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Two step electrochemical redox mechanism of Cu^{2+} through kinetic parameters and digital simulation technique

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ABSTRACT

Cycle voltammetric behaviour of Cu(II)SO_4 in aqueous NaCl (supporting electrolyte) has been explored in comprehensive manner. 5 mM Cu^{2+}, 1.0 M NaCl and glass carbon (GC) reveals the optimum response. Two stage electromechanical redox EE mechanism [(Cu^{2+}/Cu^{+}) and (Cu^{+}/ Cu^{0})] has been explored by using different theoretical and experimental methods. The mass transfer co-efficient, dimensionless parameters and heterogeneous electron transfer rate constant (k^0) confirmed the quasi-reversible response of (Cu^{2+}/Cu^{+}) redox couple. The experimental Gileadi (k^0) and simulated Digi Sim (k^0) values found as 0.052 cm/s and 0.0012 cm/s respectively. The diffusion co-efficient (D) of (Cu^{2+}/Cu^{+}) redox couple computed from 9.96 X 10^{-6} to 4.43 X 10^{-6} cm^2/s through different methods. The novelty of the present work is to confirm the quasi-reversible response of (Cu^{2+}/Cu^{+}) through obtained electrochemical and kinetic parameters by using simple, fast, and cost-effective technique.

1. Introduction

Electrochemical studies of copper ion have gained significant importance since copper remarkably substituted aluminum in the fabrication of integrated circuits (ICs) as an interconnect metal [1]. Since copper is a bivalent metal, it undergoes two electron transferred redox reaction either directly in single step (Cu^{2+}/Cu^{0}) or in a series of steps (Cu^{2+}/Cu^{+} and Cu^{+}/Cu^{0}), these redox couples are of interests because of their significance in electrodeposition, and in corrosion of copper [2], some research has extended by altering the pH of the solution, [3, 4], also the effects of chloride ions were explored for corrosion behavior of copper [5, 6]. Some previous studies explored the kinetic parameters and nucleation formation of copper in deep eutectic solvents [7, 8]. Apart from electrochemistry copper and its associated coordination complexes in aqueous media play significant role in biological system like interconversion of Cu^{2+} into Cu^{+} significantly changes the state of healthy person and produces Alzheimer disease, therefore most of the research has been attributed for the redox mechanism of copper ion [9]. Because of technological and biological involvement of different oxidation state of copper ions provoke researchers to work on redox mechanism of copper ions, therefore extensive work has been reported on this aspect. Bockris Mattson mechanism suggested (in earlier research) that the dissolution and deposition of copper occurred by a two-step mechanism comprising two single-electron transfer events and the reversible production of a soluble Cu^+ intermediate, in non-complexing sulphate medium [10,11]. Grujicic and Besic represented two electron reduction mechanism in a single step [12], whereas they also extended the copper nucleation studies in ammonical solution with two step series wise electron reduction procedure [13]. However, less emphasis drawn to confirm redox mechanisms by theoretical and simulated techniques.

In present studying the main aim is to explore redox mechanism of copper ions by using cyclic voltammetric (CV) kinetic parameters and Digi simulation techniques for further confirmation of redox mechanism of copper. To explore the electrochemical redox mechanism of $Cu^{2+/}Cu^+$ redox couple by analyzing different electrochemical parameters like heterogeneous electron transfer rate constant, mass transfer coefficient etc. by CV which is cost effective, fast and reliable technique comparative to other expensive, tedious and less available methods. It could be beneficial for the analysis of interaction of metal ions with other substrates. In present study the CV experiments were performed to select the optimum working electrode (WE), supporting electrolyte, scan-rate and Cu^{2+} concentration. This study comprehensively presented the redox-reaction of $Cu^{2+,}$ heterogeneous electron transfer rate constant (k^o), electron transfer coefficient (Tafel plot and CV). The Diffusion coefficient was calculated by two different voltammetric methods. The results were further ensured by digital simulation (DIGISIM software embedded in CHI software). In the best of our knowledge, redox kinetic parameters of Cu^{2+} in the presence of supporting electrolyte (aqueous NaCl) and its reaction mechanism hasn't yet reported.

2. Materials and Method

2.1 Reagents and Chemicals

Copper(II)sulphate ($CuSO_4.5H_2O$, 99.9%) was purchased from Merck, Germany. Sodium chloride (NaCl, 99.5%), Potassium chloride (KCl, 99.5%) purchased from Merck, Germany. Lithium perchlorate (supporting electrolyte: $LiClO_4$ > 95%) was purchased from Sigma Aldrich, Germany.

2.2 Apparatus

Cyclic voltammetric experiments were performed by using electrochemical workstation CH Instruments with the setup of three-electrode system and analyzed through the software CHI-760D. Platinum wire (Pt) was used as counter electrode while saturated calomel electrode (SCE) served as reference electrode and three different working electrodes were used, glassy carbon (GC, 0.0706 cm^2), platinum (Pt, 0.0201 cm^2) and gold (Au, 0.0201 cm^2). All electrochemical experiments performed in unstirred condition at room temperature. Possible interference of oxygen was removed by bubbling nitrogen (99.99%) in the working solution prior to perform experiment. For the determination of heterogeneous electron transfer rate constant (k^o) Nicholson, Gileadi and Kochi methods were used. Diffusion coefficient (D) calculated by the Randles-Sevcik equation and also from equation for irreversible system. Electron transfer coefficient obtained from the data of Tafel plot and CV. For the confirmation of results simulated voltammogram (DIGISIM) was produced by the CHI software.

3. Results and Discussion

3.1 Selection of Electrode, Supporting Electrolyte, Scan-Rate, and Concentration of Cu^{2+}

Several CV experiments were performed to select the optimum working electrode (WE), supporting electrolyte, scan-rate, and Cu^{2+} concentration. On behalf of extensive data, best results and interpretation GC as the WE, aqueous 1.0 M NaCl as the supporting electrolyte and 5 mM concentration of Cu^{2+} were selected as the optimum conditions. These optimum conditions later used throughout this study.

3.2 Confirmation of Redox Process

GC as the WE, aqueous 1.0 M NaCl as the supporting electrolyte, and 5 mM $Cu(II)SO_4$ concentration was used to study the redox behaviour for all further experiments. The voltammogram showed two peaks in forward scan and two peaks in the reverse scan (Fig. 1). The first two cathodic peaks (c_1 and c_2) correspond to Cu^{2+} to Cu^+ and Cu^+ to Cu^0 [14]. Therefore, electrochemical reactions of this study can be presented by the following two eq.s 1 and 2 (cathodic peaks c_1 and c_2).

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (1)$$

$$Cu^+ + e^- \rightarrow Cu^0 \quad (2)$$

Whereas the second two anodic peaks a_2 and a_1 represents the Cu^0 to Cu^+ and Cu^+ to Cu^{2+} respectively by the following two eq.s 3 and 4.

$$Cu^0 \rightarrow Cu^+ + e^- \quad (3)$$

$$Cu^+ \rightarrow Cu^{2+} + e^- \quad (4)$$

These Eq.s present multistep electron transfer mechanism or consecutive electron transfer EE process [15]. The peaks c_1 and a_1 are diffusion controlled, whereas c_2 and a_2 involves mix diffusion and adsorption as depicted in Fig. 1 by pointed line shape (anodic stripping) which occurs due to the sudden re-oxidation of the metallic copper that has been deposited on the electrode surface during the Cu^+/Cu^0 reduction. The above mechanism further analyzed by different electrochemical parameters.

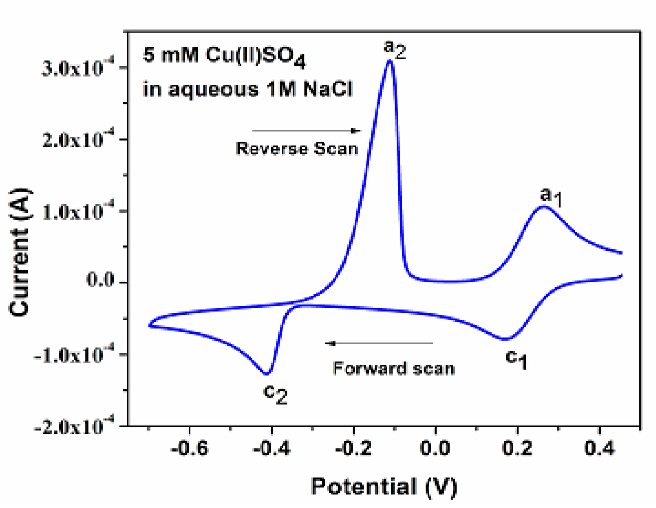

Fig. 1. CV of Cu^{2+} at a scan rate of 100 mV/s; at GC in 1.0 M aqueous NaCl solution used as supporting electrolyte with SCE as reference electrode.

3.3 First Redox Reaction (Cu^{2+}/Cu^+)

The main aims of this section are: (i) to determine the kinetic parameters and use the investigated parameters to explore the quasi-reversible behaviour of (Cu^{2+}/Cu^+); (ii) to find out the value of k^o through different methods: (iii) to investigate the diffusion coefficients.

3.3.1 Determination of kinetic parameters of first redox reaction (Cu^{2+}/Cu^+)

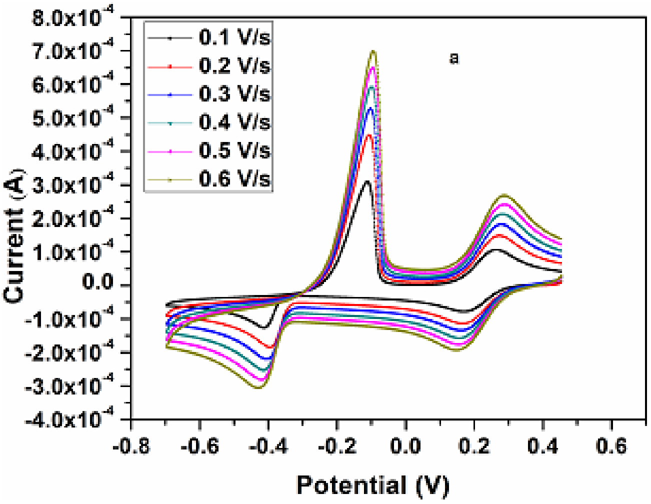

Fig. 2a. Overlay of $Cu(II)SO_4$ voltammograms at different sweep rates (WE: GC) using 1.0 M NaCl as the supporting electrolyte and SCE as the reference electrode.

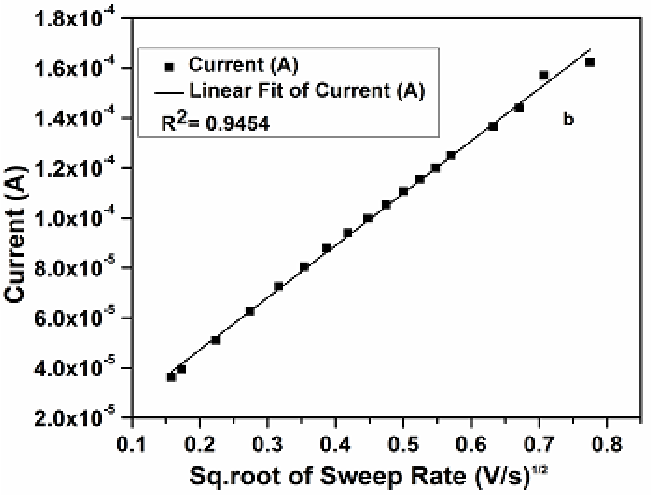

Fig. 2b. Graph between peak current and square root of sweep rate.

The voltammograms were recorded from lower to higher scan-rate values (0.3-0.6 V/s), as shown in Fig. 2a). Peak separation (ΔEp) varied from 0.079 to 0.137 V which is more than one electron reversible system as the theoretical value for the reversible system is 0.058 V/n, whereas peak current ratio (Ipa_1/Ipc_1) varied from 1.81 to 1.40 which is more than 1, therefore the redox process is more likely to be quasi-reversible.

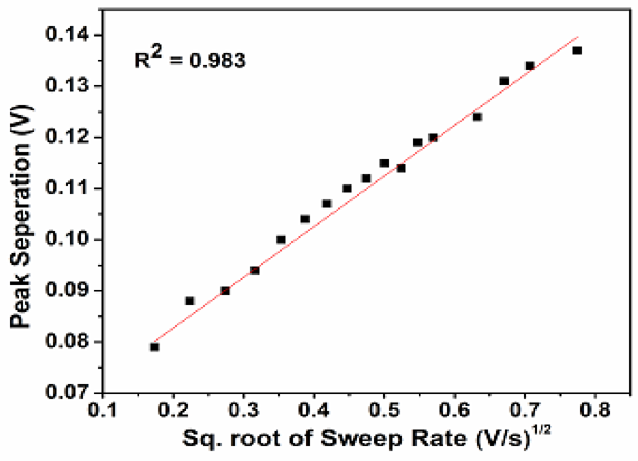

Fig. 3. Plot of ΔEp of Cu(II)SO_4 voltammetric peaks (data from Fig. 2a) against the square root of sweep rate; at glassy carbon electrode with SCE as reference electrode in 1.0 M NaCl as supporting electrolyte.

To ensure that quasi-reversible behaviour is due to uncompensated resistance or due to slow charge transfer kinetics; first condition does not fulfil as different concentration of supporting electrolyte was analyzed and 1.0 M NaCl having minimum resistance, therefore it is likely that slow kinetics would be possible. Further confirmation of slow kinetics, a graph was plotted between ΔEp and square root of sweep rate (Fig. 3), this plot exhibits linear relationship, which meets with the theory of process of quasi-reversible system, therefore the obtained results show kinetic effects on the redox process.

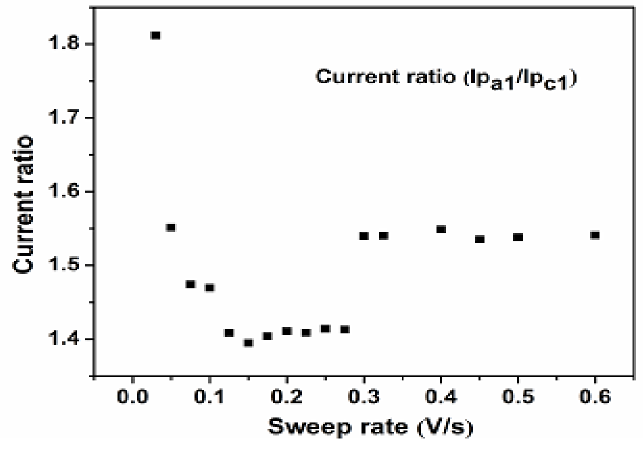

Fig. 4. Plot of peak current ratio and sweep rate (0.03-0.6 V/s)

Fig. 2b shows a linear curve between peak current (Ipc_1) and square root of scan rate that indicates the diffusion controlled. Fig. 4 represents non-linear trend between peak current ratio and scan rate. At lower scan rate (0.03 V/s) peak current ratio was 1.81, as the scan rate increases this ratio decreases until reached up to 1.41 at higher scan rate (0.6 V/s), all these values are greater than theoretical value that should be 1 required for the reversible system.

This quasi-reversibility would be determined by assessing heterogeneous electron transfer rate constant (k^o). The value of k^o from Nicholson method was found as 0.00567 cm/s, this value shows moderate speed of electron transfer which is obviously a clear indication of quasi-reversible system. Based on these observations following reaction mechanism may suggest that refers that quasi-reversibility is due to structural reorganization and peak current ratio also strengthen this mechanism as backward peak current (Ipa_1) is more than forward peak current (Ipc_1) representing the species formed during electrochemical redox process as shown in Eq. 5 [15].

$$[Cu(H_2O)_6]^{2+} + e^- \rightleftharpoons [Cu(H_2O)_4]^+ \quad (5)$$

3.3.2 Mass transfer coefficient

A comparison between k^o and mass transfer coefficient (m_T) indicating the fast and slow electrode kinetics indicated that $k^o >> m_T$ for reversible kinetics whereas $k^o << m_T$ for the irreversible process [16]. The m_T can be calculated from the following relation.

$$m_T = \left(\frac{FDv}{RT}\right)^{1/2} \quad (6)$$

The above formula provided m_T = 0.0045 cm/s whereas k^o = 0.00567 cm/s. These values are close to each other therefore the process is neither reversible nor irreversible, hence classified as quasi-reversible.

3.3.3 Dimensionless parameter

Matsuda and Ayabe introduced the dimensionless parameter ζ [17].

$$\zeta = \frac{k^0}{(FDv/RT)^{1/2}} \quad (7)$$

The value of ζ is found to be 1.216 which corresponds to the quasi-reversible limit; thus, it is further confirmed the process is quasi-reversible in nature.

3.3.4 Determination of charge transfer coefficient

The charge transfer coefficient (α) was determined by different methods. Tafel plot (Fig. 5) is one of the useful methods in electrochemistry to find out the charge transfer coefficient by using Eq. 8.

$$Slope = \frac{-\alpha F}{2.3RT} \quad (8)$$

In this method the cathodic current from the peak c_1 (Fig. 1) was plotted against the variable potential. The obtained slope is -10.72 that corresponds to α = 0.625, indicating a quasi-reversible system.

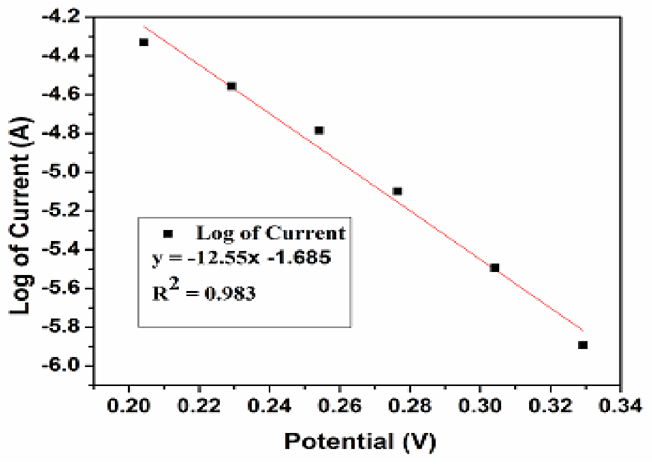

Fig. 5. Tafel plot (Fig. 1 data from the cathodic part of peak c_1): graph between log (i) and potential (V *vs* SCE) at 0.100 V/s scan rate.

Another method [18,19] by I. Shibli et. al. employs separation between peak potential (E_p) and half peak potential ($E_{p/2}$) by using the Eq. 9.

$$E_p - E_{p/2} = \frac{48\,mV}{\alpha n} \tag{9}$$

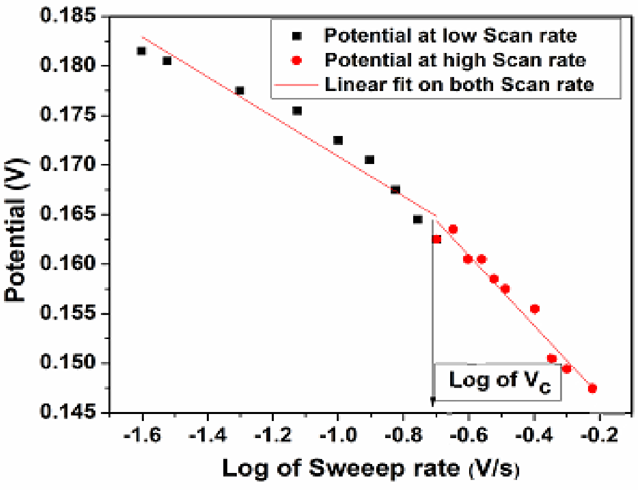

Fig. 6. Plot of cathodic peak potential (Ep_c) against log (sweep rate) for the critical sweep rate (v_c) at GC with SCE as reference electrode for 5 mM Cu^{2+}/Cu^{+} redox couple, 1.0 M NaCl as supporting electrolyte.

The different values of alpha α was obtained at different sweep-rates (Table 3), the average value of α = 0.62 with the standard deviation of 0.061, this value is in good agreement with α value obtained from Tafel plot. To ensure the correctness of experimentally obtained α, simulated voltammogram (simulation by the DIGISIM embedded in CHI software) was generated by using the experimental values in CHI software for 0.100 V/s. The best fit optimized simulated voltammogram provided α = 0.65 comparable to the above mentioned experimental value. All these methods indicated quasi-reversible behaviour with the diffusion control process.

3.3.5 Determination of heterogeneous electron transfer rate constant

Heterogeneous electron transfer rate constant defines the extent of charge transfer. Three useful methods (Table 1) were taken into account. Gileadi method [20] may provide reliable k^o values as it is not affected by the uncompensated resistance. This method depends on a critical scan-rate, which was determined by graphing peak potential Ep_c versus log (sweep-rate), signifies the transition from reversible to irreversible electrode response. Two linear curves were obtained; a linear curve is obtained at lower scan rate with larger slope, while another at higher sweep-rate with smaller slope (Fig. 6).

$$k^o = -0.48\alpha + 0.52 + log\,(\frac{nF\alpha V_c}{2.303RT})^{1/2} \tag{10}$$

The two fitted lines were extrapolated to get the value of critical scan-rate (from intersection) and Eq. 10 was used to calculate k^o. Eq. 10 provided k^o = 0.0052 cm/s that shows quasi-reversible behaviour.

Table 1

Summary of all Investigated electrochemical parameters.

Parameter	$E_{1/2}$ (V)	Charge Transfer Coefficient (α)	n	Diffusion Coefficient (D x 10^6) / cm^2/s	Heterogeneous rate constant (k^0) cm/s			Mass transfer Coefficient (m_T) cm/s	ζ
					N & Shain	Kochi	Gileadi		
CV	*0.220	*0.651		a) *4.436	*0.0056	*0.0014	*0.0052	*0.0044	*1.216
Tafel Plot	-	*0.690	-	-		-		-	-
Convolution Voltammetry	-	-		b) *3.59 c) *9.9		-		-	-
DIGISIM	*0.223	*0.650	*1	d)*3.5		*0.0042		-	-

*For first redox couple Cu^{2+}/Cu^{+}; [a]Results from Eq. 13; [b]Results from Eq. 14, [c]Results from Eq. 15, [d]Results from DIGISIM.

The second frequently used Nicholson method [21] for the determination of k^o is based upon peak-to-peak separation that corresponds to dimensionless parameter according to Eq. 11.

$$k^0 = \Psi\left[\frac{\pi D_o nFv}{RT}\right]^{1/2} \qquad (11)$$

The obtained values of k^o (Table 2) by the Nicholson method provided k^o = 0.0056 cm/s which shows good agreement with the Gileadi method.

Table 2

Values of k^o determined from Nicholson's method through experimental peak separation at different scan rates.

Scan Rate (V/s)	ΔE_p (V)	Ψ	(k^o) cm/s	Average (k^o) cm/s
0.025	0.080	1.33	0.005118	0.00567
0.05	0.079	1.52	0.006408	
0.075	0.088	0.88	0.004789	
0.1	0.090	0.81	0.005399	
0.125	0.094	0.71	0.005465	
0.15	0.096	0.67	0.005766	
0.175	0.099	0.62	0.005845	
0.2	0.098	0.65	0.006618	
0.225	0.110	0.44	0.004789	
0.25	0.112	0.43	0.004964	
0.275	0.115	0.41	0.00499	
0.3	0.114	0.42	0.005361	

Third method, by Kochi and Klinger [22], depends on the separation of peak. In this method, it is necessary to determine the value of transfer coefficient.

$$k^0 = 2.18\left(\frac{\alpha D^0 nFv}{RT}\right)^{\frac{1}{2}} exp\left[-\frac{\alpha^2 nF}{RT}\left(E_{pa} - E_{pc}\right)\right] \qquad (12)$$

Table 3

Values of k^o determined from Kochi and Klinger method.

Scan Rate (V/s)	Transfer Coefficient (α)	ΔE_p (V)	(k^o) (cm/s)	Average (k^o) cm/s
0.025	0.75	0.08	0.00069	0.00148
0.05	0.69	0.079	0.00124	
0.075	0.70	0.088	0.00123	
0.1	0.68	0.09	0.00148	
0.125	0.68	0.094	0.00154	
0.15	0.68	0.096	0.00163	
0.175	0.70	0.099	0.00151	
0.2	0.68	0.098	0.00181	
0.225	0.71	0.11	0.00130	
0.25	0.67	0.112	0.00164	
0.275	0.66	0.115	0.00172	
0.3	0.65	0.114	0.00192	

Table 3 shows heterogeneous electron transfer rate constant calculated from this method. Average k^o was found to be 0.00148 cm/s. This value is in the range of quasi-reversible limits but some difference is present similar to previous reports [38]. These experimental k^o values by the three methods (Gileadi, Nicholson, Kochi and Klinger) confirmed the quasi-reversible behaviour of the studied copper redox.

3.3.6 Determination of diffusion coefficient

3.3.6.1 Diffusion coefficient through CV

The well-known Randles-Sevcik Eq. was used to determine diffusion coefficient by the Eq. 13 [23].

$$I_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2} \quad (13)$$

Where I_p is the peak current (A), n is the number of electron exchanged during the electrochemical process (electron stoichiometry), A is the active surface area of the working electrode (cm^2), D is the diffusion coefficient (cm^2/s), C is the bulk concentration of the diffusing species (mol/cm^3), ν is the voltage scan rate (V/s). D was calculated by plotting the peak current against square root of scan-rate (Fig. 2b), the slope value 2.00 x 10^{-4} corresponds to D = 4.436 x $10^{-6} cm^2/s$. As stated above the process is electrochemically quasi-reversible. Therefore, Eq. 14 was used [15].

$$I_p = (2.99 \times 10^5) nAC(\alpha n D \nu)^{1/2} \quad (14)$$

From the above Eq., the slope = 2.00 x 10^{-4} that corresponds to *D* = 3.59 x 10^{-6} cm^2/s.

3.3.6.2 Diffusion coefficient by DIGISIM

The value of diffusion coefficient was determined from Digital simulation (DIGISIM, Fig. 7). This program is based on the fast implicit finite difference (FIFD), used for the understanding of redox mechanism by utilizing experimental parameters. The different parameters like $\alpha = 0.65$, $n = 1$, $E^o = 0.525$ V were used and optimized. The best fit simulated voltammogram of 5 mM at 0.100 V/s provided D = 3.5 x 10^{-6} cm^2/s and k^o value 0.0042 cm/s comparable with the experimental values.

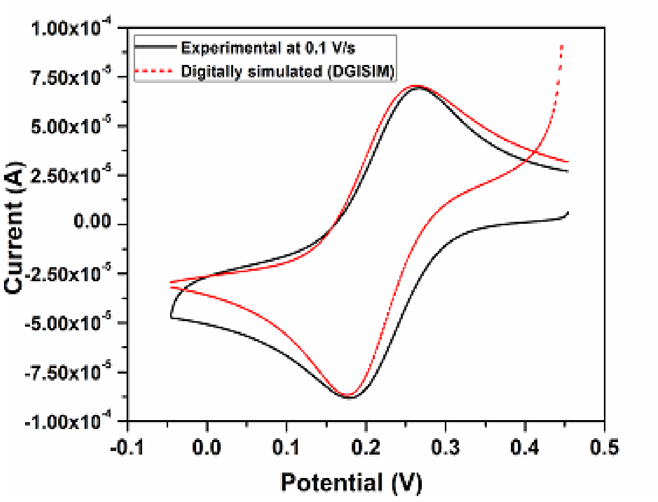

Fig. 7. Digitally simulated voltammogram at 0.1 V/s scan rate compared with the experimental CV recorded at glassy carbon electrode with SCE as reference electrode, 5 mM Cu^{2+}/Cu^+ in 1.0 M NaCl.

3.3.6.3 Diffusion coefficient through convolution voltammetry

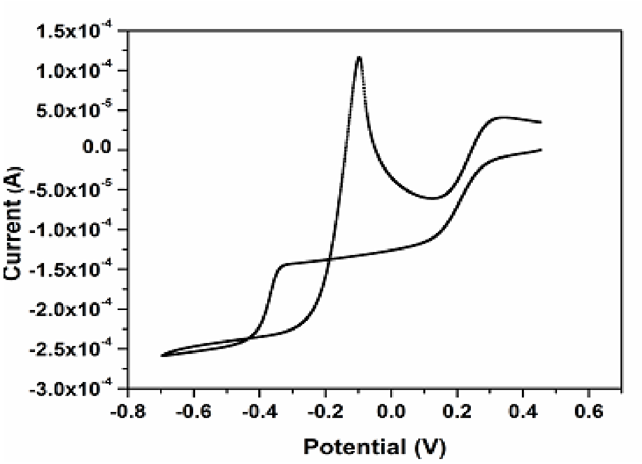

Fig. 8. Convoluted voltammogram of Cu^{2+}/Cu^+ in 1.0 M NaCl as supporting electrolyte; at glassy carbon electrode with SCE as reference electrode at sweep rate of 0.1 V/s.

Diffusion coefficient was also determined by the convolution voltammetry. The key feature of convolution voltammetry is to transform the cyclic voltammogram into a steady state voltammogram. In the steady state forward scan behaves backward scan, when convolution was applied on the cyclic voltammogram of Cu^{2+} solution it was observed that the behaviour of reverse scan was not identical to forward scan (Fig. 8). It means that the reduction process was not truly reversible but quasi-reversible. The D was investigated from frequently used Eq. 15 [24,25].

$$I_{lim} = nFAD^{1/2}C \quad (15)$$

Where I_{lim} is the limiting current obtained from the convoluted voltammogram and other terms have usual meanings. The obtained value of *D* from Eq. 15 is 9.9 x 10^{-6} cm^2/s. The value shows difference when compared to other methods likely because convolution voltammetry does not take into account the important contribution of scan-rate, transfer coefficient and charging current.

4. Conclusion

The redox reaction of Cu^{2+} in aqueous NaCl indicated that during cathodic sweep Cu^{2+} reduces to Cu^+ which further reduces into Cu^0. Therefore, it is two step-one electron transfer process and termed as consecutive electron transfer (EE). The first redox couple (Cu^{2+}/Cu^+) found as diffusion control process. Magnitude of diffusion coefficient was obtained from 9.9 x 10^{-6} to 4.43 x 10^{-6} cm^2/s and other kinetic parameters confirm the quasi-reversibility of (Cu^{2+}/Cu^+) due to the structural reorganization from $[Cu(H_2O)_6]^{2+}$ to $[Cu(H_2O)_4]^+$. The heterogeneous electron transfer rate was computed through Nicholson Shain (0.00567 cm/s), Gileadi (0.0052 cm/s) and DIGISIM (0.0042 cm/s). These electrochemical parameters confirm the theoretical aspects of quasi-reversibility of the studied reaction. As a conclusion, the explored electrochemical reaction mechanism of Cu^{2+} has good agreement with obtained magnitude of kinetic parameters.

5. Acknowledgment

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