

Quantification of V(IV)-Maltol Complex Using Cyclic Voltammetry

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(Received on 26th June 2008, accepted in revised form 11th November 2009)

Summary: Cyclic voltammetry is used in the present research work for the quantitative study of BMOV, (*bis(maltolato)oxovanadium(IV)*), the compound which shows insulin like properties. Electrochemical study of BMOV was done using cyclic voltammetry at Pt electrode vs. Ag|AgCl reference electrode. This study was performed using NaCl, KCl and KNO₃ as supporting electrolytes. Results reveal that the use of Pt electrode can be helpful to quantify this complex (2.0×10^{-4} to 16.0×10^{-4} M) and the method can be applied in the pharmaceutical quality control assay of the complex.

Introduction

World Health Organization (WHO) has declared that the number of people with diabetes is rapidly increasing all over the world. An estimated at least 171 million people worldwide suffer from diabetes (upto the year 2000) or 2.8% of the population and this figure is expected to double over the next 25 years. What is more alarming is that three fourths of future diabetes will come from developing countries, like Pakistan where roughly over 8.8 million (12 percent of the population) have been affected up to 2004 [1-4].

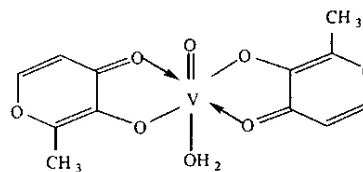
Vanadium compounds have a long history related to their insulin like properties. A possible reason could lie in the structural resemblance between vanadate and phosphate, which leads vanadium complexes to have the ability either to inhibit the protein tyrosine phosphatase or to activate the insulin receptor kinase and/or glucose carrier, thus triggering glucose intake into cells [5-9].

A key advantage of vanadium over insulin is its effectiveness when administered orally. Unfortunately, poor absorption from the gastrointestinal (GIT) tract into the blood, coupled with doses close to toxic levels for glucose- and lipid-lowering effects, has hampered efforts to develop vanadium compounds as therapeutic adjuncts for treatment of diabetes mellitus. Although both VO²⁺ and VO₄³⁻ have shown positive results in limited clinical trials in humans, the research is underway for better-absorbed and less toxic vanadium compounds [10, 11].

For the design of vanadium complexes appropriate for use as insulin-enhancing agents and ligands of intermediate binding strength was likely more appropriate possessing neither high intrinsic bioactivity nor appreciable toxicity [12]. Maltol (Hma, a food additive approved in many countries) is an excellent spectator ligand in biological applications; it forms stable, neutrally charged metal complexes with optimum combination of water solubility, reasonable hydrolytic stability, and significant lipophilicity [5, 13-17].

Differential pulse voltammetry has been done as a simple and practical method for the determination of flavor enhancer Maltol in beverages such as grape wines, drinks and beers. For this investigation glassy carbon (GC) was used as working electrode [18-20].

BMOV, VO(ma)₂, *bis(maltolato)oxovanadium(IV)*, contains bidentate ligand and has 1:2 metal-to-ligand stoichiometry. It is prepared nearly quantitatively in water (>90 % yield) by combining Vanadyl sulfate and Maltol (3-hydroxy-2-methyl-4-pyrone) (1:2) [21, 22].



Bis(maltolato)oxovanadium (IV)

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The direct electrochemical synthesis of Zn, Cd, Sn, In and Cu derivatives of Maltol have also been reported. The electrochemical oxidation of a metallic sacrificial anode (Zn, Cd, Sn, In and Cu) in a non-aqueous solution of Maltol yields the ML_n complexes ($M = Zn, Cd, Cu, Sn, n = 2; M = In, n = 3$). In this way complexes of Maltol and various d^{10} metal ions can now be readily prepared in high yield by the electrochemical technique in a convenient single step process [23].

The coordination chemistry and electrochemistry of complexes of vanadium(III, IV, V) with different ligands have been examined using different electrodes like mercury, carbon paste and microelectrodes etc. Through these techniques equilibrium constant, stoichiometry and kinetics of the reaction between O_2 and the complexes were examined and a possible mechanism was also suggested [24-39].

An electrochemical study on $VO(ma)_2$ shows that at $5 < pH > 8$ an irreversible wave was observed. As the acidity of the solution is increased, the wave becomes increasingly quasi-reversible. The wave obtained at pH 2.5 most closely resemble reversibility and corresponded to a solution containing a mixture of $VO(ma)_2$, $VO(ma)^+$ and VO^{2+} . In the extremes of acids and bases, the waves obtained appeared similar to those Vanadyl(IV) and Vanadate(V), respectively, [21].

Analytical methods have been improved during recent years and now extremely small amounts of element and compound can be detected in various media using various electrochemical and spectrophotometric assays are being widely used for the determination of vanadium [40-46]. In the present research work Cyclic Voltammetry is used to measure the electrochemical properties of Vanadium(IV)-Maltol complex.

Results and Discussion

In this study calibration curve method is used in which the signal of primary interest is the height of the peak. The peak height, I_p , for an electrochemically reversible system (rapid transport of electrons on the surface within the framework of the experiment) is directly proportional to the analyte concentration, C , as described by the *Randles-Sevcik* equation:

$$I_p = 0.4463 n F A C_o^* (n F v D_o / R T)^{1/2}$$

If the temperature is assumed to be $25^\circ C$ (298.15 K), the *Randles-Sevcik* equation can be written in a more concise form [47]:

$$I_p = (2.687 \times 10^5) n^{3/2} v^{1/2} D_o^{1/2} A C_o^*$$

where the constant has unit (*i.e.*, $2.687 \times 10^5 C mol^{-1} V^{-1/2}$), I_p is peak current (in A), n is electron stoichiometry, D is diffusion coefficient (cm^2/s), C_o^* is concentration (mol/cm^3), A is electrode area (cm^2) and v is potential scan rate (V/S).

A plot of I_p vs. C_o^* should give a straight line with an intercept of zero. Large deviation from zero could indicate adsorption. The slope can be used to determine the diffusion coefficient, if n , A and C_o^* are known [47-49].

In the present work the electrochemical properties of Vanadium(IV)-Maltol complex were measured in different supporting electrolytes (S.E.) *i.e.* NaCl (0.1M), KCl (0.1M) and KNO_3 (0.1M) at Pt electrode vs. Ag|AgCl reference electrode at $25 \pm 1^\circ C$.

Effect of concentration on current (I_p) provides quantitative information. The dependence of peak current on concentration of the V(IV)-Maltol complex was studied by taking $2.0 \times 10^{-4} M$ to $16.0 \times 10^{-4} M$ solutions using NaCl (0.1M) as S.E at 100 mV/S and current sensitivity of 20 $\mu A/V$.

Before studying the complex, base-lines were drawn in all these supporting electrolytes. The base-lines of pure supporting electrolytes were recorded at Pt electrode vs. Ag|AgCl reference electrode at $25 \pm 1^\circ C$. These base-lines were recorded in NaCl (0.1M) and KNO_3 (0.1M) at 100 mV/S and current sensitivity of 20 $\mu A/V$. Base-lines obtained in all these supporting electrolytes are horizontally straight. As Pt is very sensitive to impurities so the linearity in the base-line shows that it has no impurity (Fig. 1).

The cell assembly was rinsed thrice with the solution of analyte and then solution was run to get cyclic voltammogram in which potential range was set from -0.40V to +0.70V and then reverse back to -0.4V. The oxidative wave is seen in the

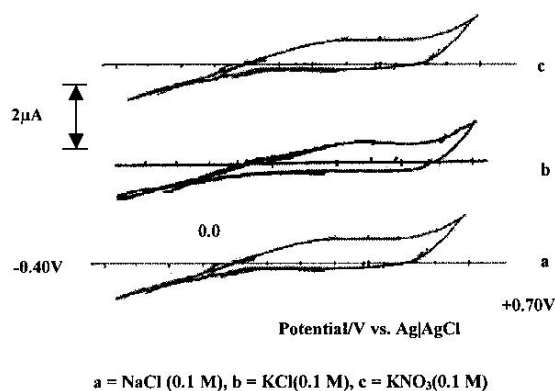


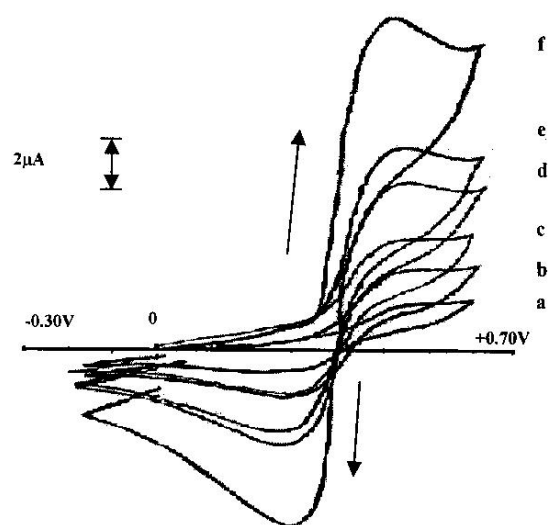
Fig. 1: Baseline of NaCl (0.1 M), KCl(0.1 M) and KNO_3 (0.1 M) at 100 mV/S and 20 $\mu\text{A/V}$.

potential range of the forward scan, going from -0.40V to +0.70V. The oxidized species is reduced back (into reduced species) during the reverse scan from +0.70V back to the initial potential of -0.40V.

The anodic (I_{pa}) and cathodic (I_{pc}) peak currents of these complexes were recorded and then plotted against concentrations. A linear dependence of peak current on the concentration of Vanadium(IV)-Maltol complex with zero intercept was found in supporting electrolyte, NaCl (0.1M), which reveals that the peak currents I_{pa} and I_{pc} are proportional to the concentration of Vanadium(IV)-Maltol complex within the concentration range of 2.0×10^{-4} M to 16.0×10^{-4} M (Figs. 2a and 3a). This linear behavior revealed that diffusion is the rate-limiting step in the electrode reaction and there is no deviation from zero so no adsorption takes place at the surface of working electrode [48, 50].

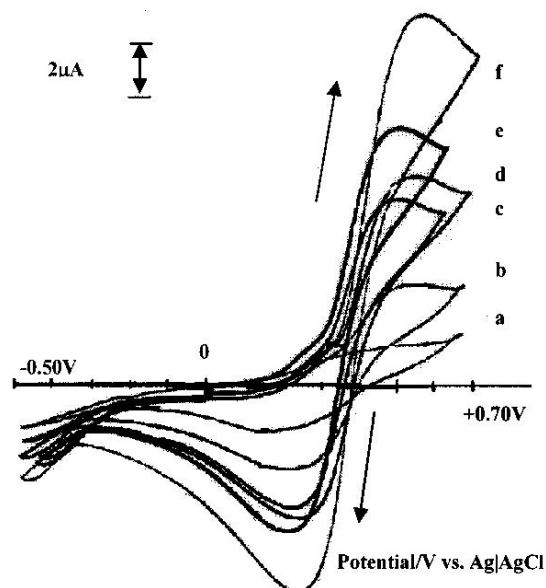
The dependence of peak current on concentration of the complex in the presence of KCl(0.1 M) and KNO_3 (0.1 M) was also determined, which also showed the linear response (Figs. 2b, 2c, 3b, 3c). These calibration curves along with the corresponding least square fitted curves revealed that the present method can be applied in the quantification of Vanadium(IV)-Maltol complex (Figs. 3a-3c).

For the determination of dependence of peak potential on concentration, the peak potentials (E_{pa} and E_{pc}) of Vanadium(IV)-Maltol complex were noted at different concentrations and also at different



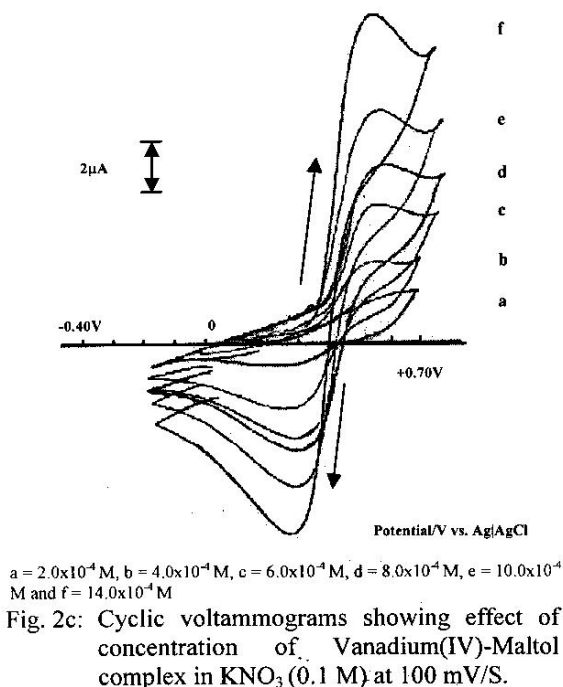
a = 2.0×10^{-4} M, b = 4.0×10^{-4} M, c = 6.0×10^{-4} M, d = 8.0×10^{-4} M, e = 10.0×10^{-4} M and f = 16.0×10^{-4} M

Fig. 2a: Cyclic voltammograms showing effect of concentration of Vanadium(IV)-Maltol complex in NaCl (0.1 M) at 100 mV/S.



a = 2.0×10^{-4} M, b = 4.0×10^{-4} M, c = 7.0×10^{-4} M, d = 8.0×10^{-4} M, e = 10.0×10^{-4} M and f = 14.0×10^{-4} M

Fig. 2b: Cyclic voltammograms showing effect of concentration of Vanadium(IV)-Maltol complex in KCl (0.1 M) at 100 mV/S.



scan rates. Their plots against log of concentrations showed straight lines at all scan rates (Fig. 4). Values of $E_{pa/2}$ and $E_{pc/2}$ are also constant at different concentrations at a particular scan rate as given in the Tables 1-3.

$E_{1/2} \cong E^\circ$ ($\cong E_{85.2\%}$ i.e. the potential corresponding to 85% of I_p) is constant for a particular system and independent of concentrations. For Vanadium(IV)-Maltol complex E° was determined at different concentrations of the complex in NaCl, KNO_3 and KCl (Table 1-3).

Another aspect of cyclic voltammetry (CV) is its ability to provide the chemistry of redox couples. This is perhaps the most attractive feature of the technique. Effect of low concentration of the complex (1.0×10^{-4} M to 0.1×10^{-4} M) shows doubtful full complexation because very insignificant shapes of the waves appear. For this study the potential range was set from -0.60 V to +0.60 V (Fig. 5). These voltammograms show that at 1.0×10^{-4} M concentration of the complex, only the oxidative wave is

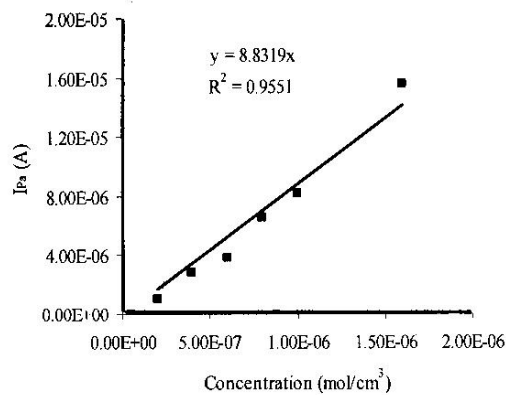
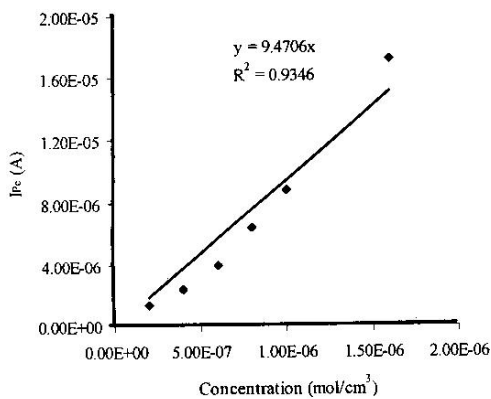


Fig. 3a: Plot of anodic and cathodic peak current against concentration of Vanadium(IV)-Maltol complex in NaCl(0.1 M).

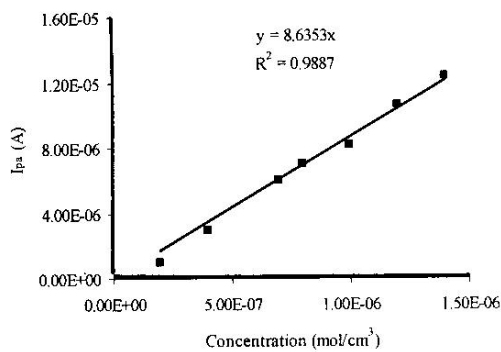
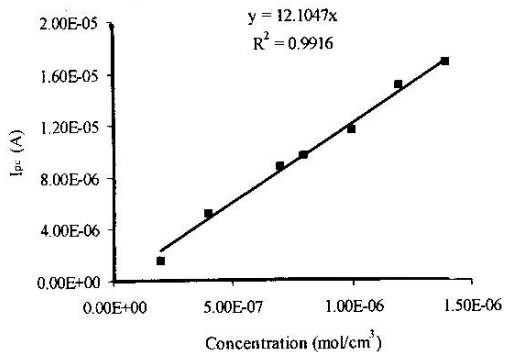


Fig. 3b: Plot of anodic and cathodic peak current against concentration of Vanadium(IV)-Maltol complex in (0.1 M) KCl.

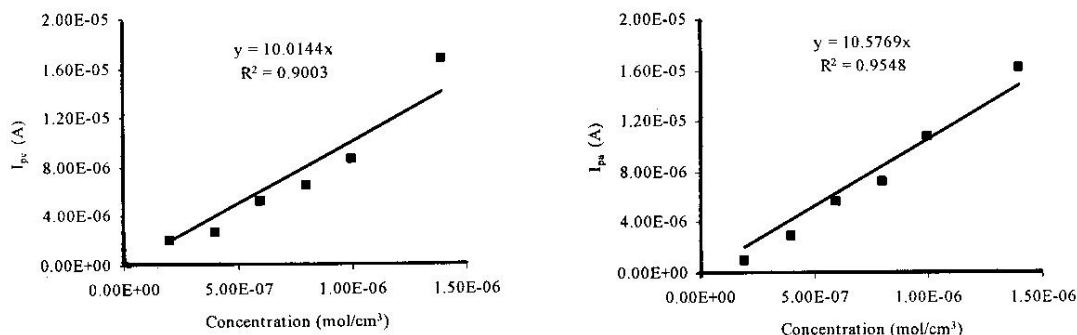


Fig. 3c: Plot of anodic and cathodic peak current against concentration of Vanadium(IV)-Maltol complex in (0.1 M) KNO_3 .

Table-1: The values of E_p , $E_{p/2}$ and E° from the cyclic voltammograms of Vanadium(IV)-Maltol complex in NaCl (0.1 M) with different concentrations.

Conc. $\times 10^{-4}$ M	E_{pa} V	$E_{p/2}$ V	$(E^\circ)_a$ V	E_{pc} V	$E_{p/2}$ V	$(E^\circ)_c$ V
2.0	0.57 ± 0.01	0.48 ± 0.01	0.42 ± 0.01	0.25 ± 0.01	0.34 ± 0.01	0.31 ± 0.01
4.0	0.57 ± 0.02	0.47 ± 0.02	0.42 ± 0.02	0.24 ± 0.02	0.35 ± 0.02	0.31 ± 0.02
6.0	0.56 ± 0.01	0.36 ± 0.01	0.34 ± 0.01	0.27 ± 0.01	0.36 ± 0.01	0.35 ± 0.01
8.0	0.60 ± 0.01	0.50 ± 0.01	0.44 ± 0.01	0.26 ± 0.01	0.35 ± 0.01	0.33 ± 0.01

Reference electrode = Ag/AgCl, Working electrode = Pt, Temperature = $25 \pm 1^\circ \text{C}$, Current sensitivity = $20 \mu\text{A/V}$, Scan rate = 100 mV/S , Supporting electrolyte = 0.1 M NaCl, under Nitrogen ($\Delta E_p = 72 \text{ mV}$, $I_{pc}/I_{pa} = 1.00$ for ferrocenium/ferrocene)

Table-2: The values of E_p , $E_{p/2}$ and E° from the cyclic voltammograms of Vanadium(IV)-Maltol complex in KNO_3 (0.1 M) with different concentrations.

Conc. $\times 10^{-4}$ M	E_{pa} V	$E_{p/2}$ V	$(E^\circ)_a$ V	E_{pc} V	$E_{p/2}$ V	$(E^\circ)_c$ V
2.0	0.55 ± 0.01	0.43 ± 0.01	0.50 ± 0.01	0.28 ± 0.01	0.20 ± 0.03	0.18 ± 0.01
4.0	0.52 ± 0.01	0.40 ± 0.02	0.51 ± 0.01	0.29 ± 0.01	0.23 ± 0.01	0.12 ± 0.02
6.0	0.57 ± 0.01	0.42 ± 0.01	0.50 ± 0.01	0.29 ± 0.01	0.23 ± 0.01	0.13 ± 0.01
8.0	0.55 ± 0.02	0.44 ± 0.01	0.51 ± 0.01	0.28 ± 0.02	0.21 ± 0.01	0.13 ± 0.01
10.0	0.55 ± 0.01	0.43 ± 0.01	0.49 ± 0.01	0.27 ± 0.01	0.22 ± 0.01	0.14 ± 0.01
14.0	0.54 ± 0.01	0.43 ± 0.01	0.50 ± 0.01	0.30 ± 0.01	0.26 ± 0.01	0.14 ± 0.01
16.0	0.54 ± 0.02	0.44 ± 0.02	0.48 ± 0.01	0.25 ± 0.03	0.20 ± 0.02	0.14 ± 0.01

Working electrode = Pt, Reference electrode = Ag/AgCl, Temperature = $25 \pm 1^\circ \text{C}$, Current sensitivity = $20 \mu\text{A/V}$, Scan rate = 100 mV/S , Supporting electrolyte = 0.1 M KNO_3 , under Nitrogen ($\Delta E_p = 72 \text{ mV}$, $I_{pc}/I_{pa} = 1.00$ for ferrocenium/ferrocene)

Table-3: The values of E_p , $E_{p/2}$ and E° from the cyclic voltammogram of Vanadium(IV)-Maltol complex in KCl (0.1 M) with different concentrations.

Conc. $\times 10^{-4}$ M	E_{pa} V	$E_{p/2}$ V	$(E^\circ)_a$ V	E_{pc} V	$E_{p/2}$ V	$(E^\circ)_c$ V
2.0	0.52 ± 0.02	0.45 ± 0.01	0.5 ± 0.01	0.25 ± 0.02	0.34 ± 0.01	0.31 ± 0.01
4.0	0.54 ± 0.01	0.42 ± 0.01	0.49 ± 0.01	0.27 ± 0.01	0.36 ± 0.00	0.35 ± 0.00
6.0	0.58 ± 0.01	0.43 ± 0.01	0.51 ± 0.01	0.27 ± 0.01	0.36 ± 0.01	0.35 ± 0.01
8.0	0.60 ± 0.03	0.44 ± 0.03	0.53 ± 0.03	0.27 ± 0.01	0.36 ± 0.01	0.32 ± 0.01

Working electrode = Pt, Reference electrode = Ag/AgCl, Temperature = $25 \pm 1^\circ \text{C}$, Current sensitivity = $20 \mu\text{A/V}$, Scan rate = 100 mV/S , Supporting electrolyte = 0.1 M KCl, under Nitrogen ($\Delta E_p = 72 \text{ mV}$, $I_{pc}/I_{pa} = 1.00$ for ferrocenium/ferrocene)

seen in the potential range of the forward scan (from -0.60 V to $+0.60 \text{ V}$) while reduction peak is not prominent when the oxidized specie is reduced during the reverse scan. On the other hand at further low concentrations, *i.e.* $0.2 \times 10^{-4} \text{ M}$ and $0.1 \times 10^{-4} \text{ M}$, both cathodic and anodic peak disappeared. The same

observations were obtained in the presence of other supporting electrolytes *i.e.* KCl and KNO_3 (Fig. 6).

These studies reveal that the use of Pt electrode can be helpful in quantify this complex (2.0×10^{-4} to $16.0 \times 10^{-4} \text{ M}$) and the method can be

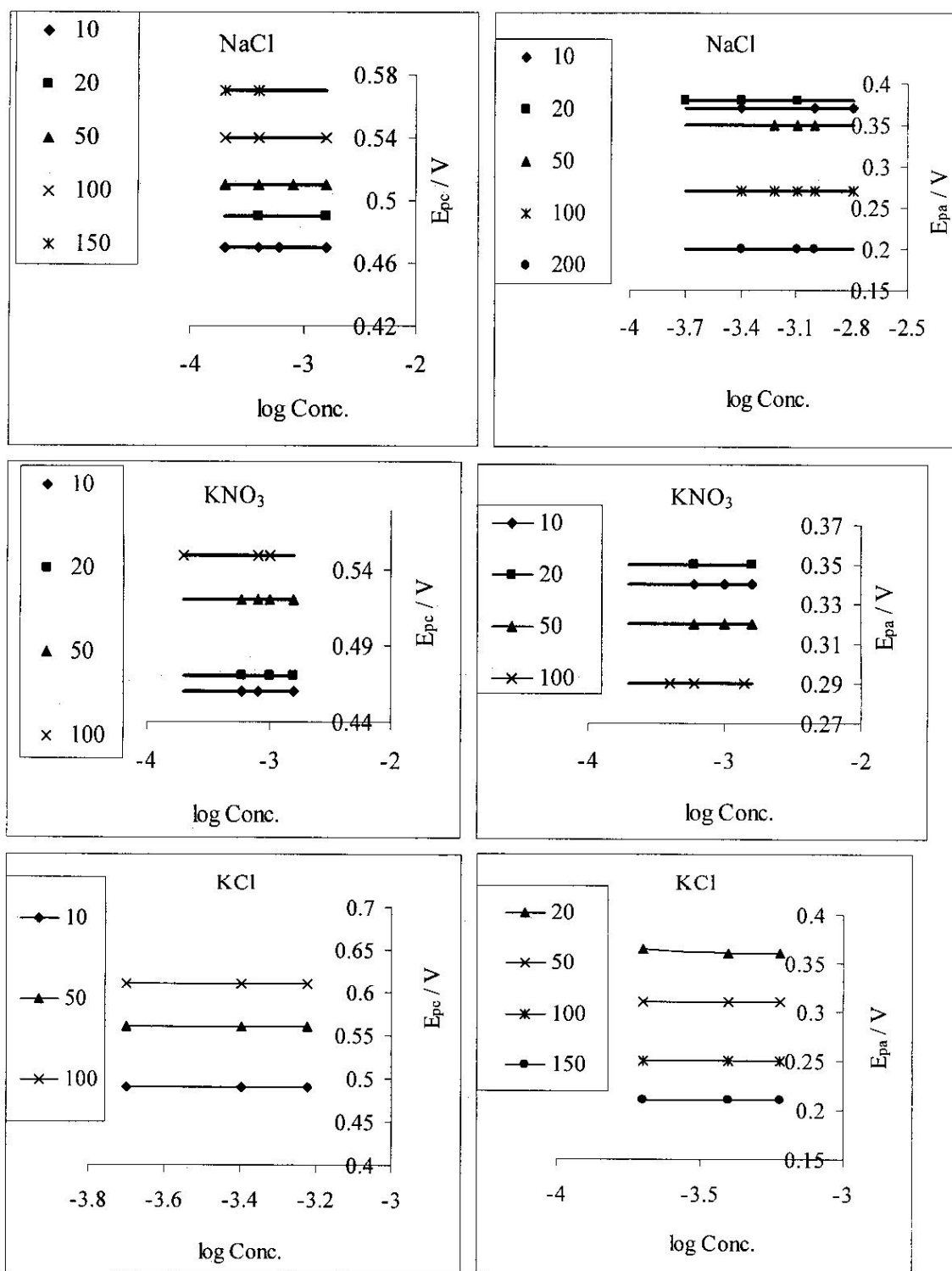
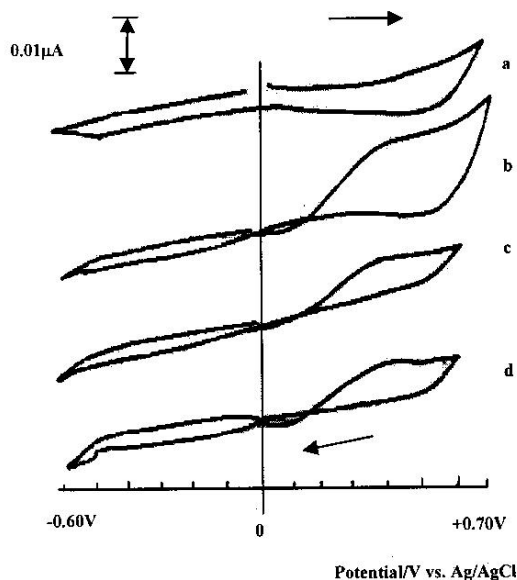


Fig. 4: Variations of anodic and cathodic peak potential with log of concentration on cyclic voltammogram of Vanadium(IV)- Maltol complex in different supporting electrolytes.



a = Base-line (0.1 M, NaCl), b = 1.0×10^{-4} M complex, c = 0.2×10^{-4} M complex, d = 0.1×10^{-4} M complex

Fig. 5: Cyclic voltammograms of Vanadium(IV)-Maltol complex in NaCl(0.1 M) with low concentrations at 100 mV/S.

applied in the pharmaceutical quality control assay of the complex.

Graphical method was also used for the determination of diffusion coefficient of Vanadium(IV)-Maltol complex in different supporting electrolytes. The slope of the straight line between current (I_p) and concentration (C) (using Randles-Sevcik equation) was used for diffusion coefficient of Vanadium(IV)-Maltol complex. The diffusion coefficient can thus be calculated as:

$$\text{Slope} = (2.687 \times 10^5) A n^{3/2} v^{1/2} D^{1/2}$$

$$D^{1/2} = \text{Slope} / (2.687 \times 10^5) A v^{3/2} v^{1/2}$$

$$D = \sqrt{\text{Slope} / (2.687 \times 10^5) A v^{-3/2} v^{1/2}}$$

Table-4: Diffusion coefficient of Vanadium(IV)-Maltol complex from graphical method in different supporting electrolytes.

Supporting electrolyte	Peak current A	$I_p = (2.687 \times 10^5) (n)^{3/2} A D^{1/2} C (v)^{1/2}$ y = mx	$D^{1/2}$	D (cm ² /S)
NaCl (0.1M)	I_{pc}	y = 9.4706x	0.9853E-03	0.9709E-06
	I_{pa}	y = 8.8319x	0.9189E-03	0.8443E-06
KCl (0.1M)	I_{pc}	y = 12.1047x	1.2594E-03	1.5861E-06
	I_{pa}	y = 8.6353x	0.8985E-03	0.8074E-06
KNO ₃ (0.1M)	I_{pc}	y = 10.0144x	1.0419E-03	1.0856E-06
	I_{pa}	y = 10.5769x	1.1000E-03	1.2109E-06

Working electrode = Pt, Reference electrode = Ag|AgCl, Temperature = $25 \pm 1^\circ$ C, Current sensitivity = $20 \mu\text{A/V}$, n = number of electron transfer = 1, v = Scan rate = $100 \text{ mV/S} = 0.1 \text{ V/S}$, A = Area of the electrode = 0.0113 cm^2 , under Nitrogen ($\Delta E_p = 72 \text{ mV}$, $I_{pc}/I_{pa} = 1.00$ for ferrocenium/ferrocene)

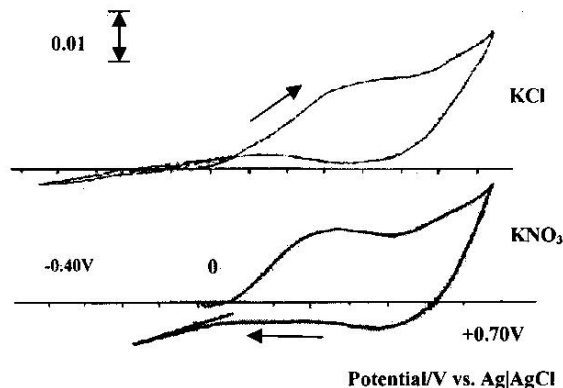


Fig. 6: Cyclic voltammograms of Vanadium(IV)-Maltol complex in KCl(0.1 M) and KNO₃(0.1 M) with low concentration (1.0×10^{-4} M) at 100 mV/S.

The slopes of the Figs. 3a-3c were used for the determination of diffusion coefficient of Vanadium(IV)-Maltol complex in presence of supporting electrolytes NaCl (0.1M), KNO₃ (0.1M) and KCl (0.1 M), respectively, (Table-4).

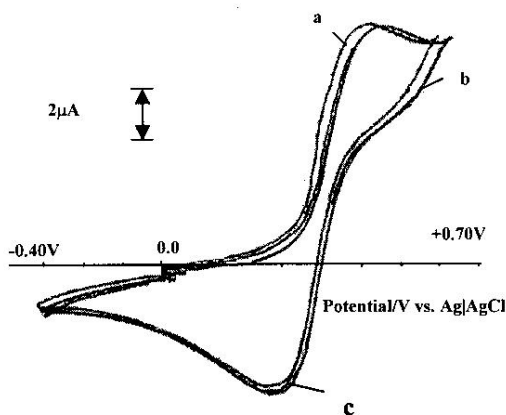
Comparative study of Vanadium(IV)-Maltol (10.0×10^{-4} M) complex in the three different supporting electrolytes *i.e.* NaCl(0.1 M), KNO₃(0.1 M) and KCl(0.1 M) is discussed (Fig. 7). The electrochemical parameters like I_{pa} , I_{pc} , E_{pa} and E_{pc} were calculated in all these mediums keeping all conditions same like potential scale, temperature, electrodes etc. (Table-5). The data shows that the complex has a slight deviation in supporting electrolyte KCl.

Comparative study of the complex was also done in the medium of these three electrolytes by taking different concentrations of the analyte from 2.0×10^{-4} M to 10.0×10^{-4} M. These complexes were prepared in all of the three supporting electrolytes

Table-5: Comparative study of electrochemical parameters of Vanadium(IV)-Maltol complex at different supporting electrolytes.

Electrochemical parameters	NaCl	KCl	KNO ₃
E _{pa} (V)	0.56 ± 0.01	0.56 ± 0.01	0.57 ± 0.01
E _{pc} (V)	0.26 ± 0.01	0.26 ± 0.01	0.25 ± 0.01
I _{pa} (μA)	11.3 ± 1	11.2 ± 1	11.5 ± 1
I _{pc} (μA)	8.5 ± 1	8.3 ± 1	8.5 ± 1
E _{pa2} (V)	0.42 ± 0.01	0.39 ± 0.01	0.42 ± 0.01
I _{pa} /I _{pc}	1.33 ± 0.01	1.35 ± 0.01	1.35 ± 0.01
ΔE _p	0.30 ± 0.1	0.24 ± 0.1	0.30 ± 0.1
E ⁰	0.47 ± 0.01	0.44 ± 0.01	0.46 ± 0.01
D	(1.39 ± 1) × 10 ⁻⁶	(1.36 ± 1) × 10 ⁻⁶	(1.52 ± 1) × 10 ⁻⁶

Working electrode = Pt, Reference electrode = Ag/AgCl, Temperature = 25 ± 1°C, Current sensitivity = 20 μA/V, Scan rate = 100 mV/S, Supporting electrolytes = NaCl (0.1 M), KNO₃ (0.1 M), KCl (0.1 M), Concentration of V(IV)-Maltol complex (1:2, M:L) = 10.0 × 10⁻⁴ M, under Nitrogen (ΔE_p = 72 mV, I_{pc}/I_{pa} = 1.00 for ferrocenium/ferrocene)



a = 10.0 × 10⁻⁴ M V(IV)-Maltol Complex in KCl (0.1 M), b = 10.0 × 10⁻⁴ M V(IV)-Maltol Complex in NaCl (0.1 M), c = 10.0 × 10⁻⁴ M V(IV)-Maltol complex in KNO₃ (0.1 M)

Fig. 7: Cyclic voltammograms of Vanadium(IV)-Maltol complex in different supporting electrolytes at 100 mV/S.

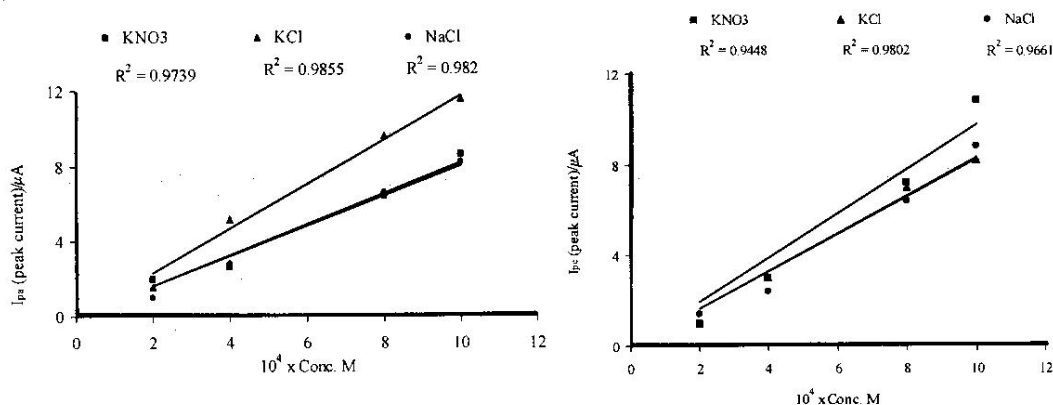


Fig. 8: Plot of anodic and cathodic peak current density against concentration of Vanadium(IV)-Maltol complex in different mediums.

and then I_{pa} and I_{pc} were measured. The calibration curve of current (I_{pa} and I_{pc}) vs. concentration reveal that although all the conditions were same but in the medium of KCl the complex have slightly higher current (I_{pa}) than other two mediums (Fig. 8).

Experimental

Materials and Reagents

In the present research work, all reagents used were of A. R. grade supplied by different sources like Merck, Sigma or Riedel-de-Haen were employed without further purification. Maltol (C₆H₆O₃, M = 126.10 g/mol, 99%) was obtained from Sigma and Vanadyl sulfate pentahydrate (VOSO₄·5H₂O, M = 253.08 g/mol) was obtained from Merck. Distilled water was redistilled and subsequently passed through a column of cation exchanger (Amberlite resin IRA-401 from BDH) in order to make it free from cations especially iron.

This distilled deionized water was used in the preparation of all stock/standard solutions of different reagents.

0.1 M solution of NaCl was prepared in distilled deionized water. 0.0050 M solution of Vanadyl sulfate and equimolar solution of Maltol were prepared as analyte by taking 0.1 M NaCl as supporting electrolyte. A colorless solution of Maltol and a blue color solution of Vanadyl sulfate were formed. For each set of experiment fresh solutions were prepared. Similarly 0.1 M solutions of KCl and KNO₃ were also used as supporting electrolytes for cyclic voltammetric study.

For the calibration curve method different concentrations were prepared. For this purpose 2.0, 4.0, 6.0, 8.0, 10.0, 14.0, and 16.0 $\times 10^{-4}$ M concentrations in 25.0 mL volumetric flask were prepared by mixing respectively 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 mL of metal (0.005 M) with twice of ligand (0.005 M) and the solution was made up to the mark with respective supporting electrolyte.

After taking base-line in a given supporting electrolyte and rinsing with analyte solution, 15.0 mL of analyte was run at Pt electrode vs. Ag|AgCl reference electrode to get overlay at 100 mV/S and current sensitivity of 20 μ A/V. The pH of the complex solution was found to be 2.55. The potential range was set from -0.40 V to +0.70 V and then reversed back to -0.40 V, to get cyclic voltammogram.

Instrumentation

CV-1B Cyclic Voltammetry controller (EF1011-00) unit, Bioanalytical Systems Inc. USA., was used for cyclic voltammetric studies of the complex. This apparatus includes CV-1B cyclic voltammograph, C-1B cell stand assembly and an XY chart recorder. The three-electrode cell consists of a Pt working electrode, Ag|AgCl as reference electrode and platinum wire as auxiliary electrode. The system was checked periodically relative to the 1×10^{-3} M CH₃CN solution of ferrocene containing 0.1M TEAP for the ferrocenium/ferrocene reduction potential was 0.2 V and $\Delta E_p = 72$ mV at a scan rate of 100 mV/S and $I_{pc}/I_{pa} = 1.00$ [51]. The reported value of Diffusion coefficient (*i.e.* 2.5×10^{-5} cm² S⁻¹) of ferrocene was used for the calculation of electrode

area from which Diffusion coefficient values of complex was obtained.

Pt electrode surface renewal was needed time to time, particularly when the analyte/supporting electrolyte was changed. The alumina polishing compound was used for polishing the electrode [52]. In few occasions, the platinum counter electrode surface was regenerated when it was found poisonous while determining base-lines and analytes. It was done by placing platinum counter electrode in dilute nitric acid. For cyclic voltammetric study 99.999 % Nitrogen gas was used for inert atmosphere, which was supplied by Pakistan Oxygen Ltd.

Conclusion

VO(ma)₂ is a neutrally charged and water soluble vanadium complex. The complex has been proven to be an excellent compound which can show insulin like properties. In the present study its electrochemical behavior on a Pt electrode vs. Ag/AgCl reference electrode was investigated. Three different supporting electrolytes were used i.e. NaCl, KCl and KNO₃. The cyclic voltammetric determination of BMOV was performed using calibration curve method. The results obtained show that this method could be used as a simple practical method for pharmaceutical quality control of this complex from 2.0×10^{-4} M to 16.0×10^{-4} M.

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