Square Wave Voltammetric Method for the Determination of Substituted Oxadiazol in Aqueous Solution

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ABSTRACT

A rapid, sensitive and accurate method for the determination of substituted oxadiazol (I&II) has been developed based on the reduction of electroactive group (-C=S) at hanging mercury electrode by using square wave voltammetric technique. The reduction peaks obtained at –0.028 and –0.172 V Vs Ag/AgC1 fir compounds I & II respectively at pH 2 in Britton – Robinson buffer are recommended for the trace determination of these compounds. Regression analysis on standard curve indicated a linear relationship between peak current and concentration over the rang 1.2×10^{-6}–2.5×10^{-5} M with a correlation coefficient of more than 0.98.

.(I-II)

(C=S)

0

–   II,I   -0.172   –0.028

.   (2)

1.2×10^{-6}

. 0.98 2.5×10^{-5}

INTRODUCTION

Pulse polarography and square wave voltammetry can facilitate the rapid analysis of many biologically active compound, drugs and enzymes (Zen and Chung, 1995; Sulaiman and Abdul Razzak, 2000; Shram et al, 1998) with the use of inexpensive and simple system.

One of the very important biologically active compounds are the substituted oxadiazol. Various oxadiazolyl compounds have been reported as insecticides, miticides

and bactericides (Okada and Yoshiyuki, 1970). Antibacterial and fungicidal properties have been exhibited by various urea derivatives (Farbwerke, 1968; Henry, 1966; Disdier et al, 1970; Nikawitz et at, 1969).

   The aim of this work is to study the square wave voltammetric behaviour of the two compounds I & II and the application of the method for trace determination in aqueous solution.
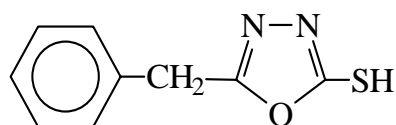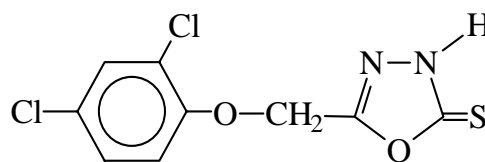
(I)   **(II)**

EXPERIMENTAL

Chemicals: Compounds I & II were prepared and characterized in our department by Ayoub and Saied (2000), Stock solution (10^{-3}M) of each of I & II were freshly prepared by dissolving appropriate weight of the corresponding compound in methanol. Dilute solutions were prepared from stock solutions either by using appropriate quantitative dilution or by pipetting into sample directly. Britton–Robinson buffer (B.R.B) (pH 1.8–12) was used as supporting electrolyte and prepared as given by Britton (Britton 1952).

Apparatus: An EG & G Princeton Applied Research (Princeton, N5) mode 384 polarographic analyses, model (303A) mercury drop electrode, and model (RE 0082) digital plotter were used The experimental parameters used in this method are shown in (Table 1) Measurements were performed with a dropping mercury electrode (0.08 mm internal diameter), Ag/AgC1-KC1 as the reference electrode and platinum counter electrode.

Table 1: Experimental parameters for determination of compounds I & II
        Mod: Square wave voltammetry.

Parameters		Information
Initial potential	0 or + 0.1 V	Replication 1
Final potential	-1.0 V	Standard curve
Deposition time	25.S	Blank substraction : No
Condition time	30.S	Tanget fit :No
Equilibrate time	15 S	Peak location :yes
Scan increment	3m V s^{-1}	Derivative : No

Procedure: Five milliliters of the supporting electrolyte (Britton-Robinson buffer at pH 2) was pipetted into the model (303 A) cell and the system was purged with N_2 gas for 240 Sec. A blank run was performed by using the experimental parameters in (Table 1). This run was stored in the memory of the model (384) polarographic analyzer. Then a standard solution of the compounds I or II (50-200 u1 of 10^{-3} M solution) was injected

into the supporting electrolyte. The solution was purged for 10 Sec, and a sample run was performed using the experimental parameters in (Table 1). The data were then printed on the digital plotter.

RESULTS AND DISCUSSION
Electrochemical reduction of compounds I & II:

Compounds I & II contain an electro active group namely the oxadiazol 2-thion which undergo a two electron reduction at dropping mercury electrode in the presence of proton donor as follow:

For analytical purposes, the current generated at the electrode by this electron transfer and measured by the polarographic analyzer is directly related to thio content of a sample.

Figure (1) is a square wave voltammogram for compound I & II. The square wave peak which occur at -0.028   V for compound I & -0.172 V Vs Ag/AgC1 for compound II. It is very clear that the peak potential of compound I is more positive than that of compound II This is probably due to the presence of 2,4-dichloro phenoxy group which make the reduction more difficult.

Effected pH: The square wave voltammogram of 3×10^{-6} M of compounds I & II were recorded at different pH(2-5) using Britton– Robinson buffer. The variation of peak potential (Ep) and peak current (Ip) with pH are summarized in (Table 2); These results indicate that the Ep values move to more negative values with increasing pH. Linear plot are obtained between Ep and pH values with slopes 93.1 and 48.8 mV pH^{-1} for compounds I & II respectively (Fig 2).

On the other hand, the peak pH 2 was chosen for the present study because it gives better resolution and almost highest peak currents.

Table 2: Effect of pH on the peak potential Ep and peak current Ip for 3×10^{-6} M of compound I and 20×10^{-6} M of compound II

PH	COMPOUND I		COMPOUND II	
	Ep(V)	Ip(10^2 nA)	Ep(V)	Ip(10^4 nA)
2	-0.028	12.5	-0.172	2.75
3	-0.104	6.5	-0.212	2.7
4	-0.184	4.8	-0.260	2.2
5	-0.284	2.0	-0.284	1.0

Quantitative determination of compounds I & II:

      Using the optimum conditions obtained above, pH 2 of britton- Robinson buffer and the experimental parameters shows in (Table 1), the squars wave voltammograms of compound I & II were recorded separately at different concentratuon.

      The result indicate that the peak current Ip was proportional to the concentration for both compounds studied and a good calibration graphs were obtained Some typical results of the method for a series of standard solution of the compound I & II are shown in (Table 3). These solutions were prepared by adding an appropriate aliquot of a stock solution of each of compound I or II to 5 ml Britton–Robinson buffer at pH 2 as supporting electrolyet.

      Regression analysis on the standard curve for both compounds I & II indicated a linear relationship between peak current and concentration.
The slop chang in peak current nA per unit changes in concentration in u mole and the intercept on the ordinate of the least square regression (in nA) are shown in (Table 3) together with the correlation coefficient (R). The lowest experimental determination limit was found to be 12×10^{-7} M.

Table 3: Determination of compounds I & II in aqueous solution at pH 2

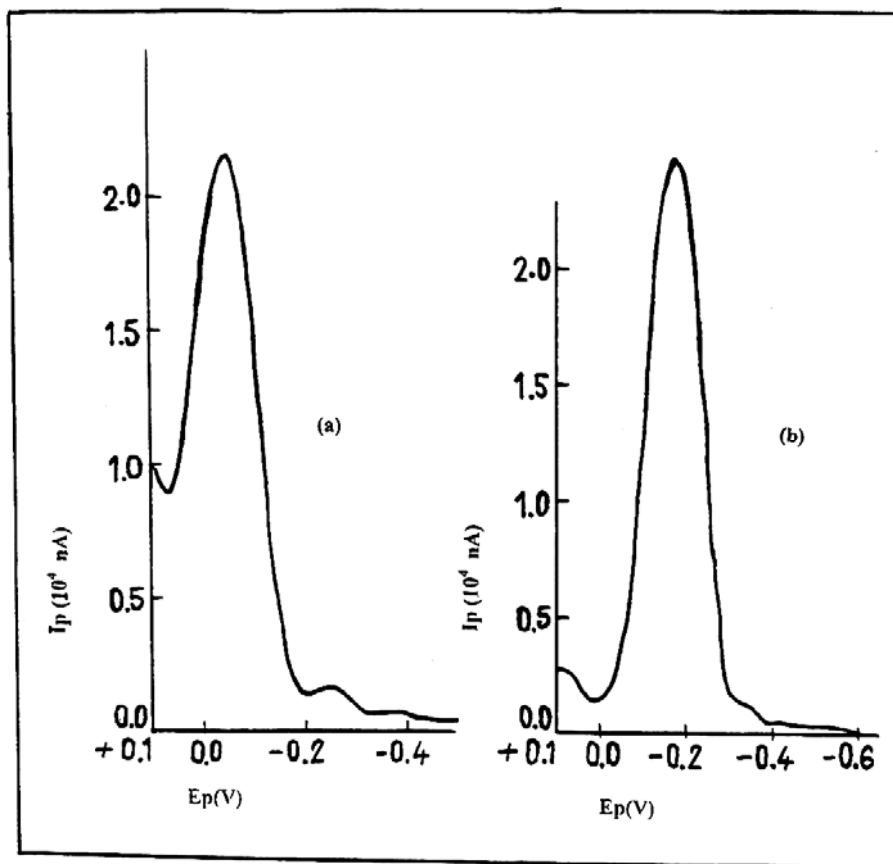| Conc. x 10^{-7} M	Compound I		Compound II	
	Ep(V)	Corrected Ip(10^3 nA)	Ep(V)	Corrected Ip(10^3 nA)
12	0.0	1.4	---	---
16	-0.030	1.5	---	---
20	-0.035	1.6	-0.080	4.4
29	-0.035	2.2	-0.076	5.0
39.	-0.030	3.0	-0.76	5.0
49	-0.030	4.2	-0.088	5.3
59	-0.030	5.2	-0.132	6.0
98	-0.030	5.0	-0.172	9.9
137	-0.035	12.9	-0.176	15.0
176	-0.-040	14.5	-0.176	22.1
212	-0.050	17.2	-0.168	27.3
250	---	---	-0.164	31.3
egression Analysis				
R	0.98098		0.99042	
Slop	8.168×10^8		1.232×10^9	
Intercept	-0.29338		-0.253777	

Fig 1: Square wave voltammetry of 2.12×10^{-5} M at 2 for
(a) compound I   (b) compound II
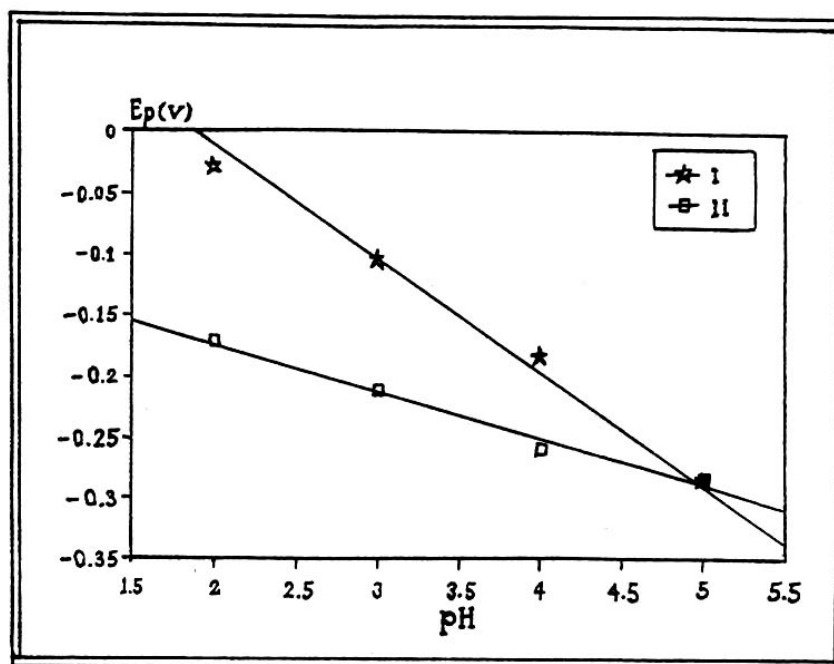
Fig. 2: The plot Ep versus pH for compounds I & II

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