

## Investigation of Electrochemical Behavior of Mordant Dye (C.I. 17135)

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In this study, the electrochemical behavior of Mordant dye (C.I. 17135) was investigated in Britton-Robinson (BR) buffer (pH 2.0-12.0) media by using different techniques, which are square wave voltammetry (SWV), cyclic voltammetry (CV), differential pulse polarography (DPP), direct current polarography (DCP) techniques. The polarograms and voltammograms of the dye on a static mercury drop electrode (SMDE) and hanging mercury drop electrode (HMDE) show one reduction peak corresponding to the two-step four electron electrode reaction mechanism. In SW voltammograms and DP polarograms of the dye, a broad shoulder peak was seen in the pH range of 2.0 to 12.0, due to the adsorption of the azo dye on the electrode surface. The shift of the peak potentials to more negative values indicate that the protons are involved in the electrode reaction. The effect of scan rate on the reduction peak has been studied at different pH values.

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**Keywords:** Mordant dye, reduction, scan rate, reaction mechanism.

### 1. INTRODUCTION

Azo dyes constitute the largest class of the dyes which are characterized by the azo functional group (-N=N-). The azo dyes are named according to the number of azo groups such as monoazo, disazo, trisazo, polyazo and azoic.

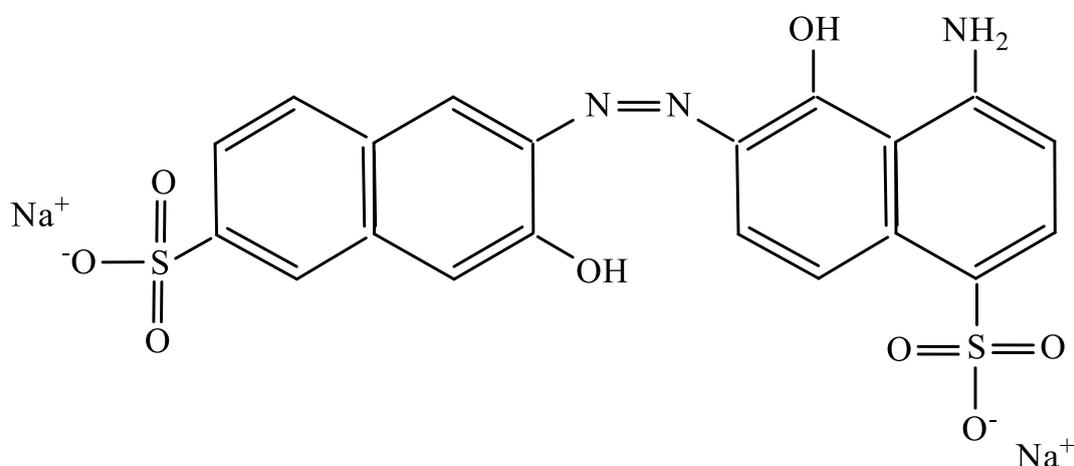
Mordant dyes represent the largest part of synthetic azo dyes, which are widely used for the coloration of textile fibers, such as wool, silk, polyester, cotton, and nylon [1,2]. These dyes include groups, which are able to react with metallic cations (mordants), in the presence of fiber to produce metal-dye complexes [3]. Cobalt(II) and chromium(II) complexes of o,o'-dihydroxy azo dyes were used to produce dyeing protein and fibers which have excellent light and wash fastness [1,4,5].

The aim of the present study is to examine the electrochemical behavior of Mordant dye (C.I. 17135). The polarographic and voltammetric studies of the dye were investigated by SWV, DPP, DCP and CV techniques in BR buffer. Additionally, this work contributes to previous studies on the electrochemical behavior of other azo dyes [6-9]. Mordant dye has not been investigated by voltammetric methods up to now. The molecular structure of the Mordant dye (C.I. 17135) is shown below (Scheme 1).

## 2. EXPERIMENTAL

4-amino-5-hydroxy-6-[(Z)-2-(3-hydroxy-6-sulfonatophthalen-2-yl)diazen-1-yl]naphthalene-1-sulfonate (Mordant dye C.I. 17135) was purchased from Aldrich and used without further purification. A  $10^{-3}$  M stock solution of Mordant dye was prepared in deionised water. A 0.04 M BR buffer solution was prepared by using 0.04 M phosphoric acid, 0.04 M acetic acid and 0.04 M boric acid and adjusted to the desired pH with concentrated sodium hydroxide. All chemicals used for buffer preparation were of p.a. purity.

The polarographic and voltammetric experiments were performed using a Metrohm 757 VA Computrace Electrochemical Analyser at room temperature. A three-electrode system was employed with a working electrode, (DME (dropping mercury electrode) SMDE and HMDE), a Ag/AgCl (saturated KCl) reference electrode and a platinum wire auxiliary electrode. The SMDE and HMDE have been used for polarographic and voltammetric experiments of the dye, respectively. All solutions were deaerated for 5 min with oxygen-free nitrogen prior to polarographic and voltammetric experiments. Polarographic and voltammetric studies were carried out by using SWV, DPP, DCP, and CV techniques.



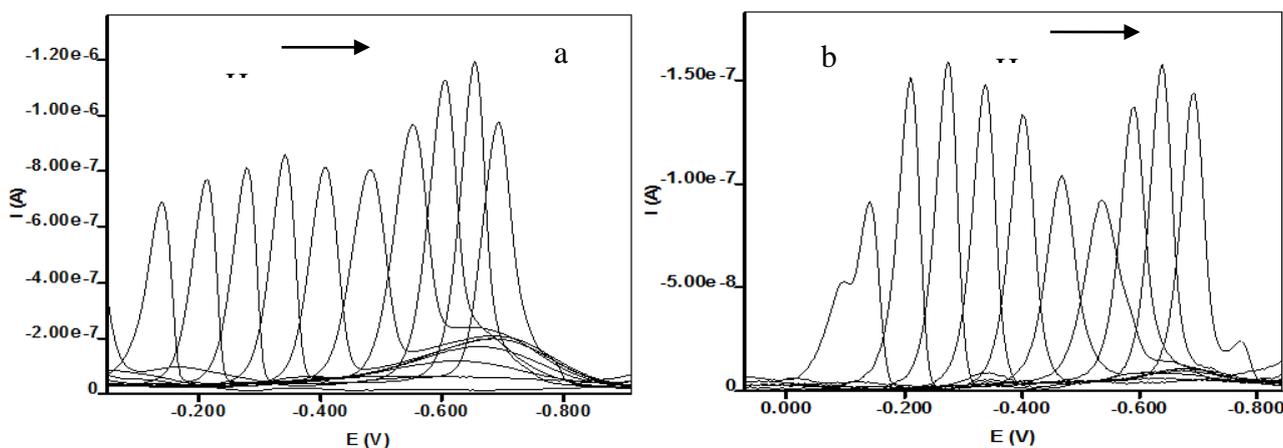
**Scheme 1.** Molecular structure of the Mordant dye (C.I. 17135).

### 3. RESULTS AND DISCUSSION

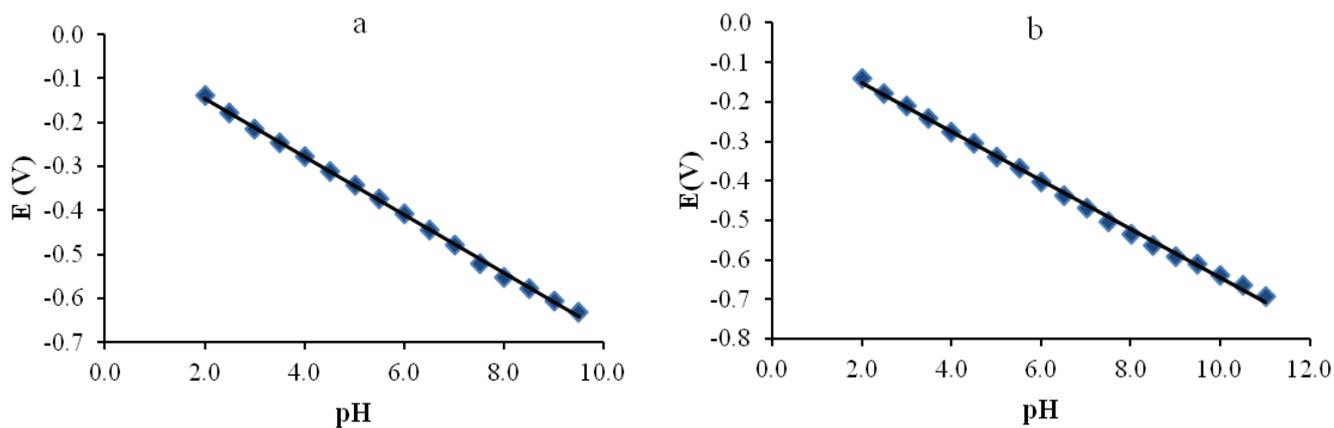
The voltammetric behavior of the Mordant dye at a HMDE was studied by using SWV and CV techniques in BR (pH 2.0-12.0) buffer. The polarographic behavior of the Mordant dye at a SMDE was investigated by using DPP and DCP techniques in BR (pH 2.0-12.0) buffer. Voltammograms and polarograms of the azo dye are given in Fig. 1. As seen in Fig.1, one well-defined reduction peak ( $I_p$ ) was observed corresponding to the reduction of the azo group with SWV and DPP techniques in BR buffer. In SW voltammograms and DP polarograms of the dye, a broad shoulder peak was seen in the pH range of 2.0 to 12.0, due to the adsorption of the azo dye on the electrode surface [10-14]. The potentials of the reduction peaks ( $E_p$ ) are a linear function of pH, which are given by the equations  $E_p$  (V) = -0.0116-0.0664pH and  $E_p$  (V) = -0.0284-0.0617pH for the SWV and DPP techniques, respectively, in BR buffer media (Table 1). The slope values -66.4 mV/pH and -61.7 mV/pH are very close to the theoretical value of -59 mV/pH required under assumption of the  $2e^-/2H^+$  or  $4e^-/4H^+$  process of the electrochemical reduction of Mordant dye.

The reduction peak potentials shifted towards more negative values with increasing pH indicated that protons are involved in the electrode reaction (Fig. 2).

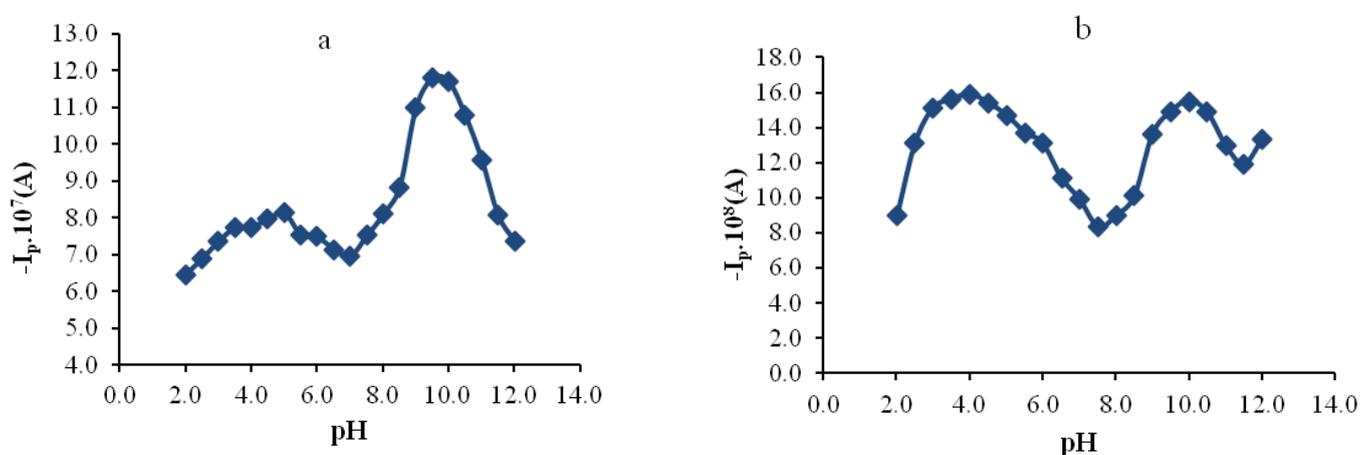
There was a minimum in the peak current of the azo dye at pH 7.0 and at pH 7.5 for SWV and DPP techniques, respectively. As given in Fig. 3, with the SWV technique, the peak currents of the dye increased in the pH range from 7.5 to 9.5 and then diminished with pH values greater than 9.5. And the DPP technique indicated that the peak currents of the dye diminished to pH 7.5 with increasing pH, and at pH  $\geq$  8.0, peak currents of the azo dye increased and at pH  $\geq$  10.5, peak currents diminished again. The increasing and decreasing of the peak current around at pH 7.0 is due to the changing in acidic and basic forms of the azo dye. And it shows similar consistency with pKa values in the literature [15].



**Figure 1.** Voltammograms and polarograms of Mordant dye in BR buffer (0.04 M) pH 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, and 11.0, (a) SWV, sweep rate ( $\nu$ ) = 200 mV/s, with a HMDE, (b) DPP,  $\nu$  = 4 mV/s, with a SMDE.



**Figure 2.** The change in cathodic peak potentials versus pH in BR buffer for Mordant dye a) SWV,  $\nu = 200$  mV/s, with a HMDE, b) DPP,  $\nu = 4$  mV/s, with a SMDE.



**Figure 3.** The change in cathodic peak currents versus pH in BR buffer for Mordant dye a) SWV,  $\nu = 200$  mV/s, with a HMDE, b) DPP,  $\nu = 4$  mV/s, with a SMDE.

**Table 1.** The change in peak potentials with pH.

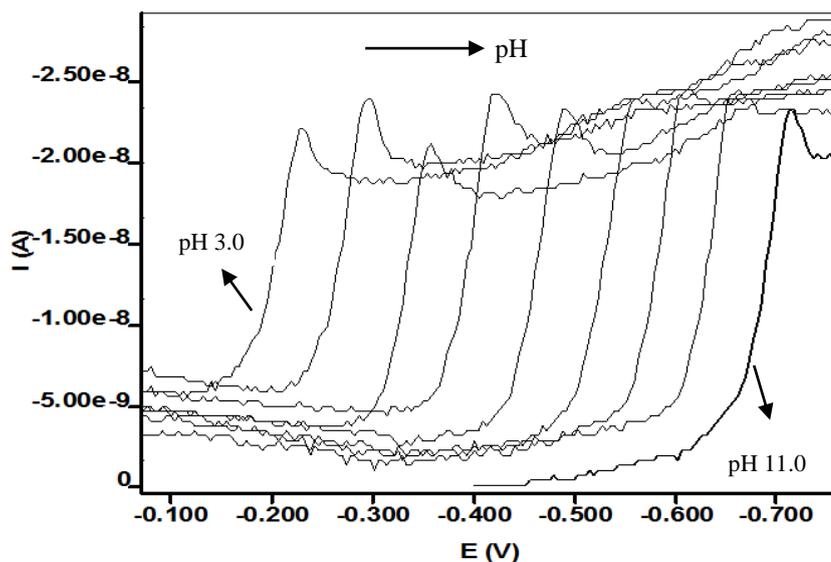
Medium	pH	Peak equation	$r^2$ (Regression coefficient)	Technique
BR (0.04 M)	2.0-12.0	$E_p$ (V) = -0.0116-0.0664pH	0.999	SWV
BR (0.04 M)	2.0-12.0	$E_p$ (V) = -0.0284-0.0617pH	0.998	DPP
BR (0.04 M)	2.0-12.0	$E_p$ (V) = -0.0604-0.0630pH	0.997	CV

### 3.1. DCP studies

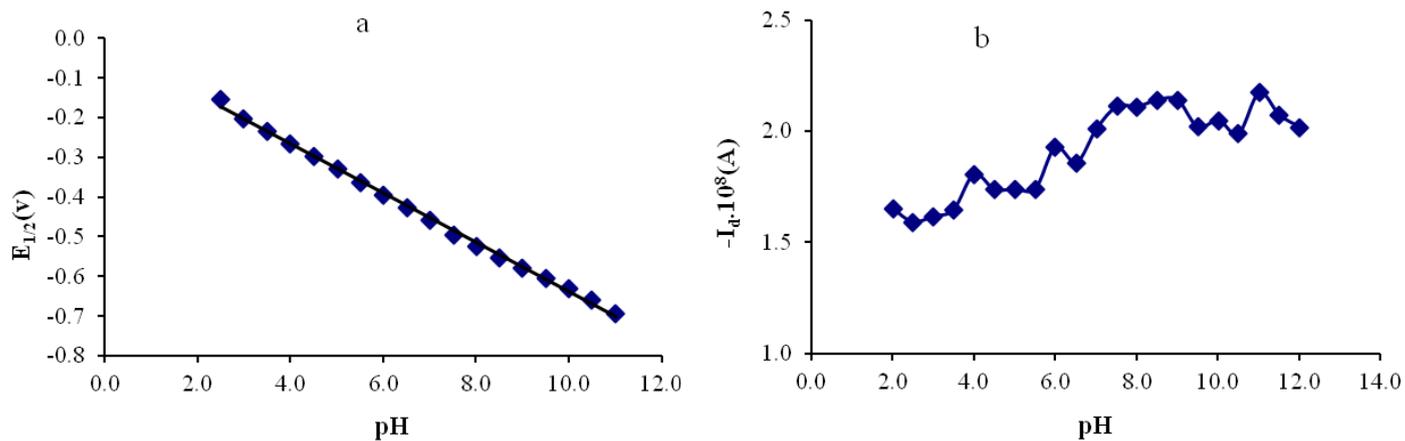
As seen in Fig. 4, one well-defined cathodic wave was observed in BR buffer (2.0-12.0) with a scan rate of 4 mV/s. Peak maxima were observed at DC polarograms due to the adsorption of azo dye on the electrode surface. The limiting current becomes more or less constant within the range of pH 2.0–12.0. This behavior proves that the reduction of the azo compound involves four electrons in acidic and alkaline media. In acidic and alkaline media, the azo compound is first reduced to a hydrazo species, and then, in the second step, the azo group is reduced to aniline derivatives. The  $E_{1/2}$  values shifted to more negative potentials with increasing pH values (Fig. 5).

Logarithmic analyses of the reduction waves calculated from the direct current polarograms in BR buffer (2.0–12.0) resulted in straight lines. The  $\alpha n$  values were calculated by using the Heyrovsky-Ilkovic equation [16-18]. The linear equation of the  $E_{1/2}$ -pH graph for the reduction wave of Mordant dye was given as  $E_{1/2}$  (V) = -0.017-0.0623pH. To propose the electrode reaction mechanism of the dye, the number of protons ( $a_{H^+}$ ) and the number of electrons ( $n$ ) participating in the rate-determining step should be determined. For this purpose, the slope values  $S_1$  ( $S_1 = -0.05916/\alpha n$ ,  $\alpha$ : transfer coefficient) and  $S_2$  ( $S_2 = -0.05916a/\alpha n$ ) of both the  $E$  versus  $\log(I/I_d - I)$  and  $E_{1/2}$ -pH plots were determined (Figs. 5, 6). The  $\alpha n$  values obtained in acidic, neutral and alkaline media (pH 3.0-10.5) are approximately equal two (Fig. 6).

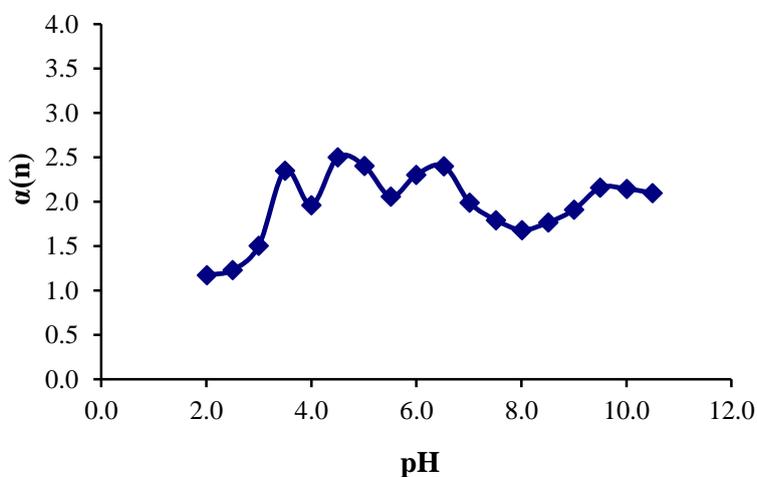
The slope value -62.3 mV/pH was very close to the theoretical value of -59 mV/pH. This behavior indicated that  $2e^-/2H^+$  or  $4e^-/4H^+$  were involved in the electrochemical reduction of the Mordant dye [19].



**Figure 4.** DC polarograms of  $9.90 \times 10^{-6}$  M Mordant dye in BR (0.04 M) buffer pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, and 11.0 solutions,  $\nu = 4$  mV/s, with a SMDE.



**Figure 5.** The change in a)  $E_{1/2}$  values and b) diffusion currents ( $I_d$ ) of Mordant dye versus pH in BR buffer for the DCP technique,  $v = 4$  mV/s, with a SMDE.

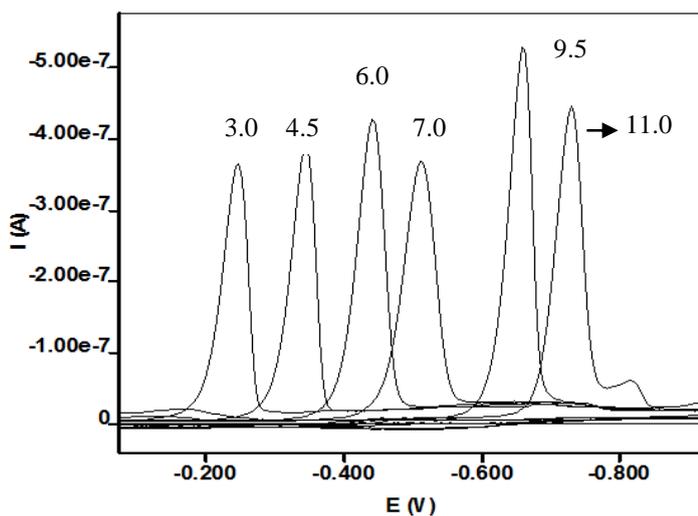


**Figure 6.** The change in  $\alpha n$  with pH for Mordant dye in BR buffer.

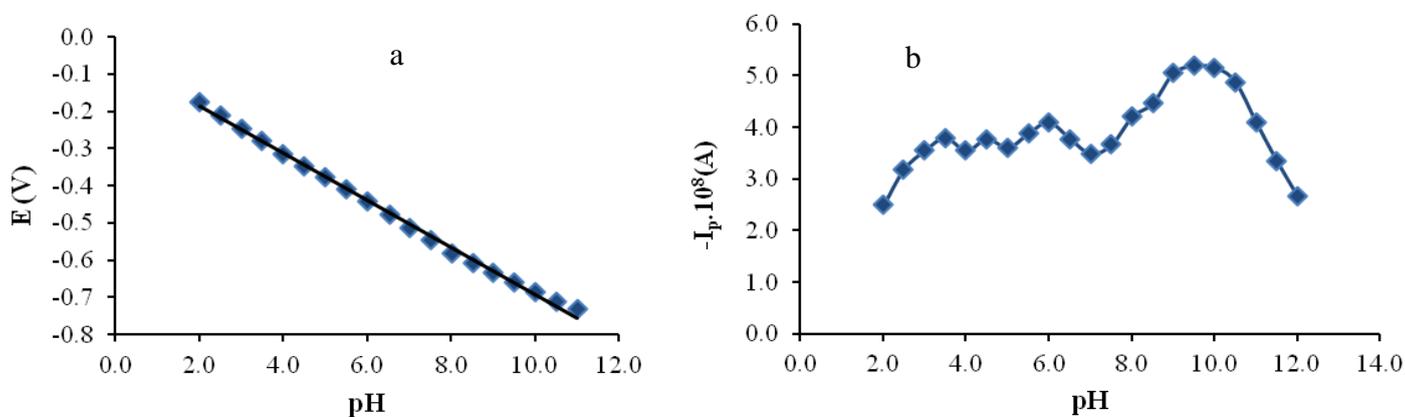
### 3.2. CV studies

The cyclic voltammograms of the Mordant dye recorded in 0.04 M BR buffer at different pH values (pH 3.0, 4.5, 6.0, 7.0, 9.5, and 11.0) were given in Fig. 7. One well-defined reduction peak was observed in acidic, neutral and basic media. Irreversible electrode reaction occurred at the electrode surface, as no anodic peak was seen on the reverse scan [8, 20-24].

The shift in peak potential values with increase in the pH from 2.0 to 12.0, was the evidence for involvement of protons in the electrode reaction (Fig. 8).

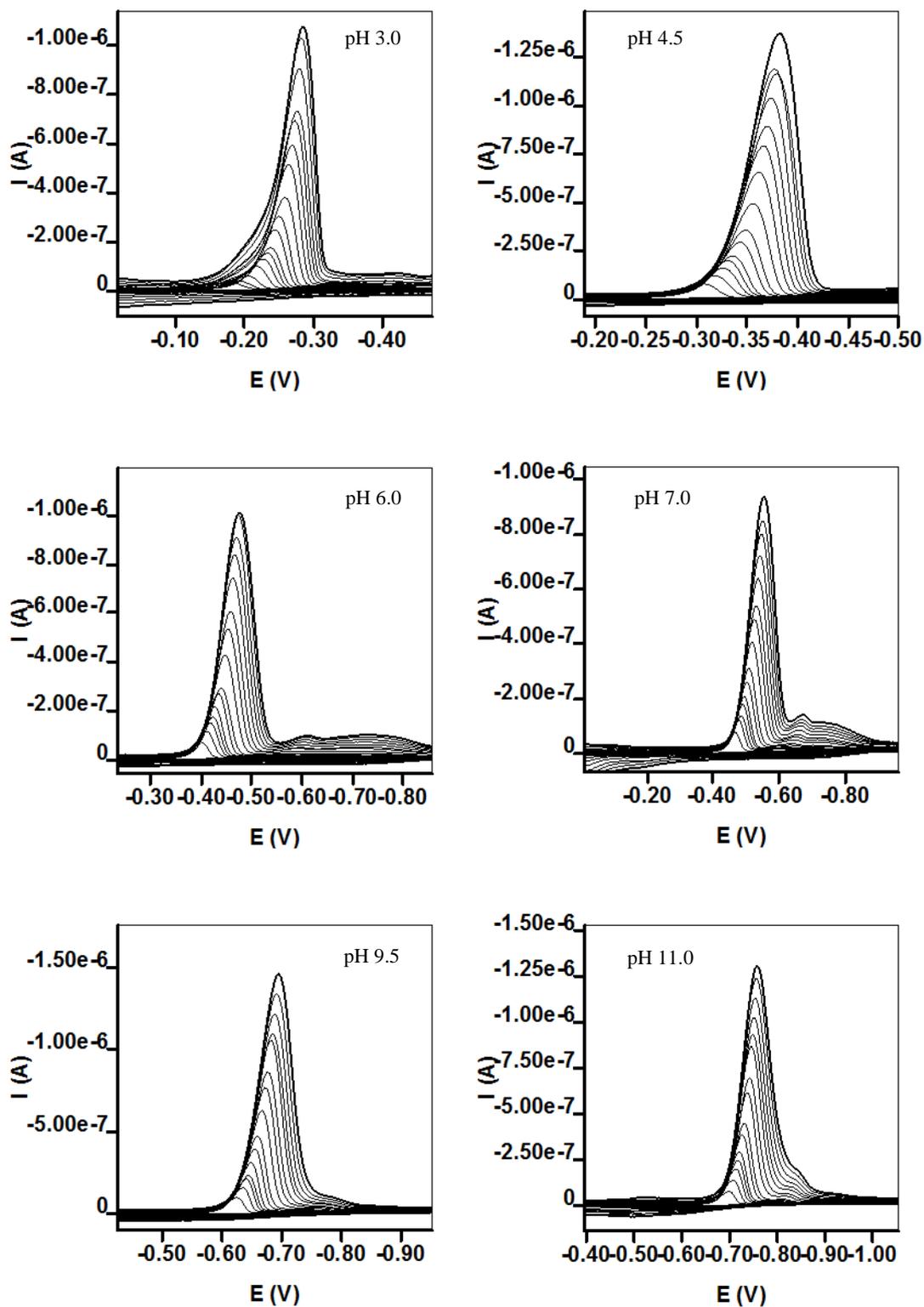


**Figure 7.** CV voltammograms of Mordant dye in BR (0.04 M) buffer (pH 3.0, 4.5, 6.0, 7.0, 9.5, and 11.0) solutions,  $\nu = 200$  mV/s, with a HMDE.

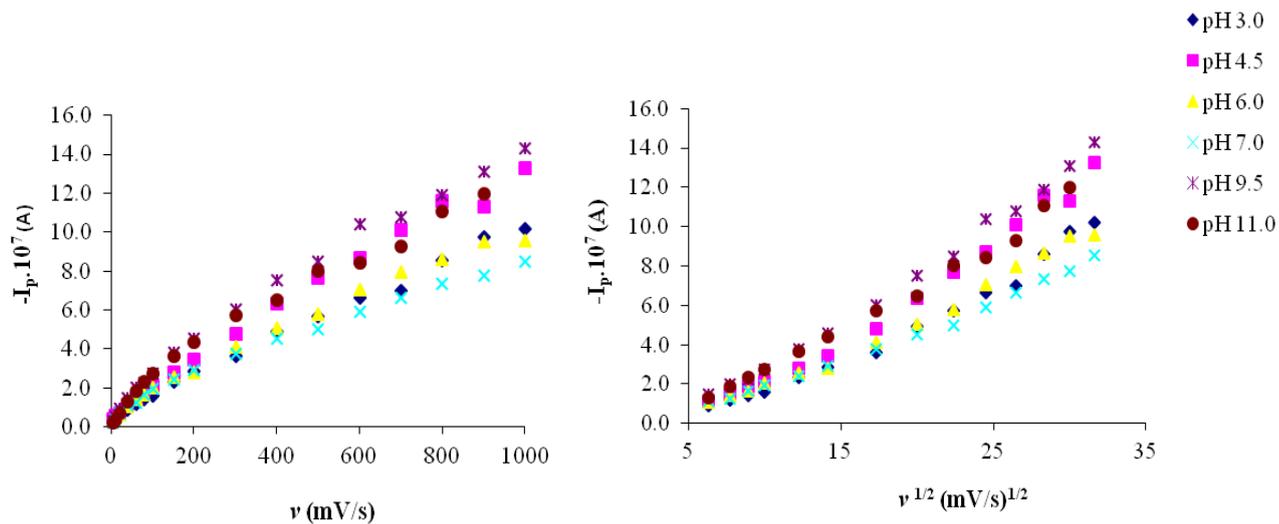


**Figure 8.** The change in a) cathodic peak potentials and b) cathodic peak currents versus pH in BR buffer obtained for Mordant dye for the CV technique,  $\nu = 200$  mV/s, with a HMDE.

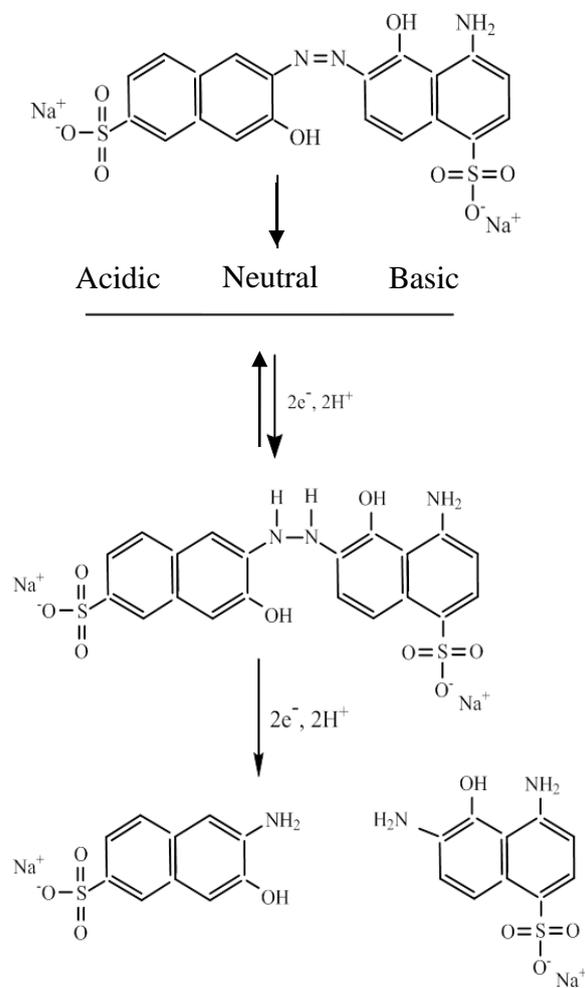
The electrode reaction followed by a rapid chemical reaction, may prevent the anodic peak from being observed on cyclic voltammograms of the dye. As scan rate was increased from 5 to 1000 mV/s, no anodic peak was seen on reverse scan, indicating that the azo group was split into amines with an irreversible electrode reaction [13].



**Figure 9.** The change in cyclic voltammograms of Mordant dye with scan rate at pH 3.0, 4.5, 6.0, 7.0, 9.5, and 11.0 ( $\nu = 5-1000$  mV/s, with a HMDE).



**Figure 10.** The change in cathodic peak currents of Mordant dye with scan rate at pH 3.0, 4.5, 6.0, 7.0, 9.5, and 11.0 ( $v = 5\text{-}1000$  mV/s, with a HMDE).



**Scheme 2.** Reaction mechanism of Mordant dye.

The cyclic voltammograms of the dye at different pH (pH 3.0, 4.5, 6.0, 7.0, 9.5, and 11.0) values were given in Fig. 9. The change in cathodic peak currents with increase in scan rate ( $\nu = 5\text{-}1000\text{ mV/s}$ ) and root square of scan rate at different pH values (pH 3.0, 4.5, 6.0, 7.0, 9.5, and 11.0) was also given in Fig. 10. As scan rate was increased from 5 to 1000 mV/s, the peak potential shifted towards more negative values as expected for an irreversible electrode reaction [25,26]. The linear variation of peak current with square root of scan rate demonstrates that the diffusion-controlled electrode reaction occurred on the electrode surface [23,26, 27-30].

As given in this equation  $I_p = A\nu^x$ , the peak current and the scan rate ( $\nu$ ) have a linear relationship with each other.  $x$  can take the values 1.0 and 0.5 for adsorption and diffusion-controlled reactions, respectively. The slope values obtained from the analysis of  $\log(I_p)$  versus  $\log(\nu)$  plots were 0.70, 0.68, 0.64, 0.64, 0.72 and 0.75 for pH 3.0, 4.5, 6.0, 7.0, 9.5 and 11.0, respectively. These results indicated that the cathodic peak current had contributions from both diffusion and adsorption [22,23,31].

#### 4. CONCLUSIONS

The electrochemical behavior of Mordant dye at a HMDE and SMDE has been studied in BR buffer (pH 2.0-12.0) media by using SWV, DPP, DCP and CV techniques. One reduction peak was observed in BR buffer which is attributed to the reduction of the azo group to amines with SWV, DPP, DCP and CV techniques. The reduction of dye showed irreversible behavior at a HMDE in acidic, neutral and basic media. The electrochemical reaction mechanism of dye has been suggested from the polarographic and voltammetric data at a mercury electrode (Scheme 2). The effect of the scan rate on the peak current studies indicate that the electrode process of the dye at a mercury electrode is diffusion-adsorption controlled.

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