

Voltammetric investigation of electrooxidation of Methyl(E)-2-cyno(N-ethyl carbazol-2-yl) acrylate at a gold electrode

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Electrooxidation of cyano methyl acetate carbazole derivative was analyzed electrochemically at a gold electrode in 0.1 M tetrabutylammonium chloride (TBACl) in CH₂Cl₂ by convolutional voltammetry and numerical simulation methods. Investigation via Cyclic voltammetric indicated the existence of singly fast oxidation wave coupled with the reductive peak in the reverse direction. It was observed that the electrode pathway of the investigated methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound proceeds as EEC scheme. The electrochemical parameters of the oxidation process of the carbazole compound were calculated via cyclic voltammetry and convolutional voltammetry methods. The obtained data and the mechanistic of the electrode pathway were ascertained via numerical theoretical method.

Keywords: convolutional voltammetry, numerical simulation, Au electrode.

1. INTRODUCTION

Carbazole compounds may be used to investigate the experimental studies of molecular orientational order in thermotropic and lyotropic liquid crystals, in liquid-crystalline polymers, and in lipid membranes because of their excessive photostability and the long molecular formula [1,2]. The majority of the carbazole compounds were taken into consideration for utilization in natural electronic gadgets devices [3-5]. This may be further performing as a illuminated factor in liquid crystal shows operating in passive or active manners [6]. Carbazole dyestuff gift an immense variety of colorants so they're implemented in high-level colorants used in the car fabrication finalize [7].

The accumulation traits of those molecules are strongly controlled by the chemical formation of the substituents in carbazole framework, type of solvent, the awareness of the dye, and temperature [8].

It was worked out that, carbazole compounds have a perfect hole conducting efficiency, great photochemical fixedness, elevated charge transporter movability, and a markedly lowered ionization

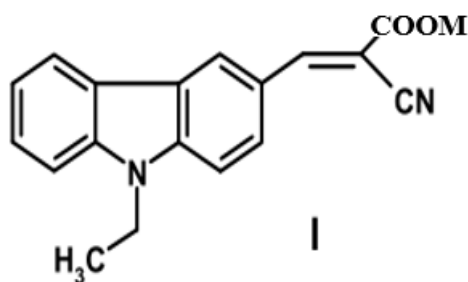
ability via π -conjugation [9-13]. In a similar fashion, carbazoles are surprisingly easy to operationalize at the 3-, 6-, or 9-sites. Characteristically substances with carbazole had been foremost as hole transporting substances [14-16] and hostess substances that permit green [17], red [18] and even blue [19] and [20] fluorescence.

It became noted that until now no electrochemical work has been carried out on methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate spinoff under consideration in CH_2Cl_2 solvent at an Au WE in 0.1 M TBACl utilizing convo-lution, deconvolution transforms, and numerical simulation methods. For that goal, the heterogeneous rate constant of electron transfer (k_s), the diffusion coefficient (D), the redox potential (E°), the coefficient of symmetry (α), and the mechanistic pathway of the carbazole compound under examination were calculated, and explained through cyclic voltammetry, convolution and deconvolution transform. The homogeneous rate constant of chemical reaction (k_c) was evaluated from numerical simulated. Numerical simulation was performed to establish and validate the values of the preparative electroch-emical factors and to identify the kind of the electrode reaction.

2. EXPERIMENTAL

2.1 Chemical compounds

The examined methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound have been synthesized and refined in conformity with the method accepted in published works [21]. The solvents utilized in this work have been of a spectroscopic stratum. The framework of the examined carbazole compound had been exhibited in scheme 1 [21].



Scheme 1. Structure of methyl(E)-2-cyno(N-ethyl carbazol-2-yl) acrylate.

2.2. Electrochemical measurements

Electrochemical voltammetric experiments have been performed utilizing a PAR Computer – managed Potentiostat brand 283 and PAR Model 175 Universal Programmer (from EG and G). Three electrode cell arrangements were utilized for achieving the electrochemical measurements. The working gold electrode with area of $5.65 \times 10^{-3} \text{ cm}^2$ was used, Pt wire was used as CE and Ag/AgCl as an RE.

The potential was measured against the Ag/AgCl RE at 25° Cand 0.1 M TBACl as heritage substance to causing the condenser current. The voltammograms were captured afterwards background subtraction and minimization of iR solution to reduce the condenser and solution resistance.

The WE was cleaned using a Ecomet grinder polisher. Cyclic voltammetric experiments had been captured at scan rate ranged from 0.02 - 5 V⁻¹ in the selected media at 24 ± 1°C.

Numerical simulation of the cyclic voltammetry was achieved on PC computer using EG & G condesim package. Nitrogen gas was passed into the running solutions for 15 min. after that an N₂ atmosphere was continue above the solution for the duration of the experiments.

3. RESULTS AND DISCUSSION

The redox behavior of methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound at a working gold electrode was done through cyclic voltammetry (CV) and convolution-deconvolution voltammetry methods in 0.1 M TBACl in dichloromethane solvent at ambient temperature 23 ± 2°C. Figure1 exhibits the cyclic voltammogram of the investigated methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate at scan rate (ν) of 0.2 V.s⁻¹.

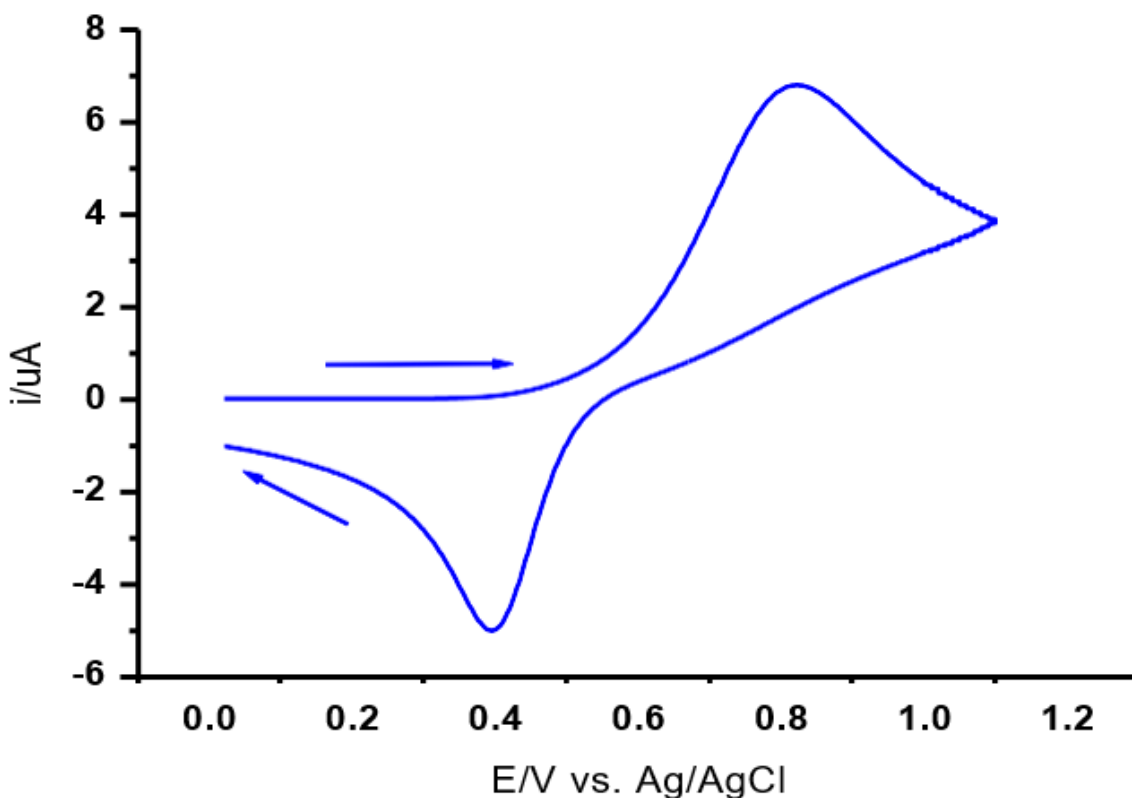


Figure 1. Cyclic voltammogram of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound at a Au electrode, ν 0.2 V.s⁻¹, in 0.1M TBACl and T = 23 °C

As shown in figure 1 the CV revealed a single oxidative peak ($E_{pa} = 0.823$ V) coupled with a reductive peak ($E_{pc} = 0.397$ V) at 25°C. The coupled peaks demonstrate the presence of a two sequential quasi-reversible electron transfer followed by a slow chemical step (EEC scheme) as indicated from the low steep of the peak concerning to the oxidation process. It was noted that the peak distance (ΔE_p) of cyano methyl acetate carbazole derivative under consideration ($\Delta E_p = E_{pc} - E_{pa}$) lie in the range of 130

– 650 ± 5 mV which more than that calculated value of (58 mV) for single-fast electron transfer [22]. This may be due to the sluggishness of the rate of electron transfer and further due to the existence of some solution resistance of the methylene chloride media.

3.1. Effect of sweep rate

Figure 2 (A & B) produces the cyclic voltammograms of methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound at a gold electrode, at variance sweep rates and $T = 23$ °C. It became observed that, the peak potential shift to greater positive value of potential with increasing the sweep rate which indicates the non-Nernstian nature of electrode behavior. Additionally, the ratio i_p^b/i_p^f at low sweep rate is less than unity due to the existence of chemical step following the sequential two electrons

transfer. The variance of the onward peak current (i^f) with sweep rate is indicated in figure 3. The plot produces straight line passes with the origin indicating that the diffusion nature of the mass transport of electroactive species [22].

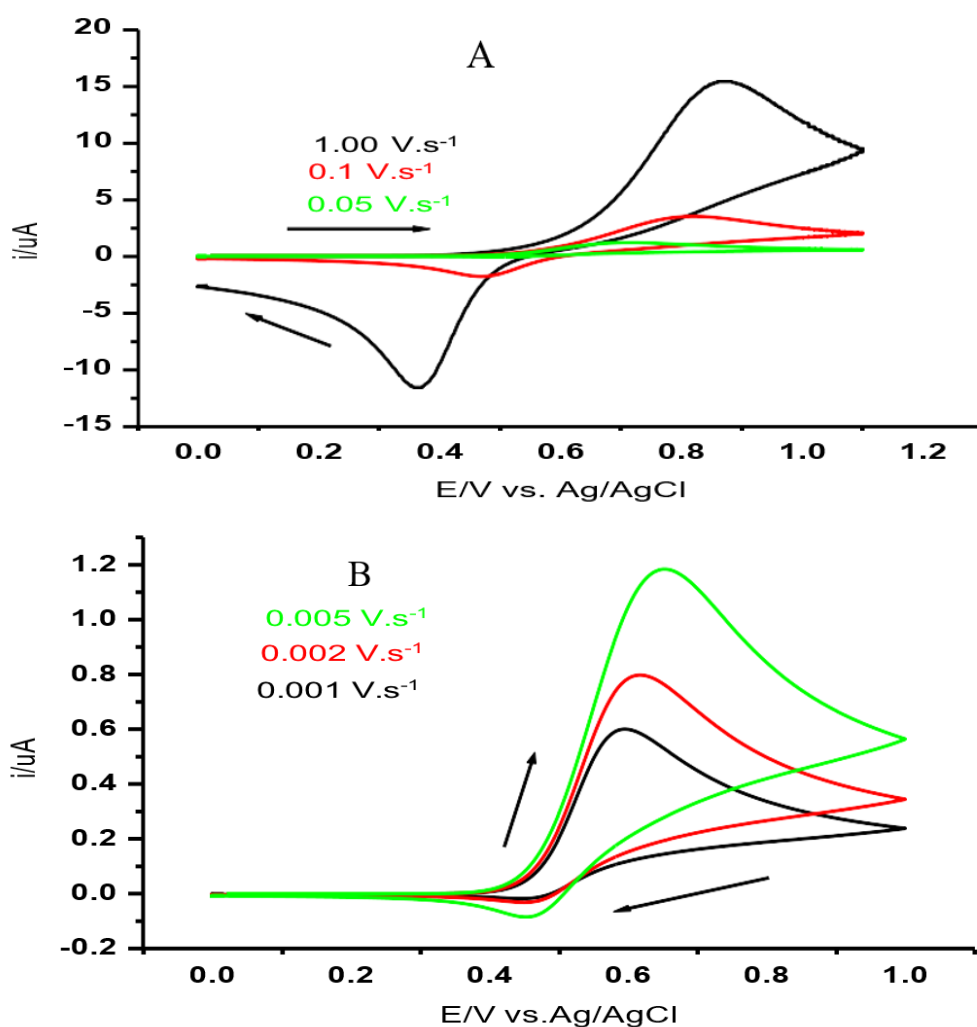


Figure 2. Cyclic voltammograms of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate at a gold electrode at different sweep rates, in 0.1M TBACl and $T = 23$ °C.

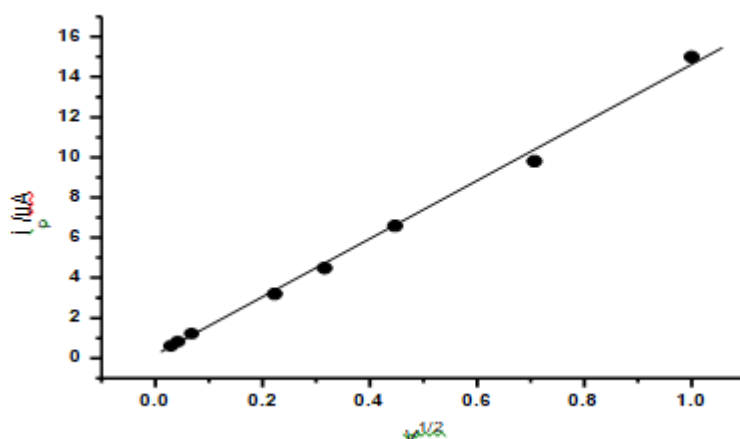


Figure 3. Variance of oxidative peak current of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound at Au electrode, with various sweep rates in 0.1M TBACl and $T = 23$ °C.

3.2. $i - t$ curve derived from cyclic voltammogram

The conversion of CV to $i - t$ plot of the oxidation approaches of the compound under examination at v of 0.2 V.s^{-1} is manifested in Fig.4. By way of taking the points of the decreasing part of the $i-t$ plot and presentation it as current (i) versus $1/(t)^{1/2}$ which produce a Cottrell plot as shown in figure 5. The slope of Cottrel plots of the examined species yields a D cited in Tables 1 & 2. As manifested in figure 4, the $i - t$ plots yields disconnectedness Δic at $t = 7.00$ s caused by the changeability of the scan. Exploration of Fig.4 exhibited that, the lack of equality of the highness of the moving onward and reversed directions, i.e. the highness of the forward peak is more than the highness of the backward peak confirming the presence of a chemical step beyond electron transfer process.

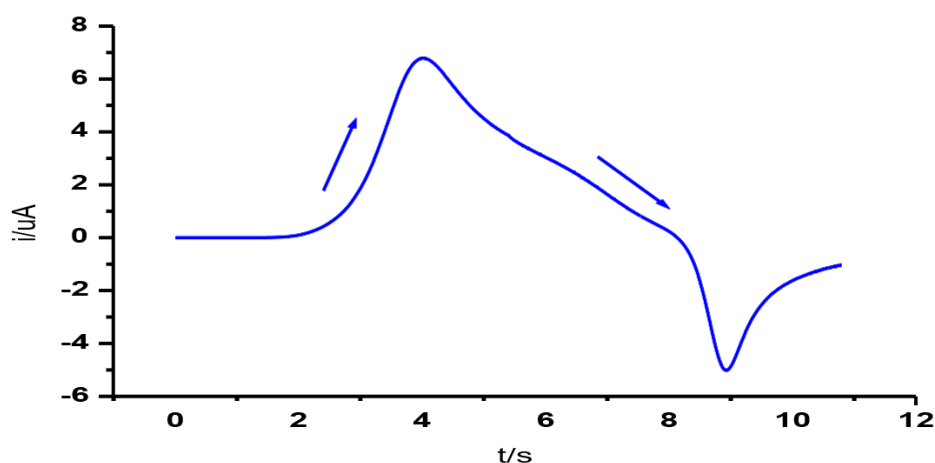


Figure 4. i vs. t plot of the oxidative step of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound at Au electrode, in 0.1M TBACl, v 0.2 V.s^{-1} and $T = 23$ °C.

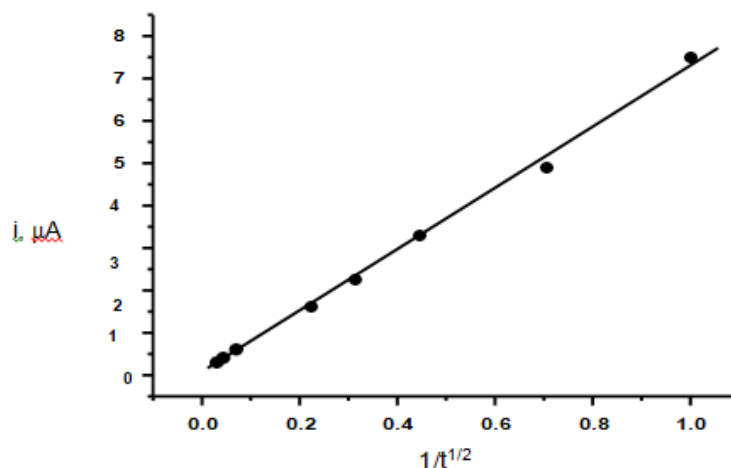


Figure 5. i_p vs. $1/t^{1/2}$ plot of the oxidative step of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound at Au electrode, in 0.1M TBACl, ν 0.2 V.s $^{-1}$ and T = 23 °C.

The determination of $E^{0'}$ of the investigated compound was achieved from the mean values of E^0 and used in virtual voltammograms.

The value of D was calculated from the relationship (2) [22],

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} S C^{\text{bulk}} D^{1/2} \nu^{1/2} \quad (2)$$

wherein i_p refer to the highness of the peak, n is the total number of electrons used in electrode reaction, α is the transfer coefficient and the ultimate characters have their ordinary definition. The value of D was found to be $5.96 \times 10^{-5} \pm 0.15$ cm 2 .s $^{-1}$.

Table 1. Kinetic parameters values received for cyano methyl acetate carbazole compound at an Au electrode at ν 0.2 V.s $^{-1}$

Technique	$k_s \times 10^{-4}$ (cm.s $^{-1}$)	$E^{0'}$ / V	$D \times 10^5$ (cm 2 s $^{-1}$)	α	k_c s $^{-1}$
Sim	3.95	0.532	5.58	0.31	0.052
CV	----	----	5.96	0.30	----
Conv.	----	----	5.25(a)	----	0.051
Decon.	----	0.535	5.27	----	----
Cottrell equation	----	0.54	5.65	0.31	----

Sim: numerical, CV: Cyclic voltammetry, conv: Convolution voltammetry, Decon: Deconvolution voltammetry.

3.3. Convolution-deconvolution voltammetry

Convolution voltammetry has been great degree of advantageous for understanding the mechanistic of numerous electrochemical processes [22-26]. The diffusion factor of cyano methyl acetate carbazole compound was determined through the relationship (3) [24],

$$I_{lim} = nFAD^{1/2}C^{bulk} \quad (3)$$

wherein the I_{lim} is the limiting magnitude attained for I_1 when the potential is enforced to a an adequate point beyond the peak, and the remaining characters have their ordinary definitions.

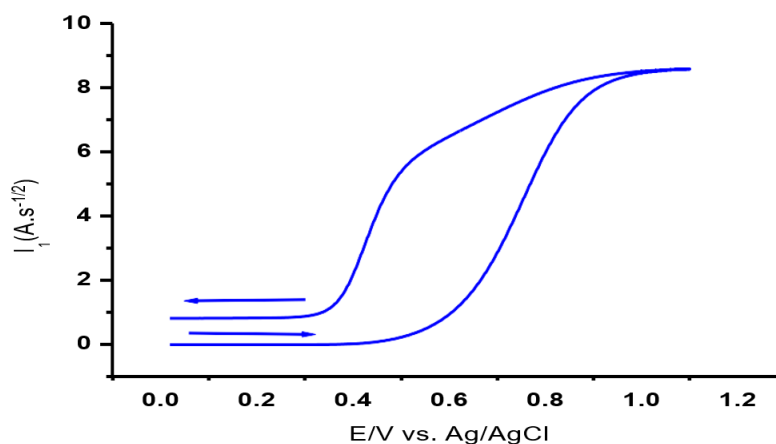


Figure 6. Convolution voltammogram of 5×10^{-4} M methyl(E)-2-cyno(N-ethyl carbazol-2-yl) acrylate compound at a Au electrode, in 0.1M TBACl, ν 0.2 $V.s^{-1}$ and $T = 23$ $^{\circ}C$.

The curve of I_1 convolution of the examined compound was clarified and showing in Figure 6, and producing an apparent space among the onward and reverse sweep and illustrate the low velocity of electron exchange of the redox step. As revealed in figure 6 the reverse sweep of the I_1 convolution at the ending of the sweep does not arrives to the initial point because of the existent of chemical step coupled with electrode pathway. The D values extracted through equations 3 are collected in table 1. The rate constant of chemical reaction (k_c) was exactly evaluated thru the I_2 convolution at a ν 0.2 Vs^{-1} , which portrayed in Figure 7 and evaluated from the proper value of k_c which attained by introducing test values of the k_c into the I_2 convolution till I_2 reached to zero directly after the peak [26]. The real k_c value driven from I_2 value was established to be $0.051 s^{-1}$ which consents well with the value utilized in numerical cyclic voltammograms.

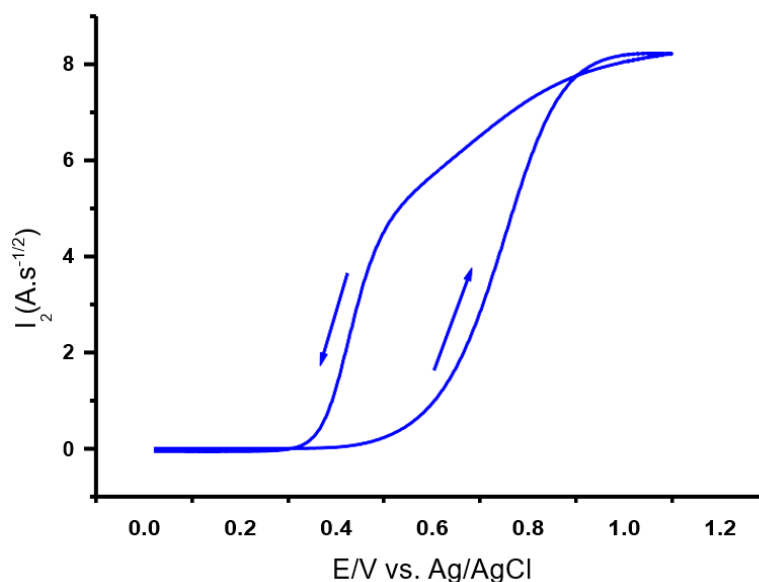


Figure 7. I_2 of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound in 0.1M TBACl at an Au electrode, ν of 0.2 Vs^{-1} and $T = 23 \text{ }^\circ\text{C}$.

3.4. Deconvolution voltammetry

It was established that, the current (dI_1/dt) as a feature of E for a fast electron system is described as [26-30].

$$e_p = (dI_1/dt) = nFAC\sqrt{D} a\zeta / (1+\zeta)^2 \quad (4)$$

wherein the symbol $a = n\nu F/RT$ and $\zeta = \exp [nF/RT (E - E^0)]$

the illustration of this equation at $\nu = 0.2 \text{ V.s}^{-1}$ of the oxidation manner of methyl(E)-2-cyno(N-ethyl carbazol-2-yl) acrylate compound at a Au electrode, ν of 0.2 V.s^{-1} , $T = 25 \text{ }^\circ\text{C}$ are indicated in Fig.8.

It was found that the magnitude of deconvolution height width ' w_p ' are in the extent of $250 - 295 \pm 2 \text{ mV}$, demonstrating the mild speed character of two sequential electron transfers of the oxidative process. The lack of symmetry of the onward and reversed peak, demonstrating the sluggishness of EE character of the oxidation step. From the above it was obvious, the I_1 vs E and (dI_1/dt) vs E curves have been easier to offer proper information concerning the character of electrode response than i vs E curve.

The diffusion transfer factor was further determined from the equation(5) [29, 30],

$$e_p = \frac{\alpha n^2 F^2 \nu C^{\text{bulk}} D^{1/2}}{3.367 RT} \quad (5)$$

wherein the symbol e_p represents the magnitude of the onwards peak of $(dI_1/dt) - E$ curve and the other symbols have their normal explanation. The significance of D obtained from Eq. (5) is noted in Table 1.

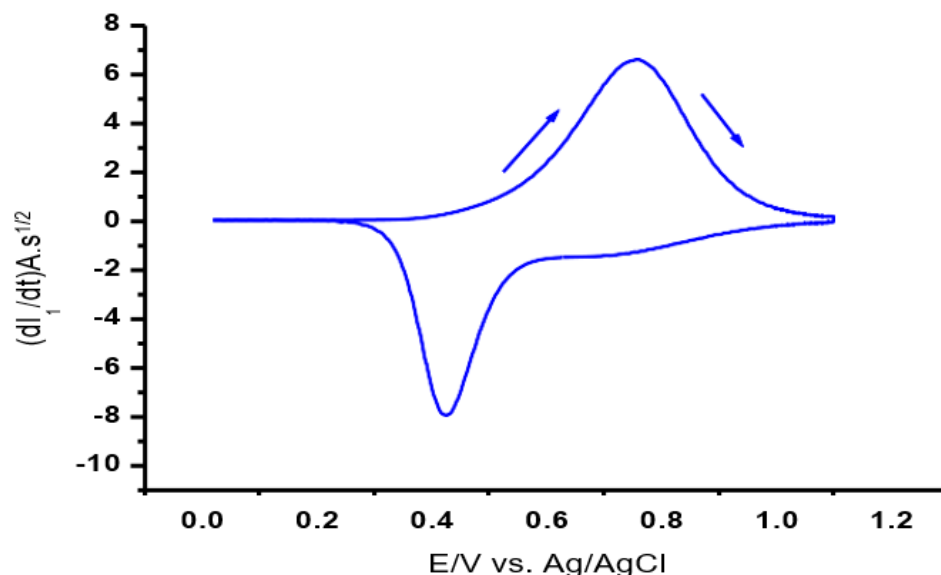


Figure 8. Deconvolution voltammogram of 5×10^{-4} M methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound in 0.1M TBACl at an Au electrode, ν 0.2 Vs⁻¹, T = 23 °C.

Also, the arrangement between the convolution and deconvolution transforms the following relationship was deduced:

$$n = \frac{0.086 \text{ ep}}{I_{\text{lim}} \alpha \nu} \tag{6}$$

wherein n is the number of charges ate up in electrode pathway, and the alternative parameters have their ordinary definitions. From the above equation (6) the total n used was equal to 2.12 *ca.* 2.

Table 2. Wave characteristics for the methyl(E)-2-cyno(N-ethyl carbazol-2-yl) acrylate compound extracted from deconvolution voltammetry and numerical simulation techniques at 0.2 V s⁻¹.

Wp/mV	186(*)	184(**)
$\Delta\text{ep Decon} / \text{mV}$	89(*)	93(**)
epf/epb (Decon)	1.09(*)	1.10(**)

Values evaluated from (*) deconvolution and (**) from numerical simulation

3.5. Numerical simulation

To realize the precise type of electrode reaction, numerical simulation of EEC and EC scheme had been performed and compared between the experimental voltammograms. Figure 9 displays the numerical oxidative CV of the EEC via the following electrochemical conditions:

$k_{s1} = 3.95 \times 10^{-6} \text{ m.s}^{-1}$, $k_{s2} = 3.86 \times 10^{-6} \text{ m.s}^{-1}$, $E^\circ = 0.52 \text{ V}$, $E^\circ = 0.54 \text{ V}$, $\alpha_1 = 0.31$, $\alpha_2 = 0.32$, $D_1 = 5.2 \times 10^{-9} \text{ m}^2.\text{s}^{-1}$, $D_2 = 5.2 \times 10^{-9} \text{ m}^2.\text{s}^{-1}$, $k_c = 0.051 \text{ s}^{-1}$

and $n_1 = 1$, $n_2 = 1$

& for EC scheme the following electrochemical variables were used:

$k_s = 3.95 \times 10^{-6} \text{ m.s}^{-1}$, $E^\circ = 0.52 \text{ V}$, $\alpha = 0.31$, $D = 5.2 \times 10^{-9} \text{ m}^2.\text{s}^{-1}$, $D_2 = 5.2 \times 10^{-9} \text{ m}^2.\text{s}^{-1}$, $k_c = 0.051 \text{ s}^{-1}$

and $n = 2$.

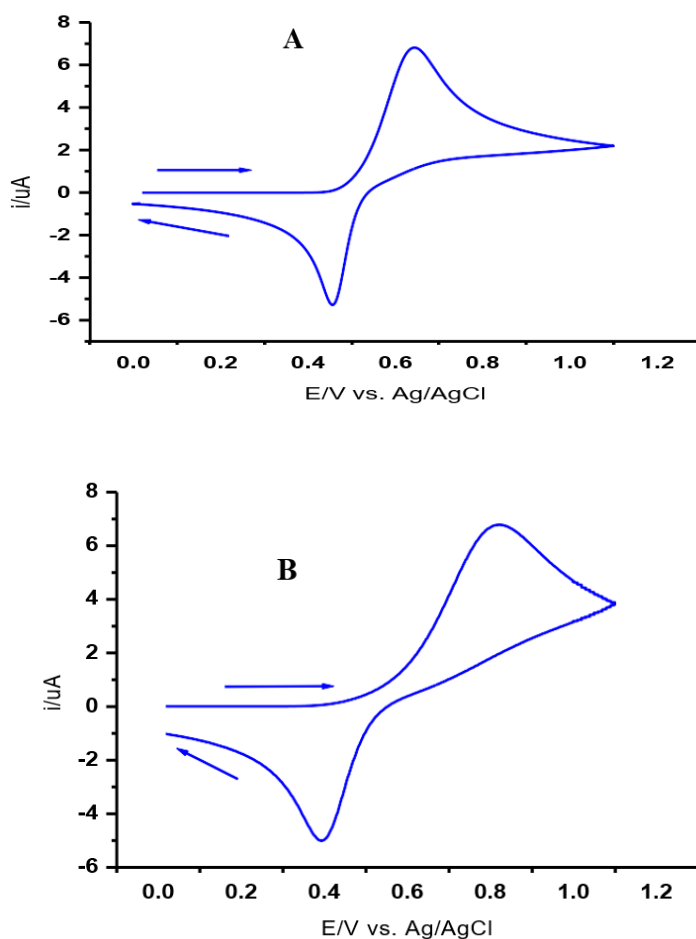


Figure 9. Numerical cyclic voltammograms of EC scheme (A) and for EEC scheme (B).

A directly exploration of the type of electrochemical reaction was achieved by comparing the obtained simulated CV of the type EEC and EC with the experimental voltammogram of cyano methyl methylene carbazole compound. Figure 10 exhibits agreeable matching between the numerical versus experimental $i - E$ curves at a v of 0.2 V.s^{-1} approving the transport of two sequential electrons before a mediocre fast chemical step.

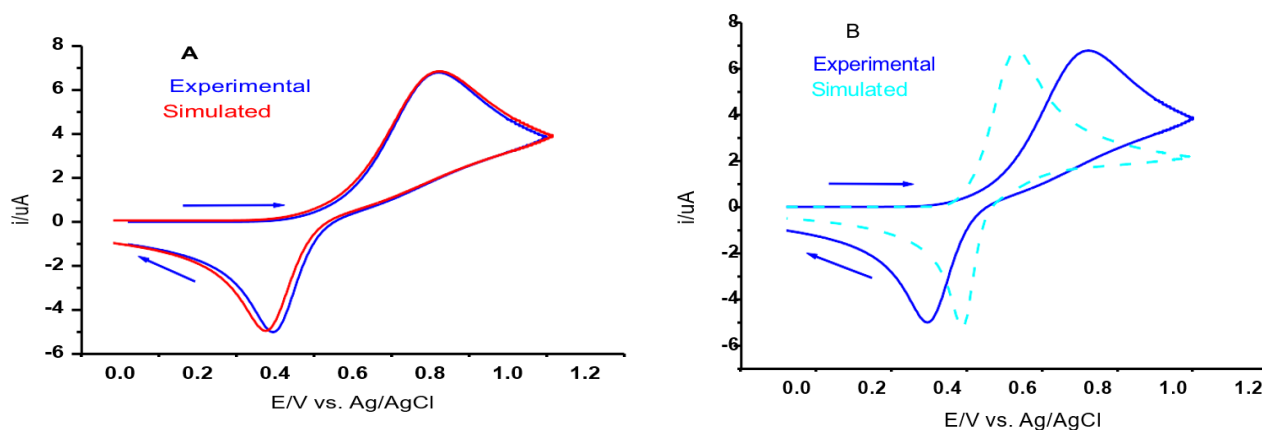


Figure 10. Matching of numerical curves of the types EEC (A) and EC (B) with experimental cyclic voltammogram of $1 \times 10^{-4} \text{ M}$ methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate compound in 0.1 M TBACl at a v of 0.2 V.s^{-1} and $T = 23 \text{ }^\circ\text{C}$.

Inspection of Figure 10 revealed a good matching between the types of EEC with the experimental cyclic voltammogram (figure 10 A) while there is a mismatching between EC type and the experimental cyclic voltammogram. Based on this, we conclude that the electro-oxidation of methyl(E)-2-cyno (N-ethyl carbazol-2-yl) acrylate proceeds as EEC mechanism at a gold electrode, a sweep rate of 0.2 V.s^{-1} and $T = 23 \text{ }^\circ\text{C}$.

4. CONCLUSION

In this reporting the chemistry of methyl(E)-2-cyno(N-ethyl carbazol-2-yl) acrylate compound was explained at a working gold electrode in 0.1 M TBACl in methylene chloride solution using cyclic voltammetric, and convolution-deconvolution voltammetry experiments. The proper parameters of the investigated compound have been computed experientially and validated theoretically via numerical simulation method. The mechanistic pathway electrode behavior was found to go as two sequential mediocre fast electron transfer precedes a chemical reaction step i.e., EEC pathway.

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