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Voltammetric Studies of Anthracen-9-ylmethylene-(3,4-dimethyl-isoxazol-5-yl)-amine Compound at Platinium Electrode

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Abstract: *The voltammetric behavior of anthracen-9-ylmethylene-(3,4-dimethyl-isoxazol-5-yl)-amine compound at Platinium electrode has been performed via convolutive cyclic voltammetry and digital simulation techniques using a conventional platinium electrode in 0.1 mol L^{-1} tetrabutylammonium perchlorate (TBAP) in acetonitrile solvent (CH_3CN). The compound loss one electron forming radical cation followed by fast chemical step and the radical cation loss another two electrons producing trication which followed by chemical reaction (ECEC). Cyclic voltammetry and convolutive voltammetry were used for determination of the chemical and the electrochemical parameters of the electrode reaction pathway of the investigated compound. The Electrochemical parameters such as α, ks, E^o , D, and kc of the investigated isoxazol derivative were verified via digital simulation technique. Voltammetric studies of the investigated isoxazol derivative compound under consideration was presented and discussed.*

Keywords: 3,4-dimethyl-isoxazol-5-yl)-amine, Voltammetric studies, Platinium electrode, Digital simulation.

1. INTRODUCTION

Example of compounds used in medicinal chemistry is those nitrogen containing heterocycles with an oxygen atom because of their diversified applications in biological systems. An important class of heterocycles are isoxazoles, which are largely employed in the area of therapeutics and pharaceuticals such as insecticidal, antibacterial [1,2], antifungal, antitumour, antibiotic [3,4], anticancer, antituberculosis, and ulcerogenic [5]. Isoxazole derivatives are used in the market as anti-inflammatory drugs and COX-2 inhibitors [6]. Isoxazole derivatives such as sulfisoxazole, oxacillin, sulfamethoxazole, acivicin and cycloserine have been in commercial use for many years [7-9]. It was found that, the best known antibiotic drug that possess antitubercular, antibacterial activities and in treatment of leprosy is the cycloserine. Acivicin is an antileishmania, antitumour drug, while isoxaflutole is used as herbicidal drug [10,11]. The drugs such as Levothyroxin, Fenoprofen, Nimesulide etc. are revealed the importances of these area. Different substructures combinations are one of the approach to synthesize potential biologically active compounds from known active compounds.

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To the best of our knowledge there is no electrochemistry studies on Anthracen-9-ylmethylene-(3,4-dimethyl-isoxazol-5-yl)-amine at Pt electrode in acetonitrile solvent using TBAP as indifferent electrolyte. So, the present article describes the investigation of of Anthracen-9-ylmet-hylene-(3,4-dimethyl-isoxazol-5-yl)-amine using convolutive cyclic voltammetry & digital simulation. The determination of chemical and electrochemical parameters were performed experimentally and confirmed via the method of digital simulation.

2. EXPERIMENTAL

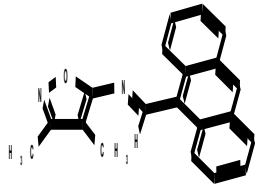
2.1. Chemicals.

The compound, anthracen-9-ylmethylene-(3,4-dimethyl-isoxazol-5-yl)-amine under consideration was synthesized as following:

A mixture of 5-amino-3,4-dimethylisoxazole (0.0024 mol) and anthracene-9-carbaldehyde (0.50 g, 0.0024 mol) was heated for 2 h in ethanol (15 mL). . TLC was used to monitore the progress of the reaction. The separated solid from the cooled mixture was collected and recrystallized from a chloroform - methanol mixture (2: 8) to give the title compound.

Yellow solid: Yield: 82%;m.p. 146-147 °C.
GC-MS m/z (rel. int.%): 301 (62) $[M+1]^+$,

Scheme 1.



IR (KBr) *v*max cm^{-1}: 2917 (C-H), 1580 (HC=N), 1158 (C-N).
^{1}H NMR (600MHZ, $CDCl_3$) (δ/ppm): 10.12 (s, CH olefinic), 8.95 (d, 2H, H1, J=8.8 Hz), 7.61 (dd, 2xH, H2, J=5.6 Hz), 7.50 (dd, 2xH, H3, J=7.2 Hz), 8.56 (d, 2H, H4 J=8.0 Hz), 7.65 (s, H5), 2.30 (s, CH_3), 2.16 (s, CH_3).
^{13}CNMR (600 MHz, $CDCl_3$) δ: 165.44, 162.07, 159.82, 132.63, 131.53, 131.10, 130.05, 129.27, 129.12, 127.94, 125.54, 124.07, 123.56, 116.50, 108.03, 10.83, 6.89.
Anal. calc. for $C_{20}H_{16}N_2O$: C, 79.98, H, 5.37, N, 9.33. Found: C, 79.94, H, 5.32, N, 9.28

The investigated isoxazol derivative has the structure shown in scheme 1.

2.2. Voltammetric measurements.

Cyclic voltammetry and convolutive transforms were run using Computer – controlled Potentiostat Model 283 Princeton Applied Research (PAR) and Model 175 Universal Programer (from EG and G). The system provides a scan rate up to 100 V/s for the cyclic voltammetric measurements.

Three conventional electrode cell configuration was used for electrochemical measurements. Working electrode was a platinum electrode with surface area 7.85 x 10^{-3} cm^2, the counter and reference electrodes were coiled platinum wire and saturated Ag/AgCl respectively.

The potential of the working electrode was measured with relative to the potential of Ag/AgCl reference electrode at 25^{o}C and 0.1 mol/L tetrabutylammonium perchlorate (*TBAP*) as background electrolyte. Solution resistance and double-layer charging current of the cyclic voltammetry experiments were minimized by background subtraction of residual current and iR compensation. The polishing of the working electrode was done on a polisher Ecomet grinder. Data of cyclic voltammetry experiments were obtained at scan rate ranging from 0.02 to 2 $V.s^{-1}$ in non aqueous media at (25 ± 2) ^{o}C.

Digital simulation of cyclic voltammetric experiments was carried out on PC computer using condesim software package purchased from EG & G. Finite differences techniques was used to perform the simulation process. Algorithms used in the simulation software were implemented and coded in the condesim package provided by EG & G.

Oxygen free nitrogen was bubbled in the solutions for 15 minutes and a nitrogen gas was maintained above the solution throughout the experiments to expel air from working solutions.

3. RESULTS AND DISCUSSION

3.1. cyclic voltammetric studies

An example response of the cyclic voltammogram of 4 x 10^{-4} M of the investigated anthracen-9-ylmethylene-(3,4-dimethyl-isoxazol-5-yl)-amine compound in acetonitrile solvent, at scan rate of 0.60 V/s is shown in Figure 1. As indicated in Figure 1, the first anodic peak (A) was coupled with a small cathodic peak (B) in the reverse scan, while the second anodic peak (C) was coupled with a small cathodic peak (D) in the backward sweep. The ratio of the forward peak to the backward peak (i_pf/i_pb) is more than unity for the two peaks, confirming that the rate of the homogeneous chemical rate constant (k_c) is fast. The cyclic voltammograms at various scan rates are displayed in Figure 2.

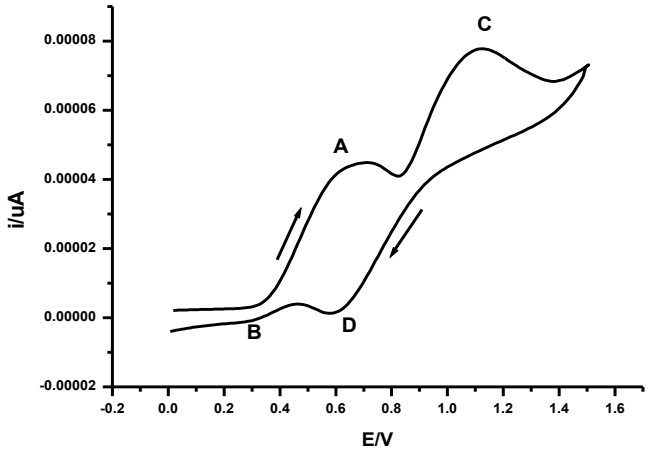


Figure 1. Oxidative cyclic voltammogram of 4´10^{-4} M of *isoxazol* derivative in CH_3CN / 0.1M TBAP at scan rate of 0.6 $V.s^{-1}$.

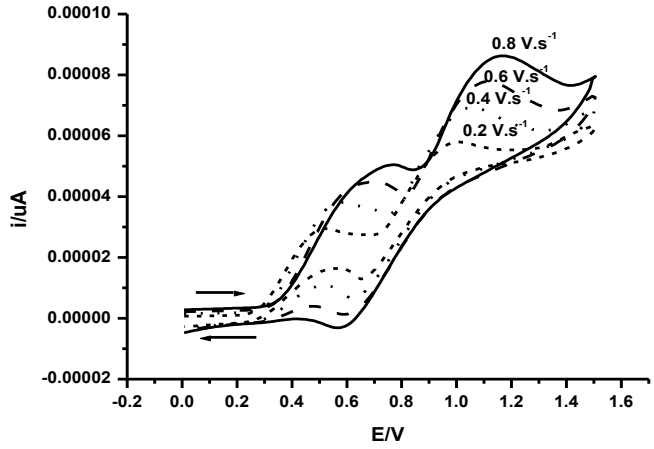


Figure 2. Oxidative cyclic voltammograms of 4×10^{-4} M of *isoxazol derivative* in CH_3CN / 0.1M TBAP at various scan rate.

3.1.1. Effect of scan rate

In this article the electrode reaction revealed that the height of peak current increases with increasing the scan rate, and the position of forward anodic peakl of oxidative process was shifted to more positive potential. From cyclic voltammetric behaviour, it was noted that, the rate of electron transfer of anodic process of the isoxazol derivative is slow at all scan rates. The disappearance of the cathodic peaks in the backward scan at low values of the scan rate confirm the presence of fast chemical step after the transfer of

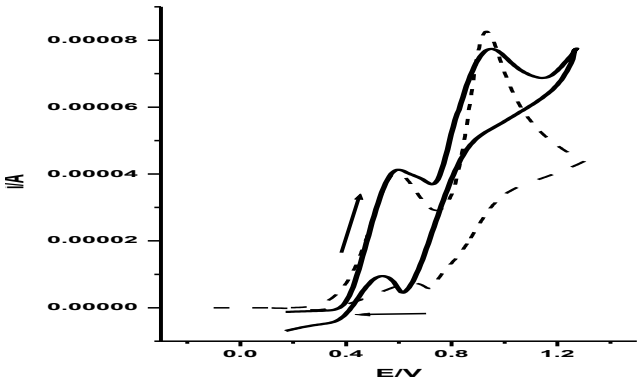


Figure 3. Matching between oxidative experimental voltammogram of *isoxazole.* (———) and simulated voltammogram (.....) at a sweep rate of 0.6 V.s^{-1}.

electron. This behaviour revealed that the first electron transfer produces a cation radical followed by a fast chemical reaction and the radical cation give another two electrons to form a trication which followed by fast chemical process. Examination of Figure 2 revealed that, the anodic peak currents, after minimizing the residual current, is increased with the square root of scan rate ($v^{1/2}$).

The sluggish nature of electron exchange in 0.1 mol/L TBAP / CH_3CN was confirmed from the values of peak separation ΔEp of the first and the second charge transfers. Tha value of ΔEp was found to be in the range of 360 – 520 & 400 – 623 mV of the first and the second charge transfers respectively. The average values of the forward and backward peak positions give the magnitude of redox potential (E^0) (Table 1). The standard heterogeneous rate constant (*k*s) was determined via the working curve established in literature [12]. The value of diffusion coefficient (*D*) of the isoxazol derivative under study was calculated from the plot of of i_p vs. $\sqrt{v}$ [12,13]. From the above methods the values of *k*s and *D* were calculated and listed in Table 1. Figure 3 employs the experimental and theoretical values of the electrochemical parameters of the isoxazol derivative compound, which demonstrate good matching between the simulated data and captured one with slight deviation of the second peak which may be attributed to some sort of iR drop due to cell solution resistance.

3.2. Convolutive voltammetry

It was known the convolution theorem gives the following equation [14-17]:

$$L^{-1}[f_s(s).gs(s)]=\int_0^t G(u)F(t-u)du \quad (1)$$

in which the Laplace transform of the functions *F* and *G are* f_s & g_s, while the variables *u* are the dummy variables which are lost when the definite integral is evaluated.
In electro-oxidation process:

$$A - ne \rightleftharpoons B$$

where the initial species behave only as simple electron transfer, Fick's second law is expressed as [17]:

$$[\partial C_A/\partial t]_x = D_A[\partial^2 C_A/\partial x^2]_x \quad (2)$$

the I_1 convolution is the given by $I_1 = i / (\pi t)^{1/2}$ or as:

$$I_1(t) = \pi^{-1/2}\int_0^t i(u)/(t-u)^{1/2}du \quad (3)$$

For the evaluation of the convolution integral *I(t)* several algorithms have been proposed . In this work, the proposed one is [16-25]:

$$I(t) = I(k\Delta t) = \frac{1}{\sqrt{\pi}}\sum_{j-1}^{j=k}\frac{\Gamma(k-j+1/2)}{(k-j)}.\Delta t^{1/2} i(j\Delta t) \quad (4)$$

Where $i(j\Delta t)$ is the magnitude of current read at equally intervals of spaced time Δt and $\Gamma(x)$ is the Gamma function of *x*.
The diffusion coefficients (*D*) of the anodic processes was determined from the following equation:

$$I_{lim} = nFAC(D)^{1/2} \quad (5)$$

and listed in Table 1. Figure 4 shows the convoluted current I_1 of the anodic wave at 1.0 V.s^{-1} scan rate. The large separation between the backward scan and the forward scan reflect slow nature of electron transfer. Also the backward scan does not return to initial current point , indicating the presence of chemical step coupled with electron transfer and the slow kinetic of the heterogeneous rate constant (k_s) between the electroactive isoxazol compound and the electrode surface , *i.e* the mechanism proceeds as *ECEC*.

The deduced convoluted current (I_{limd}) was used for calculation of the diffusion coefficient via the following relationship [13,16]:

$$I_{limd} = \frac{i_p}{3.099(an_\alpha v)^{1/2}} \quad (6)$$

where I_{limd} is the limiting convoluted current deduced from cyclic voltammetry and convolution transform ($I_{limd} = I_{lim} = nFACD^{1/2}$). The agreement between the values of diffusion coefficient calculat-

Table 1. Electrochemical parameters of the anodic oxidation processes of Isoxazol derivative compound

E^0 V	E^{02} V	$k_{s1}\times10^3$ ms^{-1}	$k_{s2}\times10^3$ ms^{-1}	$D_1\times10^9$ m^2.s^{-1}	$D_2\times10^9$ m.s^{-1}	α s^{-1}	kc1 s^{-1}	kc2
0.410[a]	0.802	2.70	3.20	6.21	6.53	0.48	----	----
0.412[b]	0.801	2.30	2.40	5.81	4.94	0.39	0.40	0.30
----[c]	----	----	----	6.53	6.70	----	----	----
0143[d]	0.803	----	----	6.12	6.222	0.42[e]	0.31[e]	----

a) Experimental values. b) Simulated values. c) Values of *D* calculated via Eq.(5). d) Values calculated via deconvolution. e) Values of k_c calculated from kinetic convolution.

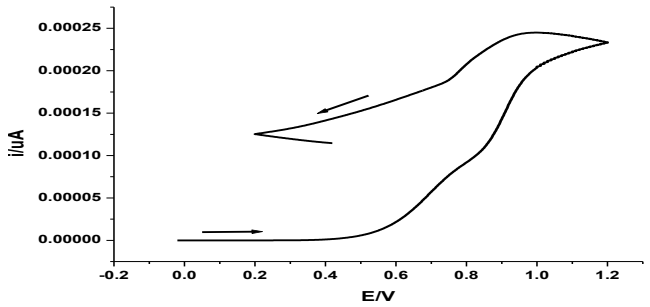


Figure 4. Convolution voltammetry (I_1) of the oxidative process of *isoxazol* at sweep rate of 1.0 V.s^{-1}.

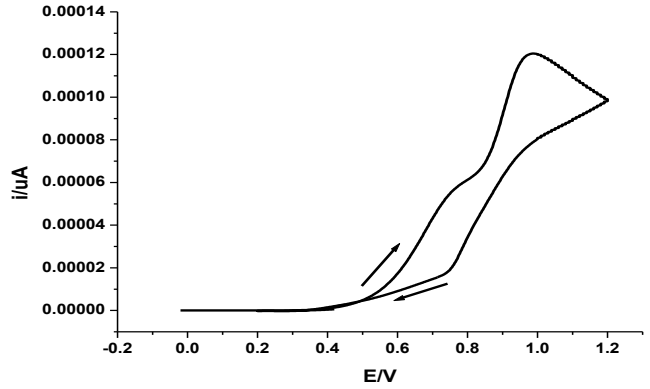


Figure 5. Kinetic convolution voltammetry (I_2) of the oxidative process of *isoxazol* at sweep rate of 1.0 V.s^{-1}.

ed from CV and I_{lim} is indicated in Table 1.

The homogeneous rate constant (k_c) of the first and second chemical processes was determined via kinetic convolution, I_2, as shown in Figure 5 which consider precise, accurate, fast, and simple method [13]. The calculated values of homogeneous chemical rate constant were shown in Table 1.

3.3. Deconvolution voltammetry

Deconvolution voltammetry is akin to semidifferentiation in a similar way to considering $t^{-1/2}$ convolution as semiintegration.. Convolutions $t^{1/2}$ is related to deconvolutions via the following scheme [26].

$$dI_1/dt \underset{\text{deconvolution}}{\overset{\text{convolution}}{\rightleftharpoons}} i \underset{\text{deconvolution}}{\overset{\text{convolution}}{\rightleftharpoons}} I_1(t)$$

The deconvoluted current ($d\,I_1\,/dt$) of reversible process is defined as [26 -30]:

$$(dI_1/dt) = nFAC\sqrt{D}\, a\zeta / (1+\zeta)^2 \qquad (7)$$

where $a = nvF/RT$ (8)

and $\zeta = exp\,[nF/RT\,(E - E^0$ (9)

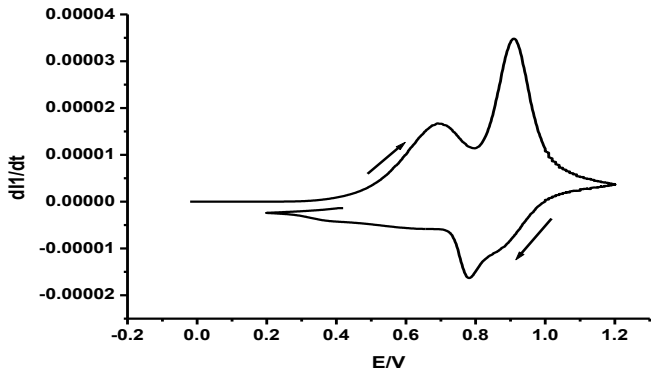


Figure 6. Deconvolution voltammetry (dI_1/dt) of the reductive cyclic voltammogram of *isoxazol* at a sweep rate 0.6 V.s^{-1}.

and the plot of deconvolution voltammetry at v = 0.6 V.s^{-1} is shown in Fig.6. In case of fast charge transfer the width of deconvoluted peak (wp) is equal to 3.53 RT/nF = 90.5 /n mV. The slow nature of electron transfer of the electrode reaction.was indicated and confirmed from the value of wp = 183 ± 2 mV,

The displacement and the asymmetry of the oxidative and reductive peak, further confirming the slow nature of electron transfer of ECEC mechanism of the oxidation processes of isoxazol derivative compound. The reduction potentials were measured from the average values of peak potwntial of deconvolution voltammograms (Table 1). It was found that the values of E^0_1& E^0_2 determined from deconvoluted voltammograms agree well with that obtained from cyclic voltamm-ograms (Table 1).

It was observed that the height of the peak of deconvoluted transforms is proportional to the bulk concentration of the oxazole species, to the surface area of the electrode, and to the scan rate v. The peak shape is very dependent on n, the number of electrons transferred, as n increase, the peak is predicted to become narrower and much higher. As indicated in Fig.6 the peak width of the second peak is narrower than the first one confirming consuming of two sequential electrons in the second step. i.e the first one consume one electron and the second one consume two electrons with very close two reduction potentials for the two electrons transfer in the second peak. The peak height of deconvolution voltammogram was used for determination of the diffusion coefficient (D) Eq.(10) [13-16].

$$e_p = \frac{an^2F^2vC^{bulk}D^{1/2}}{3.367RT} \qquad (10)$$

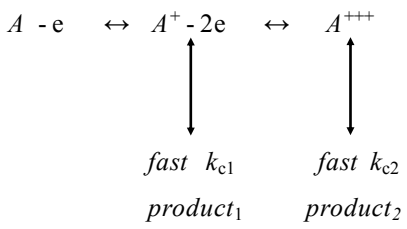
where e_p is the height of peak (in ampere) of the oxidative deconvolution sweep and the other terms have their usual definitions. Table 1 indicates the values of D calculated by equation 10.

From definition of convolution and deconvolution voltammetry, Eq. (11) was established.

$$n = \frac{e_p 3.367RT}{\alpha F \nu I_{\lim,}}$$
$$n = \frac{0.086 e_p}{I_{\lim} \alpha \nu} \quad (11)$$

where the symbol *n* is defined as the number of electrons involved in the electrode reaction, and the other symbols have their usual definitions. The total number of electrons involved in the electrode reaction was calculated from Eq. (11) and found to be 1.1 for the first wave and 2.08 for the second one i,e the total n is 3.18 (≈ 3). The successful determination of n using Eq. 11 without knowing the area of electrode surface is considered a simple and accurate method. From the above discussion it was found that, the convolution and deconvolution voltammetry were easier to support, interpret and confirm the nature of mechanistic pathway of electrode reaction.

According to the above discussion, the mechanistic pathway of the electrode reaction of anthracen-9-ylmethylene-(3,4-dimethyl-isoxazol-5-yl)-amine can be suggested to proceed as follows:



i.e. *ECEC* mechanism.

4. CONCLUSION

The electrochemical behavior of isoxazol derivative in 0.1 M TBAP /CH_3CN at a platinum electrode takes place as two oxidative anodic peaks (A & C) coupled with two small reductive peaks (B & D). This behavior demonstrates that the first charge transfer produces a radical cation that loss another two electrons to form a trication. The good matching between experimental and theoretical cyclic voltammograms were used for confirmation the accuracy of the electrochemical parameters determined experimentally. The mechanistic pathway of electrode reaction was suggested to behave as *ECEC* mechanism.

5. ACKNOWLEDGEMENT

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