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Polarographic and voltammetric investigation of 3-allyl-4-hydroxyazobenzene

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Abstract

The polarographic and voltammetric behaviour of 3-allyl-4-hydroxyazobenzene was studied at room temperature using various electrochemical techniques. In this study, the electrode reaction for the azo compound were investigated using SWV, DPP, DCP and CV. The reduction of the azo group to amino group in acidic media and hydrazo step in neutral and basic media was observed. From the observation an electrode reaction mechanism has been suggested for the compound.

Keywords: Voltammetry; Polarography; Azo dyes

1. Introduction

Azobenzene derivatives have been the most widely used class of dyes due to their versatile application in various fields, such as dyeing textile fiber biomedical studies, advanced application in organic synthesis and high technology areas as laser, liquid crystaline displays, electro-optical devices and ink-jet printers [1–3]. At the same time azo dyes are also used in colouring agents in foods and pharmaceuticals etc. Therefore a study of the mechanism of the polarographic and voltammetric of the azo group is worthy of investigation [4,5].

Polarographic and voltammetric studies of azo compounds were mainly concerned with aromatic azo compounds because of (i) the importance of this group in the dyestuff industry, (ii) the interest in the carcinogenic properties of the azo compound and (iii) the use of the azo compound for the indirect determination of non-electroactive metals [6–9].

Science aromatic azo compounds generally are electrochemically active much effort has been undertaken to study the redox chemistry of such compounds mainly by polarography. It has been studied that different substituents on the aromatic azo rings of azo compounds have a large impact on the reduction mechanism. It is also important to obtain more information on substituents and substitution pattern. The reduction mechanism of the azo compound is also known to be dependent on solution media. Therefore different azo compounds have been studied in previous works [8–12].

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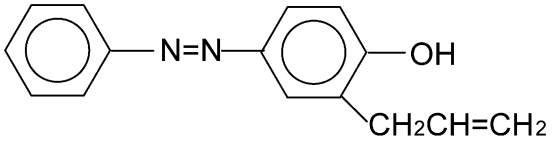


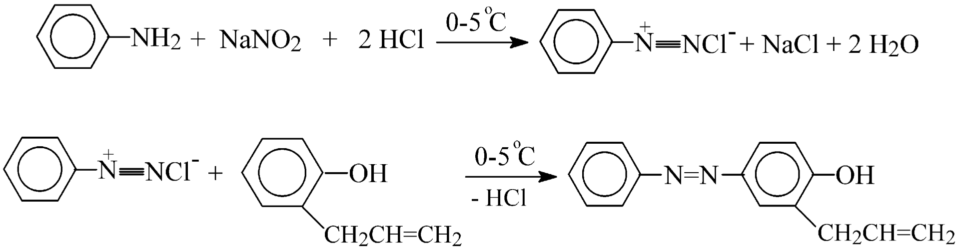
Scheme 1.

The present paper describes the electrochemical behaviour of 3-allyl-4-hydroxyazobenzene using differential pulse polarography (DPP), square wave voltammetry (SWV), cyclic voltammetry (CV) and direct current polarography (DCP). Our aims were to elucidate the mechanism of electrode reduction reaction. This study brings a contribution to our previous studies [10–15] and other works on the electrochemistry of some azo compounds. Molecular formula of the azo dye is given as above (Scheme 1).

2. Experimental

Melting point was taken with an electrothermal melting point apparatus. IR spectra was recorded on a Mattson 1000 FTIR spectrometer calibrated with polystrene film using the KBr disc. Absorption spectra in $CHCl_3$ was determined on a Unicam UV–vis spectrophotometer. The ^{1}H-NMR spectra were taken on a BRUKER AC 200 spectrometer, reference tetramethylsilane as internal standard. Elemental analysis was performed by the TUBITAK Marmara Research Center.

The azo dye was synthesized by azo-coupling reactions of benzenediazonium salt and *o*-allylphenol as below [13,15,18,20] and the compound was identified by UV–vis, IR and ^{1}H-NMR spectroscopic techniques m.p: 89–91 °C, yield 74%.



(3-allyl-4-hydroxyazobenzene)

UV–vis (λ nm) 350 (π–π^*), 445 (n–π^*, sh), IR (cm^{-1}) 3450–3250 (OH), 1416 (–N=N–), 1638 (–C=C– allyl), ^{1}H-NMR (d_6-acetone) δ 9.25 (s, OH) 6.08 (ddt, –CH=), 5.14 (dd, CH_2=) and 5.08 (dd, CH_2=), 3,49 (d, –CH_2–), 8.03–7.03 (m, aromatic).

The polarographic and voltammetric experiments were carried out using a computer controlled electroanalysis system which is Metrohm 757 VA 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. In this study, the electrochemical behaviour of the titled compound has been explained by using SWV, DPP, DCP and CV in different media. Solutions have been prepared in 30% alcohol–water (v/v) mixtures.

3. Results and discussion

The SWV and DPP voltammograms and polarograms of 3-allyl-4-hydroxyazobenzene (10^{-5} M) in BRT buffer at different pH values are given in Fig. 1. In the studied pH range of 2–12, the azo compound gives a single peak. In the range of potential which is examined, peaks or waves belongs to reduction of the azo group.

The peak potential of the azo compound shifts to more negative potentials with increasing pH at all voltammetric and polarographic techniques. The change of the peak potential with pH is given in Fig. 2.

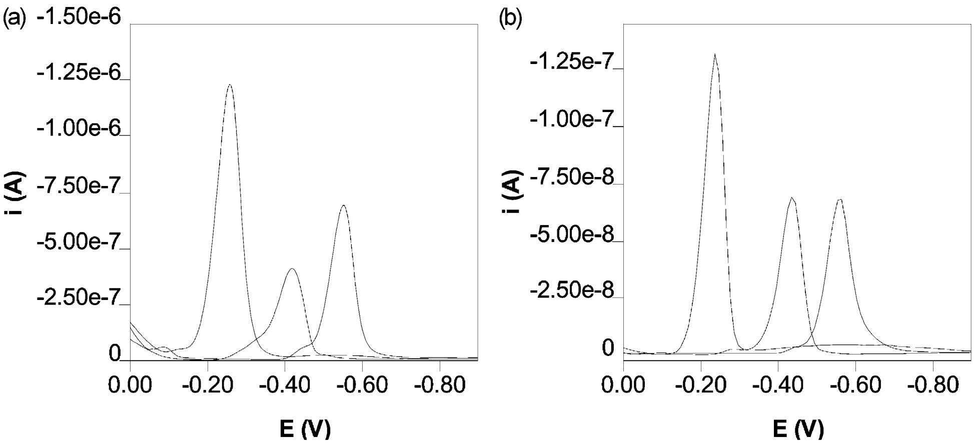


Fig. 1. Voltammograms and polarograms of the azo compound in Britton Robinson Buffer solution (a) SWV (pH:4.5, 7.0, 9.5 respectively), (b) DPP (pH: 4.5, 7.0, 9.5 respectively).

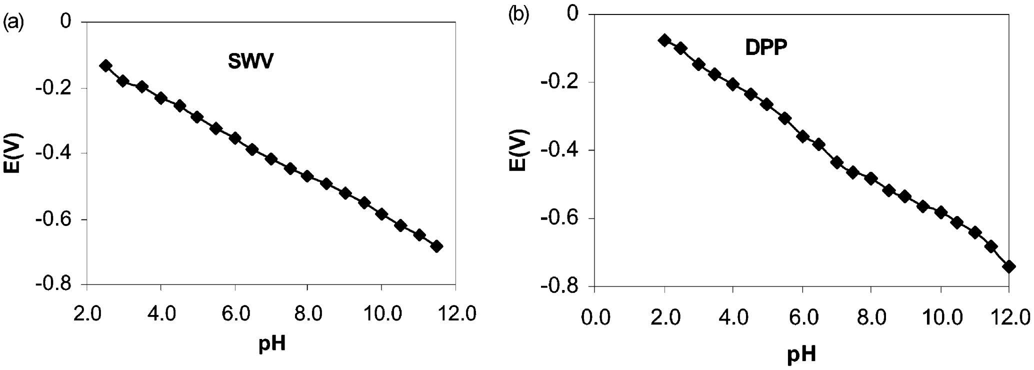


Fig. 2. Change in peak potential of the azo compound with pH in Britton Robinson Buffer solution (a) SWV, (b) DPP (scan rate 10 mv, drop time 1 s for DPP and scan rate 200 mV/s, for SWV and Ag/AgCl reference electrode).

As shown in Fig. 2, there is a linear relationship between the Ep values as below equation;

$$Ep = 0.008 - 0.060\ \mathrm{pH}\ \left(r^2 = 0.999\right)\ \text{for SWV}$$

$$Ep = 0.046 - 0.065\mathrm{pH}\ \left(r^2 = 0.995\right)\ \text{for DPP}$$

According to this results, the shift in the peak potential values of the reduction peak to more negative potentials with increasing pH denotes that the electrode reaction is involving hydrogen ions [17,19,21].

DCP polarograms, the change of limit currents and $E_{1/2}$ values with pH are given in Figs. 3 and 4, respectively. As shown in Figs. 3 and 4 limit currents decrease with increasing with pH. The observed dependence of limit current on the pH can be explained by a direct exchange of four electrons in acid medium with splitting of the azo group to form amines while in alkaline medium only two electrons are exchanged, with reduction to the corresponding hydrazo compound. A similar result was observed in previous studies [6–16].

Cyclic voltammograms are given in Fig. 5. In neutral and basic medium, anodic peak was observed but not in acidic medium. Reduction of the azo compound stops in hydrazo step. These results are supported DPP and DCP peaks and waves.

CV voltammograms of the azo compound recorded at scan rates of 10 and 1000 mV/s and different pH values are shown in Fig. 6. In cyclic voltammograms one well-defined cathodic peak Ic was observed at all pH and all scan rates values.

The reduction process of the azo compound is shown by peak potential shifts observed increasing with pH as shown DPP, SWV and DCP. Oxidation peak were observed increasing with pH. At he same time the oxidation peak currents increase with pH. Especially, small anodic peak were observed in acidic media. At slow scan rate in acidic media an irreversible oxidation wave is seen. As the scan rate is increased the oxidation becomes quasi-reversible. This is in a good agreement in previous studies [10–13,14–16].

In cyclic voltammograms, the Ic current peak clearly shows that transfer is followed by chemical reaction [22]. As shown in Fig. 7 a′ Ic peak currents are plotted non linearly against the square root of scan rates. These results, it is supported that is EC reaction mechanism. Furthermore cathodic peak current and cathodic peak potential approximately change linearly against the scan rate. These

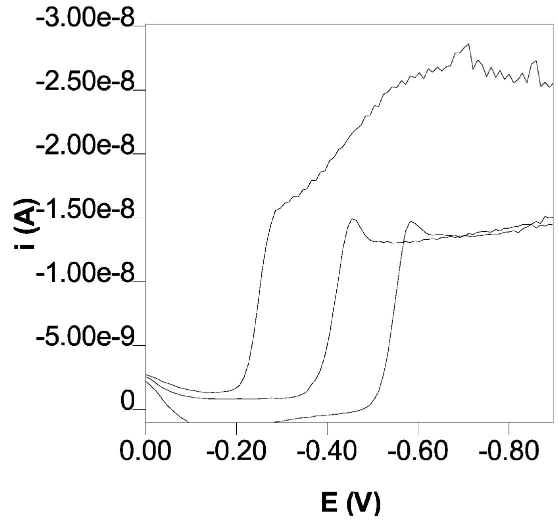


Fig. 3. Polarograms of the azo compound in Britton Robinson Buffer solutions(PH: 4.5, 7.0, 9.5, respectively) (scan rate 10 mV/s, drop time 1 s, with SMDE and Ag/AgCl reference electrode).

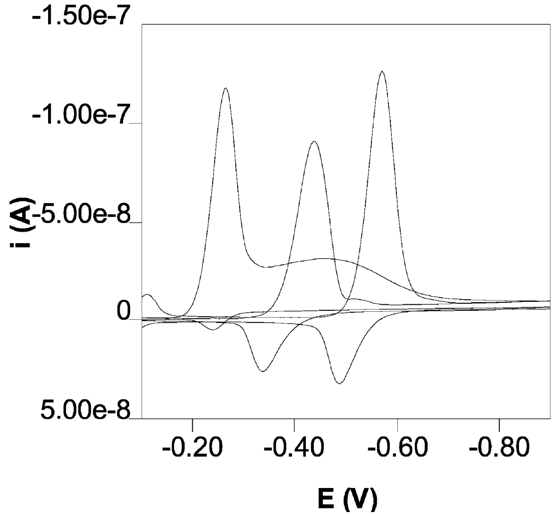


Fig. 5. CV Voltammograms of the azo compound in Britton Robinson Buffer solutions (PH 4.5, 7.0, 9,5, respectively) (scan rate 100 mV/s, 1 s, with HMDE and Ag/AgCl reference electrode).

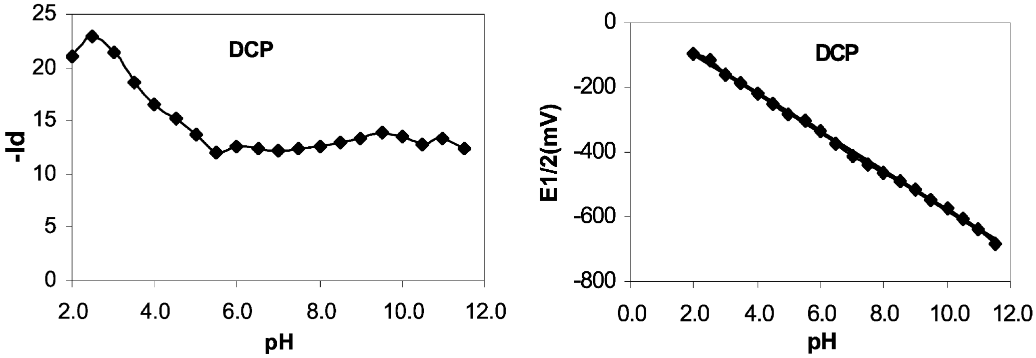


Fig. 4. Change in limit currents and peak potential of the azo compound with pH in Britton Robinson Buffer solution (scan rate 10 mv, drop time 1 s for DCP and Ag/AgCl reference electrode).

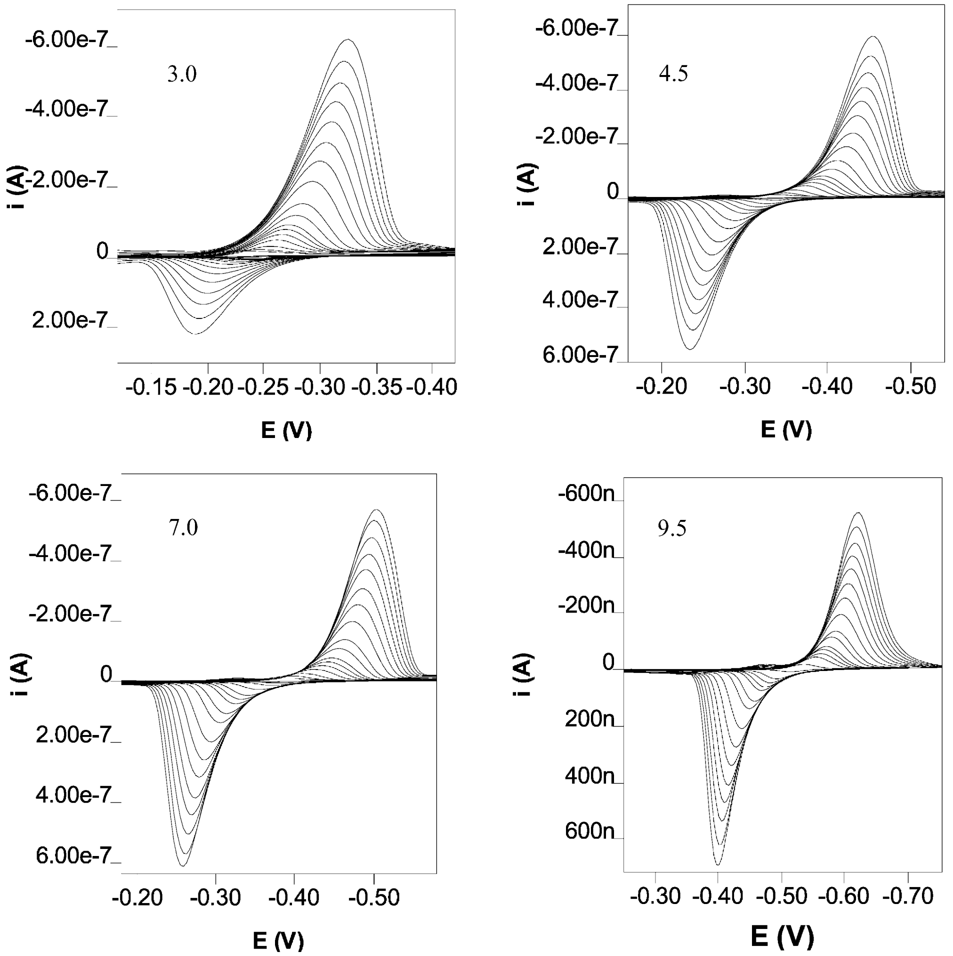


Fig. 6. Cyclic voltammograms of different scan rate of the azo compound for pH 3.0, 4.5, 7.0 and 9.5.

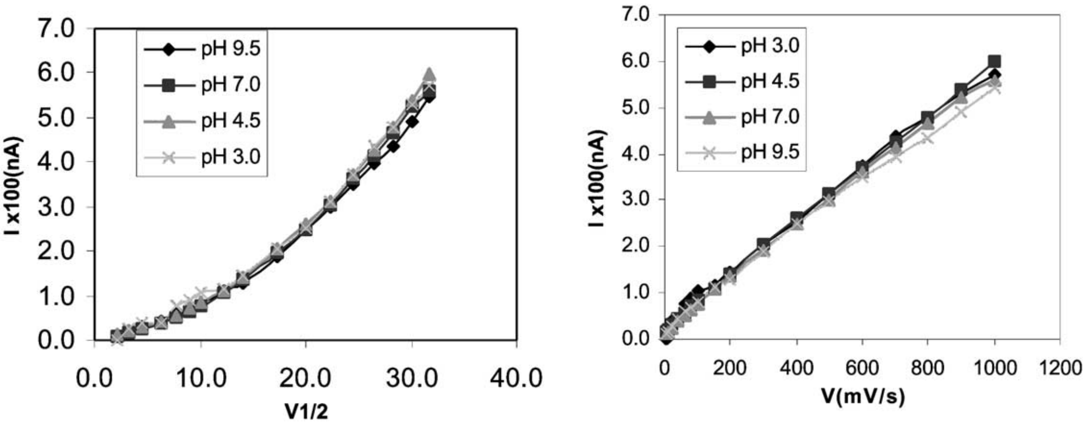
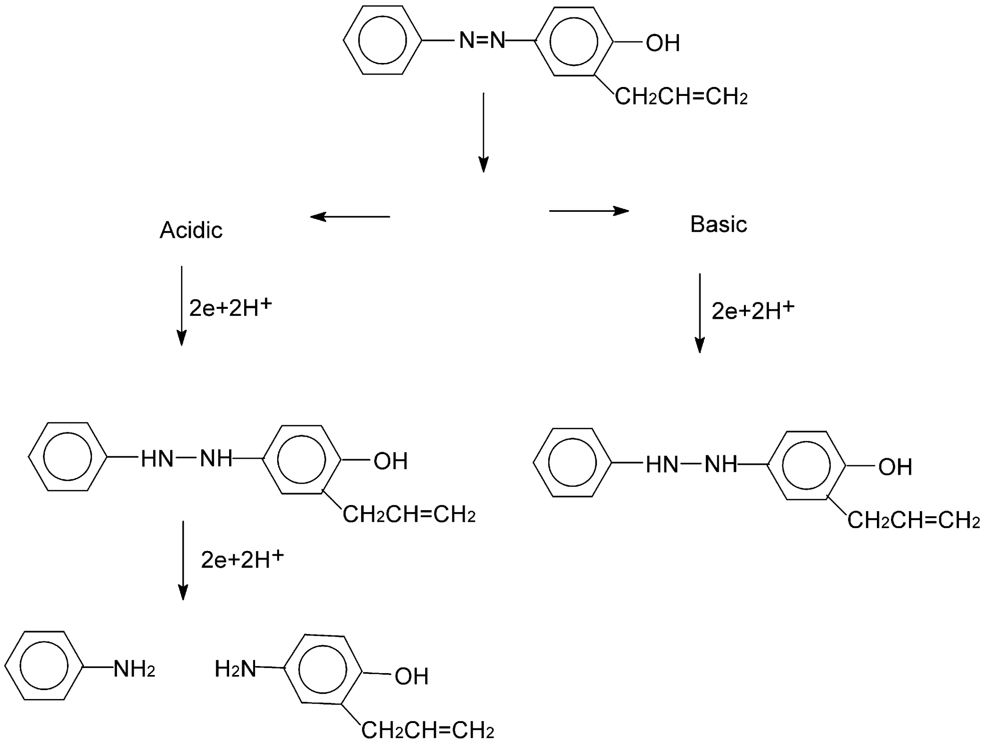


Fig. 7. The change of cathodic peak currents vs. $v^{1/2}$ and v.



show that the adsorption step is involved in the reduction process of the azo compound. Furthermore, oxidation peak current and potentials values approximately show similar behaviour to the azo compound. Peak maximum are also recorded in DCP polarograms (Fig. 3). These result is supported from DPP and DCP measurements.

From polarographic and voltammetric mesurements (DPP, SCP CV and SWV) it is known that the reduction of aromatic azo compounds containing electron donating subtituents, such as hydroxy and amino groups involve a cleavage of the azo bridge to yield the corresponding amines in weak acidic solutions, while the reduction of unsubstituted ones with electron drawing substituents generally give to corresponding hydrazo compounds [6–7]. It is therefore reasonable to assume that the majority of the azo compound studied here is reduced to corresponding amines in acidic media. But increasing pH, reduction of the azo compound stops in the hydrazo step. 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 appreciability supported from DCP, DCP SWV and CV polarograms and voltammograms. According to SWV, DPP, DCP and CV techniques, the reduction mechanism can be suggested as above.

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