Cyclic voltammetry Studies of bis [5-phenylazo-2-hydroxybenzaldehyde]-4, 4′-diiminodiphenyl ether and its amine derivative

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ABSTRACT: The azoimine ligand, bis [5-phenylazo-2- ydroxybenzaldehyde] -4, 4′-diaminophenyl ether **(2)** was synthesized by reducing the imine group of the azoimine form bis[5-phenylazo-2- ydroxybenzaldehyde] -4,4′-diiminophenyl ether **(1),** conducted by the condensation of 5-phenylazo-2-hydroxybenzaldehyde and 4,4′(diamino-diphenyl) ether. The compounds **(1)** and **(2)** were characterized using elemental analyses, IR, UV-Vis spectroscopy, ^{1}H NMR, ^{13}C NMR and mass spectra. The electrochemical study has been investigated by cyclic voltammetry technique.

KEYWORDS: Azo ligands, Reduction, Oxidation, Scan rate, Cyclic voltammetry.

RÉSUMÉ : Le ligand azoimimine, bis [5-phenylazo-2- ydroxybenzaldehyde] -4,4′-diaminophenyl ether **(2)**   a été synthétisé par réduction du groupe imine de sa forme azoimine [5-phenylazo-2- ydroxybenzaldehyde] -4, 4′-diiminophenyl ether **(1).** Elle est réalisée par condensation de 5-phenylazo-2-hydroxybenzaldehyde et 4,4′(diamino-diphenyl) ether. Les composés (1) et (2) ont été caractérisés par : analyse élémentaire, IR, spectroscopie UV-vis, RMN ^{1}H, RMN ^{13}C et spectrométrie de masse. L'étude électrochimique a été faite par la technique de voltammétrie cyclique.

MOTS CLÉS : Ligands Azo, Réduction, Oxydation, Vitesse de balayage, Voltamétrie Cyclique.

1. Introduction

Azo Schiff bases are commonly synthesized by coupling a diazonium reagent with an aromatic aldehyde to form an azo aldehyde [1, 2]. Aromatic azo compounds are widely used in various fields. For example, the azo compounds are used as organic dyes [3].Besides their use as dyes, showed antibacterial and antifungal activities [4-6]. In additon, Schiff bases are well known to have biological activites such as antibacterial [7-9] and herbicidal activities [10]. Schiff bases are used extensively as ligands in coordination chemistry [11, 12]. They have thermochromic and photochromic properties in their solid state they are also used the catalytic reactions, there are relatively few studies on the electrochemical behavior of imines or Schiff bases in aprotic media, a different mechanism was proposed in non-aqueous media where hydrolysis does not pose problems. In Schiff bases, the reduction potential is dependent on the size of the aromatic groups on either side of the –C=N– group, the types of substituent attached to the aromatic ring intra-molecular hydrogen bonds, It has also been claimed that the presence of electron withdrawing groups and hydrogen bonding facilitate the reduction. Schiff base ligands consist of a variety of substituents with different electron-donating and electron-withdrawing groups, and therefore may have interesting electrochemical properties [13].

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ATIA S., DOUADI T., DOUADI A. and LOUNAS A.

In the present study, the Schiff base **(1)** and its amine derivative **(2)** were synthesized and investigated by elemental analysis, FT-IR, UV–Vis, ^{1}H NMR, ^{13}C NMR and mass spectra in order to study their electrochemical properties in organic medium DMF- Bu_4NPF_6 10^{-3}M on a platinum support (diameter 2mm).
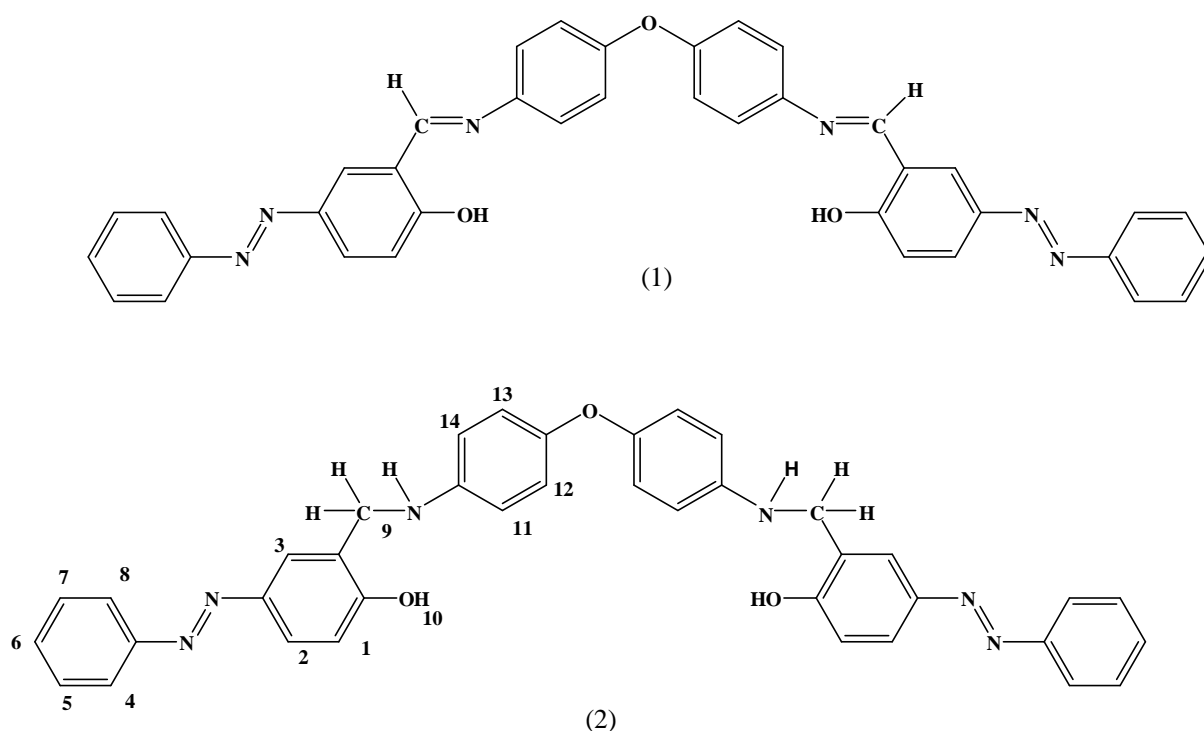

(1)

(2)

Figure 1: Synthesized compounds 1 and 2

2. Experimental:

2.1. Syntheses of the ligands: These compounds were prepared in a similar manner as previously described by Salem et al. [14].

2.1.1. Bis [5-phenylazo-2-hydroxybenzaldehyde]-4, 4'-diiminophenyl ether (1)

Yellow – Orange solid, yield 93.18 %, mp 256 °C. IR (KBr, cm-1): 3415 (OH), 3055 (C-H, aromatic), 2918 (C-H, aliphatic), 2846, 1618 (C=N), 1573 (C=C, aromatic), 1500 (N=N), 1349, 1272 (C-O), 1194 (C-N), 838, 686. Elemental analysis calcd (%) For ($C_{38}H_{28}O_3N_6$):   C 74.01, H 4.58, N 13.63, found: C 73.58, H 4.51 and N 13.45.

2.1.2. Bis [5-phenylazo-2-hydroxybenzaldehyde]-4, 4'-diaminophenyl ether (2)

Brown Solid, yield 83.80 %, mp 185°C. IR (KBr, cm-1): 3436 (OH), 3284 (N-H), 3033 (C-H, aromatic), 2922 (C-H, aliphatic), 2857, 1594 (C=C, aromatic), 1506 (N=N), 1251(C-O), 830, 683. Elemental analysis calcd (%) For ($C_{38}H_{32}O_3N_6$): C 73.53, H 5.20, N 13.54, found: C 73.17, H 5.53 and N 13.42. ^{1}H NMR(400 MHz, (CD3)2SO): δ = 10.49(s, H-10), 7.84 (br s, H-3), 7.76 (d, J = 7.6 Hz, H-4, H-8), 7.69 (d, J = 8.7 Hz, H-2), 7.51 (m, 3H, H-5, H-6, H-7), 7.00 (d, J = 8.6 Hz, H-1), 6.69 (m, J = 8.7 Hz, H-12, H-13), 6.55 (m, J = 8.8 Hz, H-11, H-14), 5.98 (br s, N-H), 4.22 (br s, 2H, H-9). ^{13}C NMR (400 MHz, (CD3)2SO): δ = 158.83, 152.29, 148.43, 145.17, 130.38, 129.29, 127.15, 123.20, 122.93, 122.04, 119.05, 115.35, 113.00. MS m/z (%): [M] $^+$ = 621, [M+nH] = 621, 622, 623.

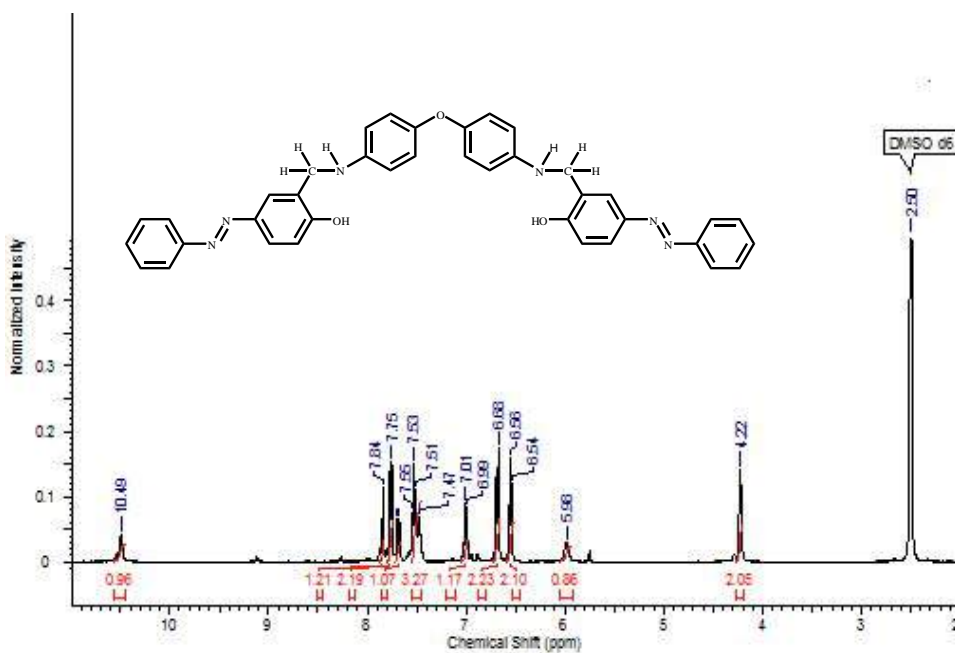The ^{1}H NMR and MS spectrums of ligand **(2)** are illustrated in Figs **2, 3** and **4**.
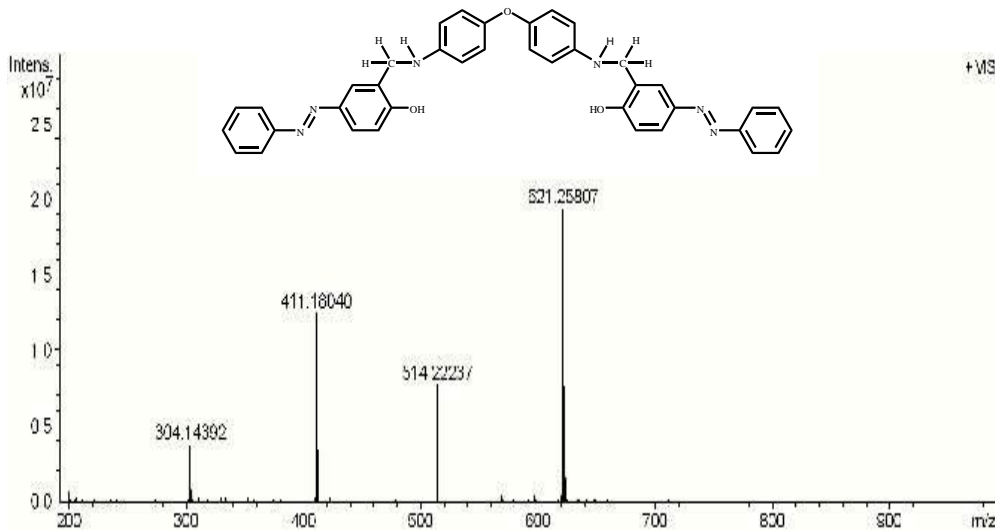
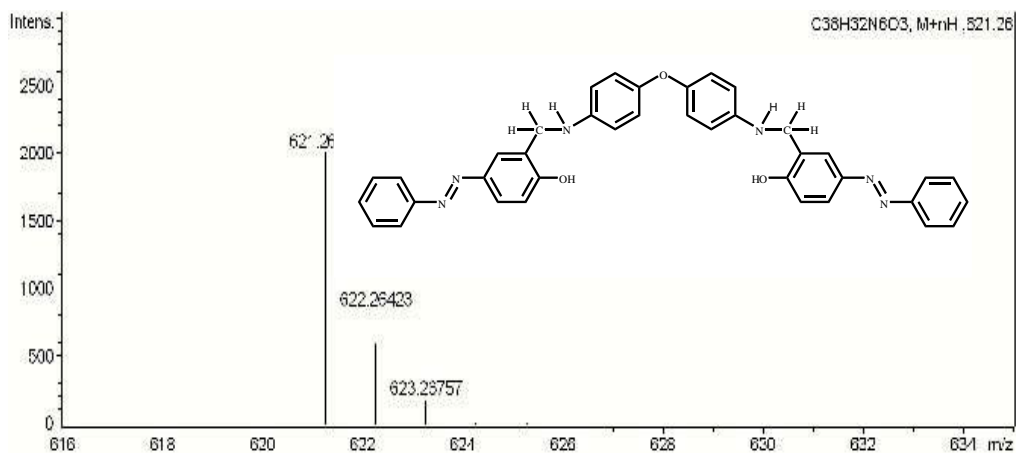**Figure 2: ¹H NMR spectrum of ligand (2)**

Figure 3: MS spectrum of ligand (2)

Figure 4: MS spectrum of ligand (2)

ATIA S., DOUADI T., DOUADI A. and LOUNAS A.

3. Electrochemical studies

Electrochemical experiments were carried out using a potentiostat type voltalab 32. All experiments were carried out in DMF. Cyclic voltammograms were recorded using an individual cell of 25 ml with a conventional three-electrode system in DMF containing 10^{-1} M Bu_4NPF_6. The electrodes were polished by diamond paste and rinsed copiously by acetone and then by DMF. Working electrode was a disc of platinum (diameter 2 mm) while the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). The experiments were carried out under a moisture free nitrogen atmosphere. Cyclic voltammetry was measured for a DMF solution of compounds **1** and **2** (10^{-3} M) at scan rates equal to 10; 25; 50; and 100 mV.s^{-1} (Figures **5** and **6**).
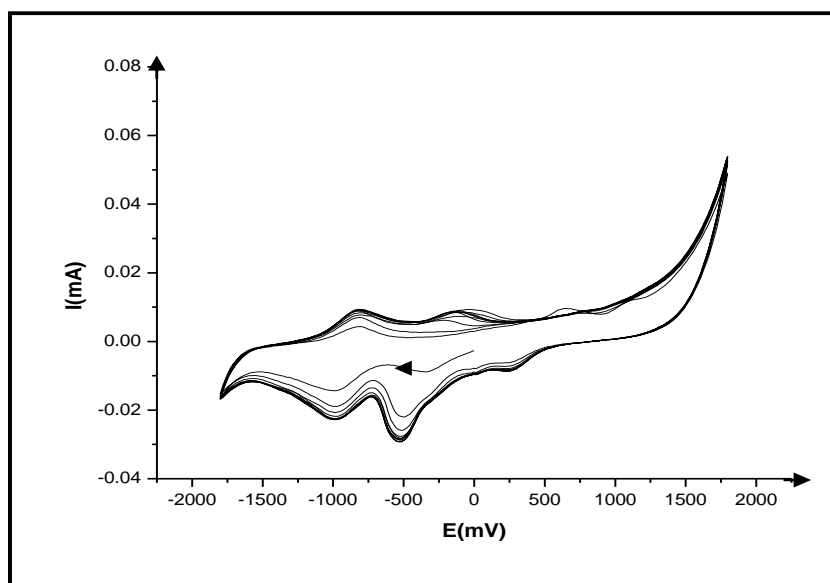

Figure 5: Cyclic voltammogram of a 10^{-3} M solution of ligand1 in DMF. Bu_4NPF_6 10^{-1}M at 100 mVs^{-1} (10 rings)
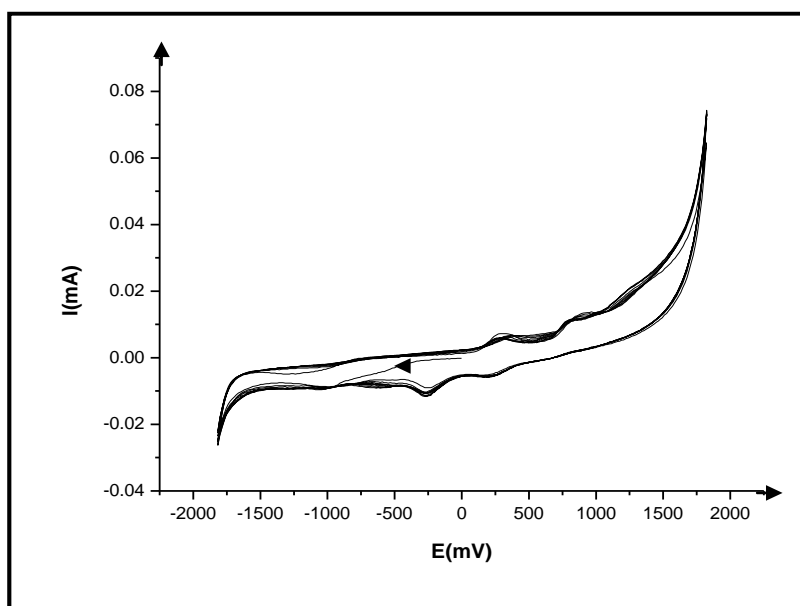

Figure 6: Cyclic Voltammogram of a 10^{-3} M solution of ligand2 in DMF. Bu_4NPF_6 10^{-1}M at 100 mVs^{-1} (10 rings)

3.1 Results and discussion

The reduction and oxidation properties of Azo ligands dyes (**1, 2**) were investigated by cyclic voltammetry at a scan rate of 100 mV s^{-1}. It can also illustrate an example of Figs. **5**, **6**. One cathodic peak was observed for (**2**) and two peaks for compound (**1**). Since the –N=N– group (all compounds) is more susceptible to reduction. Than the –C=N–, the –N=N– group is reduced at less negative potential than the –C=N group [15], appeared at -500, -250 mV/SCE, respectively, which was thought to belong to the reduction of the N=N group.

A new reduction peak, which was thought to belong to the reduction of the N=C group, appeared at –1010 mV/SCE on the cyclic voltammetry curve for compound (**1**). Anodic peak was observed for compounds (**1, 2**), appeared at 1250, 1330 mV/SCE, which was thought to belong to the oxidation of the O-H group [16]. Second anodic peak was observed, appeared at 760, 850 mV/SCE is attributed to the re-oxidation of azo group   -N=N- introduced in its reduction, Two Anodic peak was observed Appeared at 300 mV/SCE for compound (**2**) which was thought to belong to the oxidation of the N-H group. Electrochemical data of these compounds are given in Table1. The observation of this table can be seen on the one hand the potential movement of the cathodic and anodic peaks, Take for example, the change in oxidation potential of the O-H group of (**1**) and (**2**) between 1250 to 1330 mV/SCE. The change in reduction potential of the -N=N- group of compounds (**1, 2**) between -250 to -500 mV/SCE.

Table 1: Peak potential values of a 10^{-3} M solution of (1) and (2) in DMF. Bu_4NPF_6 10^{-1}M
Scan rate = 100m V s^{-1}

Dye	Compound	Oxidation		Reduction	
		Epa (mV/SCE)	Epc (mV/SCE)	Epa (mV/SCE)	Epc (mV/SCE)
1	$C_{38} H_{28} O_3 N_6$	**760**	/	/	**-500**
		1250	/	/	**-1010**
2	$C_{38}H_{32}O_3N_6$	**300**	/	/	**-250**
		850	/	/	/
		1330	/	/	/

3.2 Effect of scan rate

Effect of scan rate (Figure **7**) was studied by placing 10^{-3} M of compounds (**1, 2**) and was realized in organic medium DMF.Bu_4NPF_6 10^{-1} M in an electrochemical cell. It was studied by varying the scan rate from 10mVs[-1], 25mVs[-1], 50mVs[-1] and 100mVs[-1], Behavior of ligand (**1**) has been summarized in table **2** and Figure **8**.
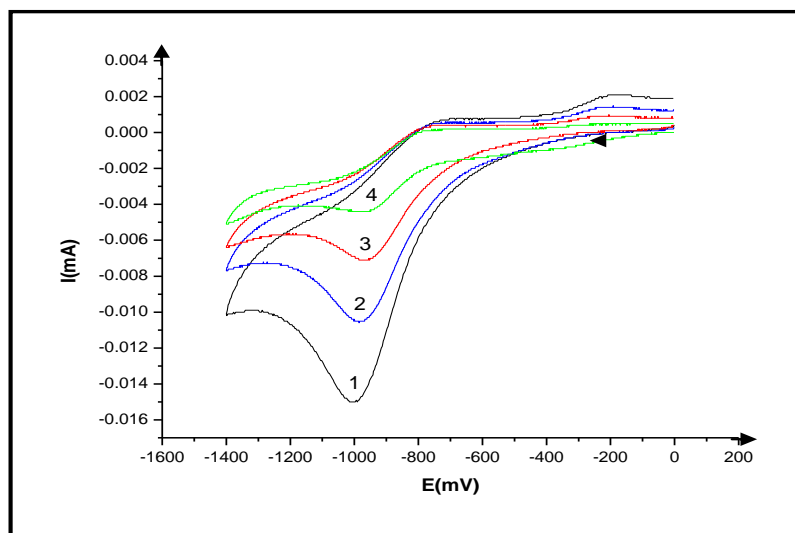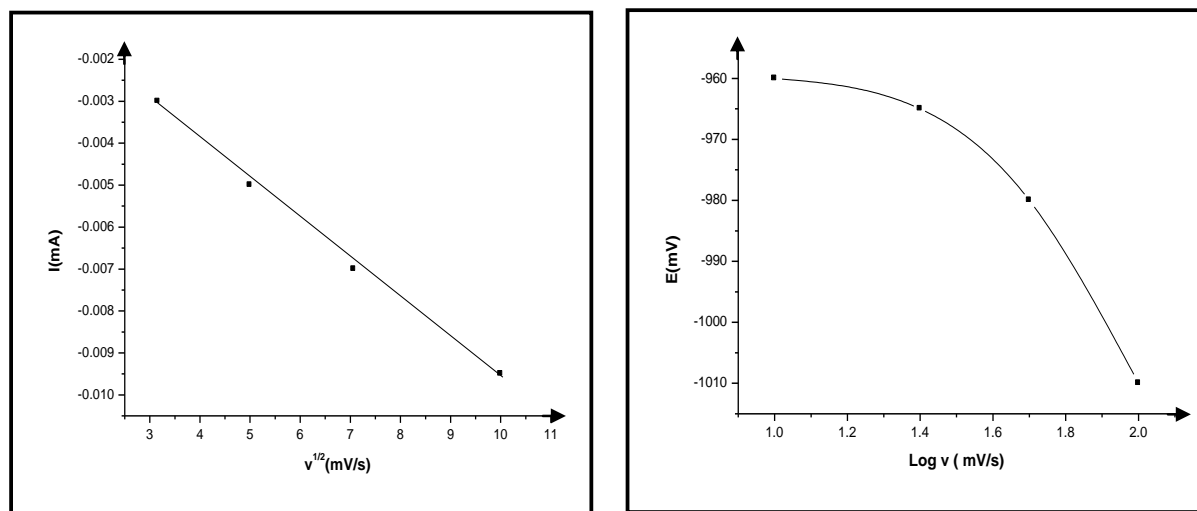

Figure 7: Cyclic voltammogram for the different scan rate of ligand (1)

ATIA S., DOUADI T., DOUADI A. and LOUNAS A.

Table 2: Electrochemical data for the reduction of ligand (1) in DMF.Bu$_4$NPF$_6$ 10^{-1}M

v (mVs^{-1})	v$^{1/2}$	Log v	E$_{PC}$	I$_{PC}$
10	3.16	01	-960	- 0.003
25	05	1.4	-965	-0.0055
50	7.07	1.7	-980	-0.007
100	10	02	-1010	-0.0095

Figure 8: Ipa = f (v$^{1/2}$) and Epa = f (logv) of a 10^{-3} M solution of ligand1
in DMF. Bu$_4$NPF$_6$ 10^{-1}M   at 10, 25, 50, 100 mVs^{-1}

The study of the variation of peak cathodic to support the conclusion that:
1. In the case **(1)** the study of the variation of peak cathodic to conclude allows the intensity of the peak current is proportional to the root of the scan rate is a straight line of slope equal to zero, on the other hand, the variation of the potential peak according to the decimal logarithm of the scan rate curve concavity facing the axis of rate, confirmed that the system is semi rapid governed by diffusion.
2. In the case **(2)** the study of the variation of peak cathodic to conclude allows the intensity of the peak current is proportional to the root of the scan rate curve concavity facing the axis of Speed therefore there is charge transfer associated with chemical reaction.

4. Conclusion

The electrochemical properties of azo ligands **(1, 2)** were investigated by cyclic voltammetry, the effect of scan rate, showed the system is semi rapid governed by diffusion controlled reduction process **(1)** and there is charge transfer associated with chemical reaction controlled reduction process **(2)**.

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