very similar. The redox behaviour of $VO(sal-anl)_2$ **2** was examined in DMF containing 0.1M TBAP as the supporting electrolyte by cyclic voltammetry (CV) on a Pt-working electrode. The electrochemical behaviours of sal-anl was also studied under identical experimental conditions for the sake of comparison with their corresponding oxovanadium (IV) complexes. The CV results for $VO(sal-anl)_2$ a positive scan initiated at 0.0V in the potential range from 0.0 to +1.25 V vs SCE shows (figure 2) two totally irreversible anodic waves in the positive potential region at Epa_1 = +0.68 and Epa_2 = +1.06V. The negative scan initiated at 0.0 V in the potential range 0.0 to -1.50 V revealed two irreversible reduction peaks at $Epc^{/}_1$ = -0.90 V and Epc_2 = -1.325 V in the forward scan while an irreversible anodic peak appeared at $Epa^{/}_2$ = -0.42 V in the reverse scan. The cyclic voltammogram of sal-anl ligand at 100mVs^{-1} showed an irreversible anodic peak at Epa = +1.03 V, while a negative scan indicated an irreversible cathodic and anodic peaks, c and a'_2 respectively at Epc = -0.86 and Epa'_2 = - 0.49 V vs SCE

$$[V^{IV}O(sal-anl)_2] \xrightarrow{irr} [V^{V}O(sal-anl)_2]^+ + e^- \qquad a_1 \qquad (1)$$

$$[V^{IV}O(sal-anl)_2] + 2H^+ + e^- \xrightarrow{irr} [V^{III}(sal-anl)_2S_2]^+ + H_2O \qquad c_2 \qquad (2)$$

A comparison of formal potentials ($E^{0'}$) for complex **2** in different solvents shows that the formal potential ($E^{0'}$) shifts anodically with change of solvent in the sequence: DMSO (+485 mV) → THF (+ 535mV) → DMF (+545 mV) → AN (+600 mV) → DCE (+810 mV). Similar observation has also been found for complex **1** in the present investigation.

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