

A Simple Method for Determination of the Electrochemical Parameters of ECEC Mechanism Using Convulsive Cyclic Voltammetry Combined with Numerical Simulation

A.A Al-Owais¹, I. S. El-Hallag^{2,*}

¹ Chemistry Department, College of Science, King Saud University, Riyadh, Kingdom of Saudia Arabia

² Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

*E-mail: i.elhallag@yahoo.com

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Convulsive cyclic voltammetry was used to yield a smooth and skillful method for test the type of electrode response, computation of the homogeneous chemical rate constant k_c , and the standard reduction potential E^0 of the ECEC mechanism in which the two chemical steps are irreversible. The laboratory results and the type of electrode reaction were verified via numerical method. The arbitrary experimental model which behaves as ECEC is the 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione. The electrode behavior of the selected model was carried out at a gold electrode in 0.1 mol/L tetrabutylammonium perchlorate (TBAP) in methylene chloride (CH_2Cl_2) solvent. The discrimination between ECEC and $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ was achieved via numerical simulation method.

Keywords: Convulsive cyclic voltammetry; gold electrode; ECEC; numerical simulation.

1. INTRODUCTION

Convolution transform was used to impress the limitation resulting from the cyclic voltammetry experiments regardless of the speed of electron transfer [1-7]. The convolution theorem assets use in the status where it is necessary to execute the reverse transformation on a function which is the result of two functions of the Laplace various each of which discretely had known reverse transformations. In such a circumstance, the convolution theorem yields [8]:

$$L^{-1} [f_s(s).g_s(s)] = \int_0^t G(u)F(t-u)du \quad (1)$$

in which f_s, g_s are the Laplace transform of the functions F and G , the variables u is a dummy variable which is lost when the definite integral is evaluated.

For the coming reaction, in which an assumed species allowances only electron transfer



without subsequent processes other than ‘linear’ diffusion out in the solution from a flat electrode, i.e. the Fick’s Second Law is expressed as [9]:

$$[\partial C_{Ox} / \partial t]_x = D_{Ox} [\partial^2 C_{Ox} / \partial x^2]_x$$

then the solution of the above via Laplace methods yields [8]:

$$(C^b - C^s) = I_1 / nFSD^{1/2}_{Ox}$$

and
$$C^b = I_{lim} / nFSD^{1/2}_{Ox}$$

where C^b & C^s is the total and surface concentrations respectively and the involution I_1 is accepted by

$$I_1 = I_{1(t)} = \int_0^t \frac{i(u)}{\sqrt{\pi} (t-u)^{1/2}} du \tag{2}$$

and I_{lim} is the limiting value of I_1 at ‘extreme’ potentials. In the circumstance of EC reaction stated in equation (3):



the reduced form ‘R’ is produced by acquiring electrons at the cathode and transport to the product C towards the solution with speed amount k_c . The Second Law of Fick’s is now conferred as [10].

$$[\partial C_R / \partial t]_x = D_R [\partial^2 C_R / \partial x^2]_x - k_c C_R \text{ (at } x) \tag{4}$$

which allows the concentration at electrode surface by Eq. (5) [10]

$$C^s_R = I_2 / nFAD^{1/2}_R \tag{5}$$

where I_2 is defined by Eq. (6)

$$I_2(t) = \pi^{-1/2} \int_0^t [i(u) \exp(-k_c(t-u))] / (t-u)^{1/2} du \tag{6}$$

Thus, I_2 displays a plateau (at zero) on the return sweep in cyclic voltammetry and this property permits the determination of k_c .

The semi differentiation of the current (dI_1/dt) vs. E of fast speed of electron transfer is reported

in literature as in Eq. (7) [10-12].

$$e_p = (dI_1/dt) = nFAC\sqrt{D} a\zeta / (1+\zeta)^2 \quad (7)$$

Where

$$a = n\nu F/RT \quad (8)$$

and

$$\zeta = \exp [nF/RT (E - E^0)] \quad (9)$$

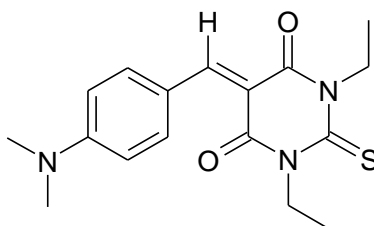
It was found that the semi-differential of current validates the type of electron transforms and assessment of the reduction potential of the electrolyzed species.

The present work planned to describe the nature of the ECEC scheme via I_1 convolution & the ratio of the apex of the forward sweep to the minimum of the backward one of deconvoluted current $(dI_1/dt)_f/(dI_1/dt)_b$ vs. the square root of sweep rate $(\nu)^{1/2}$ plots. The selected experimental example which behaves as ECEC is the electrooxidation of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at a gold electrode in 0.1 mol/L TBAP in CH_3CN solvent. The verification of the suggested method for calculation of the experimental parameters as well as the identification of the kind of the electrode reaction was achieved by combination of the numerical model with experimental data.

2. EXPERIMENTAL

2.1 Materials

The preparation of the investigated 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione was carried out by adding 1, 3-diethyl-2-thiobarbituric acid (0.0058 mol) to p-dimethylamin-obenzaldehyde (0.0058 mol) and in anhydrous ethanol (15 ml). The extracted product was refined by recrystallization from methanol and chloroform. Yield: 73.54% IR (KBr) ν_{max} cm^{-1} 1686 (C=O), 1653 (C=C), 1164 (C-N), 2932 (C-H aliphatic), 2977 (C-H aromatic), 1188 (C=S). 1H -NMR ($CDCl_3$) δ : 8.40 (H1, d, J=7.8 Hz), 6.70 (H2, d, J=8.4 Hz), 8.40 (H3,d, J=7.8 Hz), 6.70 (H4, d, 8.4 Hz), 7.20 (H5, s), 4.58 (CH_3-CH_2-N , t, J=3.6Hz), 1.33 (CH_3-CH_2-N , q, J=4.8 Hz), ^{13}C -NMR ($CDCl_3$) δ : 178.87, 161.48, 160.25, 158.91, 154.67, 148.39, 132.86, 126.16, 116.57, 114.96, 110.43, 56.24, 56.04, 44.21, 43.59, 12.47, 12.41. The prepared compound has the following structure as shown in scheme 1 [13]:



Scheme 1

2.2. Instrumentation

Cyclic voltammetry and convoluted voltammetry transforms were performed via a Princeton Applied Research (PAR) Computer-controlled Potentiostat Model 283 and PAR Model 175 Universal Programmer (from EG and G). The apparatus used afford sweep rate up to $100 \text{ V}\cdot\text{s}^{-1}$. The used working electrode (WE) was Au electrode with a surface area of $7.85\text{E-}3 \text{ cm}^2$, a CE is coiled Pt wire and a RE is saturated Ag/AgCl electrode. The voltage was measured against the Ag/AgCl RE at 25°C and in 0.1 mol/L TBAP as auxiliary electrolyte dissolved in CH_2Cl_2 solvent. The experimental cyclic voltammetry was amended by subtracting the non-Faradaic background current and IR drop. Ecomet grinder paper was used for cleaning the WE and the $i - E$ curve were plotted at sweep rate vary from 0.02 to $2 \text{ V}\cdot\text{s}^{-1}$ at $(25 \pm 2)^\circ \text{C}$. N_2 gas was passed into the solution then maintain above the solution during the experiments to evacuate the air from the working solution.

Numerical model of the data was run using techniques of finite differences via EG & G condesim software package. Into the condesim software package algorithms for the simulation software were coded and implemented. Convolution-deconvolution voltammetry were achieved by Condecon software based on the method well-established in literature [14,15].

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry

Figure 1 represents an illustration response of the cyclic voltammograms of the considered compound in $0.1 \text{ mol}\cdot\text{L}^{-1}$ tetrabutylammonium perchlorate (TBAP) in acetonitrile (CH_3CN) solvent at an Au anode at various sweep rate.

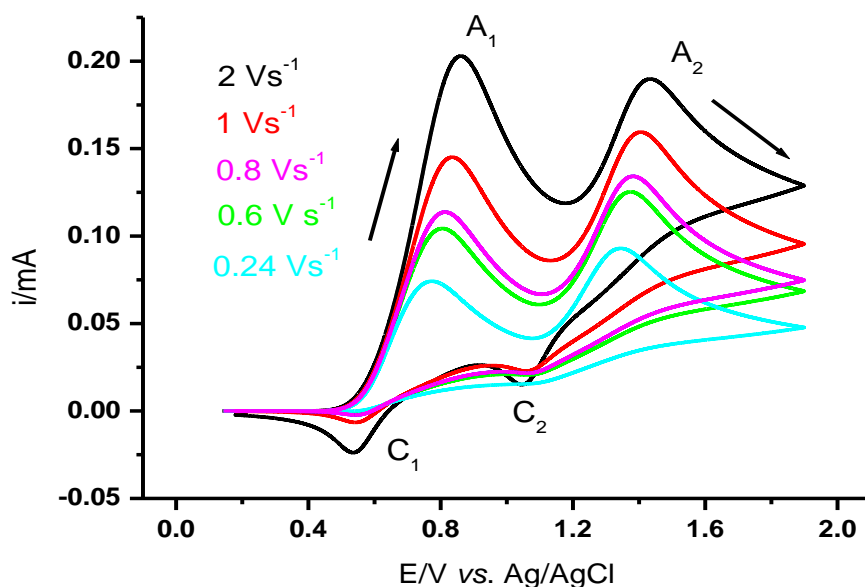


Figure 1. Cyclic voltammograms of the investigated compound in $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBAP in CH_3CN solvent at an Au WE and at various sweep rate.

The sweep rates used in this work was in the scope of 0.02 – 2.0 V s⁻¹. It was found that the compound under examination show two well defined anodic waves (A₁+C₁) & (A₂+ C₂). As shown, the magnitude of backward peaks increases with increasing the sweep rate confirming the existence of moderate rapid chemical reaction following the electron exchange of the two electrooxidation processes. The displacement of anodic peak position (E_p) to more positive potential by increasing the sweep rate and increasing the magnitude of the half peak width (E_p - E_{p/2}), approve the irreversible character and/or slow nature of electrode process [16].

The values of symmetry coefficient (α) were calculated experimentally using equation (9) and found to be 0.32 and 0.34 for the first and second anodic peaks respectively confirming the quasi-reversible character of the two anodic steps [17]:

$$E_p = E_{p/2} + 1.857 (RT/\alpha_n a F) \quad (9)$$

Here, the peak current (i_p) can be denotive by the following equation [18]:

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

where i_p stand for the peak current in amp, and C represent the concentration of the reactants species or groups which equals 3.5x10⁻⁴ M, and the other symbols have their normal explanation. On drawing of the i_p versus v^{1/2} straightforward line passing across the origin is acquired and reveals the mass transport is transformed by diffusion phenomena.

Table 1. Experimental values of (α), (E⁰) and (k_s) of the first and second oxidation processes of the selected compound.

Peak number	α	E ⁰ , V	k _s , m.s ⁻¹
1 st	0.31	0.68	3.2e-5
2 nd	0.34	1.18	3.5e-5

The standard rate constant (k_{s1} & k_{s2}) values were calculated through ΔE_p , values *versus* the dimensionless parameter (Ψ) [18, 19]. The computed values of k_{s1} and k_{s2} were recorded in table 1.

In the case of simple charge transfer or electron transfer coupled with chemical reaction (EC) scheme, the I₁ convolution [20] evaluates the magnitude of the diffusion coefficient (D) of the species from Eq. (11):

$$I_{lim} = nFAC\sqrt{D} \quad (11)$$

where I_{lim} is the limiting convoluted current, the resting symbols have their usual explanation. The diffusion coefficients (D) of the considered compounds were evaluated using Eq. (11) and listed in Table 2. The semi-integration of current (I₁) at a sweep rate of 0.12 V s⁻¹ is advertised in Figure 2. As

shown the I_1 displays a wide length between the oxidative and reductive direction and do not reach to initial zero point, due to the slow nature of the two electrons exchange and the presence of rapid chemical process after electrons transfer.

Table 2. Values of the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$) of the selected compound via various methods

Peak number	CV $D_{\text{x}}E^9$	I_{lim} $D_{\text{x}}E^9$	Simulation $D_{\text{x}}E^9$
1 st	6.2	6.7	6.6
2 nd	5.6	5.2	5.8

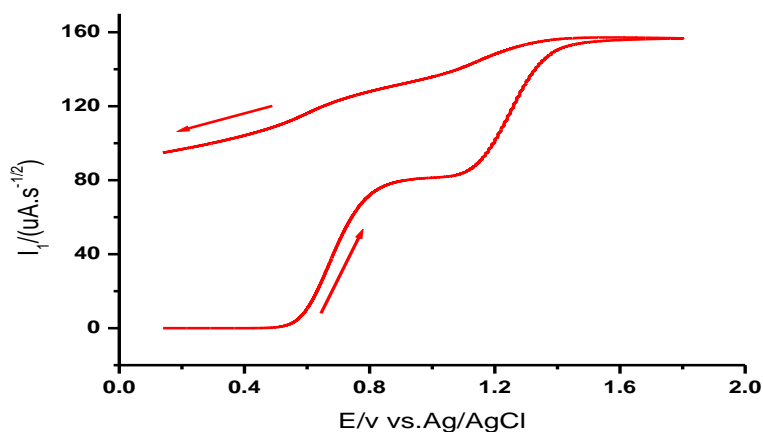


Figure 2. Convolution transform voltammogram of the selected compound in $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP in CH_3CN solvent at an Au WE and at sweep rate of $0.12 \text{ V} \cdot \text{s}^{-1}$.

3.2 Characterization of ECEC system

Figure 3 represents the experimental cyclic voltammogram of 5-(4-Dimethylamino-benzylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at scan rate $0.12 \text{ V} \cdot \text{s}^{-1}$ and 298 K, while Figure 4A&B includes the numerical cyclic voltammogram of ECEC and $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ systems at sweep rate of $0.06 \text{ V} \cdot \text{s}^{-1}$, $T = 298 \text{ K}$ using the following electrochemical parameters:

diffusion coefficients (D_1) = (D_2) = (D_3) = (D_4) = $5 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$,

standard heterogeneous rate constants (k_{s1}) = $5.2 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$, (k_{s2}) = $3.2 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$,

standard reduction potentials (E_1^0) 0.64 V & (E_2^0) 1.14 V,

transfer coefficients (α_1) = 0.31 & (α_2) = 0.35,

homogeneous chemical rate constants (kc_1) = 5 s^{-1} & (kc_2) = 4 s^{-1} and for $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ $k_{f1} = k_{b1} = 5 \text{ s}^{-1}$ & $k_{f2} = k_{b2} = 4 \text{ s}^{-1}$, where $k_{c1} = k_{f1} + k_{b1}$ and $k_{c2} = k_{f2} + k_{b2}$.

It was noted that the backward of the reductive peak in case of ECEC does not appear at sweep rate $< 1 \text{ V} \cdot \text{s}^{-1}$ (Fig. 4A) and in case of $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ the reversal reductive peaks appear at low and high

sweep rate (Fig 4B) [21].

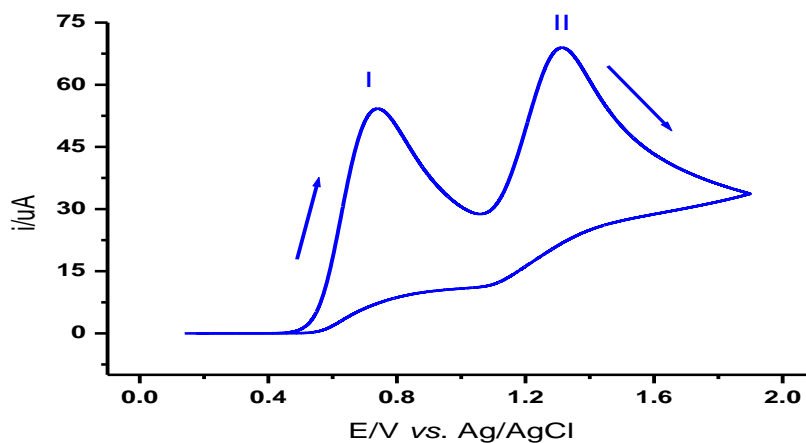


Figure 3. Experimental cyclic voltammogram of 3.5×10^{-4} M of the investigated compound in 0.1 mol.L^{-1} TBAP in CH_3CN solvent at a Au WE and at sweep rate of 0.12 V s^{-1} .

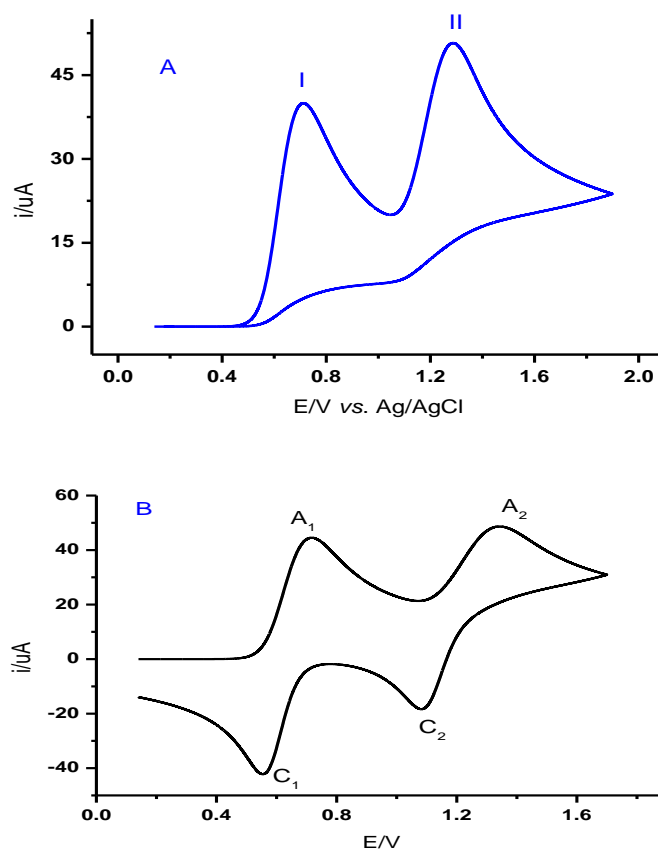


Figure 4: The numerical cyclic voltammogram of ECEC (A) & $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ (B) at sweep rate of 0.06 V s^{-1} , $T = 298 \text{ K}$

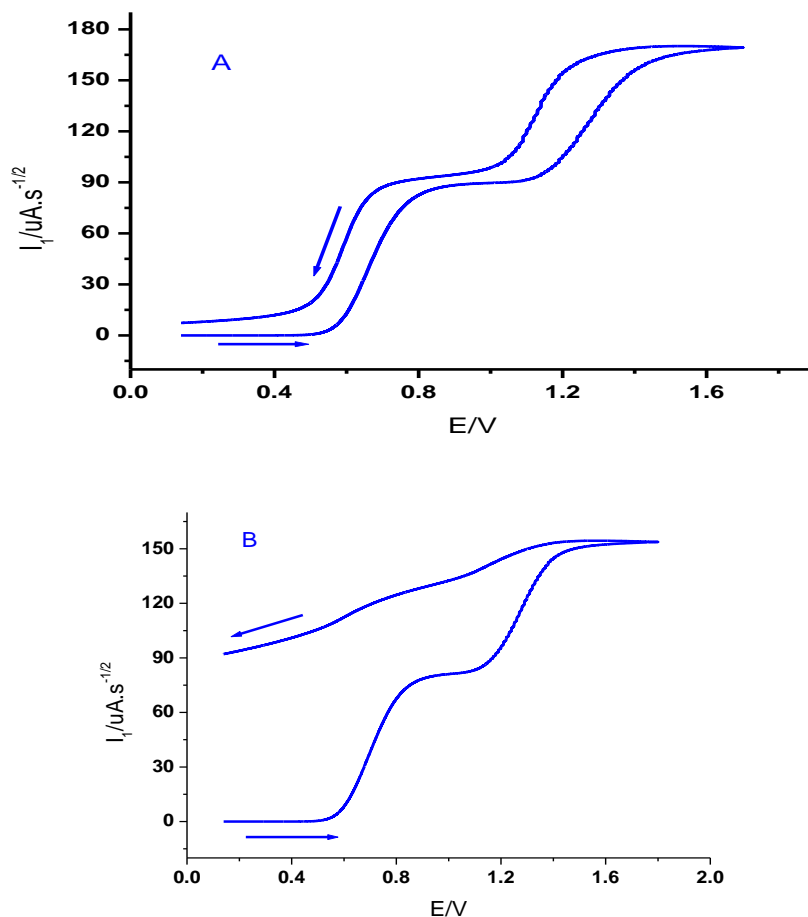


Figure 5. I_1 Convolute voltammogram of the numerical simulation of $EC_{rev}EC_{rev}$ (A) at sweep rate of $0.06 \text{ V}\cdot\text{s}^{-1}$ & $ECEC$ (B) at sweep rate of $0.24 \text{ V}\cdot\text{s}^{-1}$.

The I_1 convolution of numerical $EC_{rev}EC_{rev}$ system at sweep rates of $0.06 \text{ V}\cdot\text{s}^{-1}$ is shown in Figure 5A. It was noted that the convoluted current of $EC_{rev}EC_{rev}$ exhibits a moderate separation between the forward and reverse sweep indicating the quasi-reversible of electron transfer of the electrode process as well as the presence of a moderate fast of chemical reaction following the charge transfer as illustrated from the return of backward sweep near to zero value. In case of numerical $ECEC$ the I_1 convolution displays a large separation between the forward and reverse sweep confirming sluggishness of electron transfer and there is a wide distance between the return sweep and the initial value verifying the presence of a fast irreversible chemical reaction.

The semiderivative (e) of current ‘‘i’’ is defined as [22]:

$$e = d^{1/2}i/dt^{1/2} = dI_1/dt$$

which consist of two mirrors–image peaks with a maximum and minimum amplitude alignment at $E_{1/2}$ values and the value of half-width w^P equals to $3.526 RT/nF$ or $90.53/n \text{ mV}$ in case of rapid

electron transfer and $T = 298$ K. Figure 6 implies an instance of deconvoluted current (dI_1/dt) of 5-(4-Dimethylamino-benzylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at sweep rate of $0.5 \text{ V} \cdot \text{s}^{-1}$ which signify the irregularity of the forward and backward sweep approving the existence of EC_{irr} nature of the electrode mechanism [23, 24].

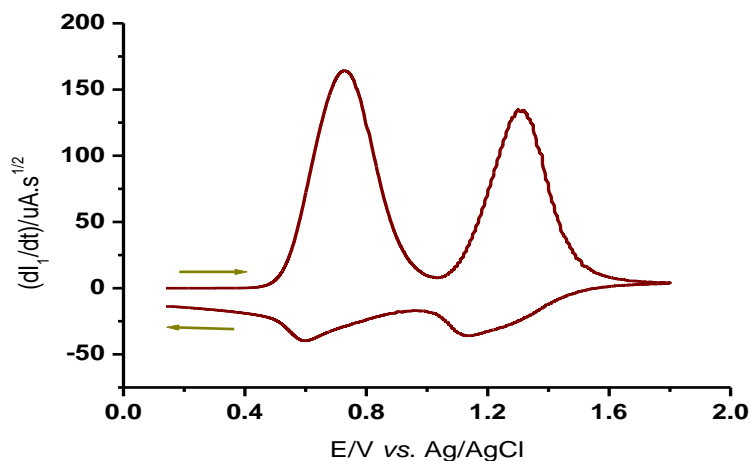
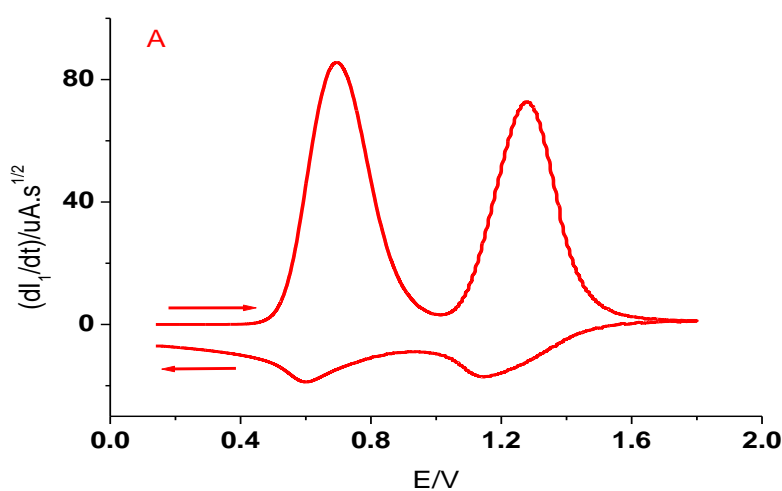


Figure 6. Exhibit the deconvoluted current (dI_1/dt) of 5-(4-Dimethylamino-benzylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at a gold electrode, sweep rate of $0.5 \text{ V} \cdot \text{s}^{-1}$ and $T=25^\circ \text{ C}$

It was established that with increasing the sweep rate, the homogeneous chemical rate constant decreases as a result of the decreasing of the time of the experiment, i.e. the ratio $(dI_1/dt)_f / (dI_1/dt)_b$ decrease with increasing the sweep rate. The numerical deconvolutive voltammograms of ECEC and $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ were indicated in Figure 7 A&B. As shown from Figure 7 in case of ECEC the ratio $(dI_1/dt)_b / (dI_1/dt)_f$ is less than that in case of $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ which consider a good and simple method for distinguishing between ECEC and $\text{EC}_{\text{rev}}\text{EC}_{\text{rev}}$ systems.



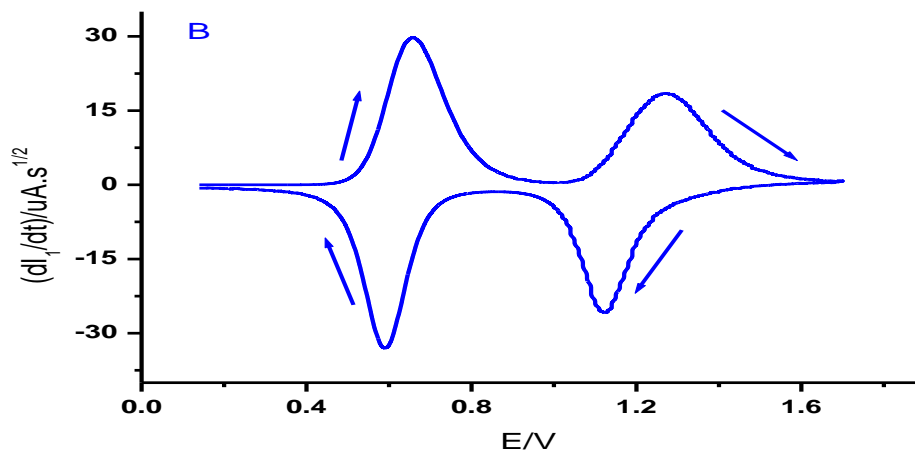


Figure 7. Numerical simulation of deconvolutive voltammogram of ECEC (A) and $EC_{rev}EC_{rev}$ (B) at sweep rate of $0.06 \text{ V}\cdot\text{s}^{-1}$.

The experimental ratio of deconvolution, numerical simulation of deconvolutive ECEC and $EC_{rev}EC_{rev}$ as a function of the square root of sweep rate (v)^{1/2} are indicated in Figure 8A-C.

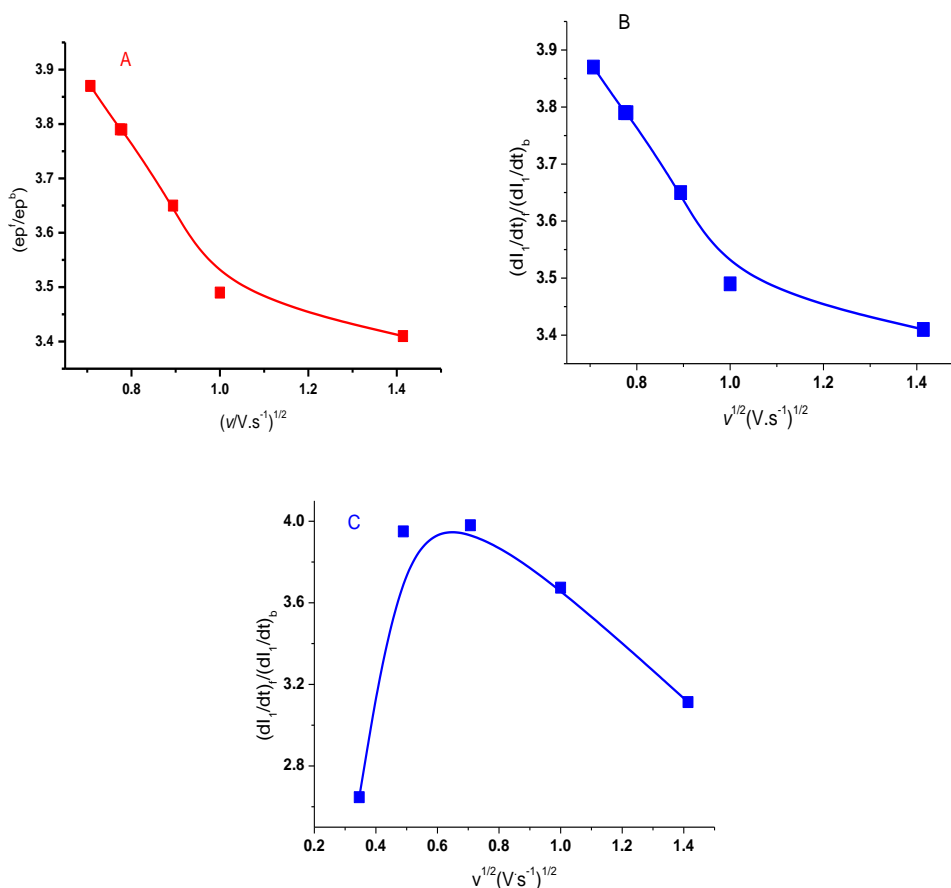


Figure 8. The experimental ratio of deconvolution (A), numerical simulation of deconvolutive of ECEC (B) and $EC_{rev}EC_{rev}$ (C) as a function of the square root of sweep rate (v)^{1/2}.

It was observed that, in Figure 8 the curves in the plot exhibited for experimental and numerical ECEC the $(dI_1/dt)_f / (dI_1/dt)_b$ decrease on increasing the square root of sweep rate. In case of $EC_{rev}EC_{rev}$ the representation of the ratio $(dI_1/dt)_f / (dI_1/dt)_b$ versus $v^{1/2}$ indicates increasing then decreasing the values of the ratio with the square root of sweep rate. This plot provides a simple method for discriminating between ECEC and $EC_{rev}EC_{rev}$ systems.

4. CONCLUSION

In this article we utilized the convolution–deconvolution voltammetry & numerical simulation procedure for the depiction and the finding of the proper chemical and electrochemical parameters of ECEC mechanism. The utilization of these methods affords the favorable circumstances for getting strict kinetic parameters very correctly without regard to the rate of charge transfer. The examination of the effectiveness of our method is executed by adopting it to the electro-reduction of 5-(4-Dimethylamino-benzylidene) -1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at a gold WE in 0.1 mol/L tetrabutylammonium perchlorate (TBAP) in CH_3CN solvent & is set up to supply acceptable conclusion verifying the accuracy of the considered method. Also, the discrimination between ECEC and $EC_{rev}EC_{rev}$ was performed via a simple convolutive voltammetry combined with numerical simulation methods.

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