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Der Pharma Chemica, 2014, 6(2):42-50
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Cyclic voltammerty study of schiff-base ligand and the effect of groups substitutes on potential and electroactivity

Talib Esmail Al-Salih and Rusul Widad Al-Taha

Chemistry Dept., College of Education for Pure Science, Basrah University, Iraq

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ABSTRACT

The electron transfer process accrue during the applied potential on a series of organic derivative compound. These derivation give us a chance to see the different in potential and activity behavior of these compound during their study, which has followed by using cyclic voltammetry technique wave to explain the chance happen in these different compounds during and after the electron transfer process.

Keywords: Cyclic voltammetry , Schiff's base, Platinum electrode, Electrooxidation.

INTRODUCTION

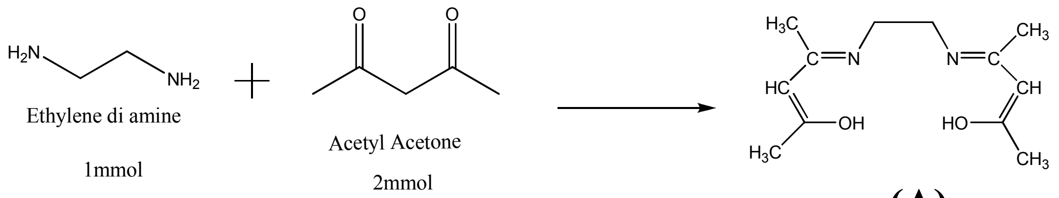
The cyclic voltammetry (CV), one of the voltammetric methods, is the most commonly used technique for acquiring qualitative and quantitative information about electrochemical reactions. It was first reported in 1938 and described theoretically in 1948 by Randles and Sevcik [1].This technique consists of scanning linearly the potential of a stationary working electrode between two chosen limits using a triangular potential waveform at a known sweep rate[2]. In this technique current flowing between the electrode of interest (whose potential is monitored with respect to a reference electrode) and a counter electrode is measured under the control of a potentiostat. The voltammogram determines the potentials at which different electrochemical processes occur. The working electrode is subjected to a triangular potential sweep, whereby the potential rises from a start value E_i to a final value E_f then returns back to the start potential at a constant potential sweep rate. The sweep rate applied can vary from a few millivolts per second to a hundred volts per second. The current measured during this process is often normalized to the electrode surface area and referred to as the current density. The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material [3,4]. Cyclic voltammetry makes possible the elucidation of the kinetics of electrochemical reactions taking place at electrode surfaces [5,6]. In a typical voltammogram, there can be several peaks. From the sweep-rate dependence of the peak amplitudes, widths and potentials of the peaks observed in the voltammogram, it is possible to investigate the role of adsorption, diffusion, and coupled homogeneous chemical reaction mechanisms [3,7].

MATERIALS AND METHODS

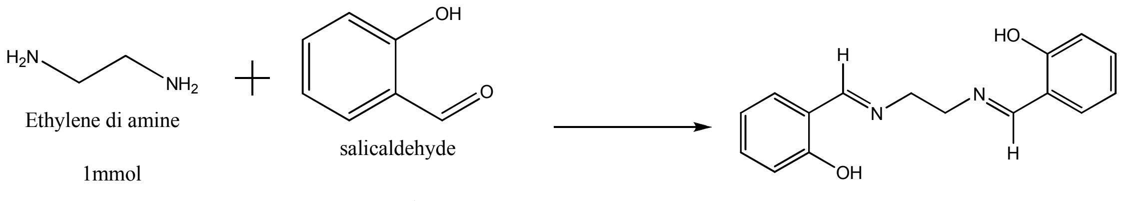
All chemicals : Acetyl Acetone(99.5%, Sigma-Aldrich), Methyl Acetoacetate (97%, Sigma-Aldrich), Salicaldehyde (99%, Merck), Ethylene di amine (99%, Merck), Ethanol (99.9%, Laboratory Reagent), Dimethylformamid (DMF) (99%, Laboratory Reagent), Tetrahydrofuran (THF) (99%, Laboratory Reagent), Methanol (99.9%, Laboratory Reagent).Double distilled water was always used to prepare aqueous solutions for electrochemical use.IR spectra (in KBr pellets) were recorded on IR Affinity-1shimadzu . Melting point were determined on melting point apparatus .^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Varian VNMRS 600 MHz solution-state NMR spectrometers. ESI–MS measurements were performed using VG Auto Spec-3000 magnetic sector MS spectrometer . Cyclic voltammograms were recorded on a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with a software GPES for Windows version 4.8. Electrochemical syntheses and studies were performed in a drybox under a dry nitrogen atmosphere. The electrochemical analysis have been carried out using a Pt (Platinum) as working electrode, SCE (saturated calomel electrode) as reference electrode, Ag/AgCl (Silver/Silver Chloride**)** as the auxiliary electrode The supporting electrolyte was 0.2 mM [tBuN][BF_4] (TBuNBF4), Tetrahydrofuran (THF) as solvent at a scan rate of 200 mV/s. All measurements were performed at room temperature (23 ±2 °C).

Preparation of (2Z,2'Z,4E,4'E)-4,4'-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))dipent-2-en-2-ol (A) :
To a solution of 1 mmol of Ethylene di amine was mixed with 2mmol of Acetyl Acetone in 25 ml of ethanol. The resulting mixture was left under reflux for 3 – 6 h and the solid product formed was separated by filtration, purified by recrystallization from Water , washed with ethanol, and then dried[8,9]. The yield of the product was 90% and the product melts at 112C°, CHN analysis for $C_{12}H_{20}N_2O_2$; C, 64.26; H, 8.99; N, 12.49; O, 14.27 Found; C 64.25; H 8.97; N 12.47; O, 14.25, IR (KBr) ; (cm-1) : 3165 (>O-H), 2916 (>C-H), 1604 (>C=N-)[10,11], δH ($CDCl_3$) (1.91) ppm (6H,s,$C\underline{H}_3C(N)=C$), (2) ppm (6H,s,$C\underline{H}_3CO$), (3.4) ppm (4H,m,$C\underline{H}_2$), (5.1) ppm (s,2H,$C\underline{H}$), (10.8) ppm (2H,s,$O\underline{H}$)[12]. ESI MS (m/z, % int.) 225.1597 (100) $[M+H]^+$[13].

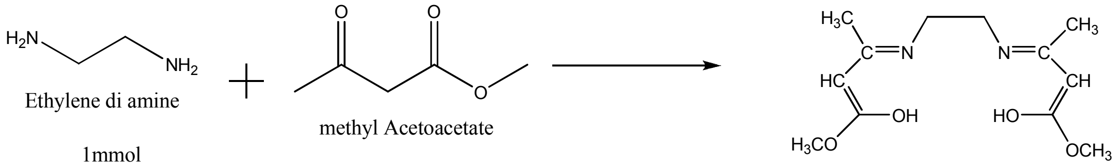
Preparation of 2,2'-(1E,1'E)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (B) :
To a solution of 1 mmol of Ethylene di amine was mixed with 2mmol of Salicaldehyde in 25 ml of ethanol. The resulting mixture was left under reflux for 2 h and the solid product formed was separated by filtration, purified by recrystallization from ethanol , washed with ethanol, and then dried[14,15]. The yield of the product was 93% and the product melts at 127C°, CHN analysis for $C_{16}H_{16}N_2O_2$; C, 71.62; H, 6.01; N, 10.44; O, 11.93 Found; C 71.61; H 6.00; N 10.40; O, 11.90, IR (KBr) ; (cm-1) : 3451 (>O-H), 3025 (>C-H, aromatic), 1635 (>C=N-),1577 (>C=C<, aromatic ring)[16,17], δH ($CDCl_3$) (3.92) ppm (4H,s,$C\underline{H}_2$), (6.84-6.90) ppm (4H,m,H_A & H_B), (7.30–7.35) ppm (2H,w,H_C), (7.40–7.43) ppm (2H,m,H_D), (8.60) ppm (2H,m,-HC=N-),(13.3) ppm (2H,s,OH)[18,19]. ESI MS (m/z, % int.) 269.1285 (100) $[M+H]^+$[20]



(A)

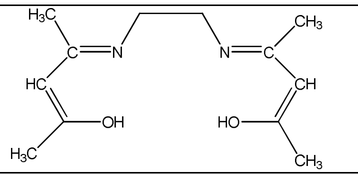
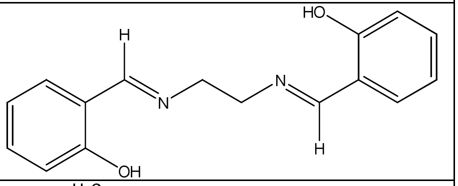
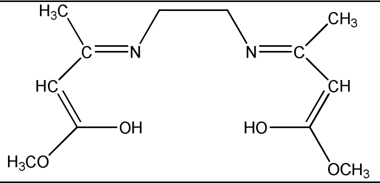


(B)



(C)

Table – 1 Physical constant of Schiff base compound

Name	Chemical Formula	m.p. (°C)	Color	Yield (%)	Structural formula
A	$C_{12}H_{20}N_2O_2$	112	Crystal White	90%	
B	$C_{16}H_{16}N_2O_2$	127	Crystal Yellow	93%	
C	$C_{12}H_{20}N_2O_4$	178	Crystal White	86%	

Preparation of (3E,5E,9E,11E)-5,10-dimethyl-2,13-dioxa-6,9-diazatetradeca-3,5,9,11-tetraene-3,12-diol (C) :
To a solution of 1 mmol of Ethylene di amine was mixed with 2mmol of Methyl Acetoacetate in 25 ml of ethanol The resulting mixture was left under reflux for 2 – 6 h and the solid product formed was separated by filtration, purified by recrystallization from Methanol , washed with ethanol, and then dried[21,22]. The yield of the product was 86% and the product melts at 180C°, CHN analysis for $C_{12}H_{20}N_2O_4$; C, 58.19; H, 7.51; N, 10.44; O, 23.85 Found; C 58.18; H 7.49; N 10.42; O, 23.83. IR (KBr) ; (cm-1) : 3134 (>O-H), 2947 (>C-H, aliphatic), 1591 (>C=N-)[23], δH ($CDCl_3$) (2.07) ppm (6H,s,C$\underline{H}_3$C(N)=C), (2.70) ppm (4H,m,C$\underline{H}$), (3.5) ppm (6H,s,C$\underline{H}_3$CO), (5.1) ppm (2H,s,C$\underline{H}$), (10.7) ppm (2H,s,O$\underline{H}$)[24]. ESI MS (m/z, % int.) 257.1140 (100) $[M+H]^+$[25].

RESULTS AND DISCUSSION

Electrochemical studies

The Cyclic Voltammetry was conducted at the beginning of the solvent (THF) with the supporting electrolyte [tBuN][BF_4] only , Where scan given the potential to distance and wide stretches of (-2.0 – +3.0 V) , Where did not show the presence of any material oxidation or reduction , which may interfere with the compounds to be studied along that space , As shown in Fig (1).

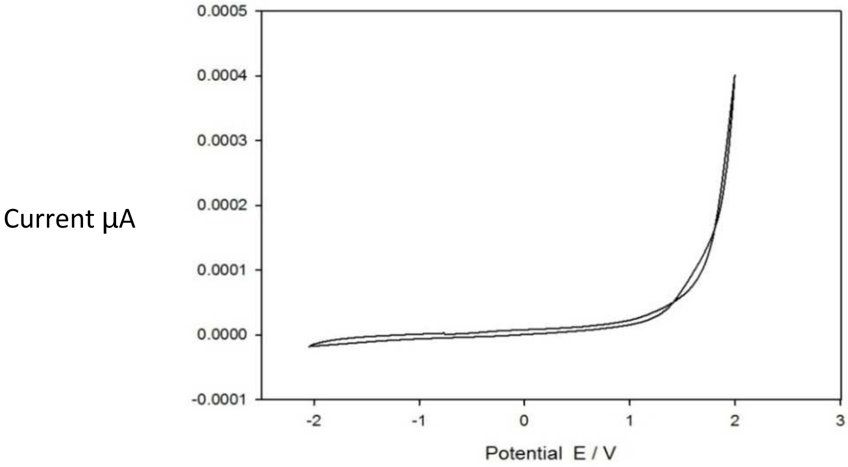


Fig.(1) – Cyclic voltammogram of 0.2mM solvent (THF) with the supporting electrolyte [tBuN][BF_4] on Pt electrode at 200mV/s Scan rate

Showed compounds (A), (B) and (C) irreversible oxidation and Quasi reversible in the negative, As shown in Fig (2) and (3).

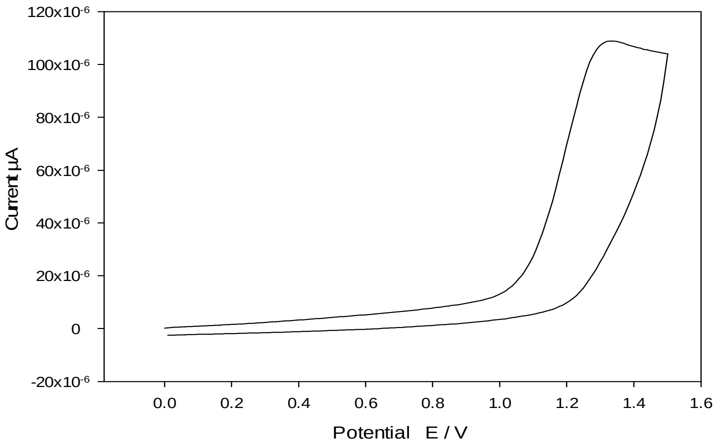


Fig.(2) – Cyclic voltammogram of Oxidation compound (A) in 0.2mM solvent (THF) with the supporting electrolyte [tBuN][BF_4] on Pt electrode at 200mV/s Scan rate

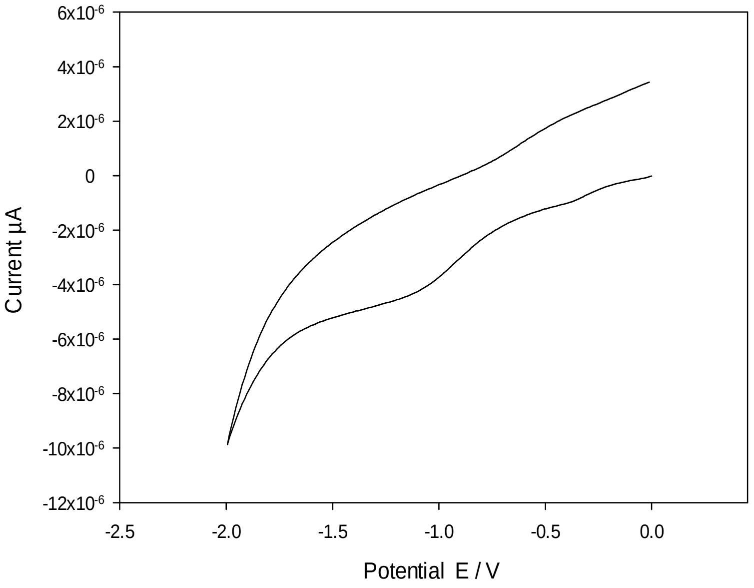


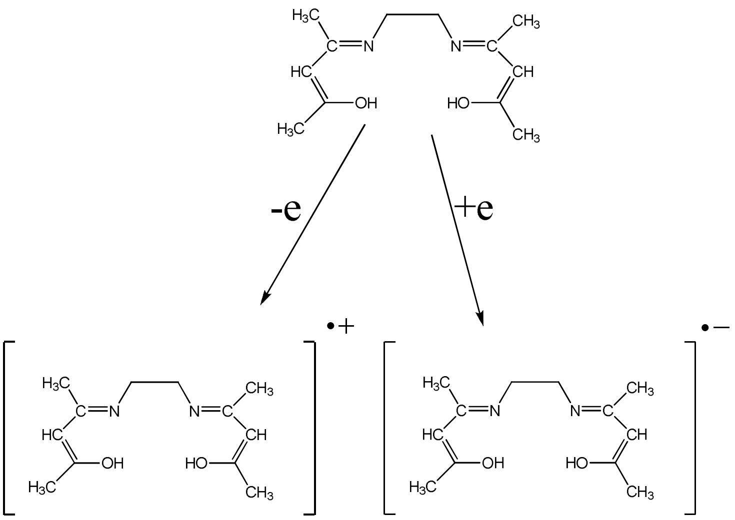
Fig.(3) – Cyclic voltammogram of Reduction compound (A) in 0.2mM solvent (THF) with the supporting electrolyte [tBuN][BF_4] on Pt electrode at 200mV/s Scan rate

This study has divided into two field , first the effect of electro activity on chemical reaction , and kinetic study of molecule behavior after both oxidation and reduction. All these compound have shown different reduction and oxidation which registered in table (4) using Ferrocene material as referenced material with calomel electrode. The first electron transfer process was evidences in chronoamperiometric technique to prove then it is ECE reaction in a long rang scan of cyclic voltammetry[26].

Table (4) - Shows the values of Oxidation and Reduction of Schiff bases Compounds.

Compound	Reduction E_p^{Red1}	Reduction E_p^{Red2}	Oxidation E_p^{Oxd}
A	-0.955	-1.886	1.448
B	-0.413	0.975	1.381
C	-0.727	-1.916	1.532

Compound A as most of organic compound shows irreversible electro activity , In opposite to the inorganic compound which gives mostly sharp reversible couple of oxidation reduction in close potential area of about 60 mV for one electron transfer. This irreversibility related to the charge transfer especially in bulk molecule where resonance tack place in presence of charge[27]. compound A which shows electro activity in potential Oxidation peak at (1.448 V) and Reduction peak at (-0.955 V) on platinum and vitreous carbon electrodes[28]. respectively is represented in equation (1).



Equation (1)

This reaction is classified as EC reaction and it`s irreversible in which one electron involved in the transfer process and this is proved by a rotating electrode and chronoamperiometry[29]., As shown in Fig (5).

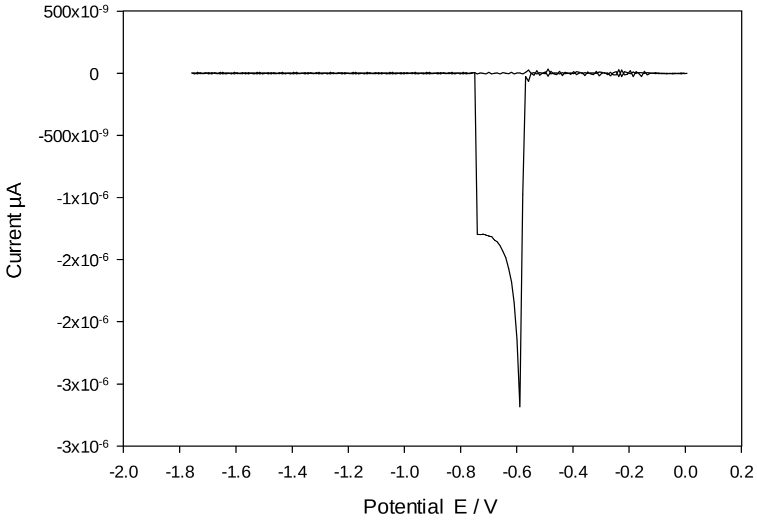
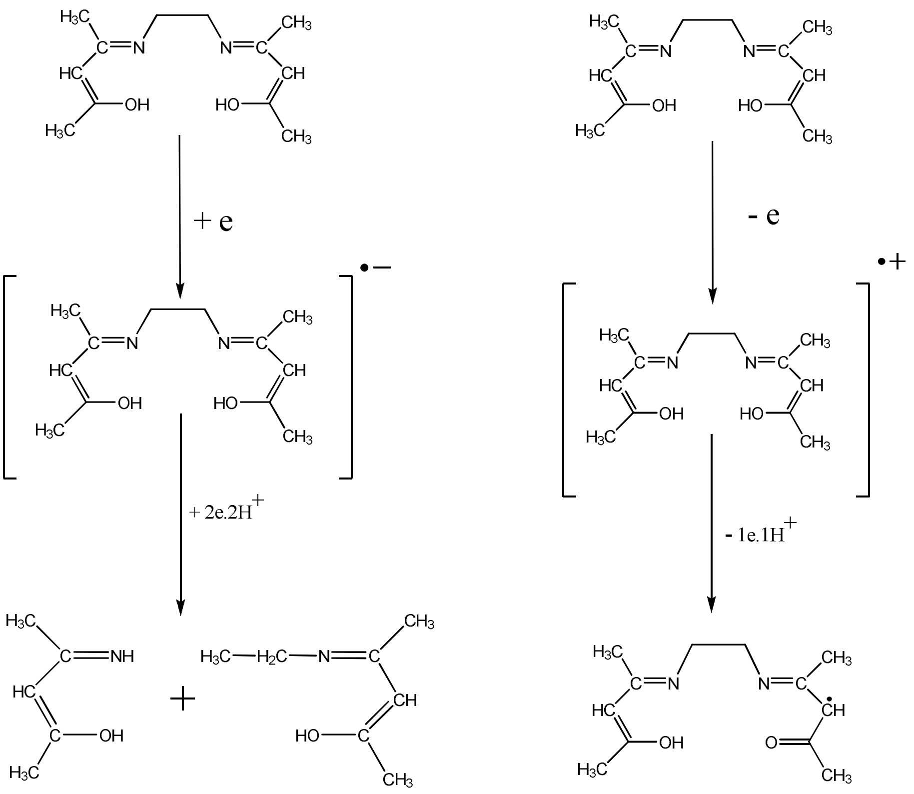


Fig.(5) – The transition processes from electrode area to Compound (A) in a solution of 0.2mM Supporting electrolyte [tBuN]$[BF_4]$ in the solvent (THF) at 200mV/s Scan rate using a technique Chronoamperometric

According to this irreversibility on can say that the intermediate is unstable in a very short time it has calculated in less than < 3 min so we have concentrate on the other possibility so the suggested mechanism shown Scheme (1) .[30,31]



Scheme . (1) Redox of Compound (A)

In a further negative potential Compound (A) shows a three irreversible reduction peak, As shown in Fig (6).

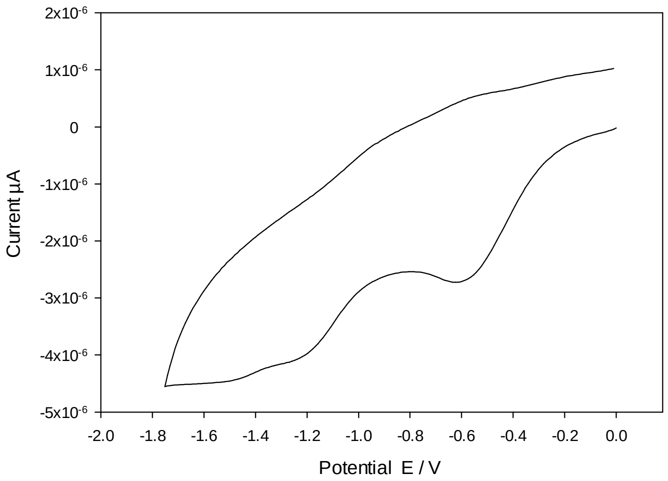


Fig.(6) – Cyclic voltammogram of Reducation compound (A) in 0.2mM solvent (THF) with the supporting electrolyte [tBuN][BF$_4$] on Pt electrode at 200mV/s Scan rate

There is a relationship between the current which flows at time t , i_t and that which Flows at time t +Γ=time hold, $i_{t+\Gamma}$ .This relation has elucidate in study[32]. As shown in Fig (7).

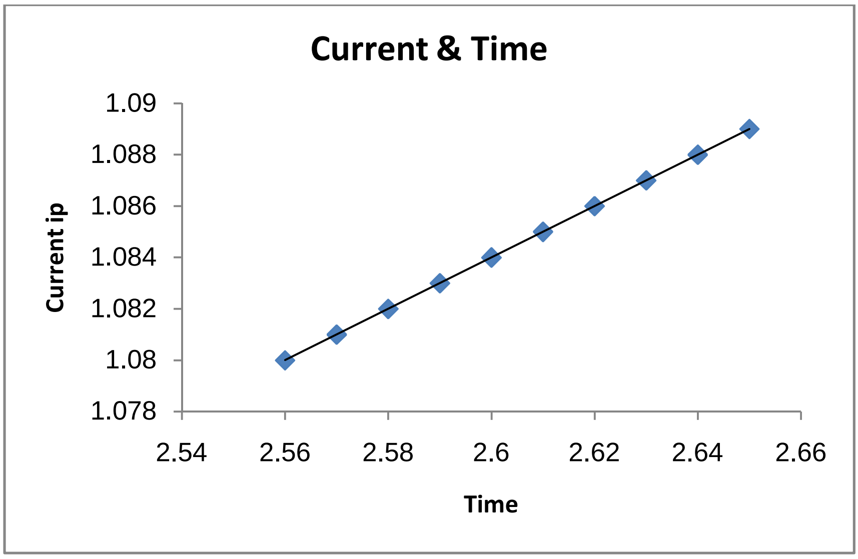


Fig.(7) – Graphic relationship between the output current with time starting from the oxidation process until they reach the top of oxidation in 0.2mM solvent (THF) with the supporting electrolyte [tBuN][BF$_4$] on Pt electrode at 200mV/s Scan rate

The ratio ($i_{t+\Gamma} / i_t$) is a function of time and stability of the electro generated products .Which was reflected in the back voltage scan as shown in figure (8) (this is showing the increase in production 3 scan). Current function wave F_p^{Oxd} have been measured using the same technique[33]. And Which is given by equation (2).

$$F_p^{Oxd} = i_p^{Oxd} / \upsilon^{1/2}$$

Equation (1)

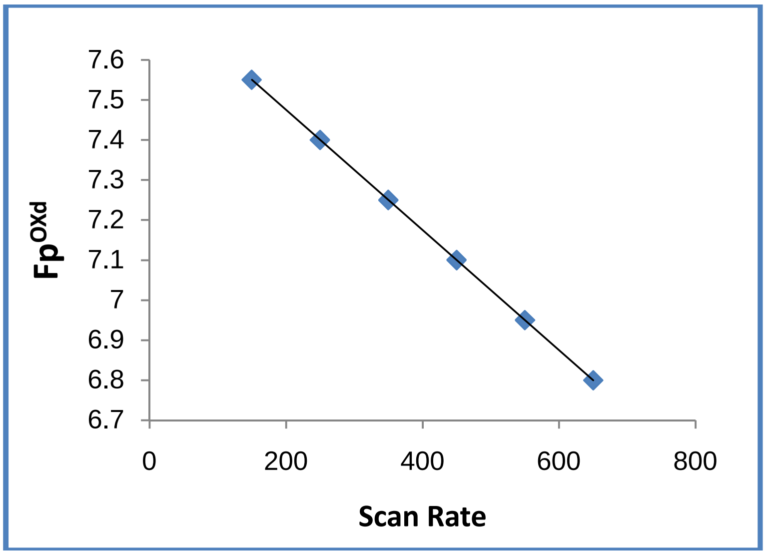


Fig.(8) – Graphic relationship between the Current function wave F_p^{Oxd} with Scan Rate at different scan rate (150,250,350,450,550,650) mV/s

Which was a result of search in different scan rate $\upsilon^{1/2}$. we have notes that current function wave is stable in a normal scan rate around (0.200 V/s) – (0.38 V/s) , but this is not the story when we come to scan rate over (500V/s) [34]., As shown in Fig (9).

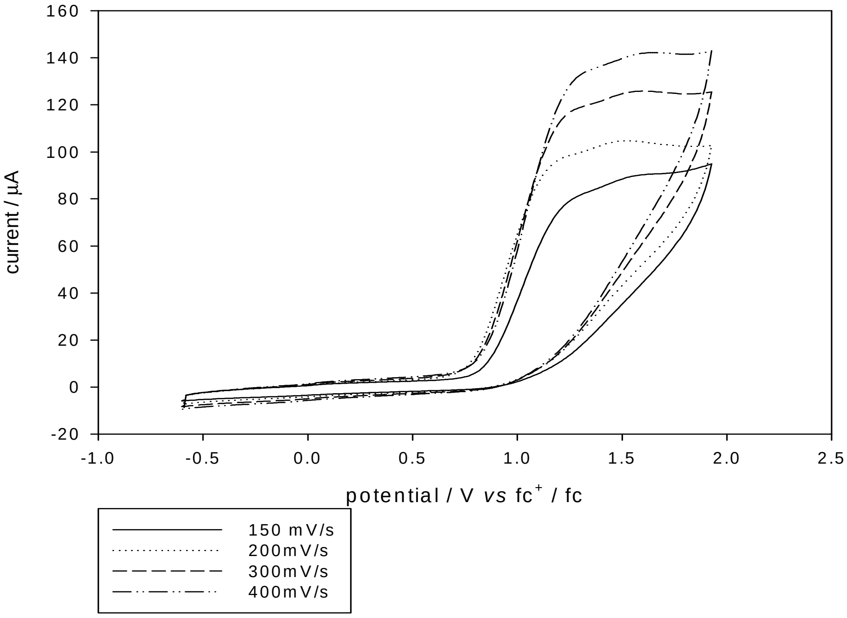


Fig.(9) – Cyclic voltammogram of compound (A) in 0.2mM solvent (THF) with the supporting electrolyte [tBuN][BF$_4$] on Pt electrode at different Scan Rate

CONCLUSION

From the previous data we conclude that both reduction and Oxidation of Compound A and B undergoes a one electron transfer reaction to give A$^{\pm}$. this step is diffusion controlled and electrochemically irreversible process . the potential of compound A and B and C, and it electro generated intermediate is listed in table (5) .Other have shows that the electro potential is shifted by moving from solvent to other , we have investigate our compounds in different solvent under different condition , and we have fond that these compound shows an equipment shift but these shift can be the same under calibration with reference electrode such as saturated calomel and silver-silver electrode ,standard with Ferrocene -ferocinium which have a fixed reversible oxidation coupled in 0.525 V.

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