

# Investigation of The Electrode Pathway of Quinoline Azo Dye Compound via Convulsive Voltammetry and Digital Simulation

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**Abstract:** The electrochemical behavior and the electrode reaction of quinolone azo dye compound was investigated using convulsive cyclic voltammetry at mercury electrode in 50% (v/v) ethanolic Britton-Robinson solutions of pH 2.5 – 12.0. Four electrons slow reduction wave was consumed in acidic and alkaline solutions corresponding to the reduction of the more easily N = N center. A second more cathodic irreversible, pH – dependent, 2-electron wave represents the reduction of quinolone ring. Cyclic voltammetry and convolution transforms were used to determine the kinetic parameters of the electroactive species. The extracted electrochemical parameters were confirmed via digital simulation. Controlled potential coulometry technique was used for calculation the overall number of electrons involved in electrode reaction.

**Keywords:** Electrochemical parameters; Quinolineazo dye; convulsive voltammetry; digital simulation

## 1. INTRODUCTION

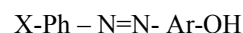
In view of extensive studies on biologically important azo compounds to other compounds of biological interest [1,2], we have selected in this work some quinoline azo dyes. The reductions of azo compounds were the subject of many investigations [3- 5]. Arylazo compounds have been found to play an important role in the field of medicine for their antidiabetic activity [6,7]. Literature surveys of azo compounds derived from hetero cyclic compounds revealed the lack of electrochemical work via convulsive voltammetry, chronoamperometry and digital simulation methods. The present work describes the electrochemical investigation of quinolineazo dye compound at mercury electrode using cyclic voltammetry, convulsive voltammetry and digital simulation methods as well as the determination of the electrochemical parameters and its verification via theoretical treatment.

## 2. EXPERIMENTAL

### 2.1. Solid Compounds

According to the method established in literature [8] the compound under consideration was prepared. The compound formed was kept 30 mins then filtered of, washed by water and dried. The

crude material was tested by measuring the m.p. until reached a constancy value. The structure of the compound was characterized by the elemental analysis [9]. The formula of the compound under consideration is as follows:



Where X = 4-COOH and Ar-OH = 8-hydroxy quinoline

### 2.2. Solutions

Stock solutions of  $5 \times 10^{-3} \text{M}$  were prepared by dissolving an accurately weighed quantity of the solid material in the appropriate volume of absolute ethanol. Britton-Robinson Universal buffer solution (pH 2.5 – 11.8) was used as supporting electrolyte. All experiments were carried out at  $25 \pm 2^\circ \text{C}$ .

### 2.3. Electrochemical Apparatus

Model 273 A of Polarographic Analyzer and Model 303 A of the electrode assembly (From EG & G) with working hanging mercury drop electrode (area =  $2.61 \times 10^{-2} \text{cm}^2$ ), Ag/AgCl as a reference and Pt – wire as a counter electrode were used for cyclic voltammetry measurements. The generated cyclic voltammograms were performed using digital simulation software program CONDESIM (from EG & G).

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### 3. RESULTS AND DISCUSSION

#### 3.1. Cyclic voltammetry

Cyclic voltammetric investigation of azo compound was carried out in buffer solution of pH's 2.5 and 8.2. The cyclic voltammograms in both solutions revealed two cathodic peaks. On increasing the scan rate ( $\nu$ ), the position of peak potential ( $E_p$ ) of both waves were shifted to more negative values revealing that the irreversibility nature of the reduction waves[10]. Also, the absence of any peak in the anodic direction confirm the irreversibility of the reduction process.

The recorded cyclic voltammogram at  $0.2 \text{ V.s}^{-1}$  scan rate, at pH 2.5 is shown in Fig. 1. The measured values of  $E_p - E_{p/2}$  obtained at different scan rates are listed in Table 1 indicates the slow nature of electron transfer. The diffusion coefficient ( $D$ ) was calculated from the slopes of the plots of  $i_p$  vs  $\nu^{1/2}$  using Eq. (1)[11, 12] and found to be in the range of  $1.3 - 2.1 \pm 0.1 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ .

$$i_p = (2.99 \times 10^5) n (\alpha n a)^{1/2} A C^b D^{1/2} \nu^{1/2} \quad (1)$$

The plotting of  $i_p$  vs.  $\nu^{1/2}$  exhibited linear correlation passing through the origin which indicates that the electrode reduction of the electroactive species under consideration is mainly controlled by diffusion. The symmetry coefficient ( $\alpha$ ) was calculated from Eqs. (2 & 3) [13], where  $E_{p2}$  and  $E_{p1}$  are the peak potential values at the corresponding scan speeds  $\nu_1$  and  $\nu_2$  ( $\text{V.s}^{-1}$ ).

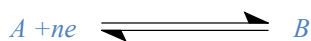
$$\alpha n a = [0.0591/(E_{p2} - E_{p1})] \log (\nu_1/\nu_2)^{1/2} \quad (2)$$

$$E_p - E_{p/2} = (0.048/\alpha n a) \quad (3)$$

The cathodic symmetry coefficient ( $\alpha$ ) values at the selected pH were calculated to be  $0.29 \pm 0.04$ . The low value of ( $\alpha$ ) confirm the irreversible nature of the reduction process. It was noted that there is a good agreement between the values of symmetry coefficient calculated via different methods.

#### 3.2. Convulsive voltammetry

For the electro-reduction reaction:



in which a given species undergoing only electron transfer at a planar electrode. The Fick's second law is written as [13 - 16]:

Table 1. Indicate the values of  $E_p - E_{p/2}$  of the investigated compound.

pH	$\nu$	$E_p - E_{p/2}$ , mV	
		a	b
2.0	50	20	----
	100	30	----
	200	70	30
	500	100	50
8.0	50	20	----
	100	30	40
	200	52	50
	500	73	60

(a) first peak, (b) second peak

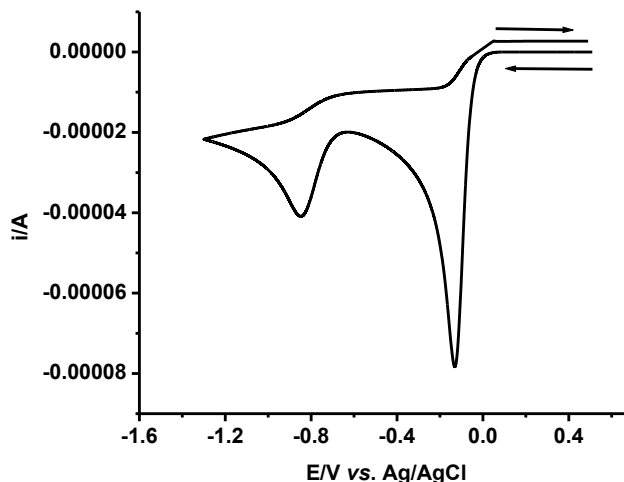


Figure 1. Cyclic voltammogram of investigated compound at scan rate of  $0.2 \text{ V.s}^{-1}$  and pH 2.5.

$$[\partial C_A / \partial t]_x = D_A [\partial^2 C_A / \partial x^2]_x \quad (4)$$

the convolution  $I_1$  is given by  $I_1 = i^*(\pi t)^{-1/2}$  or more 'fully' as:

$$I_1(t) = \pi^{-1/2} \int_0^t i(u) / (t-u)^{1/2} du \quad (5)$$

The following algorithm is used to evaluate the convolution integral  $I(t)$  in this work [17]:

$$I(t) = I(k\Delta t) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{j=k} \frac{\Gamma(k-j+1/2)}{(k-j)} \cdot \Delta t^{1/2} i(j\Delta t) \quad (6)$$

Where the symbol  $I(j\Delta t)$  is defined as the current read at equally spaced time intervals  $\Delta t$  and the symbol  $\Gamma(x)$  is the Gamma function of  $x$ .

Here equation (5) is used for calculation the diffusion coefficients ( $D$ ) of the oxidation processes.

$$I_{lim} = nFAC(D)^{1/2} \quad (7)$$

The calculated  $D$  values were listed in Table 2. Figure 2 exhibits an example of  $I_1 - E$  plot of the reductive curve at a scan rate of  $0.2 \text{ V.s}^{-1}$ . As shown there is a large distance between the backward

Table 2. Values of diffusion coefficient ( $D$ ), heterogeneous rate constant ( $k_s$ ), redox potential ( $E^0$ ) and homogeneous rate constant ( $k_c$ ) of the investigated compound via different methods at selected pH values.

pH	$D \times 10^{10} \text{ m}^2.\text{s}^{-1}$			$k_s \times 10^5 \text{ m.s}^{-1}$			$E^0 \text{ V}$	$K_c \text{ s}^{-1}$
	a	b	c	d	e	c		
2.0	1.80	1.82	1.70	1.25	1.20	1.10	-0.42	5.0
8.0	1.45	1.40	1.30	0.65	0.60	0.50	-0.91	8.0

a, Eq. (1), b using Eq. (5) c from simulation, d using ref. (18), and e using ref. (12).

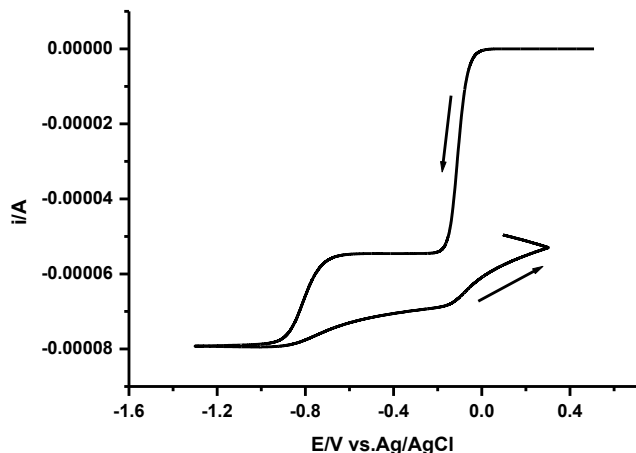


Figure 2.  $I_1$  convolution of investigated quinolone azo dye compound at scan rate of  $0.2 \text{ V.s}^{-1}$

sweep and the forward sweep of the  $I_1-E$  plot. Also the backward sweep does not return to zero current value, confirming EC mechanistic pathway and slow kinetic of the heterogeneous rate constant ( $k_s$ ) between the electrode and the electroactive azo dye quinoline compound.

Again, the deduced convoluted current ( $I_{limd}$ ) was used to calculate the diffusion coefficient from equation (8) [13,16]:

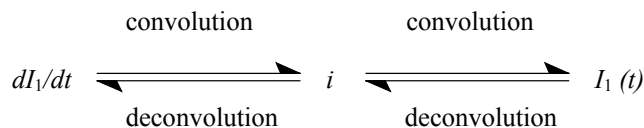
$$I_{limd} = \frac{i_p}{3.099(\alpha n_a \nu)^{1/2}} \quad (8)$$

where the symbol  $I_{limd}$  is define as the deduced limiting convoluted current, which is equals to  $I_{lim}$  ( $I_{limd} = I_{lim} = nFACD^{1/2}$ ). Table 2 shows the agreement between D values calculated via different methods.

Digital simulation method was used for calculation the homogeneous chemical rate constant ( $k_c$ ) of the first and second processes. The determined values of homogeneous chemical rate constant were cited in Table 2.

### 3.3. Deconvolution voltammetry

The conversion between  $t^{1/2}$  convolutions (semiintegration) and deconvolutions is indicated as the following [11]:



The transforms of the current to deconvolution ( $dI_1/dt$ ) as a function of  $E$  of reversible process is given as [14]:

$$(dI_1/dt) = nFAC\sqrt{Da\zeta} / (1+\zeta)^2 \quad (9)$$

$$\text{where } a = n\nu F/RT \quad (10)$$

$$\text{and } \zeta = \exp [nF/RT (E - E^0)] \quad (11)$$

The deconvolution voltammetry at  $\nu = 0.6 \text{ V.s}^{-1}$  are indicated in Fig.3. It was found that the peak width of the curve ( $w_p$ ) is  $183 \pm 2$

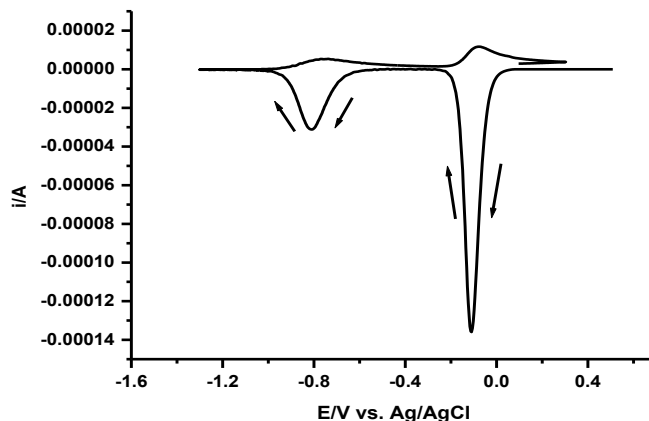


Figure 3. deconvolution voltammetry of investigated quinolone azo dye compound at scan rate of  $0.2 \text{ V.s}^{-1}$

mV, indicating and confirming the slow nature of electron transfer of the electrode reaction.

The asymmetry and the displacement of the forward and reverse sweep, further confirming the sluggish of electron transfer of ECEC scheme of the oxidative processes of investigated compound. The standard reduction potentials were determined from the deconvoluted peak potentials of the two peaks (Table 2). The values of  $E_1^0$  &  $E_2^0$  determined from Figure 3 agree well with the values calculated from cyclic voltammogram (Table 2).

The height of deconvoluted peak is proportional to the concentration of the electroactive species, to the surface area of the electrode, and to the scan rate  $\nu$ . It, was noted that, the peak shape is very dependent on  $n$ , the number of electrons transferred, as  $n$  increase, the peak is predicted to become narrower and much higher. As indicated in Fig.3 the peak width of the first peak is narrower than the second one confirming consuming of two sequential electrons in the second step. i.e the first one consume one electron and the second one consume two electrons with very close two reduction potentials for the two electrons transfer in the second peak. The peak height of deconvolution ( $e_p$ ) is used for determination the diffusion coefficient (D) using Eq.(12)[13- 16].

$$e_p = \frac{\alpha n^2 F^2 \nu C^{bulk} D^{1/2}}{3.367 RT} \quad (12)$$

Values of the diffusion coefficient (D) calculated via Eq. (12) are given in Table 2.

Also, the number of electrons consumed in the electrode reaction ( $n$ ) was calculated from Eq. (13).

$$n = \frac{e_p 3.367 RT}{\alpha F \nu I_{lim}} \quad (13)$$

$$n = \frac{0.086 e_p}{I_{lim} \alpha \nu}$$

The total number of electrons consumed in electrode reaction was found to be 4.1 for the first wave and 2.08 for the second one

i.e the total  $n$  is 6.18 ( $\approx 6.0$ ) The successful determination of ( $n$ ) using Eq. 13 without knowing the electrode surface area can be considered a simple and precise method for this purpose. From the above discussion it was found that, the  $I_1$  vs  $E$  and  $(dI_1/dt)$  vs  $E$  curves were easier to interpret, support and confirm the nature of electrode reaction and the data extracted from  $i$  vs  $E$  curve.

Diffusion coefficient ( $D$ ) of the compound under investigation was also determined from a simple and accurate method via combination between the peak current of the cyclic voltammogram and the definition of limiting convoluted current using the following relationship[17]:

$$I_{lim} = i_{pirr} / 3.099 (\alpha n_a v)^{1/2} \quad (14)$$

Where  $I_{lim}$  is the deduced limiting convoluted current,  $i_{pirr}$  is the peak current of the cyclic voltammogram and the other parameters have their usual meaning. Table 2 gives the value of  $D$  estimated via relationship (14) and indicated good agreement of those values obtained from Eq. (1).

The standard heterogeneous rate constant ( $k_s$ ) of the investigated compound was calculated from the working curve using the values of  $E_p - E_{p/2}$  versus the dimensionless parameter  $\psi$  [18]. Values of  $k_s$  determined from this method were listed in Table 2.

### 3.3.1. Controlled Potential Coulometry (CPC)

The number of electrons consumed in the reduction process in solutions of pH 5 & 10.4 was determined experimentally by using CPC technique. The number of electrons ( $n$ ) was evaluated using the relationship:

$$Q = nM/Fw,$$

in which  $w$  is the weight (in grams) of the depolarizer,  $M$  its molecular weight,  $F$  is the Faraday's constant, and  $Q$  is the charge in coulombs. The results obtained denoted that ( $n$ ) equals to  $4 \pm 0.11$  electrons at potential corresponding to the limiting current at the first wave in acidic and alkaline solutions and  $6 \pm 0.13$  electrons at potential corresponds to that of the second wave. This means that for first wave ( $n$ ) equals to 4 while for second one  $n$  equals to 2 electrons.

### 3.4. Treatment of Data via Digital Simulation

The accurate digital simulation of the investigated compounds was used for testing the experimental electrochemical parameters.

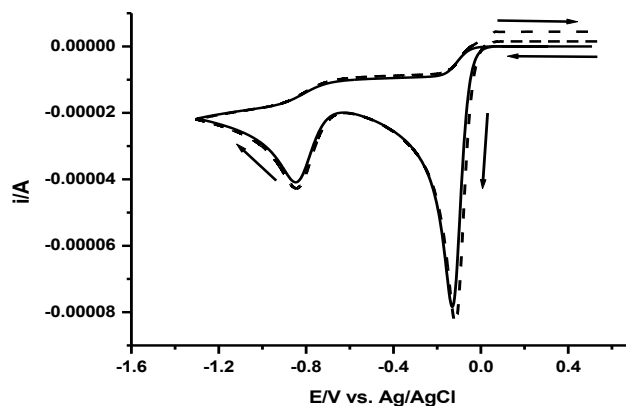


Figure 4. Matching between experimental voltammogram of quinolone azo dye (----) and simulated voltammogram (—) at a scan rate of  $0.2V.s^{-1}$ .

The method used for testing the parameters was made by fitting the simulating voltammograms on the experimental data, using the average experimentally determined parameters.

In the present article, the test for knowing the type of electrode reaction was done by making simulation, with three types of electrochemical reactions namely:

i.  $E_{irr}$ , ii.  $E_{rev}C_{irr}$  & iii.  $E_{irr}C_{irr}$ . The electrochemical parameters used in the three systems of electrochemical reactions mentioned are:

- $D$  (diffusion coefficient of the electroactive species),
- $E^0$  (standard redox potential),
- $C$  (bulk concentration of the electroactive species),
- $k_s$  (standard heterogeneous rate constant),
- $v$  (scan rate),
- $T$  (room temperature),
- $k_f$  (forward homogeneous chemical rate constant),
- $k_b$  (backward homogeneous chemical rate constant),
- $k_c$  ( $k_f + k_b$ ) and
- $\alpha$  (cathodic symmetry coefficient).

Table 3: characteristics of the first peak of the investigated compound measured experimentally and theoretically at pH 2.0 & 8.0 at different scan rate.

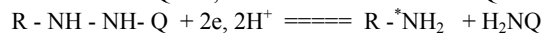
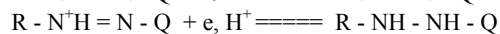
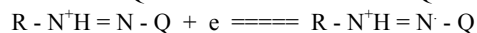
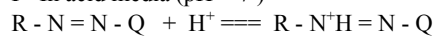
$v$	pH	Ep-Ep/2 mV		ip uA		Ep mV		$I_{lim}$ uAs <sup>-1/2</sup>	
		a	b	a	b	a	b	c	d
50	2.0	20.0	21.1	0.95	0.96	70.0	71.0	2.49	2.48
100		30.0	29.5	1.30	1.31	90.0	92.1		
200		70.0	71.0	2.20	2.22	-10.0	-9.5		
500		100.0	101.1	5.40	5.48	-36.0	-35.6		
50	8.0	20.0	21.0	0.80	0.85	-0.40	-401.0	2.50	2.49
100		30.0	31.5	1.70	1.74	-0.42	-420.2		
200		33.0	33.8	3.20	3.25	-0.43	-432.0		
500		37.0	38.1	6.65	6.70	-0.46	-464.0		

experimental values, (b) theoretical values, (c) deduced convoluted limiting current and (d) actual simulated convoluted current.

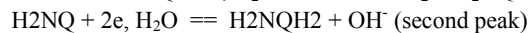
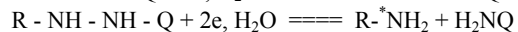
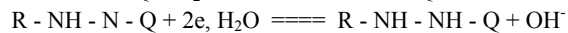
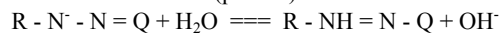
Table 3 shows the peak characteristics measured experimentally and that obtained theoretically for  $E_{irr}C_{irr}$  system. Fig. 4 indicates the good agreement between the generated theoretical voltammogram of the  $E_{irr}C_{irr}$  system and experimental cyclic voltammogram at pH 2.0, and a scan rate  $0.2 \text{ V.s}^{-1}$ . The homogeneous rate constant ( $k_c$ ) for the chemical reaction ( $5 \text{ s}^{-1}$ ) was determined by simulation and its values at the selected pH are given in Table 2.

Based on the obtained results and our discussion, the electrode reaction of the investigated compound can be suggested as follows:

I- In acid media (pH < 7)



II- In alkaline media (pH > 7).



\* identified product of electrolysis

The positive dye test given by the solution of the depolarizer after controlled potential electrolysis confirmed the presence of an aromatic amines (identified products) as one of the reduction products as well as verification of the proposed mechanism.

#### 4. CONCLUSION

In this article, the electrochemical parameters of quinolone azo dye compound at mercury electrode in ethanolic Britton – Robinson solutions of pH 2.0 – 12.0 were determined using cyclic and convulsive voltammetry techniques. The electrode pathway of the investigated compounds was found to proceed as ECEC mechanism. The test for diagnosis of the type of electrode mechanism as well as verification of the values of electrochemical parameters determined experimentally were performed via digital simulation method. From controlled potential coulometry technique, the overall number of electrons participating in electrode reaction was calculated.

#### 5. ACKNOWLEDGEMENT

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