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Electrochemical Studies of Some Carbazole Derivatives via Cyclic Voltammetry and Convolution – deconvolution Transforms

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Abstract: *Three carbazole chromophores derivatives featuring dicyno, cyano, ethyl acetate and dimethyl acetate groups as an acceptor moiety with a π – conjugated spacer and N-methyl dibenzo[b]pyrole as donor were investigated electrochemically at a platinum electrode in 0.1 mol/L tetraethylammonium chloride (TEACl) in acetonitrile solvent via cyclic voltammetry, convolution – deconvolution transforms and digital simulation techniques. Cyclic voltammetric study revealed that the presence of a single reversible oxidative peak due to two sequential electron transfer (EE scheme) and unidirectional reductive peak which proceed as ECEC mechanism. The electrode reaction pathway, the relevant chemical and electrochemical parameters of the investigated carbazole chromophores were determined using cyclic voltammetry, convolution- deconvolution transforms and chronoamperograms. The extracted electrochemical parameters and the nature of the electrode reaction were verified & confirmed via digital simulation method.*

Keywords: Carbazole derivatives, cyclic voltammetry, convolution transforms, digital simulation.

1. INTRODUCTION

Carbazole derivatives have been well known dyes which are characterized by efficient fluorescence emission and well define electronic absorption and fluorescence transition dipole moments [1,2]. As a consequence, they have attracted considerable attention of researchers working in the area of pure and applied sciences. Because of their high photostability and the elongated molecular shape, carbazole derivatives can be applied as probes in the experimental studies of molecular orientational order in thermotropic and lyotropic liquid crystals, in liquid–crystalline polymers, and in lipid membranes [3,4]. Most of the carbazole derivatives have been considered for applications in organic electronic devices and in optical disks [5-7]. They can be also applied as a fluorescent component in liquid crystal displays working in passive or active modes [8]. Carbazole dyes present a wide range of colors so they are applied in high grade paints utilized in automotive industry finishes [9]. At certain conditions, the molecules of carbazole derivatives can aggregate forming crystalline or semicrystalline two-dimensional structures. The aggregation properties of these molecules are strongly dependent on the chemical structure of the substituents in carbazole skeleton, solvent, the concentration of the dye, and some physical parameters, such as temperature [10].

It was found that carbazole derivatives have excellent hole-transporting capability, high photochemical stability, high charge carrier mobility, and a significantly reduced ionization potential through π-conjugation [11-15]. Further, carbazoles are relatively easy to functionalize at the 3-, 6-, or 9-positions. In particular, compounds with carbazole moieties have been popular as hole-transporting materials [16 – 18] and host materials that allow green [19], red [20] and even blue [21] and [22] electroluminescence. These emission features are due to the large band-gap and high triplet energy states of the carbazole group.

It was found that the electrochemical properties of carbazole derivatives exhibits semi-reversible behaviour in the buffer solution (pH . 7.35–7.40) [23,24]. To our best knowledge no electrochemical investigation have been carried out on carbazole derivatives in acetonitrile solvent at a platinum electrode in 0.1 mol/L tetraethylammonium chloride (*TEACl*) especially via convolution – deconvolution transforms and digital simulation methods. Ac-

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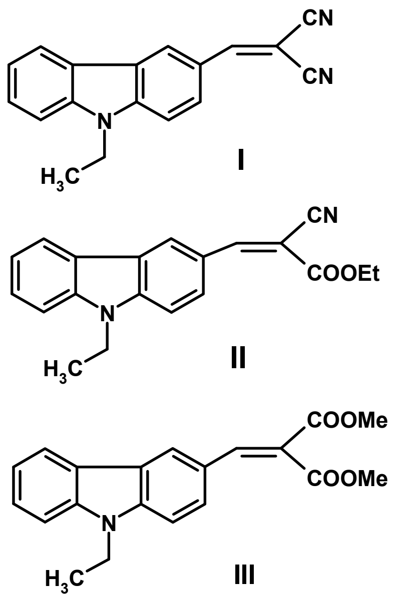


Scheme 1

cordingly, the heterogeneous rate constant (k_s) the diffusion coefficient (D) the redox potential (E^o) the transfer coefficient (α) and the electrode nature of the three carbazole derivatives under consideration were determined and discussed via cyclic voltammetry, convolution - deconvolution transforms and chronoamperometry techniques. The homogeneous chemical rate constant (k_c) was determined from generated cyclic voltammograms. Digital simulation was used to verify and confirm the experimental electrochemical parameters and identifying the nature of electrode reaction.

2. EXPERIMENTAL SECTION

2.1. Chemicals

The investigated three carbazole derivatives were prepared and purified according to the method established in literature [25]. All solvents used in this work were of spectroscopic grade. The structures of the investigated carbazole derivatives were shown in scheme 1 [25].

2.2. Electrochemical measurements

Cyclic voltammetry and convolution-deconvolution transforms were performed using a Princeton Applied Research (PAR) Computer – controlled Potentiostat Model 283 and PAR Model 175 Universal Programer (from EG and G). The system allowed the use of any scan up to 100 V/s for the cyclic voltammetric experiment.

Measurements were made using a conventional three electrode cell configuration. The platinum electrode surface was 7.85 × 10^{-3} cm^2 as a working electrode, coiled platinum wire as a counter electrode and saturated Ag/AgCl as a reference electrode.

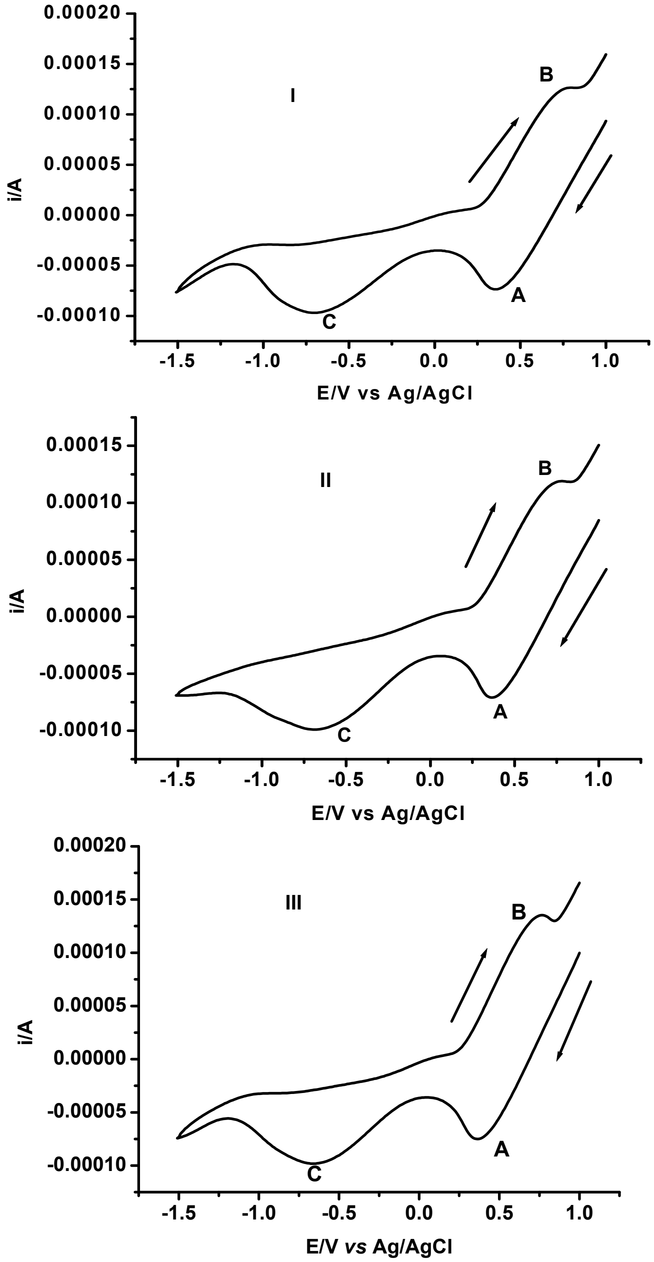


Figure 1. Cyclic voltammograms of 3.5 × 10^{-4} M of carbazole derivatives I – III in TEACl / CH_3CN at scan rate of 1.0 V/s .

The potential was calculated with relative to the Ag/AgCl reference electrode at 25°C and 0.1 mol/L tetraethylammonium chloride (*TEACl*) 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 rate ranging from 0.02 to 5 V/s in non aqueous media at (25 ± 2) °C.

Digital simulation of the data for cyclic voltammetric experiments was performed on PC computer using EG & G condesim software package. The simulation procedure was carried out using finite differences techniques. Algorithms for the simulation program were coded and implemented into the condesim software package supplied by EG & G.

All working solutions were thoroughly degassed with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

3. RESULTS AND DISCUSSION

3.1. cyclic voltammetric study

Cyclic voltammetry of the investigated carbazole derivatives were recorded at scan rates ranging from 0.02 - 5 V/s. Figure 1 gives an example response of the cyclic voltammograms of $3.5x10^{-4}$ M of the three carazole compounds I – III in 0.1M TEACl / CH_3CN at scan rate of 1 V/s. It was found that the three carbazoles species exhibited single oxidative reversible peak involved two sequential electron transfer with sluggish of the rate of electron exchange and one unidirectional reductive peak involved two sequential electron transfer with slow rate of electron exchange. The oxidation process loss two electrons (EE system) while the reduction process gain two sequential charge transfer followed by a chemical step (*ECEC*). Also the peak current increases with increasing the scan rate, while the position of peak potentials of the reduction and oxidation processes were dependent on the scan rates. From cyclic voltammetric investigation, it was found that, the rate of electron transfer of the cathodic reduction process of the examined carbazoles proceed as slow charge transfer at all sweep rates. The disappearing of the oxidative peak coupled with the reductive peak (*C*) confirms the presence of too fast chemical process following the charge transfer at all sweep rates. The chemical process my be attributed to isomerization and/ or structural rearrangement of the reduced species of carbazole derivatives. This behaviour demonstrates that the electrode pathway of the reduction step involves gain of one electron transfer producing an anion radical followed by too fast chemical process and the anion radical gain another electron producing a dianion followed by too fast chemical step.

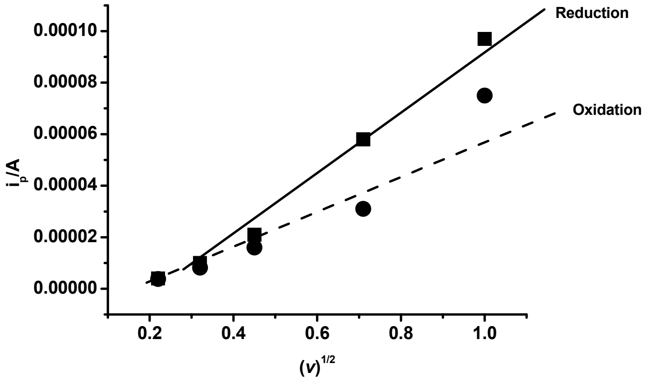


Figure 2. Plot of peak current (i_p) *vs* square root of scan rate $(v)^{1/2}$ of compound I.

As shown in Figure 1, the broading of the reductive peak (C) indicates the slow nature of both electron transfers. The $i_p – v^{1/2}$ plot of the carbazole I is shown in Fig.2. which revealed that, the peak current, after elimination of the background current and iR compensation, is proportional to square root of scan rate ($v^{1/2}$) confirming the diffusion nature of the electrode process. From the slope of the plot of ip vs. $\sqrt{v}$ (Fig.2), the diffusion coefficient (*D*) of the electroactive species was determined [26, 27] and cited in Table 1.

Due to the absence of the oxidative peak coupled with the reductive peak the redox potentials $E^{o'}_1$ and $E^{o'}_2$ were determind from digital simulation and cited in Table 1.

The standard heterogeneous rate constants (k_{s1} & k_{s2}) were deter-

Table 1. Values of the electrochemical parameters of reduction process of carbazole derivatives **I – III** at platinum electrode in acetonitrile solvent.

Compound		Electrochemical Parameters									
	Technique	$-E^o_1$ (V)	$-E^o_2$, (V)	k_{s1}, ($m.s^{-1}$)	k_{s2}, ($m.s^{-1}$)	D_1 ($m^2.s^{-1}$)	D_2 ($m^2.s^{-1}$)	α_1	α_2	k_{c1} (s^{-1})	k_{c2} (s^{-1})
	CV					4.5×10^{-10}					
	Conv					4.2×10^{-10}					
I						$4.30\times10^{-10(a)}$					
	Sim	0.30	0.31	1.2×10^{-5}	2.1×10^{-6}	5.0×10^{-10}	3.5×10^{-10}	0.28	0.26	18	19
	CA					4.8×10^{-10}					
	CV					5.5×10^{-10}					
	Conv					4.9×10^{-10}					
II						$4.7\times10^{-10(a)}$					
	Sim	0.21	0.22	1.5×10^{-5}	2.6×10^{-6}	6.1×10^{-10}	4.5×10^{-10}	0.29	0.27	20	18
	CA					5.0×10^{-10}					
	CV					4.3×10^{-10}					
	Conv					3.8×10^{-10}					
III						$3.6\times10^{-10(a)}$					
	Sim	0.32	0.33	1.3×10^{-5}	2.3×10^{-6}	5.2×10^{-10}	3.4×10^{-10}	0.29	0.27	17	15
	CA					4.6×10^{-10}					

CV: Cyclic voltammetry, Conv: convolution voltammetry, Sim: digital simulation and CA: Chronoamperometry
(a): Values of D calculated via Eq. (11)

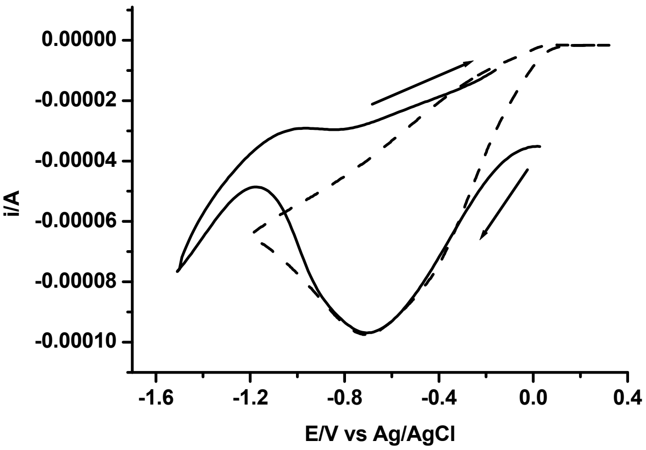


Figure 3. Matching between experimental voltammogram of carbazole I (——) and simulated voltammogram (-------) of reductive process at a sweep rate of 1.0 V/s.

mined from the generated cyclic voltammograms [26] (Table 1). The results given in Figure 3 employ the experimental and theoretical values of the electrochemical parameters of the reductive process of carbazole derivative I, which demonstrate the agreement between the captured and the simulated data. The slight deviation between the experimental and the simulated voltammograms of the reduction process may be attributed to the resistance of electrolyte solution and some sort of iR drop.

Electrooxidation of the investigated carbazole species I – III exhibited one oxidative reversible wave peak (A) coupled with peak (B) at all sweep rates (0.02 - 5 V/s. The ratios of the backward to the forward peak, $i_p b/i_p f$, are equal 1.0 at all sweep rates. This behaviour reflect the absence of chemical process after the loss of two electrons participating in the electrode reaction, indicating and confirming the presence of *EE* mechanism of the oxidative process. Also the shift of peak potentials to more positive values with increasing the sweep rates reflect the sluggish of the rate of electron transfer.

The values of the formal potentials ($E^{o'}_1$& $E^{o'}_2$) and the standard heterogeneous rate constants (k_{s1} & k_{s2}) of the oxidation process of the compounds under consideration were determined from digital simulation and cited in Table 2.

3.2. Convolution transforms

For the following reaction, in which a given species undergoing only electron transfer

$$Ox + ne \rightleftharpoons R \qquad (1)$$

and no subsequent processes other than 'linear' diffusion out in the solution from a planar electrode, i.e. the Fick's Second Law is expressed as [28].

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

then the solution of the above via Laplace methods yields [29]

Table 2: Values of electrochemical parameters of oxidation process of investigated carbazoles derivatives **I – III** at platinum electrode in acetonitrile solvent.

Compound		Electrochemical Parameters							
Technique		$-E^o_1$ (V)	$-E^o_2$, (V)	k_{s1}, (m.s^{-1})	k_{s2}, (m.s^{-1})	D_1 (m^2.s^{-1})	D_2 (m^2.s^{-1})	α_1	α_2
	CV					5.1×10^{-10}			
	Conv					5.4×10^{-10}			
I						$5.2\times10^{-10(a)}$			
	Sim	0.50	0.52	1.2×10^{-5}	8.1×10^{-6}	5.4×10^{-10}	4.5×10^{-10}	0.30	0.29
	CA				4.6×10^{-10}	5.3×10^{-10}			
	CV					5.3×10^{-10}			
	Conv					4.7×10^{-10}			
II						$4.6\times10^{-10(a)}$			
	Sim	0.51	0.53	1.5×10^{-5}	2.6×10^{-6}	6.1×10^{-10}	4.5×10^{-10}	0.31	0.32
	CA				$3.8\times10^{-}$	5.0×10^{-10}			
	CV					4.3×10^{-10}			
	Conv					3.8×10^{-10}			
III						$3.6\times10^{-10(a)}$			
	Sim	0.52	0.53	1.3×10^{-5}	2.3×10^{-6}	3.1×10^{-10}	3.4×10^{-10}	0.28	0.26
	CA				3.1×10^{-10}	4.6×10^{-10}			

CV: Cyclic voltammetry, Conv: convolution voltammetry, Sim: digital simulation and CA: Chronoamperometry
(a): Values of D calculated via Eq. (11)

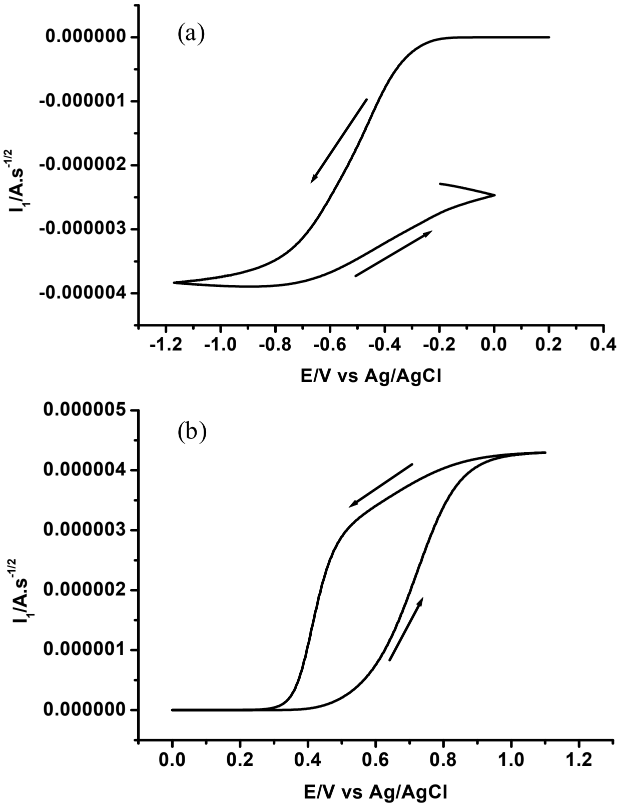


Figure 4. I_1 convolution transforms of I (a) reduction process and (b) oxidation process.

$$(C^{bulk} - C^s) = I_1 / n\,FSD^{1/2}_{Ox} \text{ and} \tag{3}$$

$$C^{bulk} = I_{lim} / n\,FSD^{1/2}_{Ox} \tag{4}$$

where C^{bulk} & C^s is the bulk and surface concentrations respectively and the convolution I_1 is given by

$$I_1 = i*(\pi t)^{-1/2} \text{ or more 'fully as'}$$

$$I_1(t) = \pi^{1/2}\int_t^0 i(u)/(t-u)^{1/2}\,du \tag{5}$$

The limiting value of I1 at 'extreme' potentials gives limiting convoluted current (I_{lim}) i.e. when the concentration at the electrode C^s is effectively reduced to zero by rapid redox conversion and the current is thus controlled solely by the maximum rates of diffusion to (and from) the electrode.

In the case of electron transfer followed by homogeneous chemical reaction Eq. (6).

$$\mathrm{Ox} + ne^- \underset{\alpha,D,E^{0'}}{\overset{k_l}{\rightleftharpoons}} \mathrm{R} \underset{\substack{k_{-1}\\(k_1>>k_{-1}),\\(k_c=k_1+k_{-1})}}{\overset{k_s}{\rightleftharpoons}} \mathrm{P} \tag{6}$$

where k_s, α, D, E^o, k_1, k_{-1} and k_c are defined as following [30]:

k_s is the standard heterogeneous rate constant
α is the transfer coefficient
D is the diffusion coefficient
$E^{o'}$ is the formal reduction potential
k_1 is the forward homogeneous chemical rate constant
k_{-1} is the backward homogeneous chemical rate constant
k_c is the homogeneous chemical rate constant

the species here are produced by electron transfer at a planar electrode and undergoes chemical reaction in the bulk via a first order chemical reaction of rate constant k_c. The Fick's Second Law expression is now [29, 30].

$$[\partial C_R/\partial t]_x = D_R[\partial^2 C_R/\partial x^2]_x - k_c C_R(at\ x) \tag{7}$$

and solution via Laplace methods gives here, necessarily starting at zero concentration in the bulk, the following electrode concentration

$$C^s_R = I_2 / nFAD^{1/2}_R \tag{8}$$

where the 'kinetic' convolution I_2 is given by [30].

$$I_2(t) = \pi^{-1/2}\int_0^t [i(u).\exp(-k_c(t-u))]/(t-u)^{1/2}\,du. \tag{9}$$

Thus in the I_2 convolution at time t, each segment of i(u) is scaled by dividing by the square root of the time which has elapsed from t to the time u to which the segment refers and likewise is scaled by the exponential factor $\exp(-k_c(t-u))$. Thus I_2 for example now goes to a plateau (at zero) on return of the sweep in cyclic voltammetry and this property allows determination of k_c in the case of appearing the backward peak coupled with the forward one.

In cases of straight forward electron transfer or subsequent chemical reaction, the I_l convolution [31 – 35] allows to determine the diffusion coefficient of the bulk species from Eq. (10) [28]:

$$I_{lim} = nFAC\sqrt{D} \tag{10}$$

where I_{lim} is the limiting value 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 values of the diffusion coefficients (D) of the investigated carbazole derivatives corresponding to the reduction and oxidation steps were calculated via Eq. (10) and listed in Tables 1 & 2. The I_1 convolution of the reductive and oxidative voltammograms of carbazole I at a scan rate of 1 V/s is indicated in Figure 4. The I_1 convolution of reduction process shows a large separation between the forward and backward sweep and do not return to zero current value, confirming the sluggish of the two electrons transfer which followed by too fast chemical process (isomerization and/or structural rearrangement) i.e *ECEC*.

The *i* - *t* plot derived from cyclic voltammogram of the reductive and oxidative processes of I at sweep rate of 1.0 V/s is presented in Fig.5. By selecting the data points of the decay part of the reductive i-t plot a Cottrell plot are obtained and presented in Fig.6. The slopes of Cottrel plot of the carbazole species yield a diffusion coefficients cited in Tables 1 & 2. As shown the i - t plots produces discontinuity Δi_c at t = 1.43 s and t = 1.28 s for reduction and oxidation process respectively due to the reversibility of the scan. Inspection of Fig.5b revealed that, the equality of the height of the forward and backward peaks, i.e the height of peak A is equal to

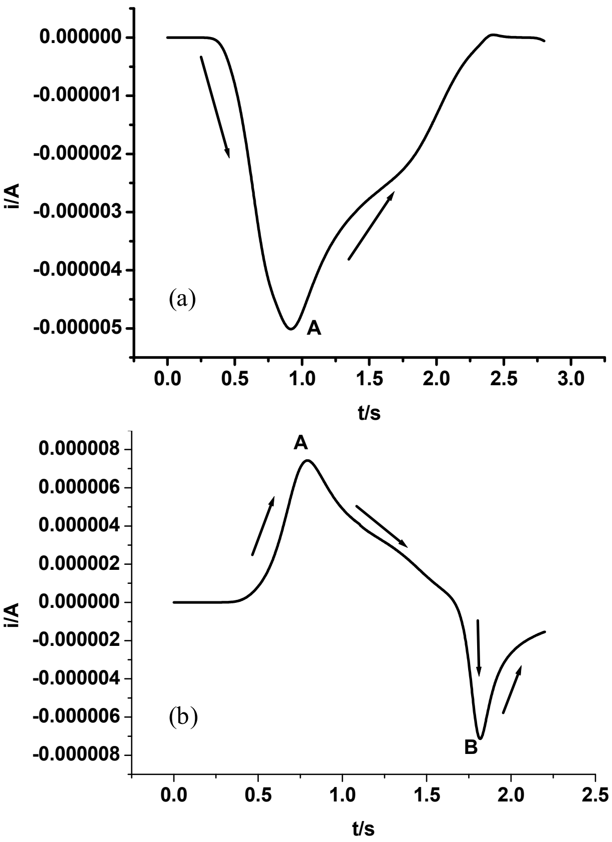


Figure 5. Plot of *i* versus *t* of the reductive cyclic voltammogram of I at sweep rate of 1.0 V/s (a) and oxidative cyclic voltammogram at sweep rate of 1.0 V/s (b).

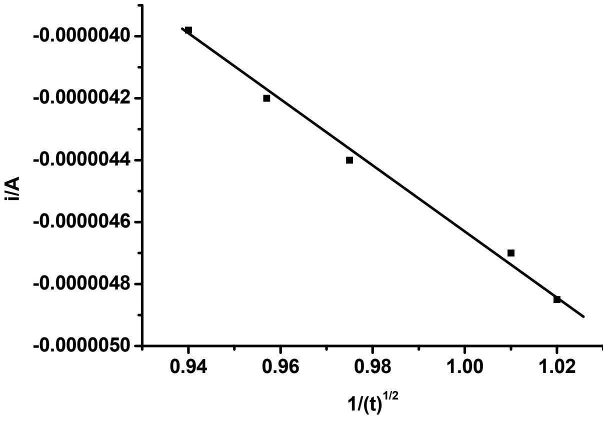


Figure 6. Presentation of i vs $1/\sqrt{t}$ of the reduction process of compound I.

the height of peak B confirming that the equality of the amount of charge for forward and backward peaks of oxidative process. This behaviour demonstrate that the presence of two simple charge transfer of the oxidation of carbazole derivatives. The situation is different in case of reduction step due to the isomerization and / or structural rearrangement of the reduced species.

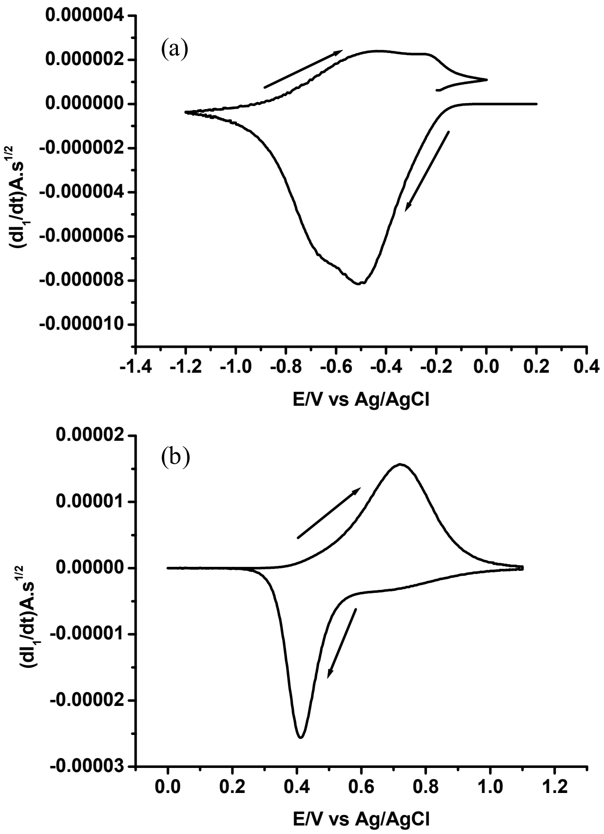


Figure 7. Deconvolution transforms (dI_1/dt) of the reductive cyclic voltammogram (a) and of the oxidative cyclic voltammogram (b) of carbazole derivative I at a sweep rate of 1.0 V/s.

The diffusion coefficients (D_{Red} & D_{Ox}) of the carbazoles species were determined from the following equation [31]:

$$I_{limd} = i_p / 3.099(/ \alpha n_a v)^{1/2} \tag{11}$$

Where I_{limd} is the deduced limiting convoluted current and the other symbols have their usual meaning. The calculated values of the diffusion coefficients (D_{Red} & D_{Ox}) were listed in Tables 1 & 2. The true values of homogeneous chemical rate constants k_{c1} and k_{c2} of the chemical processes were determined from digital simulation method and cited in Table 1.

3.3. Deconvolution transforms

The deconvolution transforms of the current ($d I_l /dt$) as a function of E of reversible process is defined as [36].

$$ep = (dI_1/dt) = nFAC\sqrt{D}\, a\zeta / (1+\zeta)^2 \tag{12}$$

where

$$a = nvF/RT \tag{13}$$

and

$$\zeta = exp\ [nF/RT\ (E - E^0) \tag{14}$$

these words shift slightly to left to start parallel to the paragraph, i.e and the representation of this equation at $v = 1$ V/s of the

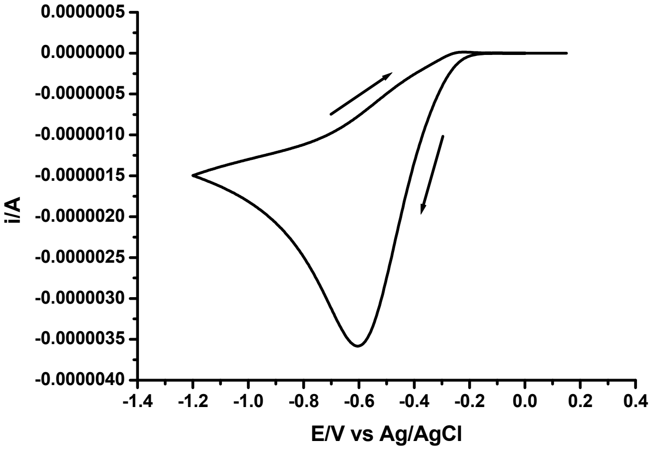


Figure 8. Generated theoretical reductive cyclic voltammogram of EC system at scan rate of 1.0 V/s , n = 1, $k_s = 1.2 \times 10^{-6}$ m/s , $E^0 = -0.305$ V $\alpha = 0.3$, $D = 4.5 \times 10^{-10}$ m^2/s and $k_c = 18$ s^{-1}.

reduction and oxidation steps of compound **I** are indicated in Fig.7. The width of deconvoluted peak (*w*p) in the case of fast charge transfer is equal to 3.53 *RT/nF* = 90.5 /n mV for fast charge transfer . It was found that *w*p in the range of 230 - 270 ± 2 mV, indicating and confirming the slow nature of charge transfer of reductive and oxidative processes. The separation between the forward and backward peaks of the deconvolutogram confirms the deviation of charge transfer from nernstain behaviour. Also the absence of backward peak in reductive deconvolutogram confirms the presence of too fast chemical process. The asymmetry of the forward and reverse peak, further confirming the sluggish of EE nature of the oxidation process. From the above discussion it was found that, the I_1 *vs E* and (dI_1/dt) *vs E* curves were easier to interpret than *i vs E* curve. Also, the values of the diffusion coefficient of the carbazole derivatives were calculated via Eq. 11 [31].

It was found that the values of diffusion coefficient of carbazole derivatives calculated from Eq. (11) agree well with the values calculated from cyclic voltammetry and convolutive voltammetry (Tables 1 & 2).

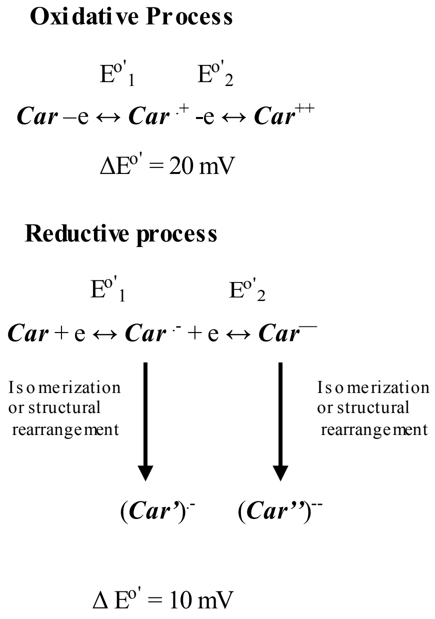
Fig.8 display an example response of the generated reductive cyclic voltammogram of the *EC* mechanism using the following values of the electrochemical parameters:

$k_s = 1.5 \times 10^{-6}$ m/s, $E^0 = -0.305$ V $\alpha = 0.3$, $D = 4.5 \times 10^{-10}$ m^2/s, $k_c = 18$ s^{-1}, and n = 1.

From the values of peak characteristics e.g. E_p, ΔE_p and $E_p - E_{p/2}$ (Table 3) it was found that there is a large deviation between the experimental and the simulated values which confirm and verify our proposed mechanism (scheme 2) and the accuracy of the calculated experimental electrochemical parameters.

Table 3. Values of peak characteristics of cyclic voltammograms of carbazole derivative **I** and theoretical voltammogram of EC scheme at n = 1 of reduction and oxidation processes.

	Peak characteristics					
	E_p (V)		$E_p - E_{p/2}$ (V)		ΔE_p (V)	
	exp	sim	exp	sim	exp	sim
Reduction	-0.702	-0.607	0.394	0.145		
Oxidation	0.419	0.358	0.247	0.175	0.419	0.358



Scheme 2.

From the above discussion the electrode behaviour of carbazole derivatives which symbolized as *Car* can be suggested to proceed as Scheme 2.

4. CONCLUSION

The electrochemical behaviour of three carbazole derivatives were investigated in 0.1M TEACl / CH_3CN at a platinum electrode. The reductive process shows unidirectional irreversible peak which proceed as *ECEC* mechanism. The first charge transfer produces a radical anion that gain another electron to form a dianion , the two charge transfer were followed by too fast chemical step (isomerization and/or structural rearrangement). Electro-oxidation of carbazole species gave one anodic oxidation peak and involved loss of two electrons, i.e., *EE* system. The experimental kinetic parameters were determined experimentally and verified via digital simulation method by comparing the generated theoretical voltammograms with the experimental voltammograms. Based on the electrochemical behaviour the electrode mechanism of the three carbazole derivatives were suggested.

5. ACKNOWLEDGEMENT

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