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Polarographic and voltammetric investigation of 6′-butoxy-2,6-diamino-3,3′-azodipyridine

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Abstract

Voltammetric and polarographic reduction on a hanging mercury electrode in aqueous-ethanol medium was performed for the 6′-butoxy-2,6-diamino-3,3′-azodipyridine by using SWV, DPP, DCP and CV techniques. Electrochemical behaviour of the azo compound has been investigated depending on ethanol–water ratio. From the polarographic and voltammeric data, electrochemical reduction mechanism has been suggested. Adsorption effect of the azo compound was investigated at different pH values. Optimum conditions are given for its polarographic and voltammetric determination. The limit determination using an HMDE was around 2.72×10^{-9} M for SWV.

Keywords: Azo dyes; Polarography; Voltammetry; Reduction mechanism

1. Introduction

Aromatic azo compounds constitute a very important class of organic compounds because of their widespread applications in many areas of technology and medicine. They are well known for their use as analytical reagents, in dye industry or as chemotherapeutic drugs [1–3].

Only a few heterocyclic dyes derived from azobenzene and containing an amino and pyridine groups conjugated with the aromatic system have been reported. The presence of conjugated bond system and chelating moiety gives rise to a considerable shift of the polarographic and voltammetric peak potentials and currents. Therefore such compounds can be used as metallochromic indicators. Electrochemical methods such as polarography and voltammetry are sufficiently informative tool for studying protolytic equilibria of compounds having a conjugated bond system in different solution media. It is known that *N*-substituted aminoazobenzenes can undergo protonation at the amino, pyridine and azo group. Proton addition induces reorganization of the conjugated bond system, so that different forms indicate different polarographic and voltammetric peak potentials and currents [4–12].

In this study polarographic and voltammetric behaviour of 6′-butoxy-2,6-diamino-3,3′-azodipyridine was investigated. The aim of this study is to explain the electrochemical reaction mechanism for the azo compound using square wave voltammetry (SWV), differential pulse polarography (DPP), direct current polarography (DCP) and cyclic voltammetry (CV) in different media. At the same time, the ionization constants were determined from the pH dependences of the electrochemical measurements and protolytic equilibria of the compound having a conjugated bond system in aqueous-ethanol medium. This compound has not hithetro been investigated by polarographic and voltammetric methods. The molecular structure of the azo compound is given as below (Scheme 1).

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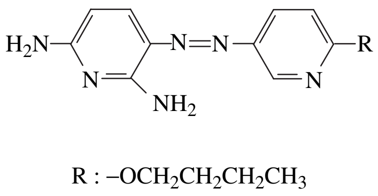


Scheme 1.

2. Experimental

6′-Butoxy-2,6-diamino-3,3′-azodipyridine (BADP) was obtained from Aldrich and was used without further purification. Boric acid, phosphoric acid, acetic acid and sodium hydroxide for Britton Robinson buffer were obtained from Merck product. All solutions were prepared using ultra pure water obtained by passing deionized water through a Milli-Q water purification system.

SWV, DPP, DCP and CV polarograms and voltammograms of the azo compound were recorded with a Metrohm VA 757 Computrace Electrochemical Analyser. A three electrode combination system was used. This consisted of a Multi Mode Electrode (DME, SMDE and HMDE), a Ag/AgCl reference electrode and a Pt wire auxiliary electrode. Pulse height of 50 mV and step height of 4 mV were used.

Solutions were degassed with nitrogen for 300 s prior to measurements and for an additional 5 s before each scan. A nitrogen atmosphere was maintained throughout the experiments. Each scan was done on a separate mercury drop at room temperature.

3. Results and discussion

The polarograms and voltammograms of the solution containing 3.85×10^{-6} M of the azo compound were taken in BR buffer solutions containing 50% ethanol at pH values between 2.0 and 12.0. BADP has one electrochemically reducible group that is azo group and its structure is shown in Scheme 1. Differential pulse polarograms and square wave voltammograms of 3.85×10^{-6} M BADP in BR buffer at different pH values are shown in Fig. 1. As shown in Fig. 1, peak currents and potentials are dependent on pH.

Differential pulse polarography and square wave voltammetry of the azo compound give one well-defined polarographic reduction peak I_c at the SMDE and HMDE at a sweep rate of 4 mV/s for DPP and 200 mV/s for SWV in aqueous-ethanol buffers in the pH range 2.0–10.0. The shape of peak I_c became broad at higher pH for DPP and SWV polarograms and voltammograms. The peak potential (E_p) of reduction peak I_c for the azo compound is dependent of pH in the pH range 2.0–12.0 studied as shown in Figs. 1 and 3.

Plots of peak potential (E_p) versus pH for 3.85×10^{-5} M of BADP are depicted in Fig. 2 for DPP and SWV. As the pH was gradually increased, the peak potential shifted towards more negative values.

As shown in Fig. 2, the dependence of the peak potentials of the BADP for SWV and DPP shows a break at a pH value of about 9.5–10.5. Below this value, a proton transfer precedes the electrode process above pH 10.5 the peak potentials are little pH dependent.

Generally the polarographic and voltammetric reduction of an organic compound can be represented by [13–16]:

$$\mathrm{O} + a\mathrm{H}^{+} + n\mathrm{e}^{-} = \mathrm{RH}a$$

The approximate relationship between E_p and pH for a reversible reaction at 25 °C is:

$$E_p = E^0 - 0.059(a/n)\,\mathrm{pH}$$

A plot of E_p against pH should be linear with a slope of $0.059a/n$ and an intercept corresponding to E^0 [17,18]. The linear pH dependence of the peak potential for SWV and DPP is given in Table 1.

The equations (Table 1) show that protons participate directly in the reduction process at pH 2.0–11.0. Fig. 2 indicates that the peak potential of the azo compound is constant at pH > 11.0 for DPP and SWV.

Protonation or deprotonation of the N atom in the aniline and pyridine groups is fast. Formally as shown in

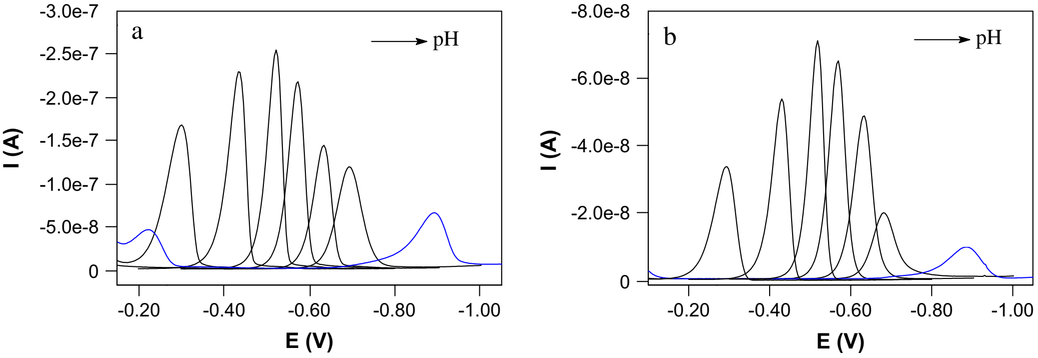


Fig. 1. (a) SWV (3.08, 5.03, 6.34, 7.09, 8.02, 9.36, 11.49) and (b) DPP (3.08, 5.03, 6.34, 7.09, 8.02, 9.36, 11.18) voltammograms and polarograms.

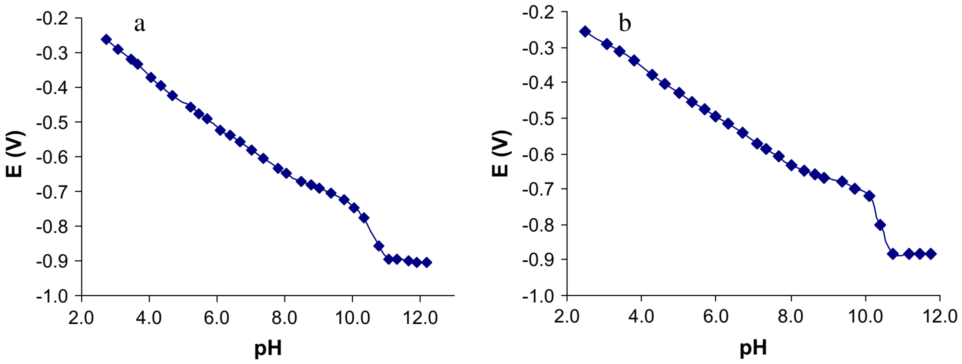


Fig. 2. Effect of pH on the peak potentials of (a) SWV and (b) DPP obtained for 3.85×10^{-6} M solution of BADP.

Scheme 2, these intermediates can be written as molecules which can be protonated on different sites. In Scheme 2 the protonations on the nitrogen atom have been represented preferentially on the nitrogen. These diverse forms can actually possess mesomeric structures which stabilize them [5,17,18]. Therefore the variation with increasing pH of equilibrium potentials consist of four linear segments with slope of −72, −40, −160 mV and ≅0 for SWV −69, −41, −254 mV and ≅0 for DPP (Figs. 2 and 9) indicating the different electrode reaction mechanisms.

Similar behaviour of currents and peak potentials relation with pH were observed in CV voltammograms compared with DPP and SWV (as given below).

The introduction of electron-donor groups in *o-o′*-positions complicates the reduction process of dyes and increases their irreversibility. The height of the reduction peaks of the azo compounds also increases because the rate of their protonization increases at pH 2.0–7.0 (Fig. 3).

3.1. The effect of ethanol

The potential peaks of reduction become negative and the height of the cathode peaks decreases with the increasing ethanol contents as shown in Fig. 4. The increase of ethanol concentration in aqua-ethanol mixes reduces proton-donor activity of water and reduces the rate of protonation. The rate of the electrode process strongly decreases in the case of the superficial reaction of protonization that precedes an electrochemical stage, because adsorption of the basic form of the depolarizer decreases [19–21]. It is confirmed by significant decrease of the rate criterion at the increase of ethanol concentration in solutions.

Table 1
Dependence of peak potentials on pH

pH range	Equation	R^2	Technique
2.0–8.0	E_p (V) = −0.0735–0.0727 pH	0.9969	SWV
2.0–8.0	E_p (V) = −0.0826–0.0687 pH	0.9997	DPP
8.5–9.5	E_p (V) = −0.3240–0.0407 pH	0.9942	SWV
8.5–9.5	E_p (V) = −0.2974–0.0414 pH	0.9513	DPP
10.0–11.0	E_p (V) = 0.8774–0.1606 pH	0.9806	SWV
10.0–11.0	E_p (V) = 1.8471–0.2536 pH	0.9982	DPP

3.2. DCP studies

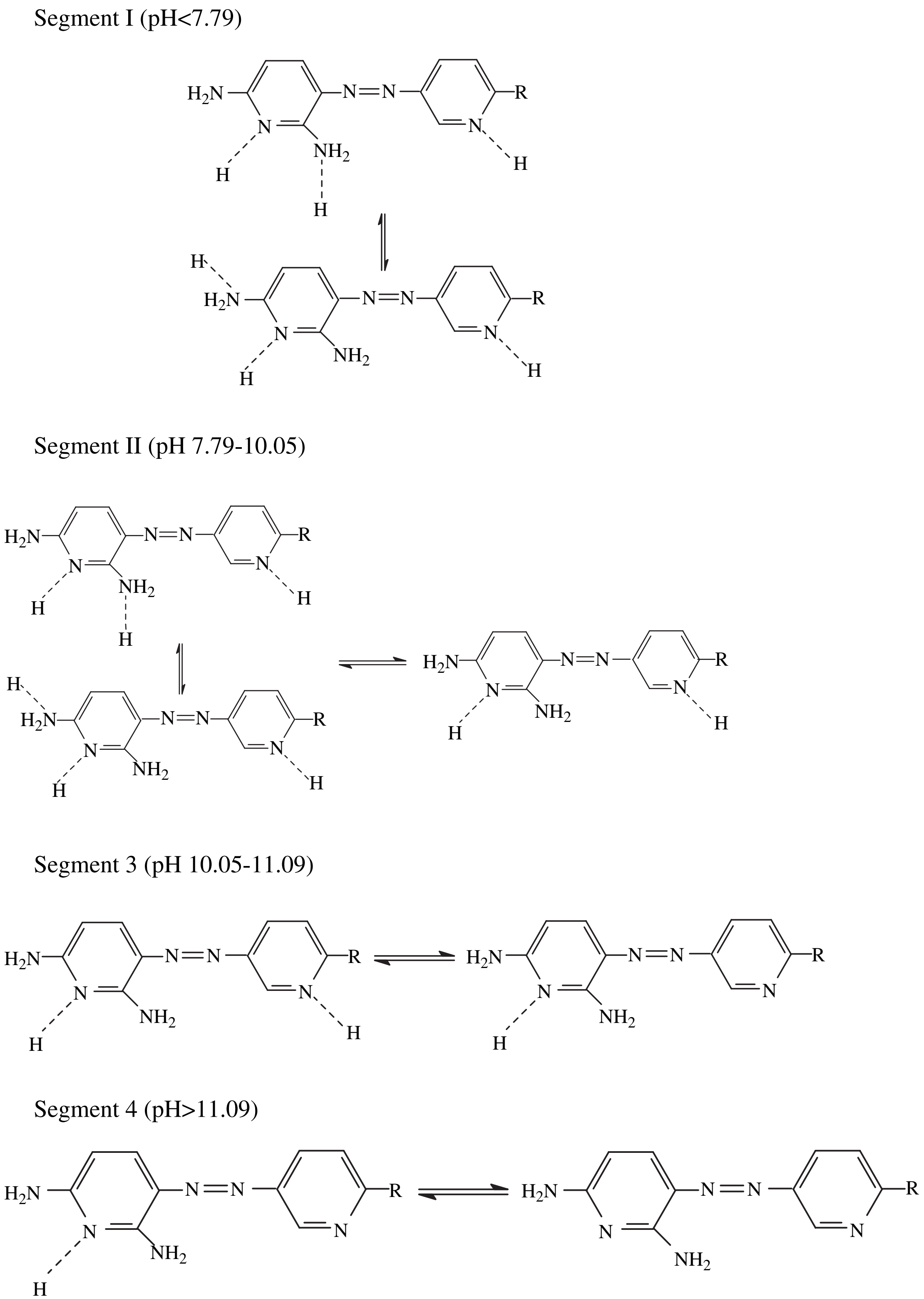
Fig. 5 shows typical DCP polarograms of the azo compound in BR buffer containing 50% ethanol; a well defined cathodic wave is produced. The reduction of the BDAP at HMDE was found to be pH-dependent. $E_{1/2}$ values were shifted to negative potentials upon the increase of pH. A plot of $E_{1/2}$ versus pH shows a region of linearity with a break at about pH as DPP and SWV.

Logarithmic analysis of the reduction waves obtained in BR buffer of different pH values (2.0–12.0) resulted in straight lines. The variable values of slopes do not prove that the reduction process is irreversible. The αn values were calculated according to the method of Heyrovsky Ilkovic equation [13–15]. At pH 2.0–11.0 αn values indicate that the electrode process consists of two electrons (Fig. 6). Also the plots of E_p–pH of the reduction wave of the BADP were straight line of slope values (S) reported in Table 1. The number of hydrogen ions (Z_H^+) participated in the rate-determining step was calculated using the slope values S_1 and S_2 of both the E_{dc} versus log (I/I_d-I) and $E_{1/2}$–pH plots, respectively. The estimated results indicated that two protons and two electrons (pH < 11.0) participated in the rate-determining step of the reactant centers [13–15].

3.3. CV studies

The cyclic voltammograms obtained for 3.85×10^{-6} M of BADP in BR buffer at pH 2.0–12.0 (scan rate 200 mV/s) are shown in Fig. 7. Only one well-defined reduction peak was seen in the range of potentials examined at pH 2.0–10.0; this can be assigned to reduction of the azo group. At pH > 10.0 CV voltammograms are broad.

To elucidate further the electrode reaction of the azo compund, a cyclic voltammetry at HMDE was recorded. As shown in Fig. 7, the cyclic voltammograms


Segment I (pH<7.79)

Segment II (pH 7.79-10.05)

Segment 3 (pH 10.05-11.09)

Segment 4 (pH>11.09)

Scheme 2. Equilibrium diagram for BADP.

of the azo compound in Britton Robinson buffer solution of pH 2.0–10.0 exhibit a single cathodic peak with no peak on the reverse scan, indicating the irreversible nature of the electrode reaction. The peak potentials (E_p) shifted to more negative values upon rise of each of the pH 2.0–11.0 which confirmed the involvement of protons in electrode reactions as DPP, SWV and DCP (Fig. 2) [15,16].

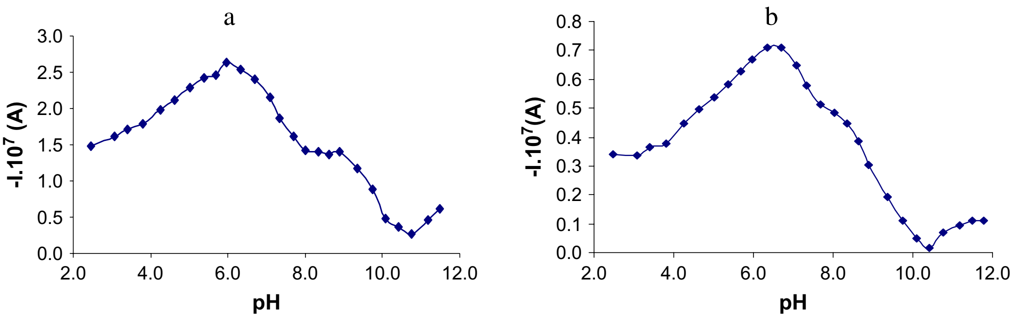


Fig. 3. Effect of pH on the peak currents of (a) SWV and (b) DPP obtained for 3.85×10^{-6} M solution of BADP.

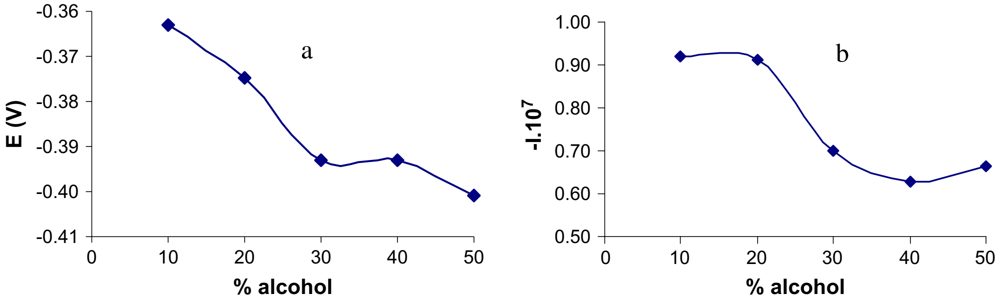


Fig. 4. Effect of the composition of the solvent on the (a) peak potentials and (b) peak currents in BR buffer at pH 7.0.

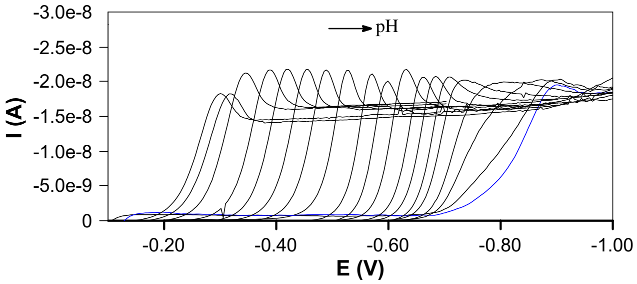


Fig. 5. Polarograms of the azo compound in Britton Robinson Buffer solution at pH 2.0–12.0, scan rate 4 mV/s, drop time 1 s, with SMDE and Ag/AgCl reference electrode.

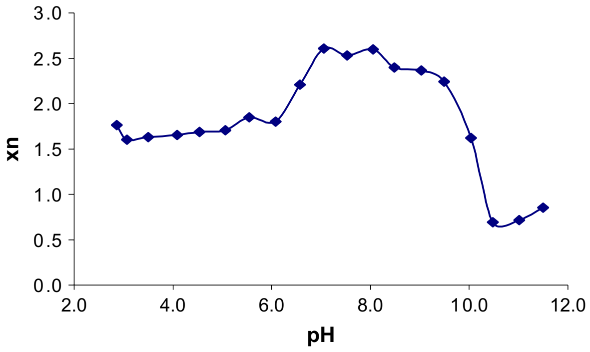


Fig. 6. The change of αn with pH for the BADP in BR buffer.

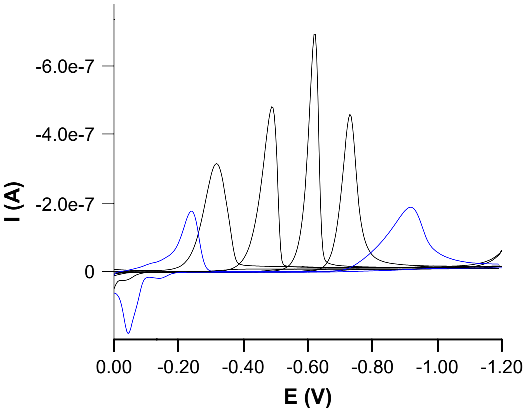


Fig. 7. CV voltammograms of the azo compound in BR buffer (pH 3.0, 4.5, 7.0, 9.5, and 11.0, scan rate 200 mV/s).

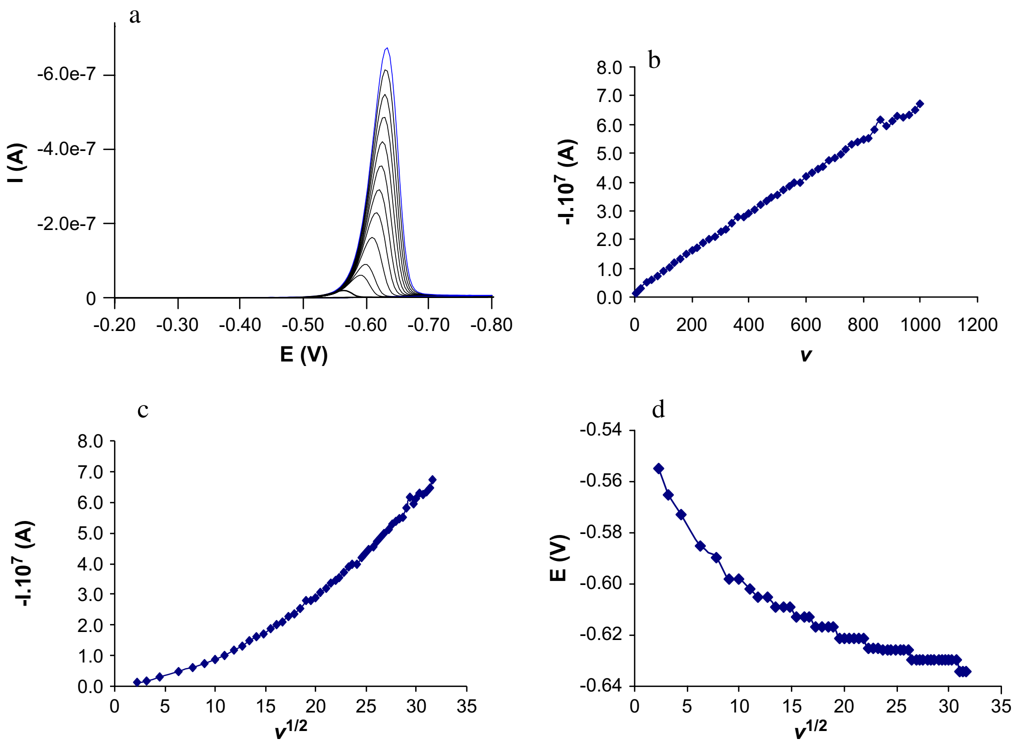


Fig. 8. (a) CV voltammograms at different scan rates at pH 7.0, (b) The change of peak currents with scan rate at pH 7.0, (c) The change of peak currents with root square of scan rate at pH 7.0, (d) The change of peak potentials with scan rate at pH 7.0.

In lots of studies, the oxidation of the hydrazo has been detected in the reverse scan at different potentials dependent on substituent effect and on the scan rate [4,5,6,11]. In the pH range of 2.0–12.0 the electrochemical reaction mechanism appears to be an irreversible process at all scan rates (5–1000 mV/s), as no current is observed in reverse scan for the BADP. In this situation it can be said that hydrazo form is unstable in studied pH values.

The peak current changes linearly with scan rate (v) according to equation $I_p = Av^x$. The x values 1.0 and 0.5 are expected for adsorption and diffusion controlled reaction, respectively. For 3.85×10^{-6} M BADP, the regression of $\log(I_p)$ versus $\log(v)$ gave a slope value of 0.78, indicating that the reduction current had contributions from both diffusion and adsorption currents [15,16]. As shown in Fig. 5, peak maxima were obtained in all the pH values at DCP polarograms. Generally adsorption effect of azo compounds appeared in lots of studies [2,4,9,10]. As scan rate was increased from 5–1000 mV/s the peak potential shifted towards more negative potential as expected for an irreversible reduction process (Fig. 8). The effect of scan rate on the peak potential and peak current was also analyzed by cyclic voltammetry on an HMDE. Upon analysis of the effect of scan rate, dependence of peak intensity on scan rate and the root square of scan rate were established within the range of scan rates studied (5–1000 mV/s). The change of I_p versus $v^{1/2}$ is not linear. With increase of scan rate, $I_p/v^{1/2}$ slope increases. This situation proved that the complex electrochemical electrode reaction of the azo compound occurs on the electrode surface. Such behaviour is adopted as indicative of EC mechanism in previous studies [4,5–10].

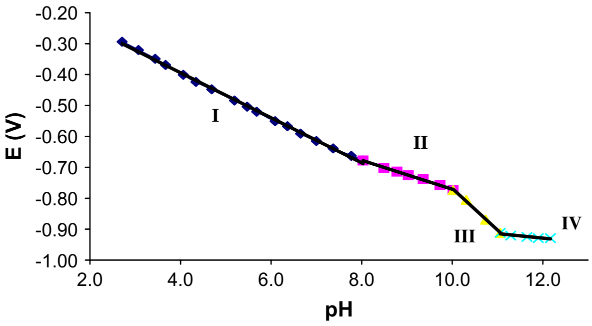


Fig. 9. Effect of pH on the cathodic peak potentials of CV.

Dependence of peak potential and peak current with pH arises from different mesomeric forms. It is priori difficult to attribute different protonations form of the azo compound since protonations can occur either on pyridine nitrogen or on the aniline nitrogen. However, protonation on the nitrogen pyridine rings should increase the stability as given different mesomeric forms in Fig. 9 and Scheme 2. As given in

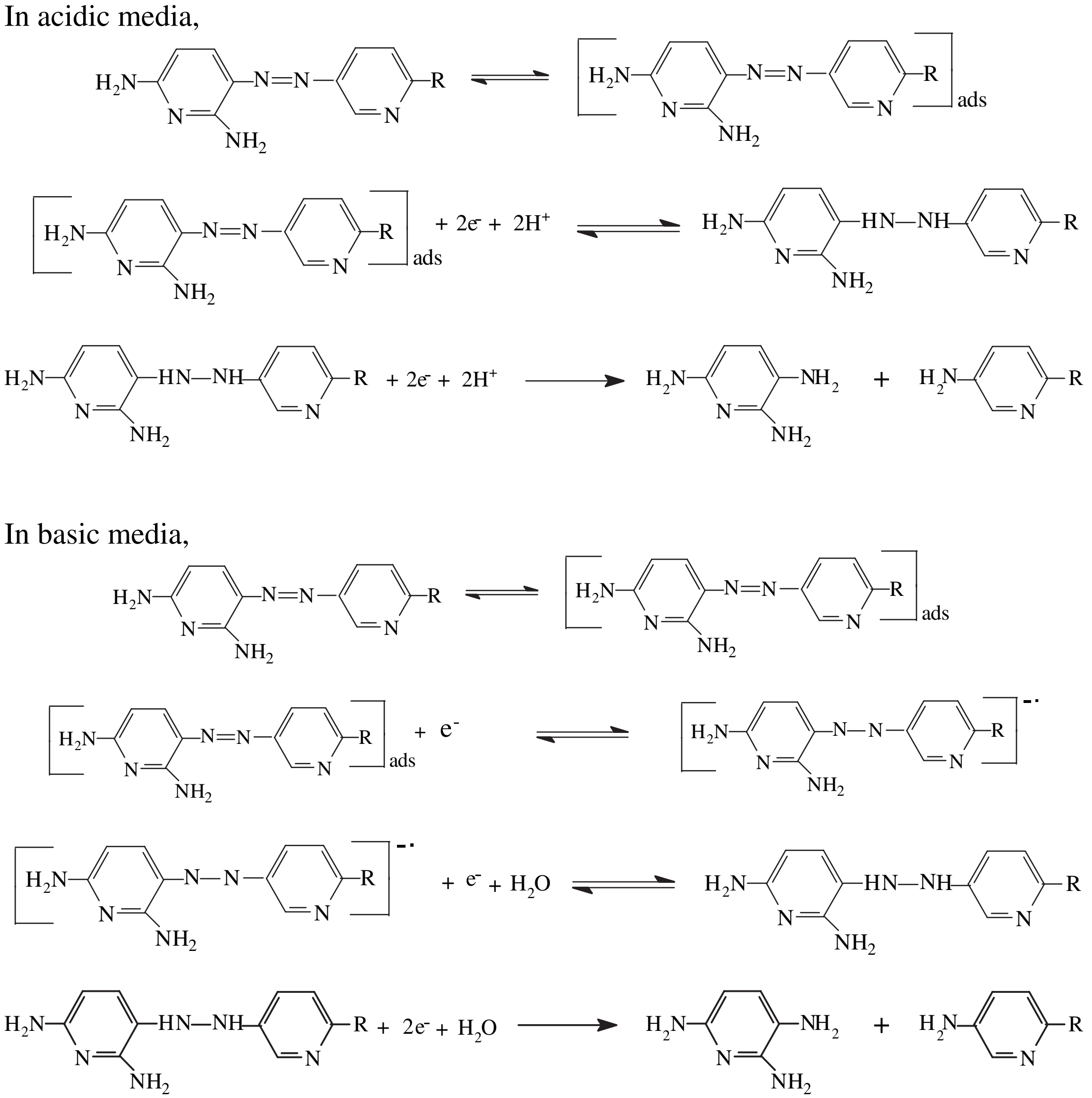
Scheme 2 forms are in agreement with literature values [1,2,4,22–25].

From polarographic and voltammetric measurements (SWV, DPP, DCP and CV) it is known that the reduction of aromatic azo compounds containing electron donating substituents, such as hydroxy and amino groups involve a clevage of the azo bridge to yield the corresponding amines [4,5–10]. It is therefore reasonable to assume that the majority of the azo compound studied here is reduced to corresponding amines at all the pH values. The cleavage of the azo bridge should be a four-electron process while a reduction to hydrazo compound should involve only two electrons. These results are appreciably supported from SWV, DPP, DCP and CV polarograms and voltammograms. According to SWV, DPP, DCP and CV techniques, the reduction mechanism can be suggested in Scheme 3.

3.4. Determination of BADP

The redox property of the azo compound on the electrode is influenced by the variations of pH values. Therefore pH is a critical factor for determination of the azo compounds. On the other hand the pH of the test solution also affects both linear range and detection power.

The DPP polarograms and SWV voltammograms showed improved peak currents compared to the DCP. SWV has been preferred because of its convenience in analytical applications. The solution condition affects the enhancement of the peak currents. It was observed



Scheme 3. Reaction mechanism diagram for BADP.

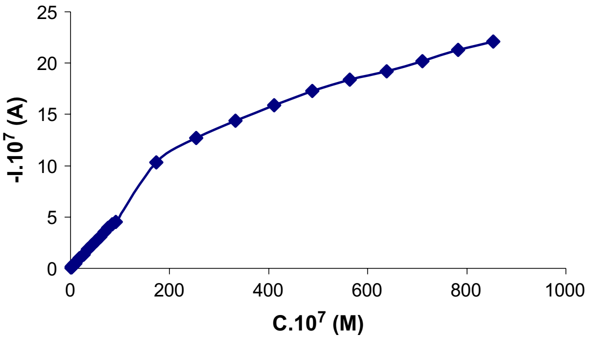


Fig. 10. Calibration graph for different BADP concentrations at pH 7.0 in BR buffer solution.

Table 2
The calibration curve (I_p–C), linear detection limit for BDAP

pH	Calibration curve	R^2
3.0	$I_p = 0.0250 + 477{,}999C$	0.9989
4.5	$I_p = 0.0952 + 511{,}694C$	0.9966
7.0	$I_p = 0.0014 + 514{,}616C$	0.9999
9.5	$I_p = 0.0302 + 200{,}775C$	0.9988
11.0	$I_p = 0.0095 + 917{,}480C$	0.9998

that SWV technique was suitable for analytical purposes among the techniques in question in this work (Fig. 1). Various pH solutions of Britton Robinson buffer such as pH 3.0, 4.5, 7.0, 9.5 and 11.0 were examined. Under the above experimental conditions, the linear regression equations, detection limits were determined show the dependence of the peak current of the azo compound on the pH value. Because of the decrease in the peak currents of the azo compound, pH > 8 is not convenient for quantitative determination. When the pH was greater than 7 the current decreased rapidly. In the pH range 6.0–7.5 the peak current was approximately constant. In our experiments pH was kept at 7 using Britton–Robinson buffer for determination of BADP. A plot of currents against concentrations is linear between 2.79×10^{-9} and 2.00×10^{-5} M (Fig. 10). The peak current reaches its maximum value at pH 6.0–7.5. selected as optimum value for quantitative determination of BADP. Different calibration graph data are summarized in Table 2. It shows that slope is bigger and intercept is smaller for pH 7.0.

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