Anal. Bioanal. Electrochem., Vol. 7, No. 2, 2015, 161 - 174

Analytical & Bioanalytical Electrochemistry

www.abechem.com

Full Paper

Electrochemical Studies of Orphendrine Hydrochloride at Gold Electrode: A Voltammetric Study

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Received: 12 November 2014 / Received in revised form: 23 February 2015 / Accepted: 1 March 2015 / Published online: 30 April 2015

Abstract- Orphendrine hydrochloride an anticholinergic drug was electrochemically studied in phosphate buffer at different pH using gold electrode. For analytical purpose, a well resolved irreversible adsorption controlled voltammetric peak was obtained in pH 7 phosphate buffer solution of ionic strength 0.2 M at 0.98 V for cyclic voltammetry. A linear relationship between the peak current and the orphendrine hydrochloride concentration, was obtained using differential pulse voltammetric method. The proposed method was used for its quantitative determination in pharmaceuticals and human biological fluids. The linear response was obtained in the range of 3.0×10^{-8} to 1.0×10^{-6} M with a detection limit of 7.10×10^{-9} M. Precision and accuracy of the developed method was checked by recovery studies. The proposed method can be used in clinical laboratories and pharmacokinetic studies.

Keywords- Reactivity, Orphendrine hydrochloride, Voltammetry, Gold electrode

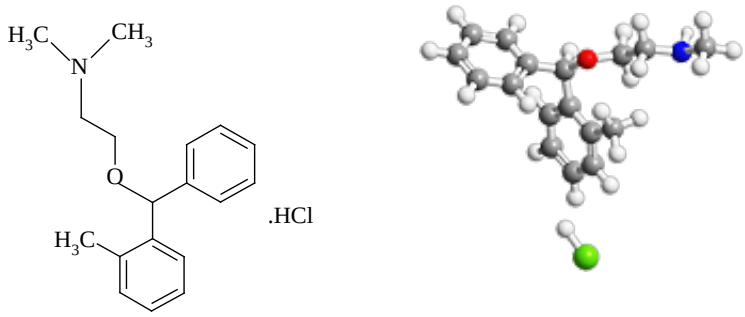
1. INTRODUCTION

Orphendrine hydrochloride (Dimethyl[2-(2-methylbenzhydryloxy)ethyl] amine hydrochloride) [ORP] (Scheme 1) is an anticholinergic drug of ethanolamine antihistamine class with prominent CNS and peripheral actions. It is used to treat painful muscle spasm and other similar conditions [1], as well as the treatment of Parkinson's disease [2]. In addition, it has mild antihistamic and local anaesthetic properties [3]. Parkinson's syndrome is the

consequence of a disturbed balance between cholinergic and dopaminergic neurotransmission in the basal ganglia caused by a decrease in dopamine. Orphendrine restores the physiological equilibrium and has a favorable effect on the rigidity and tremor of Parkinson's disease and Parkinson syndromes. Common side effects are dizziness, lightheadedness, drowsiness, blurred vision, and dry mouth may occur. So it was important to analyze ORP.

The wide spread use of ORP and the need for clinical and pharmacological study require fast and sensitive analytical techniques to determine the presence of ORP in pharmaceutical formulations and biological fluids. Until now the most common techniques for the determination of ORP in commercial dosage form are based on spectrophotometer [4-6], high-performance liquid chromatography (HPLC) [7,8], Gas liquid chromatography [9] and capillary electrophoresis methods[10]. But these methods are time consuming, solvent usage intensive and require expensive devices and maintenance. The advantages of electro analytical methods in analysis of drugs are their simplicity, high sensitivity, low cost and relatively short analysis time as compared to the other routine analytical techniques [11].

No literature was found on the voltammetric study of ORP on gold surfaces. The aim of this study is to establish the suitable experimental conditions, to investigate the oxidation mechanism of ORP on gold surface, to determine ORP in pharmaceutical dosage forms, and urine samples using cyclic, differential pulse and linear sweep voltammetry. We optimized all the experimental parameters for the determination of ORP under the physiological condition i.e. pH 7.0 and developed an electro analytical method for its determination. This method has the advantages such as fast response, and low detection limit. The proposed method was applied to the determination of ORP in the tablet and urine samples.



Scheme 1. Structure of orphendrine hydrochloride

2. EXPERIMENTAL

2.1. Reagents and chemicals

Pure orphendrine hydrochloride in powdered form was obtained from Aldrich, India and used as received. A stock solution of ORP (1.0×10^{-3} M) was made in double distilled water. Phosphate buffer solutions (Ionic strength=0.20 M) were prepared according to the literature method [12]. The ORP containing tablets were purchased from a local pharmacy with brand

name Banflex (Triveni Interchem pvt Ltd India). All the surfactants obtained from Hi-Media Pvt. Ltd. were dissolved in doubly distilled water to form 1.0×10^{-3} M solutions. All other reagents used were of analytical grade.

2.2. Instrumentation

The electrochemical experiments were performed with CH Instruments, USA (Model 1110BA, Version 4.01) Electrochemical Analyzer. The voltammetric measurements were carried out in a 10 ml single compartment three-electrode glass cell with a 2 mm diameter gold electrode as the working electrode, a platinum wire as counter electrode and Ag/AgCl (3 M KCl) electrode as reference electrode. The background subtraction was done in all the measurements. The pH of the buffer solution was measured using Elico model EI120 pH meter. All experiments were carried out at an ambient temperature of 25±0.1 $^{\circ}$C. The area of the electrode was obtained by cyclic voltammetric method using 10.0 mM $K_3Fe(CN)_6$ as a probe at different scan rates. For a reversible process, the following Randles–Sevcik formula can be used:

$$i_{pa} = (2.69x\ 10^5)\ n^{3/2}\ ADo^{1/2}\ C_o\upsilon^{1/2} \quad (1)$$

Where i_{pa} refers to the anodic peak current, n is the number of electrons transferred, A is the surface area of the electrode, D_O is diffusion coefficient, υ is the scan rate and C_O is the concentration of $K_3Fe(CN)_6$. For 10.0 mM $K_3Fe(CN)_6$ in 0.1 M KCl electrolyte, n=1, $Do=7.6\times10^{-6}$ cm^2 s^{-1} [6], then from the slope of the plot of i_{pa} *vs* $\upsilon^{1/2}$, the surface area of the electrode can be calculated. In our experiment the slope was 13.45×10^{-6} μA $(Vs^{-1})^{-1/2}$ and the area of the electrode was calculated to be 0.021 cm^2.

Activation of gold electrode surface was done by polishing the surface on micro cloths (Buehler) glued to flat mirrors. A different micro cloth was used for each size of alumina. The particle size used was 0.3, 0.1 and 0.05 μm. The final particle size was 0.05 μm. After initial cleaning of the electrode, it was only necessary to polish with 0.05 μm particle size during the time of experiments. Before transferring the electrode to the solution, it was washed with high purity water. Cyclic voltammograms were recorded in 1.0 mM ORP at 0.05 mV s^{-1} between 0 and 1.4 V, until obtaining the reproducible current–potential curves.

The experimental conditions for differential-pulse voltammetry (DPV) were: initial potential: 0 V, final potential: 1.4 V, sensitivity: 5 μA/V, pulse amplitude: 50 mV, sample width: 20 ms, pulse width: 30 ms, pulse period: 600 ms and scan rate: 20 mV s^{-1}.

2.3. Sample preparation

An amount of 10 tablets were weighed and ground to a homogeneous fine powder in a mortar. Portion equivalent to a stock solution of a concentration about 3.0 mM was accurately

weighed and transferred into a 100 ml calibrated flask and completed to the volume with doubly distilled water. The contents of the flask were sonicated for 10 min to get complete dissolution. Appropriate aliquot of the clear supernatant liquid was then transferred into a voltammetric cell containing 10 ml of buffer solution of pH 7.0. The differential-pulse voltammogram was subsequently recorded following the optimized conditions. The content of the drug in tablet was determined referring to the calibration graph or regression analysis.

To study the accuracy of the proposed method, and to check the interference from excepients used in the dosage forms, recovery experiments were carried out by the standard addition method. This study was performed by addition of known amounts of ORP to known concentration of the tablets. The resulting mixture was analyzed as in pure ORP.

3. RESULTS AND DISCUSSION

3.1. Electro-oxidation of ORP

The electrochemical behavior of ORP at gold electrode was studied by cyclic voltammetry (CV) at pH 7.0. The cyclic voltammograms obtained for 1.0 mM ORP solution at a scan rate of 50 mV s−1 exhibits a well-defined anodic peak at about 0.98 V(peak a) The results are shown in Fig. 1. On the reverse scan, one reduction peak was observed at 0.64 V indicating the reduction of gold oxide [13], the electrode process of ORP is an irreversible one. The CV of blank solution also taken for comparison (curve b); the voltammograms corresponding to the first cycle was generally recorded.

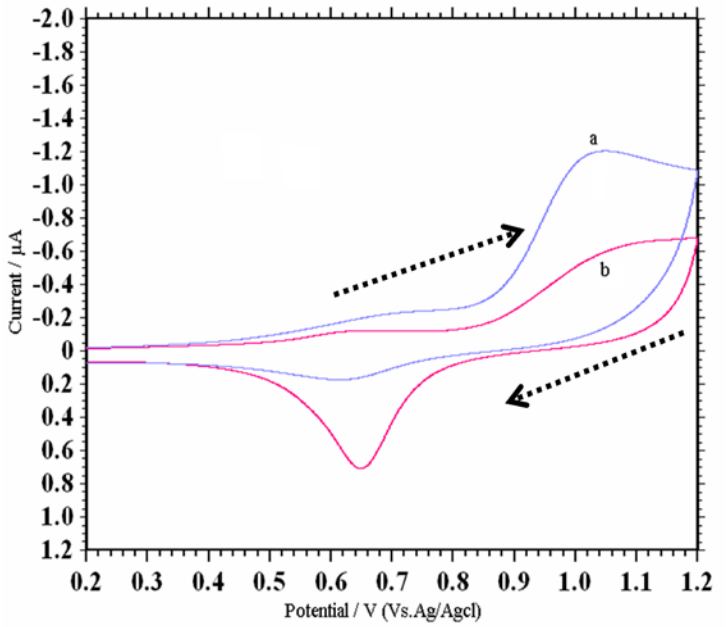


Fig. 1. Cyclic voltammogram obtained for 1.0 mM ORP on gold electrode in pH 7.0, 0.2 M buffer: (a) ORP and (b) blank run at υ=0.05 V s^{-1}

3.2. Effect of pH

To understand the dependence of pH on the ORP the electro oxidation of 1.0 mM ORP was studied over the pH range of 3.0 to 10.20 in phosphate buffer by cyclic voltammetry. The results showed that high peak current was obtained in phosphate buffer with pH 7.0 (Figure 2A). With increase in the pH of solution, the peak potential linearly shifts to less positive values and the linear relation between Ep *vs* pH (Figure 2B) can be expressed as Ep (υ)=1.174-0.029 pH r=0.983

The slope of this equation is found to be 0.029 mV/ pH. From the plot of Ip *vs* pH (Figure 2C) it is clear that, peak current is affected by the pH value. However, the best result with respect to sensitivity accompanied with sharper response was obtained with pH 7.0. So pH 7.0 was selected for further experiments.

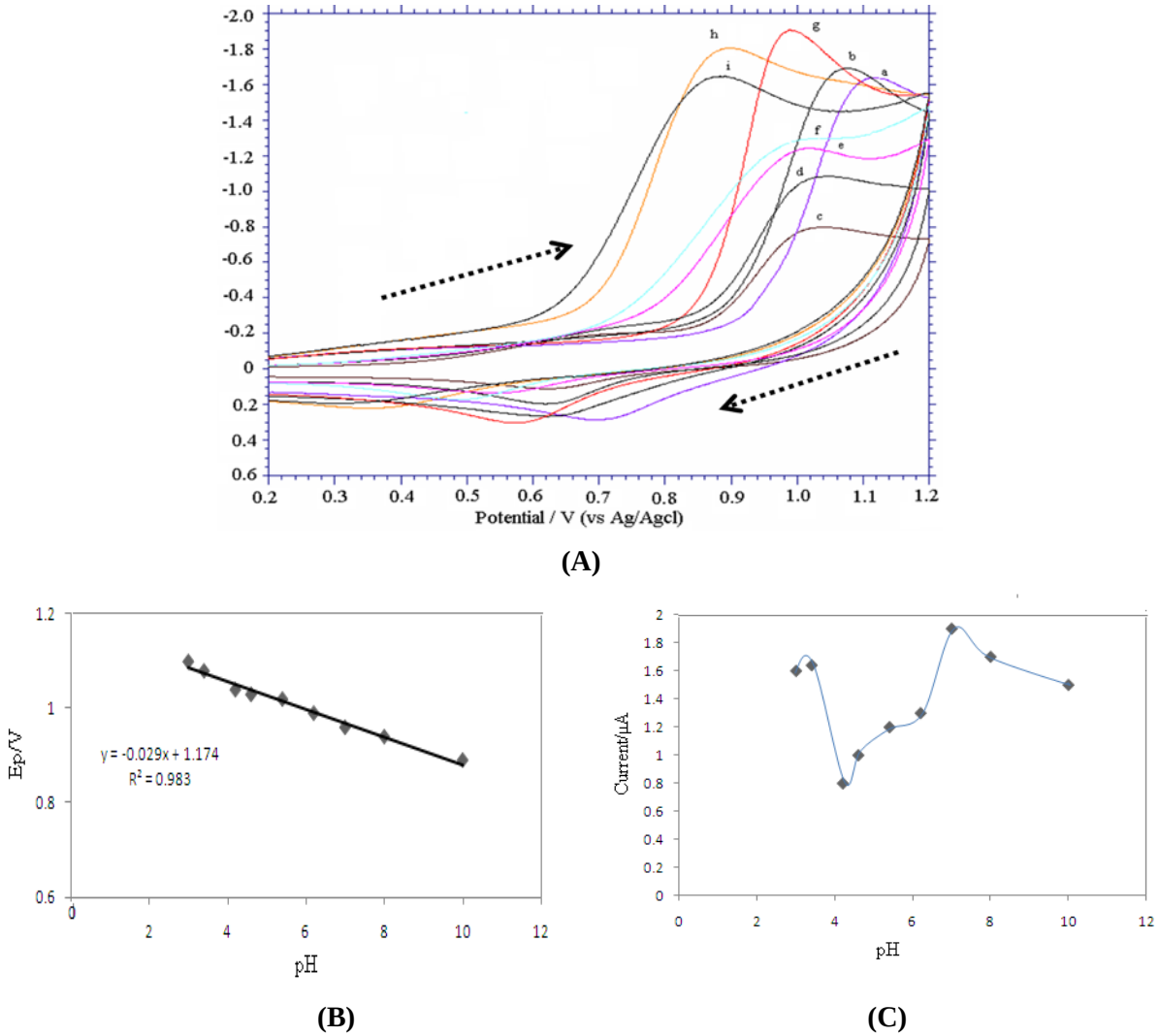


Fig. 2. (A) Cyclic voltammograms obtained for 1.0 mM ORP in buffer solution at (a) pH 3.0, (b) pH 3.4, (c) pH 4.2, (d) pH4.6 (e) pH 5.4 (f) pH 6.2 (g) pH 7.0 (h)pH 8.0(i) pH 10.0 with potential scan rate: 0.1 V s-1; **(B)** Variation of peak potential with pH for 1.0 mM ORP**; (C)** Variation of peak current with pH for 1.0 mM

3.3. Effect of scan rate

The influence of the potential scan rate on the electrochemical oxidation was studied at pH 7.0 by cyclic voltammetry (Figure 3A) and linear sweep voltammetry (Figure 4). Scan rate studies were carried out to evaluate whether the processes on gold electrode were under diffusion or adsorption-controlled. When the scan rate was varied from 0.01 to 0.20 V s^{-1} in 1.0 mM solution of ORP, a linear dependence of the peak intensity Ip upon the scan rate (υ) was found , demonstrating an adsorption behavior (Figure 3B).

The equation for this line is given below in phosphate buffer at pH 7.0, Ip = 129.99 υ (V s^{-1}) + 4.029, r = 0.9876.

A plot of logarithm of anodic peak current *vs*. logarithm of scan rate gave a straight line with a slope of 0.6678 (Figure 3C) close to the theoretical value of 1.0, which is expected for an ideal reaction for the adsorption-controlled electrode process [14]. The equation obtained was log Ip = 0.6678 log υ (V s^{-1}) + 1.9268, r = 0.9966.

The Ep of the oxidation peak was also dependent on scan rate. The plot of Ep *vs*. log υ was linear having a correlation coefficient of 0.9941 (Figure 3D) and the relation between Ep and υ can be expressed by the equation

Ep (V) = 0.1151 logυ (V s^{-1}) + 1.1709.

For an adsorption-controlled and irreversible electrode process, according to Laviron, Ep is defined by the following equation [15]

$$Ep = E^0 + \left(\frac{2.303RT}{\alpha nF}\right)\log\left(\frac{RTk^0}{\alpha nF}\right) + \left(\frac{2.303RT}{\alpha nF}\right)\log \nu \qquad (2)$$

where α is the transfer coefficient, k^0 is the standard heterogeneous rate constant of the reaction, n the number of electrons transferred, υ the scan rate and E^0 is the formal redox potential. Other symbols have their usual meaning. Thus, the value of αn can be easily calculated from the slope of Ep *vs*. log υ. In this system, the slope is 0.03821, taking T=298 K, R=8.314 J $K^{-1}mol^{-1}$ and F=96,480 C, αn was calculated to be 1.7081. Generally, α is assumed to be 0.5 in totally irreversible electrode process. Thus, n was calculated to be 1.7082~2.0. The value of k^0 can be determined from the intercept of the above plot if the value of E^0 is known. The value of E^0 in Eq. (2) can be obtained from the intercept of Ep *vs*. υ curve by extrapolating to the vertical axis at υ=0 [16]. In our system the intercept for Ep *vs*. log υ plot was 0.9978 and E^0 was obtained to be 0.8403 V, the k^0 was calculated to be 1.68×10^{-3} s^{-1}.

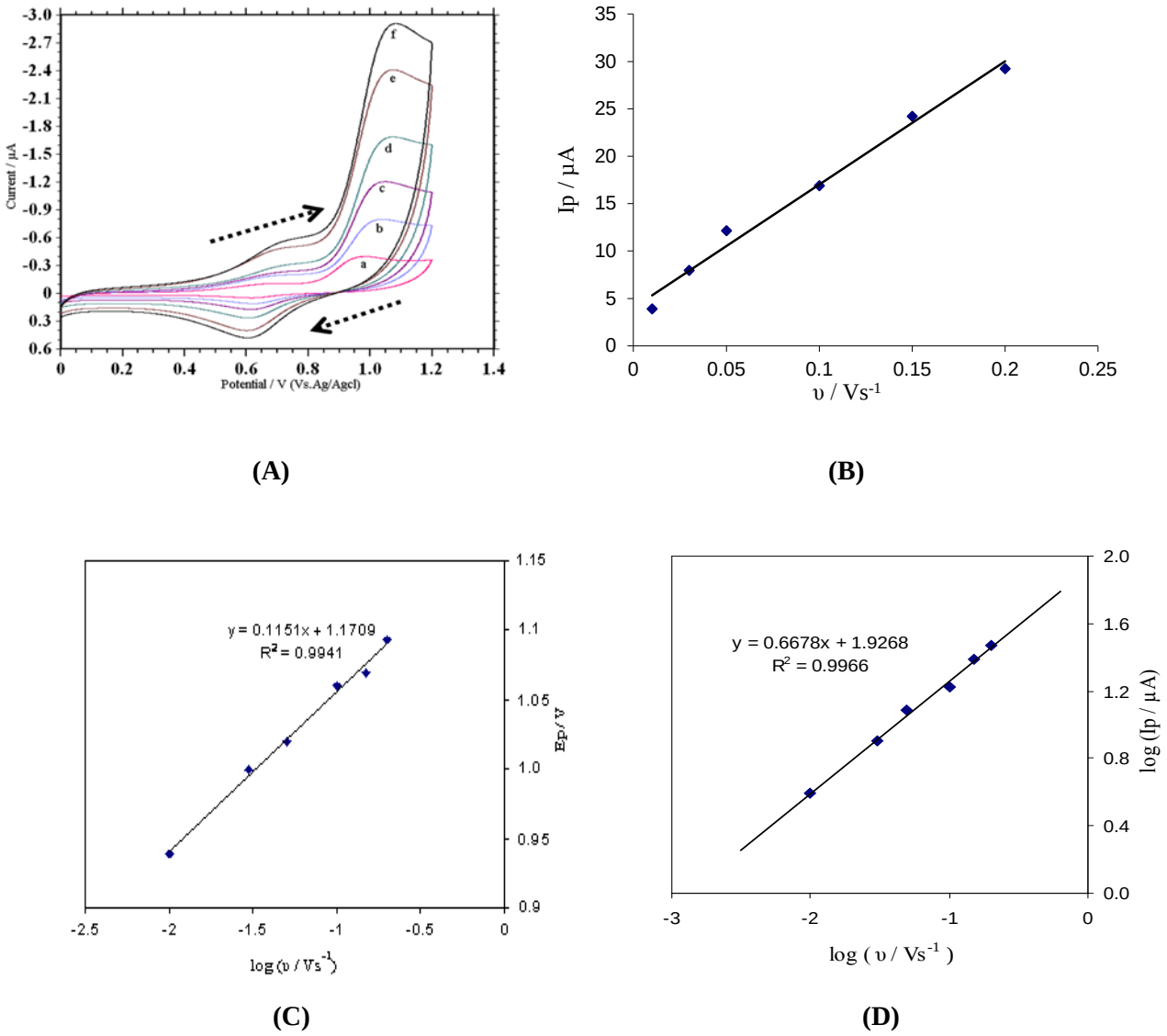


Fig. 3A. Cyclic voltammograms of 1.0 mM ORP in 0.2 M buffer solution of pH 7.0 at scan rates of: (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.1, (e) 0.15, and (f) 0.2V s^{-1}; **(B)** Observed dependence of peak current on the scan rate; **(C)** Plot of logarithm of peak current *vs.* logarithm of scan rate; **(D)** plot of variation of peak potential with logarithm of scan rate

3.4. Effect of surfactant

Surfactants even in trace quantities can exert a strong effect on the electrode process. Adsorption of such substances at the electrode may inhibit the electrolytic process, bring about the irregularity in the voltammograms, and cause shift in the wave to more negative potentials [17,18]. Surface-active substances have the common tendency of accumulation at interfaces. The lack of affinity between the hydrophobic portion of the surfactant and water leads to a repulsion of these substances from the water phase as a consequence of oxidation of the microscopic ORP-water interface. It was found that addition of the cationic surfactant, cetyltrimethyl ammonium bromide(CTAB) shifted the anodic peak potential of ORP to more

negative values and current decreases its due to formation of hydrophobic surface by CTAB repulse the analyte from electrode surface (Table 1). Whereas the anionic surfactant, sodiumdodecyl sulfate(SDS) shifted the anodic potential to more negative values and there was an increase in current which is because adsorption of the anionic surfactant SDS at the electrode surface may form a negatively charged hydrophilic film on the electrode with the polar head group directing to the bulk water phase. This negatively charged hydrophilic layer not only increases the concentration of the ORP on the electrode surface via electrostatic interaction, but also reduces the overvoltage associated with ORP oxidation and pathway of the electron transfer process. The non-ionic surfactant Triton X-100 had no effect on the Voltammograms as it is neutral in nature which is not showing any interaction with the electrode surface.

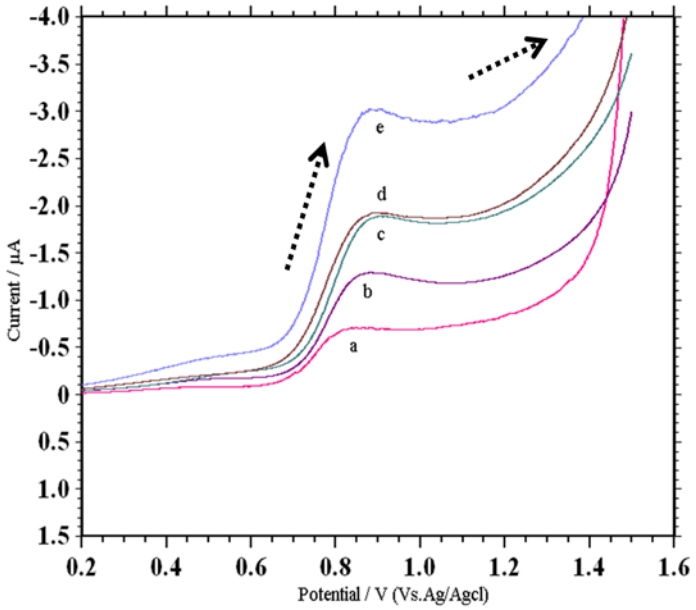


Fig. 4. Linear sweep voltammograms of 1.0 mM ORP in 0.2 M buffer solution of pH 7.0 At scan rates of: (a) 0.01, (b) 0.02, (c) 0.05, (d) 0.10, and (e) 0.15, V s^{-1}

3.5. Oxidation mechanism

Based on the cyclic voltammetry experiments the number of electrons transferred (n) was calculated to be 2.0. The bulk electrolysis of ORP oxidation gave the product as 1, 3-dimethyl-2-(1-phenyl-ethyl)-benzene 2-amino-ehanol. The product formed was confirmed by LC/ESI/MS after electrolysis solution which showed a molecular ion peak at 321amu (Figure 5). Based on these observations, a suitable mechanism is proposed as in the Scheme 2 Such type of oxidation mechanisms are documented in the literature [19,20].

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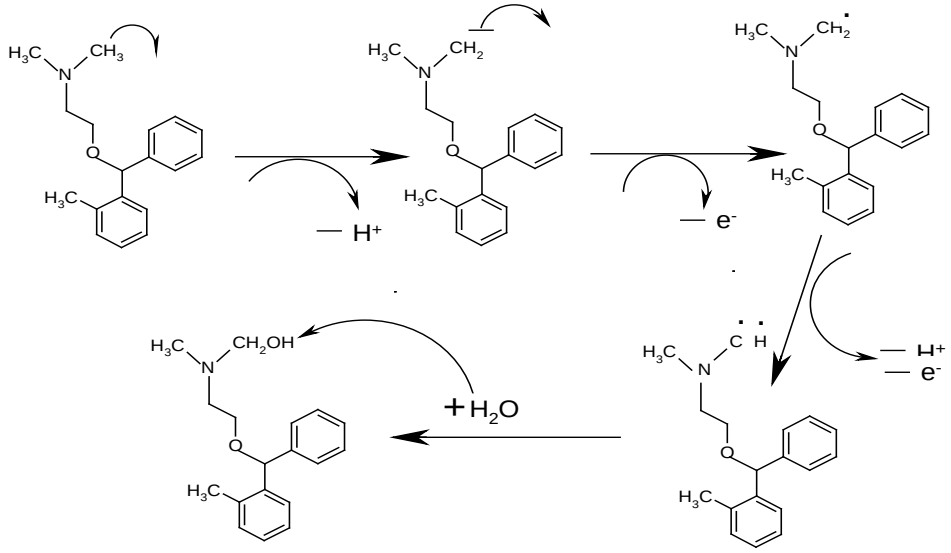
Table 1. Effect of surfactants on the voltammetric behavior of 1.0 µM ORP on gold electrode with scan rate 0.05 Vs^{-1}

Concentration (µM)	Ip (µM)	Ep (V)
CTAB[a]		
0.00	3.266	0.761
0.10	2.320	0.754
0.25	1.585	0.760
1.00	1.193	0.748
1.00	0.759	0.740
SDS[b]		
0.00	3.266	0.698
0.10	3.851	0.754
0.25	3.931	0.699
0.50	4.401	0.725
0.50	4.841	0.682

[a] Cetyltrimethylammonium bromide
[b] Sodiumdodecyl sulfate



Scheme 2. Mechanism of electro oxidation of orphendrine hydrochloride

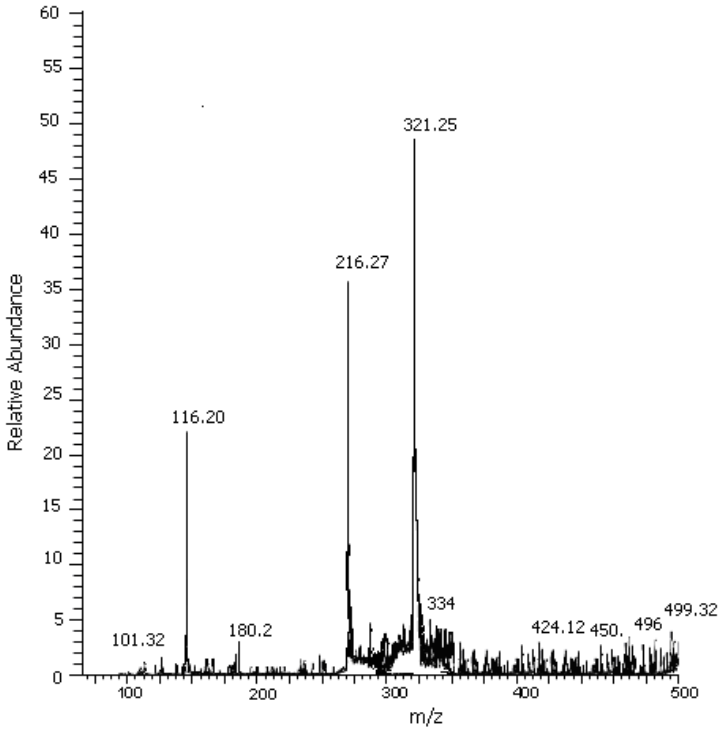


Fig. 5. LC/ESI/MS after electrolysis of solution which shows a molecular ion peak at 321 amu oxidation product of ORP

3.6. Analytical application

In order to develop a voltammetric methodology for determination of the drug, we selected the DPV mode, since the peaks were sharper and better defined at lower concentration of ORP then those obtained by cyclic and linear sweep voltammetry, with a lower background current, resulting in improved resolution. According to the obtained results, it was possible to apply this technique to the quantitative analysis of ORP. The phosphate buffer solution of pH 7.0 was selected as the supporting electrolyte for the quantification of ORP as it gave maximum peak current at pH 7.0. Differential-pulse voltammograms obtained with increasing amounts of ORP showed that the peak currents increased linearly with increasing concentration (Figure 6).

Using the optimum conditions described earlier, linear calibration curves were obtained for ORP in the range of 0.03–1 µM. Deviation from linearity was observed for more concentrated solutions. The linear equation was Ip=0.79+2.958 C (r=0.975, C is in µM). Related statistical data of the calibration curves were obtained from five different calibration curves. The limit of detection (LOD) and quantification (LOQ) were 7.1 nM and 24.17 nM, respectively. The LOD and LOQ were calculated on the peak current using the following:

LOD=3s/m; LOQ=10 s/m

Where s is the standard deviation of the peak currents of the blank (five runs) and m is the slope of the calibration curve [21]. Sample solutions recorded after 48 h did not show any appreciable change in the assay values.

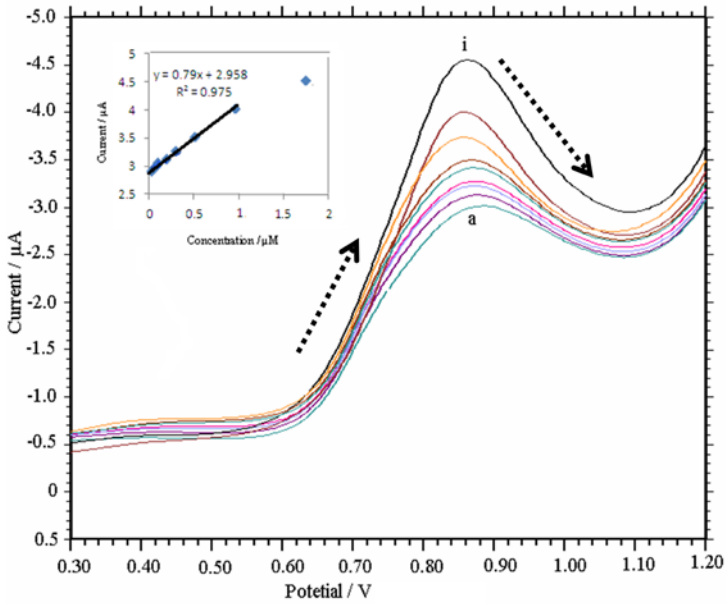


Fig. 6. Differential pulse volammamograms with increasing concentration of ORP in pH 7.0 0.2 M phosphate buffer solution on gold electrode with ORP concentration: (a) 0.03, (b)0.06, (c) 0.09,(d) 0.1, (e) 0.2, (f) 0.3, (g)0.5, (h) 1 and (i) 1.5 µM. Inset: plot of current *vs.* concentration of ORP.

3.7. Tablet analysis and recovery test

In order to evaluate the applicability of the proposed method, the commercial medicinal sample containing ORP from Sun Pharmaceutical Industries, India, was studied. The tablets were grounded to powder, dissolved in water and then further diluted so that ORP concentration falls in the range of calibration plot. Differential-pulse voltammograms were then recorded under exactly identical conditions that were employed while recording differential-pulse voltammograms for plotting calibration plot. It was found that ORP concentration determined for various tablets using this method are in good agreement with the reported values. The values of experimentally determined ORP and reported ORP amounts agreed reasonably well (Table 2). The results of recovery experiments were also shown in Table 2.

3.8. Effect of Excipients

ORP was formulated in single as well as multi-component tablets. The oxidation peaks of excifients should not appear where the peak corresponds to ORP oxidation peak. So in order

to investigate the effect of co-formulated substances such as glucose, starch, sucrose etc. on the voltammetric response of ORP, was carried out. Differential-pulse voltammetric experiments were carried out for 1.0 µM ORP in the presence of 1.0 mM of each of the interferents. The results are listed in Table 3. It was observed that 100 folds of glucose, starch, sucrose, citric acid, magnesium stearate, oxalic acid, and gum acacia did not interfere. However, 100 folds of talc interfered.

Table 2. Determination of ORP in tablets

	Banflex
Labeled claim (mg)	25.00
Amount found[a](mg)	24.89
R.S.D(%)	0.82
% of recovery in R.S.D	0.64
Added (mg)	10.00
Found (mg)	98.50
Recovered[b](%)	9.85

[a] Each value is the mean of five experiments
[b] Recovery value is the mean of five determinations

Table 3. Influence of potential interferents on the voltammetric response of 1.0 µM ORP

Interferent	Concentration (mM)	Signal Change (%)
Glucose	1.0	-1.21
Starch	1.0	-3.13
Sucrose	1.0	-0.89
Magnesium stearate	1.0	-1.32
Citric acid	1.0	+1.61
Talc	1.0	+10.24
Oxalic acid	1.0	+2.25
Gum acacia	1.0	+0.92

3.9. Detection of ORP in urine samples

The developed differential voltammetric method for the ORP determination was applied to urine samples. The recoveries from urine were measured by spiking drug free urine with

known amounts of ORP. The urine samples were diluted 100 times with the buffer solution before analysis without further pretreatments. A quantitative analysis can be carried out by adding the standard solution of ORP into the detect system of urine sample, and the peak linearly increased in height. The calibration graph was used for the determination of spiked ORP in urine samples. The detection results of five urine samples obtained are listed in Table 4. The recovery obtained was in the range from 97.6% to 104.1% and the standard deviation and relative standard deviations are given in Table 4.

Table 4. Determination of ORP in urine samples

Sample	Spiked (10^{-5} M)	Found[a] (10^{-5} M)	Recovery (%)	S.D. ± R.S.D (%)
1	0.4	0.403	98.6	0.017±0.01
2	0.6	0.589	100.3	0.019±0.01
3	4.0	4.125	104.1	0.0155±0.01
4	2.0	2.004	100.2	0.155±0.10
5	0.8	0.770	96.1	0.036±0.02

[a] Average of five experiments

4. CONCLUSIONS

The oxidation of ORP at gold electrode surface was investigated by cyclic voltammetry under the physiological condition i.e pH 7.0. ORP undergoes two electrons and two protons change with adsorption-controlled process. A suitable oxidation mechanism was proposed. The proposed differential-pulse voltammetric procedure can be used successfully to determine ORP in pharmaceutical samples. The proposed method offered the advantages of accuracy and time saving as well as simplicity of reagents and apparatus. In addition, the results obtained in the analysis of ORP in spiked urine samples demonstrated the applicability of the method for real sample analysis. The method is applicable in quality control laboratories in pharmaceutical industries and pharmacokinetic studies.

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