ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Cyclic Voltammetry Studies of Synthesized New Azo Schiff bases.

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ABSTRACT

Two new Schiff bases compound, namely bis [5-phenylazo-2-hydroxybenzaldehyde]-4,4'-diiminophenyl sulfanyl **(3)**, bis [5-(4-nitro-phenylazo)-2-hydroxy benzaldehyde]-4,4'-diiminophenyl sulfanyl **(4)**, have been prepared by condensation of Schiff bases (5-phenylazo-2-hydroxybenzaldehyde **(3)** or 5-(4-nitro)-phenylazo-2-hydroxybenzaldehyde **(4)** and 4, 4'-diiminophenyl sulfanyl in absolute ethanol. The two compounds were then characterized by IR, ^{1}H-NMR, ^{13}C-NMR and UV-Vis spectroscopies and elemental analysis. The electrochemical study has been investigated by cyclic voltammetry technique in organic medium DMF- $Bu_4NPF_6$0.1M On a platinum support of 2mm.

Keywords: Schiff bases, Reduction, Oxidation, Cyclic voltammetry.

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INTRODUCTION

Recently, many publications concerning azoaromatic compounds containing one or more –N=N- groups have appeared due to their biochemical and physicochemical properties[1]. These compounds play an important role due to their wide range of color, brightness, simplicity and ease of manufacturing and dyeing performance[3]. They are used in dyeing textiles, leather, paper, food, cosmetic products[4]. They are also used in high tech applications such as lasers and non-linear optical systems[5], photodynamic therapy[6], dye sensitized solar cells[7], metallo chromic indicators[8], thermal transfer printing and fuelcells[9].

Schiff base ligands consist of different electron-donating and electron-withdrawing have interested electrochemical properties[10,11]. A different mechanism for hydrolysis in non-aqueous media was proposed. The reduction potential for these compounds are 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 and intra-molecular hydrogen bonds. It has also been claimed that the presence of electron withdrawing groups and hydrogen bonding facilitate the reduction.

In the present study, we report our studies on the synthesis, characterization and electrochemistry of two Schiff base compounds **(3)** and **(4)**. All products were characterized by IR, 1H NMR and MS. The preliminary studies on the cyclic voltammetric behaviour of these compounds are also described.

EXPERIMENTAL

Reagents and Solvents

The chemicals (ethanol, aniline, hydrochloride, water, sodium nitrite, sodium carbonate, salicylaldehyde, 2-hydroxyben-zaldehyde, sodiumhydroxide, p-nitroaniline, sodiumchloride and 4, 4′ (diaminodiphenyl) sulfanyland) used for the synthesis were of spectroscopic gradeand was used without further purification.

Instruments

IR spectra were recorded on a Shimadzu 8000S FTIR spectrophotometer using KBr pellets. Nuclear Magnetic Resonance (^{1}H NMR, ^{13}C NMR) spectra were recorded on a Bruker (ARX-500) spectrometer (400 MHz) in DMSO-d6. The mass spectra were recorded on Os_MSMS_20CE.m, Acquisition SW6200 series TOF/6500, Version series Q-TOF B.O5.01 (B5125.1) mass spectrometer. The electronic spectra were obtained using Unicam Spectrophotometer. Elemental carbon, nitrogen and hydrogen analyses were performed witha Leco CHNS-932 analyzer. 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 2mm) while the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE).

Synthesis

Synthesis of 5-phenylazo-2-hydroxybenzaldehyde (1)

The azo-coupled **(1)** was synthesized using the known coupling methods[12, 13].

To a solution of 4.43 mL of freshly distilled aniline (0.05mol) in18.0 mL of concentrated hydrochloride and 20.0 mL of water, was added 4.00g of sodium nitrite 0.10 mol in 20mL of water. The reaction was carried out for 1 h below 5˚C. The reaction mixture was then added to a solution of 18.0g of sodium carbonate 0.17mol and 5.24 mL of salicyl aldehyde in 150 mL of water and the reaction was set within 0 ~5 ˚C. The yellow precipitate was filtered off after1h, and recrystallized in ethanol.

(1): Yellow solid, yield 63.09 %, mp128 ˚C.IR (KBr, cm^{-1}): 3100-3300 (OH), 3040 (C-H aromatic), 1664 (C=O), 1570 (C=C, aromatic), 1478 (N=N), 1380, 1284 (C-O), 1155 (C-N), 682.^{1}HNMR(400 MHz, $(CD_3)_2SO$): δ = 11.51 (s, H-9), 10.37 (s, H-8), 8.19 (d, J = 2.4 Hz, H-3), 8.10 (dd, J = 2.6, 8.8 Hz, H-2), 7.86 (m, 2H, H-4, H-7), 7.56 (m, 3H, H-5, H-R, H-6), 7.20 (d, J = 8.8 Hz, H-1).^{13}CNMR (400 MHz, $(CD_3)_2SO$):δ = 118.19, 122.14, 122.39, 123.51, 129.22, 129.51, 130.92, 144.57, 151.63, 163.08, 190.35. Elemental analysis calcd (%) For ($C_{13}H_{18}O_2N_2$): C 69.02, H 4.46, N 12.38, found: C 68.76, H 5.04 and N 12.29.

Synthesis of 5-(4-nitro-phenylazo)-2-hydroxy benzaldehyde (2)

The azo-coupled **(2)** was synthesized using the known coupling methods[14].

2-hydroxyben-zaldehyde 10 mmol was dissolved in distilled water 30 mL containing 8.8 mmol of sodiumhydroxide and 40 mmol of sodium carbonate over 30 min at 0 ~5˚C. The resulting solution was added slowly to the solution of diazonium chloride of 1.38 g 10 mmol of p-nitroaniline in water at 0 ~5˚C.The reaction mixture was stirred for 1 h at 0 ~5˚C and then allowed to warm slowly to room temperature. The product was collected by fltration and washed with 100mL of NaCl solution 10% under vacuum. The obtained yellow is horange solid was dried under vacuum at 80 ˚C overnight.

(2): Brown solid, yield 73.28 %,mp184 - 186 ˚C.IR (KBr, cm^{-1}):3400 (OH), 3042 (C-H aromatic),1662 (C=O),1574 (C=C, aromatic),1481 (N=N),1375,1286 (C-O),1151 (C-N),680.^{1}HNMR(400 MHz, $(CD_3)_2SO$): δ = 11.77 (s, H-9), 10.37 (s, H-8), 8.41 (d; J = 8.8 Hz, 2H, H-4, H-7), 8.25 (s, H-3), 8.15 (d, J = 8.8 Hz, H-2), 8.06 (s, 2H, H-5, H-6), 7.23 (d, J = 8.9 Hz, H-1). ^{13}CNMR (400 MHz, $(CD_3)_2SO$): δ = 118.84, 122.99, 123.48, 124.91, 125.27, 130.27, 145.02, 148.36, 155.37, 164.55, 190.41. Elemental analysis calcd (%) For ($C_{13}H_{17}O_4N_3$): C 57.78, H 2.98, N 15.55, found: C 58.31, H 3.75 and N 14.88.

General procedure for synthesis of azoimine ligands (3) and (4)

The Azo compounds **(3)** and **(4)** was synthesized using the known coupling methods[15]

Two **(3)** and **(4)** were prepared in a similar manner.(0.005 mol) of 4, 4′ (diaminodiphenyl) sulfanyland 0.01 mol of **(1)** or **(2)** were refluxed in 100 ml absolute ethanol for 1h. The solution was then left at room temperature as a solid. The precipitate was filtered and washed with ethanol.

Bis[5-phenylazo-2-hydroxybenzaldehyde]-4,4′-diiminophenyl sulfanyl (3)

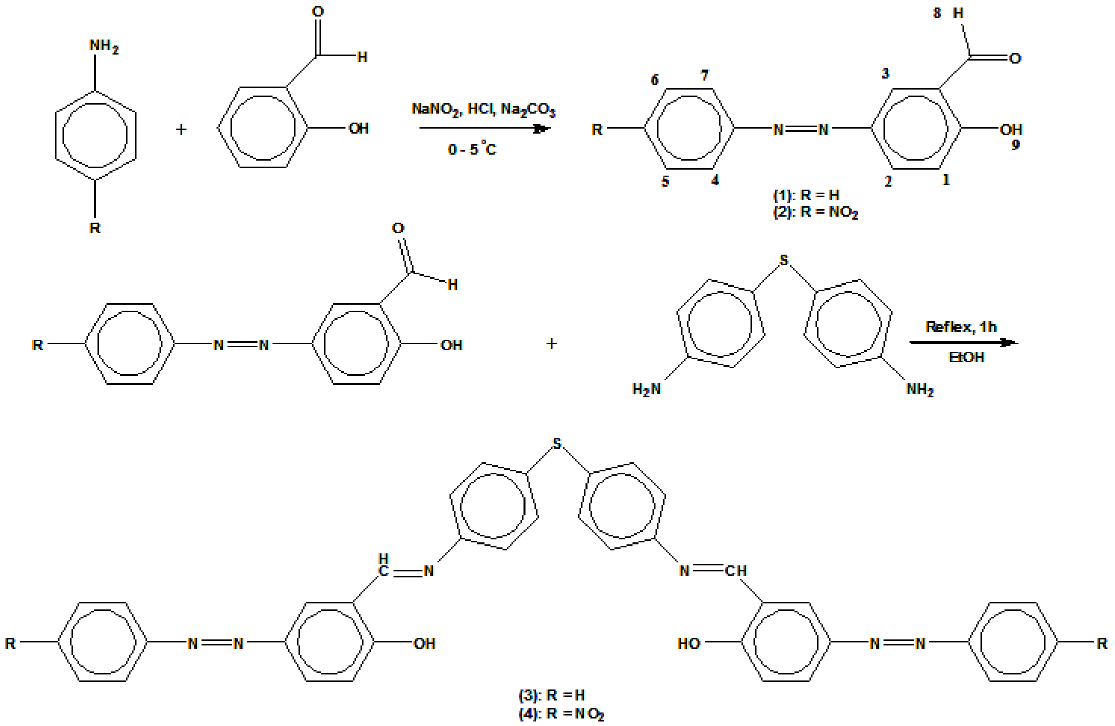
(3): Redaguri solid, yield 95.6 %,mp 244˚C.IR (KBr, cm^{-1}): 3300-3500 (OH), 3053 (C-H, aromatic), 2894 (C-H, aliphatic), 1614 (C=N), 1566 (C=C aromatic), 1486 (N=N), 1355, 1287 (C-O), 1180 (C-N), 691 (C-S),829, 685.Elemental analysis calcd (%) For ($C_{38}H_{28}O_2N_6S$): C 72.13, H 4.46, N 13.28, S 5.07 found: C 72.14, H 4.53, N 12.84 and S 4.57.

Bis[5-(4-nitro-phenylazo)-2-hydroxy benzaldehyde]-4,4′-diiminophenyl sulfanyl (4)

(4): Brown solid, yield 95.83 %, mp 297 ˚C.IR (KBr, cm^{-1}): 3100 (OH), 3055 (C-H, aromatic), 2918 (C-H, aliphatic), 2846, 1614 (C=N), 1560 (C=C aromatic), 1481 (N=N), 1347, 1275 (C-O), 1194 (C-N), 691 (C-S), 838, 686. Elemental analysis calcd (%) For ($C_{38}H_{26}O_6N_8S$): C 63.15, H 3.63, N 15.50, S 4.44 found: C 62.85, H 3.64, N 14.95 and S 3.87.

RESULTS AND DISCUSSION

Two compounds **(3)** and **(4)** were prepared in a similar manner by the condensation Schiff bases 5-phenylazo-2-hydroxybenzaldehyde **(1)**, 5-(4-nitro-phenylazo)-2-hydroxybenz -aldehyde **(2)** and 4, 4′ (diaminodiphenyl) sulfanylin absolute ethanol (scheme 1). These organic compounds can act as pentadentate N_2O_2S ligands were characterized by IR, UV-vis spectroscopy and lemental analyses and ^{1}H NMR, ^{13}C NMR.



Scheme 1.Synthesized azo compounds dyes (3 and 4).

FT-IR

In order to clarify the mode of bonding, the IR spectra of azo-compounds precursors **(1), (2)**, **(3)** and **(4)** were studied and assigned based on a careful comparison of the latter with the former. A strong band observed in the spectra of **(1)** and **(2)** at1662 cm^{-1} can beassigned to the (C=O) group. The total absence of (C=O) absorption in the IR spectra of **(3)** and **(4)** together with the appearance of new (C=N) absorption at 1614 cm^{-1}clearlyindicated that a new Schiff base ligand had formed in each case. The IR spectra of **(1)**, **(2)**, **(3)** and **(4**) show strong band at 1261–1286cm^{-1}assigned to the C–O stretching mode. The results are given in Table 1.

UV-vis

The UV-vis absorption spectra of the compounds **(1)**, **(2)**, **(3)** and **(4)** in DMF solution at ambient temperature are shown in (Fig. 1). The UV-vis absorption spectra of the compounds show two bands in the range 342 - 380 nm and 456 - 585 nm which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively[16].

^{1}H NMR and ^{13}C NMR

Nuclear Magnetic Resonance ^{1}H NMR, spectra results, obtained for all prepared compounds at ambient temperature in DMSO-d6, are presented the slightly broad signal at δ= 11.51and 11.77 ppm of compounds**(1)** and **(2)** is assigned to the OH protons. The CHO protons of compounds **(1)** and **(2)** exhibit a signal resonance at δ = 10.37 ppm. The spectra of compounds **(1)** and **(2)** show a signal resonance in the region δ = 8.41–7.20 ppm signal to the ring protons. The ^{13}C-NMR spectra of compounds **(1)** and **(2)** have 11 signals.

(Fig. 2 and 3) Shows the ^{1}HNMR and ^{13}C-NMR spectra for compound (1) as representative example.

Table 1: Tentative assignments of some selected IR (KBr, cm^{-1})

Compound	υ (O-H)	υ (N=N)	υ(C-O)	υ(C=C, ar)	υ(C=O)	υ(C=N)	υ(C-S)
1	3200	1478	1284	1570	1664	-	-
2	3400	1481	1286	1574	1662	-	-
3	3400	1486	1287	1566	-	1614	691
4	3100	1481	1275	1560	-	1614	690

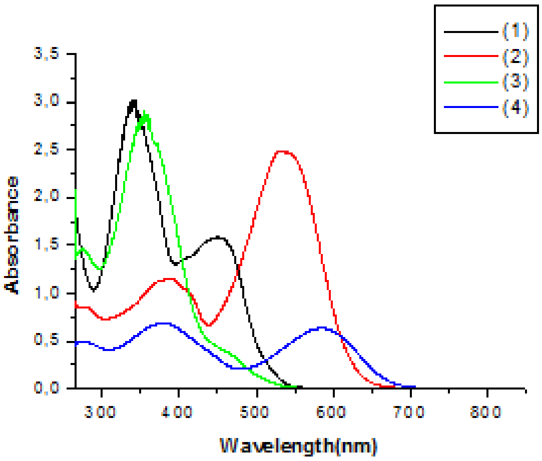


Figure 1: Absorption spectra of azo compounds dyes (1), (2), (3) and (4) in DMF

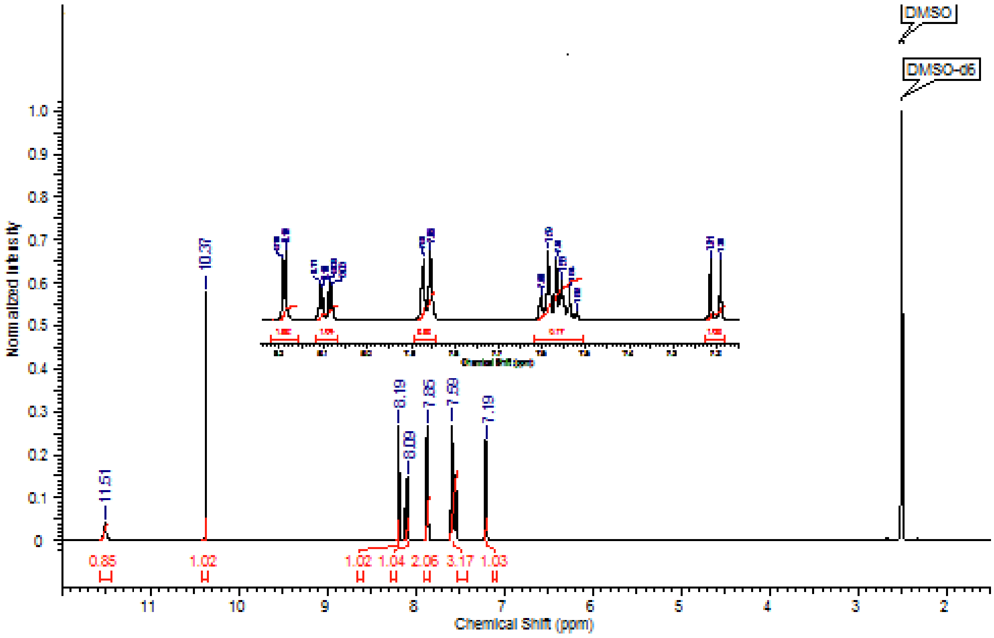


Figure 2: ^{1}HNMR spectra for the compound (1) as a representative example

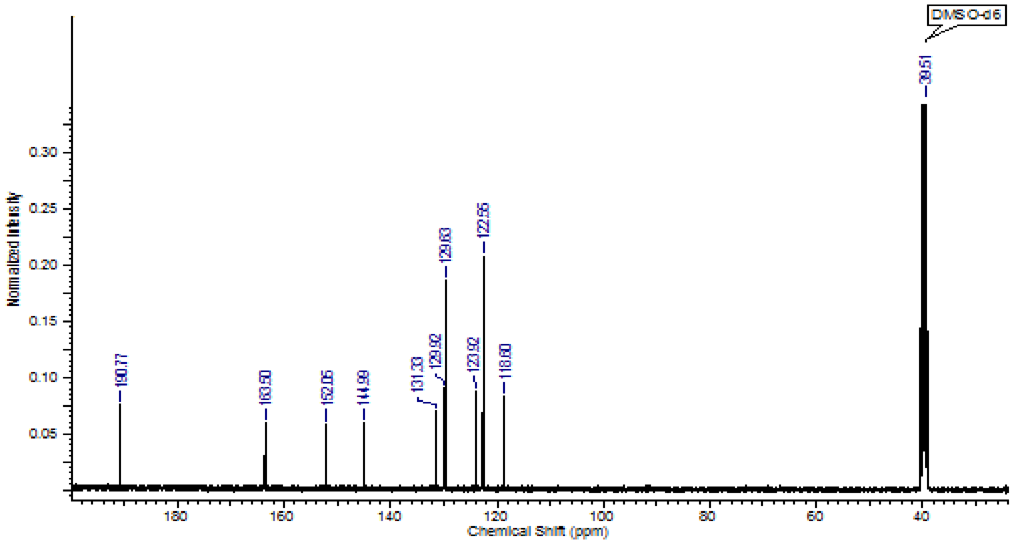


Figure 3: ^{13}C-NMR spectra for the compound (1) as a representative example

Cyclic voltammetry studies

The reduction and oxidation properties of Schiff bases compounds **(3)** and **(4)** were investigated by cyclic voltammetry at a scan rate of 100 mV s^{-1}**. (**Figure 4) shows the cyclic voltammogram for compound **(3)** as representative example and the data are summarized in Table 2. Two cathodic peaks were observed for compound **(3)** (Fig. 5a) and three peaks for compound **(4)**. It is known that the reduction of the –N=N– group is reduced at less negative potential than the –C=N group[11]. The two-one electron reduction peak at -350, -920 mV*vs.*SCE for compound **(3)** and at -395, -920 mV*vs.*SCE for compound **(4)** are assigned to the reduction of the –N=N– to produce –NH-NH- and reduction of group -C=N- to produce –CH-NH- respectively. The third reduction peak in compound **(4)** which appears at - 688mV*vs.*SCE is assigned to the reduction of the NO$_2$ group. The three anodic peaks at -412, 681, 838 mV*vs.*SCE for compound **(3)** (Fig. 5b) and at -420, 690, 856 mV*vs.*SCE for compound **(4),** the first anodic peak (-412, -420) are assigned to the re-oxidation of the –C=N group when it is reduced to -920 mV*vs.*SCE. The effect of scan rate (Fig. 6) was studied by placing 10^{-3}M of compound **(3)**. It was studied by varying the scan rate from 10mVs^{-1}, 25mVs^{-1}, 50mVs^{-1} and 100mVs^{-1}, the study of the variation of peak anodic confirmed that the system is rapid governed by diffusion **(3)** and the system is semi rapid governed by diffusion **(4).**

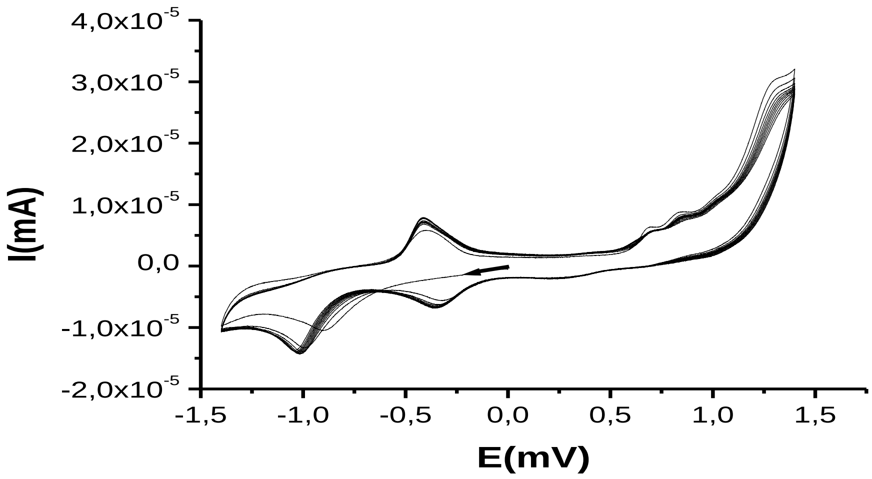


Figure 4: Cyclic voltammogram of a 10^{-3} M solution of compound (3) in DMF. Bu$_4$NPF$_6$ 10^{-1}M at 100 mVs^{-1} (20 cycles)

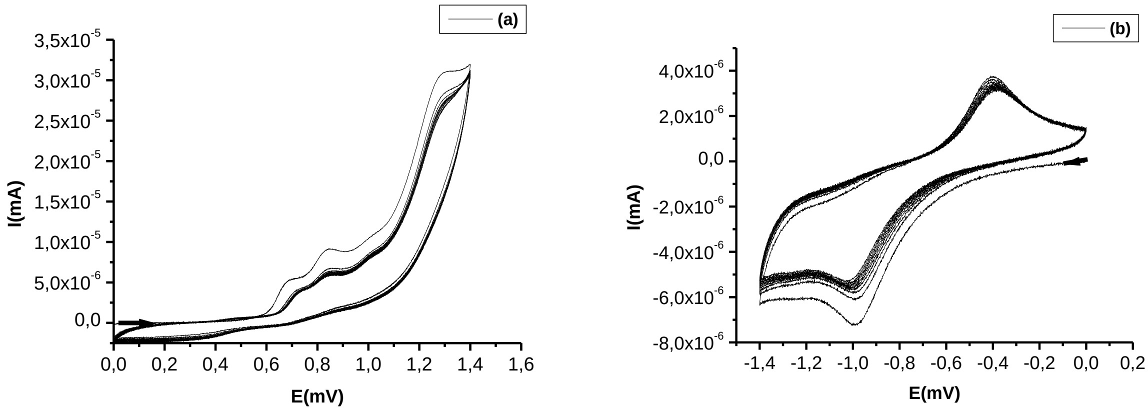


Figure 5: Cyclic voltammogram of a 10^{-3} M solution of compound (3) in DMF. Bu_4NPF_6 10^{-1}M at 100 mVs^{-1} (20 cycles), (a): [0 at 1400], (b): [-1400 at 0]

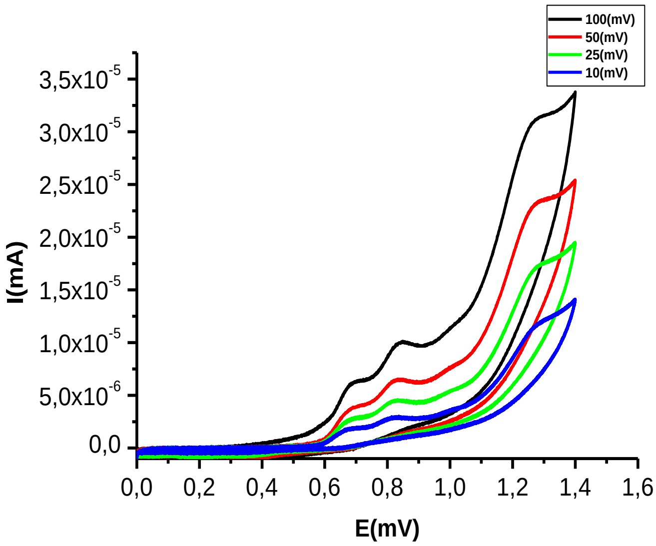


Figure 6: Effect the different scan rate of compound (3)

Table 2: Peak potential values of a 10^{-3} M solution of (3) and (4) Scan rate v = 100m V s^{-1}in DMF. Bu_4NPF_6 10^{-1}M

Compound	Oxidation		Reduction	
	E° (mV*vs.*SCE)	E° (mV*vs.*SCE)	E° (mV*vs.*SCE)	E° (mV*vs.*SCE)
3	838		-412	-350
	681			-1050
4	856		-420	-395
	690			-688
				-920

CONCLUSION

The present work was aimed at first to prepare two novel azo-containing Schiff bases namely bis[5-phenylazo-2-hydroxy benzaldehyde]-4,4′-diiminophenyl sulfanyl **(3)** and bis[5-(4-nitro-phenylazo)-2-hydroxy benzaldehyde]-4,4′-diiminophenyl sulfanyl **(4)**. Then the electrochemical properties of prepared azo-compounds **(3 and 4)** were investigated using cyclic voltammetry in an organic medium of DMF Bu_4NPF_6 10^{-1}M over a platinium electrode of 2 mm diameter. The results highlighted the reduction of azo (N=N) group within the 2 compounds **(3 and 4**) to (NH-NH) at 350 mV*vs.*SCE and **-**395 mV*vs.*SCE respectively. Regarding the imine group (C=N) it was subjected to a reduction followed by a reoxidation in both compounds. The study of the variation of anodic peak versus scan rate confirmed a rapid shift of the charge owing to the diffusion in the case of compound **(3)** and a semi rapid shift of the charge in virtue of the diffusion in the case of compound **(4).**

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