

# Electrochemical Investigation of Antibacterial Laser Dye Compound in 1,2-Dichloroethane at a Platinum Electrode

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**ABSTRACT:** *Diolefinic antibacterial laser dye namely 1,4-Bis[2-(4-Pyridyl) Vinyl] Benzene (4PVB) have been investigated electrochemically using cyclic voltammetry, chronoamperometry, convolution and deconvolution voltammetry combined with digital simulation techniques at a platinum electrode in 0.1 mol / L Tetra Butyl Ammonium Perchlorate (TBAP) in solvent 1,2-dichloroethane. The diolefinic species were reduced by consuming two sequential electrons to form radical anion and dianion. The second electron transfer was followed by chemical step i.e the electrode reaction proceed as EEC scheme. In scanning the potential to positive direction, the diolefinic laser dye compound was oxidized by loss of one electron, which was followed by a fast chemical process ( isomerization or association). The pathway of electrode reaction and the electrochemical parameters of the investigated compound were discussed & determined using cyclic voltammetry and chronoamperometry techniques. The extracted electrochemical parameters were verified and confirmed via digital simulation and convolutive voltammetry methods.*

**KEY WORDS:** *Cyclic voltammetry, Convolutive voltammetry, Digital simulation, Antibacterial laser dye, Electrochemical parameters.*

## INTRODUCTION

Certain diolefinic derivatives were found to act as antibacterial compounds [1]. It was established that photodynamic therapy is an alternative treatment for many infections or diseases [2-4]. In vitro studies was exhibited the usage of laser combined with a photosensitizer has an strong effect against bacteria, yeast, viruses and parasites [5]. However, a large number of parameters

can influence the number of microorganisms affected by this technique such as; type and concentration of the photosensitizer, microorganism's physiologic stage, photosensitizer incubation period before the radiation, exposure period and density of laser energy [6]. Photodynamic therapy promotes the destruction of the target cell via oxidation mechanisms that lead to cell membrane lysis and protein inactivation [7].

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The parameters related to the laser such as wavelength, power density or high intensity that arrive to the tissue and the energy density that is responsible for the desired radiation effect are very important for sensitization process [8,9].

Many diolefinic derivatives have been used as monomers for solid state four-center type photopolymerization [10-13], laser dye [14-20] and fluorescent whitening agents [21,22]. Other applications of laser dyes compounds are in UV stabilization of polymers [23], electrochromic display [24], optical imaging devices [25] and electroluminescent devices [26]. Both photophysical and photochemical properties of these dyes are very sensitive to ambient conditions e.g. medium viscosity, polarity and temperature as well as material concentration and excitation wavelengths [27,28]. These factors are important when diolefinic dyes undergo molecular association [29-33].

In the present paper we report the electrochemical investigation of diolefinic antibacterial laser dye compound namely, 1,4-Bis[2-(4-Pyridyl) Vinyl] benzene (4PVB) at platinum electrode in 1,2-dichloroethane / 0.1 mol / L TBAP using cyclic voltammetry, convolution - deconvolution voltammetry and chronoamperometry combined with digital simulation techniques.

## EXPERIMENTAL SECTION

### Materials

The preparation and purification of 1,4-bis[2-(4-pyridyl) vinyl] benzene have been carried out according to the general condensation procedure reported for the preparation of the series of diolefinic compounds [34]. The solvent, 1,2-dichloroethane used in this work was of analytical grade. The prepared compound has the general structure formula:



where Py is the pyridine ring and Ph is the phenyl ring.

### Instrumentation

A conventional three electrode cell configuration linked to an EG & G model 170 PAR apparatus were used for cyclic voltammetry measurements. The platinum electrode surface was  $1 \times 10^{-6} \text{ m}^2$  as a working electrode, Ag/AgCl/KCl as a reference electrode, coiled platinum wire as a counter electrode and 0.1 mol / L Tetra Butyl

Ammonium Perchlorate (TBAP) as background electrolyte. Cyclic voltammograms were recorded after background subtraction and iR compensation to minimize double-layer charging current and solution resistance. The working electrode was polished on a polisher Ecomet grinder. Cyclic voltammetric data were obtained at scan rates ranging from 0.02 to 2 V/s in non aqueous media at  $22 \pm 2 \text{ }^\circ\text{C}$ . Digital simulation of the data for cyclic voltammetric experiments was carried out on a PC computer using EG & G condesim package. Convolution-deconvolution voltammetry was performed using EG & G condecon software package. All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

## RESULTS AND DISCUSSION

### Electroreduction of 4PVB

The diolefinic antibacterial laser dye compound, 4PVB, was measured via cyclic voltammetry in solvent,  $\text{CH}_2\text{ClCH}_2\text{Cl}$  at scan rates ranging from 0.02-2 V/s. It was found that the peak current increased with scan rate, while the cathodic and anodic peak potentials of the reduction process were independent of scan rate. From cyclic voltammetric investigation, it was found that the cathodic reduction of the diolefinic laser dye proceeded as fast charge transfer at low and high sweep rates. This behaviour demonstrates that the first charge transfer produces a radical anion that gains another electron to form a dianion in a reversible process. Fig. 1 gives an example of the cyclic voltammograms at various sweep rates of the investigated diolefinic laser dye compound. The second charge transfer is followed by a chemical step due to a isomerization process of trans form to cis or the product association of the product arising after the second charge transfer [35,36]. It was observed that the first reductive peak (I) was coupled with the oxidative peak (II) in the reverse scan, while the second reductive peak (III) was coupled with the small oxidative peak (IV) in the backward sweep. The height of the oxidative peak (IV) increased with increasing the sweep rate. The cyclic voltammograms indicate that the second electron transfer is followed by a chemical step (isomerization or association process), which means that the electrode reaction behaves as EEC mechanism. The homogeneous chemical rate constant of the chemical process is fast

Table 1: Electrochemical parameters of compound 4PVB of the reduction process.

Electrochemical Parameters							
$E_1^0$ V	$E_2^0$ V	$k_{s1} \times 10^4$ m/s	$k_{s2} \times 10^4$ m/s	$D_1 \times 10^9$ m <sup>2</sup> /s	$D_2 \times 10^9$ m <sup>2</sup> /s	$k_c$ l/s	$\alpha$
a) -2.15	-2.28	4.6	5.8	4.9	4.5	3.8	0.48
b) -2.14	-2.29	4.4	5.9	4.7	4.7	3.7	0.49
c) ----	-----	----	----	4.6	4.6	----	----
d) -2.11	-2.27	-----	-----	4.3	4.5	----	----

a) Experimental values; b) simulated values; c) values of D calculated via Eq. (3); d) values calculated from convolutive voltammetry.

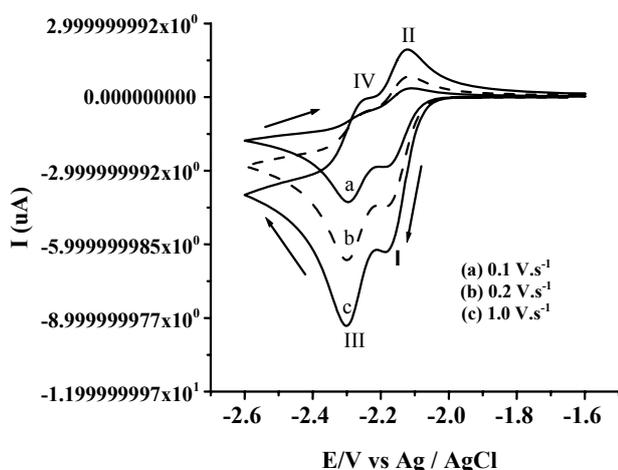


Fig. 1: Cyclic voltammogram of the reduction process of diolefinic laser dye 4PVB in  $CH_2ClCH_2Cl$  at various scan rates.

as indicated from the low height of the second oxidative peak (IV) [36].

The peak separation  $\Delta E_p$  of the first and second charge transfers were found to be 59 and 56 mV confirming the rapidity of charge transfer in 0.1 mol/L TBAP/ $CH_2ClCH_2Cl$ . The redox potential ( $E^0$ ) was determined from the mean position of the peak potentials (Table 1). The standard heterogeneous rate constant ( $k_s$ ) was extracted from the cyclic voltammograms via peak separation using  $\Delta E_p$  values vs. dimensionless parameter ( $\Psi$ ) constants [37]. In this case, the peak current  $i_p$ , is governed by the Randle-Sevcik relationship [38]. For the second peak, the decrease of current function ( $i_p/v^{1/2}$ ) exponentially with increasing the scan rate is compatible with an electrode reaction coupled with a following chemical reaction (EC) [38]. Also, the ratio  $i_{pc}/i_{pa}$  was found to be less than unity confirming EC mechanism. From the plot of  $i_p$  vs.  $v^{1/2}$ , the diffusion coefficient (D) of the

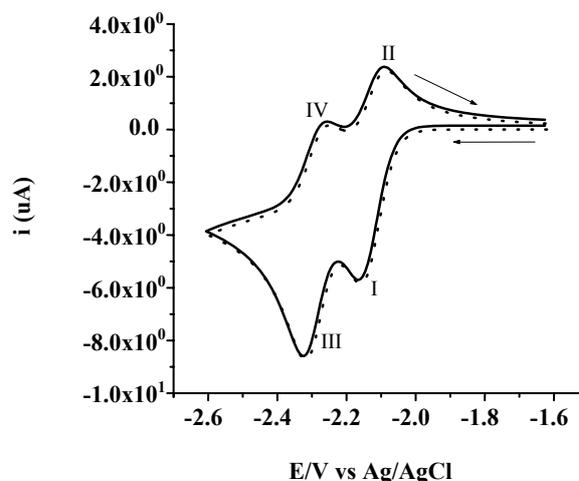


Fig. 2: Matching between reductive experimental voltammogram (—) and simulated voltammogram (···) of 4PVB at a sweep rate of 1 V/s.

electroactive species is determined. The calculated values of D are cited in Table 1.

A direct test of the experimental electrochemical parameters was verified via matching of the theoretically generated voltammograms with the experimental ones using the average experimentally determined values of  $k_s$ , D,  $E^0$ , and  $k_c$  cited in Table 1 for a symmetry coefficient  $\alpha$  of  $0.49 \pm 0.02$ . The results given in Fig. 2 employ the experimental and theoretical values of the electrochemical parameters of the compound 4PVB, at sweep rate of 1 V/s which demonstrate excellent agreement between the captured and the simulated data.

In cases of simple electron transfer or chemical reaction coupled with electron transfer, the  $I_1$  convolution which is defined [39,40] as:

$$I_1 = \frac{1}{(\pi)^{0.5}} \int_0^t \frac{i(u)}{(t-u)^{0.5}} du \quad (1)$$

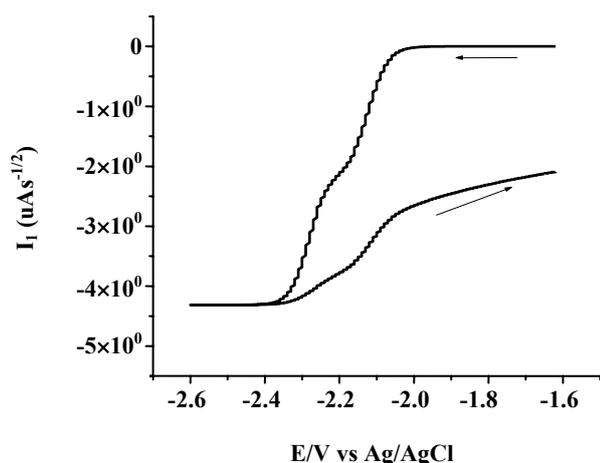


Fig. 3: Convolution voltammetry ( $I_1$ ) of the reductive cyclic voltammogram of 4PVB at a sweep rate of 0.1 V/s.

allows to determine the diffusion coefficient of the bulk species from the Eq. (2) [40]:

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

where  $I_{lim}$  is the value of the limiting convoluted current achieved for  $I_1$  when the potential is driven to a sufficiently extreme value past the wave; the other terms have their usual significance.

The value of the diffusion coefficient ( $D$ ) corresponding to the reduction step was calculated via Eq. (2) and are listed in Table 1.

The  $I_1$  convolution of the reductive voltammogram of 4PVB at a scan rate of 0.1 V/s is indicated in Fig. 3. The  $I_1$  convolution at all scan rates did not return to initial zero current value, confirming the existence of chemical reaction (isomerization or association) which follows the second charge transfer, i.e. EEC mechanism. The deconvolution of the current ( $dI_1/dt$ ) of the voltammogram at a sweep rate of 0.1 V/s revealed the asymmetry of the forward and reverse scan, further confirming the EEC nature of the reduction process (Fig. 4). The standard reduction potential of the investigated laser dye was determined from the maximum point value of the two deconvoluted peaks (Table 1).

It was found that the forward and backward peaks of the first reductive charge transfer and the second reductive charge transfer were into alignment at the first reduction potential ( $E_1^0$ ) and the second reduction potential ( $E_2^0$ ) respectively.

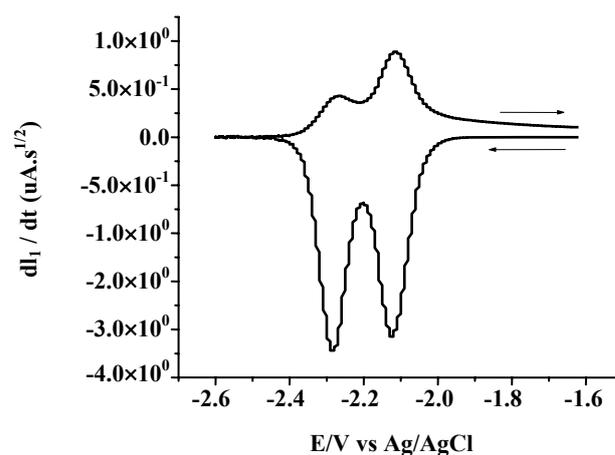


Fig. 4: Deconvolution voltammetry ( $dI_1/dt$ ) of the reductive cyclic voltammogram of 4PVB at a sweep rate of 0.1 V/s.

The values of  $E_1^0$  &  $E_2^0$  determined from deconvolution voltammetry via Fig. 4 agree well with the values calculated from cyclic voltammetry (Table 1). Also, the value of diffusion coefficient were calculated from deduced convoluted current ( $I_{limd}$ ) via the following relationship [39,40]:

$$I_{limd} = \frac{i_{prev}}{2.788(nv)^{1/2}} \quad (3)$$

where  $I_{limd}$  is the deduced limiting convoluted current, which is defined as the limiting convoluted current ( $I_{lim}$ ) from Eq. (2).

The value of diffusion coefficient calculated from  $I_{limd}$  compare well with the value calculated from cyclic voltammetry, convolutive and deconvolutive voltammetry (Table 1).

The diffusion coefficient was also determined from deconvolution transforms using Eq. (4) [39].

$$e_p = \frac{n^2 F^2 v C A D^{1/2}}{4 RT} \quad (4)$$

where  $e_p$  is the peak height (in Ampere) of the forward deconvolution sweep and the remaining terms have their usual meanings. Value of the diffusion coefficient estimated from this method is given in Table 1.

The proportionalities of  $e_p$  with sweep rate  $v$  are presented and shown in Fig. 5. It is clear that for both anodic peaks I and III the linearity is satisfactory confirming the diffusion controlled nature of 4PVB

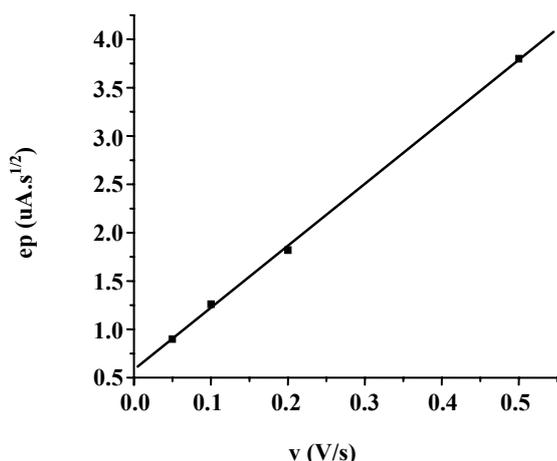


Fig. 5: Plot of  $e_p$  versus the sweep rate of the first peak.

reduction at platinum electrode in 0.1 mol/L TBAP/ $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ .

The homogeneous chemical rate constant ( $k_c$ ) of the chemical process which follows the second charge transfer was determined from the  $i_{p\text{rev}}/i_{p\text{fwd}}$  values as a function of the theoretically calculated  $k_c t$  values at different scan rates [37]. The average calculated value of  $k_c$  (3.61 1/s) agrees well with the value used in the generating simulated cyclic voltammograms

From the obtained results, it can be seen that the redox potential of the second reduction process is more negative than that of the first one, which indicates that the second process requires more energy than the first one. The separation of the peak potentials for systems with two redox centers is in terms of the comproportionation equilibrium constant of the intermediate (i.e. the product of the first electron transfer reaction). This is given by the following equation [41]: which gives  $5.12 \times 10^5$  for  $K_c$  value, indicating intermediate degree of delocalization ( $100 < K_c < 10^6$ ) [42].

$$K_c = \exp \left[ \frac{(E_1^0 - E_2^0)F}{RT} \right] \quad (5)$$

The presentation of  $i$  vs  $t$  of the voltammogram at sweep rate of 1.0 V/s is shown in Fig 6a. The plot produce discontinuity  $\Delta i_c$  at  $t = 10.02$  s due to the reversibility of the scan. By selecting the data points a Cottrell plot is obtained as current versus the reciprocal Square root of time. The slope of Cottrell plot yields

a diffusion coefficient  $D = 5.9 \times 10^{-9} \text{ m}^2/\text{s}$  and  $3.7 \times 10^{-9} \text{ m}^2/\text{s}$  of the first and second peak respectively. Fig. 6b indicate an example of  $i$  vs  $1/(t)^{0.5}$  of the first peak. Inspection of Fig. 6a confirming that the complication of the second charge transfer of 4PBV with chemical process.

#### Electrooxidation of 4PBV

The diolefinic antibacterial laser dye compound 4PBV gives only one unidirectional irreversible oxidation peak at low sweep rates  $\leq 0.2$  V/s. An example response of the oxidative cyclic voltammograms of 4PBV at sweep rate of 0.1 V/s is illustrated in Fig. 7. The presence of one peak at low sweep rate values indicates an EC mechanism with a fast chemical step. Also the shift of peak potential to more positive values with increasing the sweep rate as well as the value of peak width 124 mV of the voltammogram at sweep rate of 0.1 V/s reflects the moderate rate of electron transfer that precedes the chemical step.

At low sweep rates, the reduction potential ( $E^0$ ) of 4PBV were calculated from the plot of  $E_p$  vs.  $(E_p - E_{p/2})$  using the following equation [43]:

$$E_p = E^0 + (E_p - E_{p/2}) / Z \quad (6)$$

So, from the intercept of this plot, the value of  $E^0$  was determined and is listed in Table 2. The standard heterogeneous rate constant ( $k_s$ ) was determined from digital simulation by the good agreement between the experimental and theoretical voltammograms. Also, the diffusion coefficient was determined from the slope of  $i_p$  vs.  $v^{0.5}$  [44]. The symmetry coefficient ( $\alpha$ ) was calculated from the values of half-peak width via the following equation:

$$E_p - E_{p/2} = 48 / \alpha n_a \quad (7)$$

In the case of moderately fast electron transfer, the diffusion coefficients ( $D$ ) of the compound under investigation was determined from deduced limiting convoluted current using the following equation [38,39]:

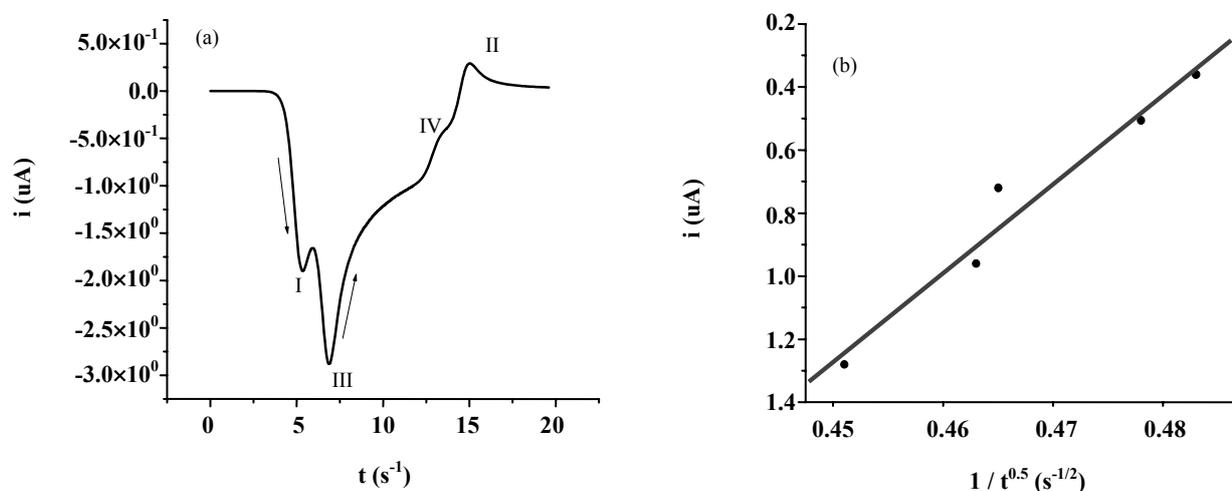
$$I_{\text{lim}} = \frac{i_p}{3.099(\alpha n_a v)} \quad (8)$$

Where  $i_p$  is the peak current in amp, and the other terms have their usual meanings. Value of the diffusion coefficient ( $D$ ) calculated via Eq. (8) are listed in Table 2.

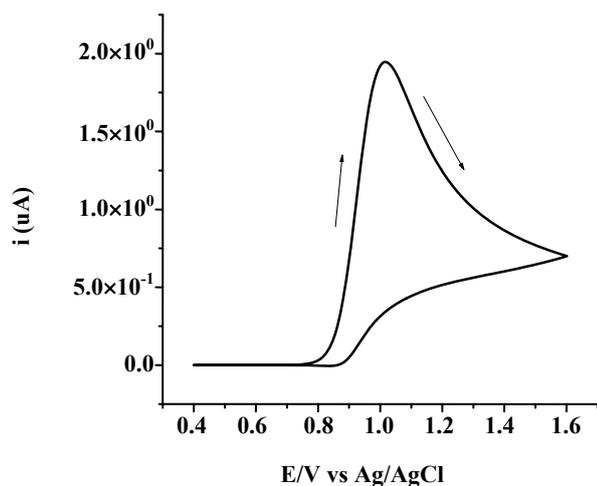
**Table 2: Electrochemical parameters of compounds 4PVB of the oxidation process.**

Electrochemical Parameters					
$E^0$ V	$k_s \times 10^6$ m/s	$D \times 10^9$ $m^2/s$	$E_p - E_{p/2}$ , mV 1/s	$k_c$	$\alpha$
a) 0.940	9.6	2.91	108	4.20	0.34
b) 0.935	8.7	3.21	109	4.15	0.35
c) ----	----	2.41	---	----	----
d) 0.925	----	3.10	---	4.10	0.35

a) Experimental values; b) simulated values; c) values of  $D$  calculated via Eq. (8); d) values calculated from convolutive voltammetry.



**Fig. 6: Representation of  $i$  vs  $t$  (a) and  $i$  vs  $t^{-1/2}$  (b) of the reductive cyclic voltammogram of 4PVB.**



**Fig. 7: Cyclic voltammogram of the oxidation process of diolefinic laser dye 4PVB in  $CH_2ClCH_2Cl$  at scan rate of 0.1 V/s.**

It was observed that the oxidative cyclic voltammetry at sweep rates  $\geq 0.5$  V/s exhibited a reduction peak in the reverse direction coupled with oxidation peak. Fig. 8 gives an example of the oxidative cyclic voltammogram at sweep rate of 2 V/s.

The peak separation  $\Delta E_p$  allows us to calculate the standard heterogeneous rate constant ( $k_s$ ) [37] which found to be in agreement with that calculated from simulation method. Also the homogeneous chemical rate constant ( $k_c$ ) can be calculated via the kinetic convolution ( $I_2$ ) of voltammogram at a sweep rate of 2 V/s, which is defined as [39]:

$$I_2 = \frac{1}{(\pi)^{0.5}} \int_0^t \frac{i(u) \exp(-kc(t-u))}{(t-u)^{0.5}} du \quad (9)$$

which are presented in Fig. 9 as calculated from the appropriate value of the chemical rate constant obtained

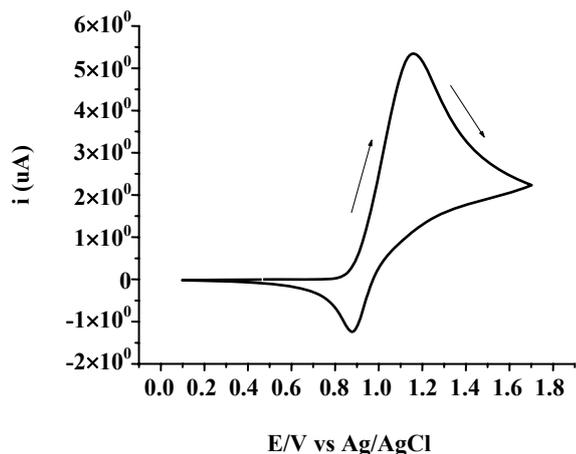


Fig. 8: Oxidative cyclic voltammogram of 4PVB in  $\text{CH}_2\text{Cl-CH}_2\text{Cl}$  at sweep rate of 2 V/s.

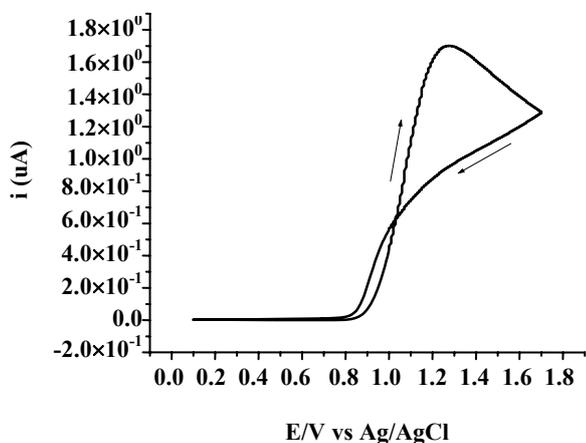


Fig. 9: Kinetic convolution ( $I_2$ ) of the oxidative process of 4PVB in  $\text{CH}_2\text{Cl-CH}_2\text{Cl}$  at scan rate of 2 V/s.

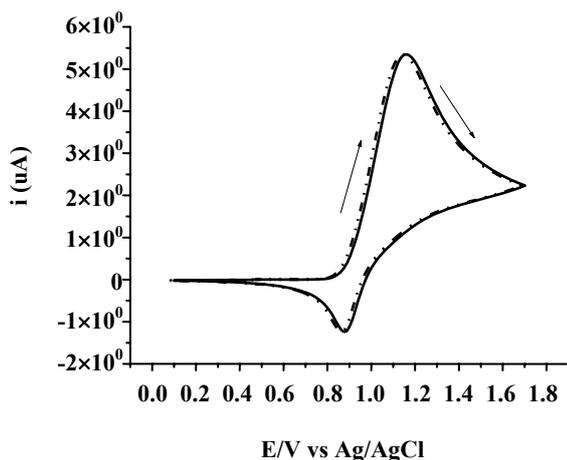


Fig. 10: Matching between oxidative experimental voltammogram (-) and simulated voltammogram (···) at a sweep rate of 2 V/s.

by inserting trial value of the homogeneous chemical rate constant ( $k_c$ ) into the convolution calculation until  $I_2$  returned to zero immediately after the wave. This is merely a reflection of the absence of the reductive species of 4PVB at the electrode at potentials before the wave when the bulk concentration of this species is zero. The true  $k_c$  value determined from  $I_2$  convolution is  $4.1 \text{ s}^{-1}$ , which agrees well with the values calculated from cyclic voltammetry and the value used in generating the cyclic voltammograms.

Fig. 10 shows an example of the comparison between experimental and theoretical voltammograms of 4PVB at sweep rate of 2 V/s, which indicates well matching between the two curves confirming the accuracy of the electrochemical parameters obtained from experimental cyclic voltammograms. The oxidative experimental and theoretical data of 4PVB are listed in Table 2.

Fig. 11 explain the convoluted and deconvoluted voltammograms of 4PVB recorded at a sweep rate of 2.0 V/s.

The values of the diffusion coefficient ( $D$ ) was determined via Eq. 2 while the value of standard reduction potential ( $E^0$ ) was determined from the average peak position values of deconvoluted voltammograms (Table 2).

The diffusion coefficient of the oxidative process was also determined from deconvolution transforms using Eq. (4) [40]. Value of the diffusion coefficient estimated from this method is given in Table 2.

The proportionalities of  $e_p$  with sweep rate  $v$  are presented and shown in Fig. 12. It is clear that the linearity of the plot is satisfactory indicating the diffusion controlled nature of 4PVB oxidation at platinum electrode in 0.1 mol / L TBAP/ $\text{CH}_2\text{ClCH}_2\text{Cl}$ .

The presentation of  $i$  vs  $t$  of the voltammogram at sweep rate of 1.0 V/s is shown in Fig 13. The plot produce discontinuity  $\Delta i_c$  at  $t = 0.8 \text{ s}$  due to the reversibility of the scan. By selecting the data points a Cottrell plot is obtained as current versus the reciprocal square of time. The slope of Cottrell plot yields a diffusion coefficient  $D = 3.9 \times 10^{-9} \text{ m}^2 / \text{s}$ . Inspection of Fig. 13 revealed that, the height of the forward and backward peaks is different, i.e the height of the oxidative peak is unequal to the height of the reductive peak confirming the complication of charge transfer of 4PVB with chemical process.

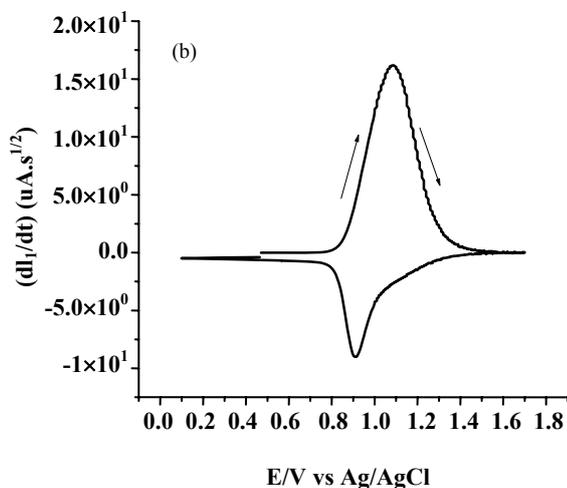
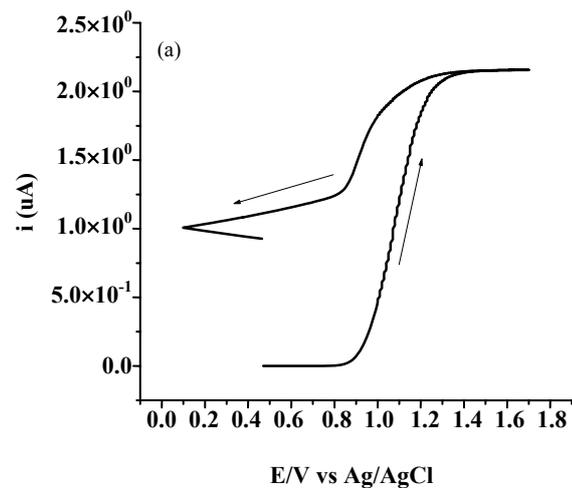


Fig. 11: Convoltuted voltammogram (a) and deconvoluted voltammogram (b) of 4PVB at sweep rate of 2 V/s.

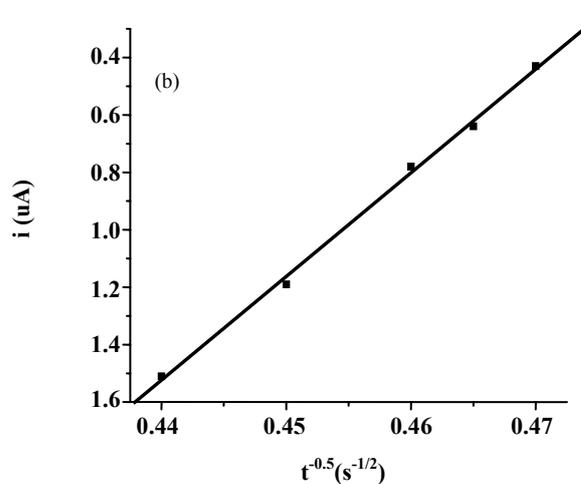
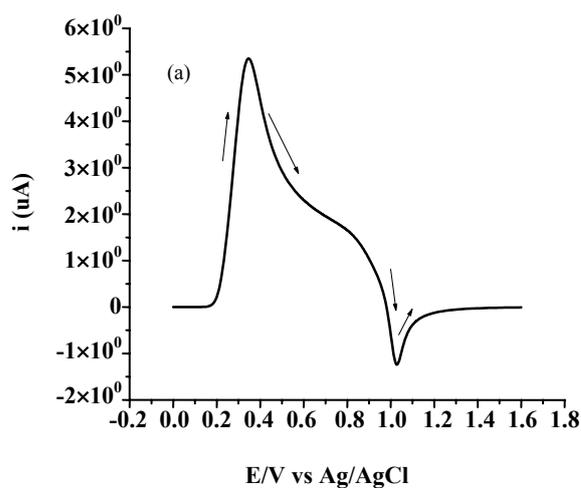


Fig. 13: Representation of  $i$  vs  $t$  (a) and  $I$  vs  $1/t^{0.5}$  (b) of the oxidative cyclic voltammogram of 4PVB.

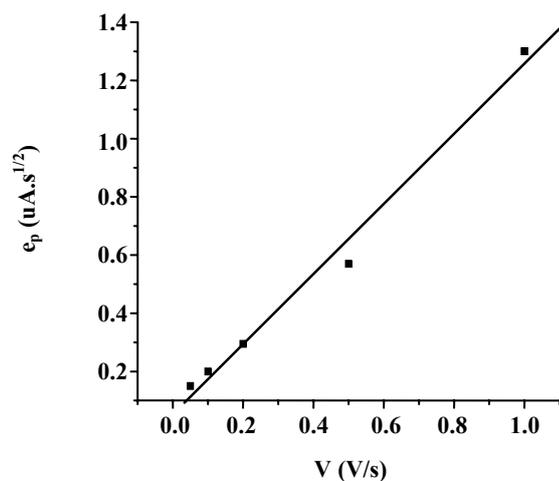
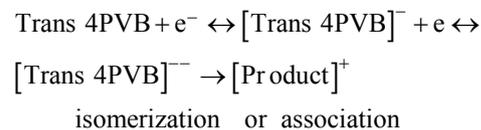


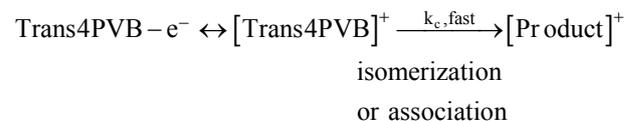
Fig. 12: Plot of  $e_p$  versus the sweep rate of the oxidative process of 4PVB.

From the above electrochemical studies the reductive and oxidative electrode behavior of the diolefinic antibacterial laser dye can be proposed to proceed as follows:

#### Reductive process



#### Oxidative Process



## CONCLUSION

It is evident from this studies that the electrochemical behavior of 4PVB in 0.1 mol / L TBAP / CH<sub>2</sub>Cl-CH<sub>2</sub>Cl at a platinum electrode takes place at two reduction peaks (I & III) coupled with two anodic peaks (II & IV). The obtained results in the present work demonstrates that the first charge transfer produces a radical anion that gains another electron to form a dianion. The second charge transfer is followed by a homogeneous chemical step due to an isomerization or association process. Electrooxidation of 4PBV gave only one unidirectional irreversible peak at low sweep rate  $\leq 0.5$  V/s. The experimental kinetic parameters were determined experimentally and verified via a digital simulation method by comparing the generated theoretical voltammograms with the experimental ones.

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