Investigation the Electrochemical Behavior of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxodihydro-pyrimidine-4,6-dione using Semi-integration of Current

Mohamed A.Ghanem[1,*], Ibrahim S El-Hallag[2] and Prabhakarn Arunachalam[1]

[1]Chemistry Department, College of Science, King Saud University, Riyadh 11451, Kingdom of Saudia Arabia
[2]Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

Abstract: *The electrochemical behavior of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at a platinum electrode was studied by semi-integration, semi differentiation of current, and digital simulation methods in 0.1 mol/L tetraethylammonium perchlorate (TEACl) in acetonitrile solvent. Cyclic voltammetric study revealed that the presence of three oxidative peaks due to the presence of two electron transfer coupled by chemical reaction (EC) and followed by electron transfer (E) step then EC, i.e., the overall process is ECEEC scheme. On going to negative potential there are two unidirectional reductive peaks associated with the oxidative peaks. The elucidation of the electrode behavior, the electrochemical and chemical data of the compound under investigation was determined using sweep voltammetry, semi integration & semi differentiation of current. The calculated electrochemical parameters and the nature of the electrode reaction were established & confirmed via generation of the theoretical cyclic voltammograms.*

1. INTRODUCTION

The unprecedented growth and development of sulfur-nitrogen (S-N) ring compounds began with the considerable rise in scientific interest for the discovery of their metallic and superconducting properties [1,2]. Quite large number of studies of these ring systems have been made and diverse reports have ascertained their relevance in the field of nanotechnology [3], electrical and electronics engineering [4-6], medicine [5], industrial and military applications [5]. One factor that has favored S-N ring compounds is the strong π-electron delocalization pattern of -S=N-units which is driven by efficient overlap of pπ orbitals of S and N coupled with the high electronegativities of nitrogen and sulfur [7]. The aforementioned factor spurred the discovery of theoretical calculations [8] to come up with electronic factors that explained the thermodynamic [7] and kinetic responses from S-N containing ring systems which have resulted in a unique magnetic [9] and conducting properties [10].

Redox-active heterocycles are candidates for catalysis, sensing and optical materials [11]. In the presence of substituents of different sizes and orientations, the redox potentials of S-N containing rings and other ring systems are tuned within a certain redox potential window [12-15], resulting in enhanced electron transfer rates, redox potentials [16] and other related parameters such as activation energy [17] by appreciable factors. Moreover, the importance of substituent effects in the stabilization of ring systems incorporating sulfur-nitrogen and other main group elements to prevent dimer formation are extremely invaluable [18].

The electrochemical data of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione has been assess using cyclic voltammetry and convolution transforms [19-21]. The possibility of using all data obtained in individual cyclic voltammetric experiment instead only including the data concerned with the peak values is the main advantage of the convolution technique. The accuracy in mechanism diagnosis and rate constant determination would thus be increased. The convolution transforms or semi integral of the current is evaluated via the history dependent integral [20].

*To whom correspondence should be addressed: Email: mghanem@ksu.edu.sa
Phone: +99 114670405

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

In equation (1) the symbol i is defined as the current, total elapsed time is represented by t and u is a dummy variable.
In the case of EC reaction described in equation (2):

$$O + ne \underset{\alpha}{\overset{k_s, D,}{\longleftrightarrow}} R \overset{k_c}{\longrightarrow} C \qquad (2)$$

the reduced form "R" are created by gain electron at cathode and transfer chemically to C into the solution with rate constant k_c. The Second Law of Fick's is now presented as [22]

$$[\partial C_R / \partial t]_x = D_R [\partial^2 C_R / \partial x^2]_x - k_c C_R \text{ (at x)} \qquad (3)$$

Which gives the concentration at electrode surface by Eq. (4) [22]

$$C^s_R = I_2 / nFAD^{1/2}_R \qquad (4)$$

where I_2 is defined by Eq. (5)

$$I_2(t) = \pi^{-1/2} \int_0^t [i(u)\exp(-k_c(t-u))]/(t-u)^{1/2} \, du \qquad (5)$$

Thus I_2 exhibits a plateau (at zero) on the reverse sweep in cyclic voltammetry and this property allows the determination of k_c.

The semi differentiation of the current (dI_1 /dt) *vs.* E of fast charge transfer is described as in literature [19, 22].

$$e_p = (dI_1/dt) = nFAC\sqrt{D} \, a\zeta / (1+\zeta)^2 \qquad (6)$$

Where

$$a = nvF/RT \qquad (7)$$

and

$$\zeta = \exp [nF/RT (E - E^0)] \qquad (8)$$

It was found that the deconvolution or semi-differential of current confirms the nature of electron transfer process and determined of the reduction potential of the electrolyzed species.

Here, we report the electrochemical investigation of the 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione compound at platinum electrode via various electrochemical methods in order to give some light on the electrode mechanism pathway and determination of the electrochemical and chemical parameters of the investigated compounds.

2. EXPERIMENTAL

The investigated compound was prepared by adding 1, 3-diethyl-2-thiobarbituric acid (0.0058 mol) to p-dimethylaminobenzaldehyde (0.0058mol) and in anhydrous ethanol (15 ml). The obtained product was purified by recrystallization from methanol and chloroform. Yield: 73.54% IR (KBr) v_{max} cm^{-1} 1686 (C=O), 1653 (C=C), 1164 (C-N), 2932 (C-H aliphatic), 2977 (C-H aromatic), 1188 (C=S). ^{1}H-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,
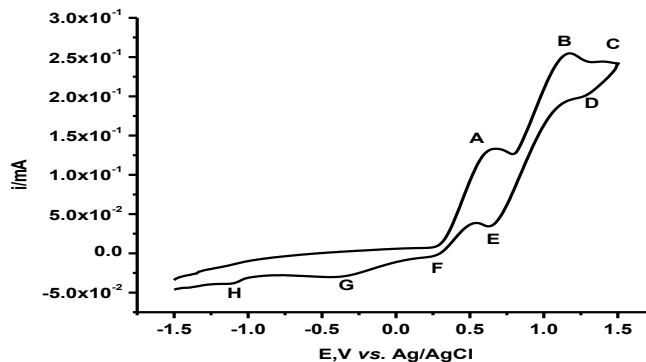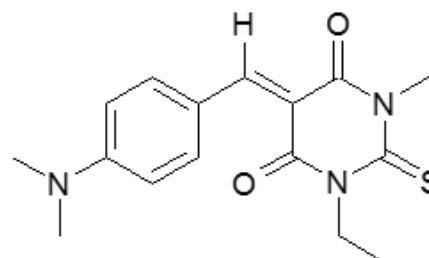
Scheme 1

Figure 1. Cyclic voltammogram of the investigated compound in 0.1 mol.L^{-1} tetraethyl-ammonium perchlorate (TEAP) in acetonitrile solvent at a platinum electrode and sweep rate of 0.08 V.s^{-1}.

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:

Cyclic voltammetry and convoluted voltammetry transforms were carried out via a Princeton Applied Research (PAR) Computer – controlled Potentiostat Model 283 and PAR Model 175 Universal Programmer (from EG and G). The equipment used provides scan speed up to to 100 V.s^{-1}. The used working electrode was platinum electrode with surface area of 7.85 x 10^{-3} cm^2, a counter electrode is coiled platinum wire and a reference electrode is saturated Ag/AgCl electrode. The potential was measured versus the Ag/AgCl reference electrode at 25°C and in 0.1 mol/L tetraethylammonium perchlorate (*TBAP*) as supporting electrolyte dissolved in acetonitrile solvent. The captured cyclic voltammetry was corrected by subtracting the non Fardiac background current and IR drop. Ecomet grinder paper was used for polishing the working electrode and the I – E voltammograms were recorded at sweep speed vary between 0.02 and 1 V.s^{-1} at (25 ± 2) ^{o}C. A stream of N$_2$ gas was purged into the solution then keep above the solution during the experiments to expel the air from the working solution.

Digital simulation 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.

Investigation the Electrochemical Behavior of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxodihydro-pyrimidine-4,6-dione using Semi-integration of Current / J. New Mat. Electrochem. Systems
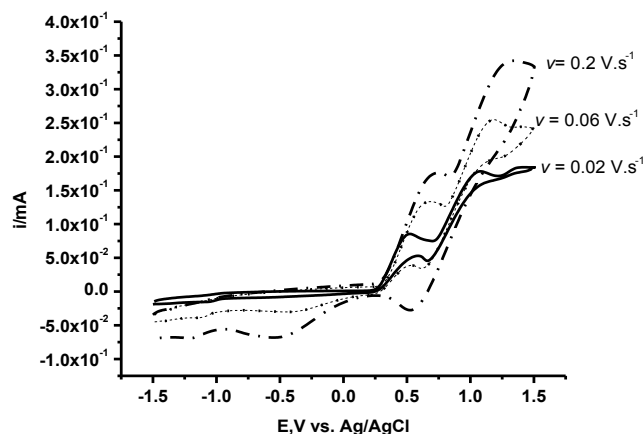
55

Figure 2. Cyclic voltammograms of the investigated compound in 0.1 mol.L^{-1} tetraethyl-ammonium perchlorate (TEAP) in acetonitrile solvent at a platinum electrode at different sweep rates.
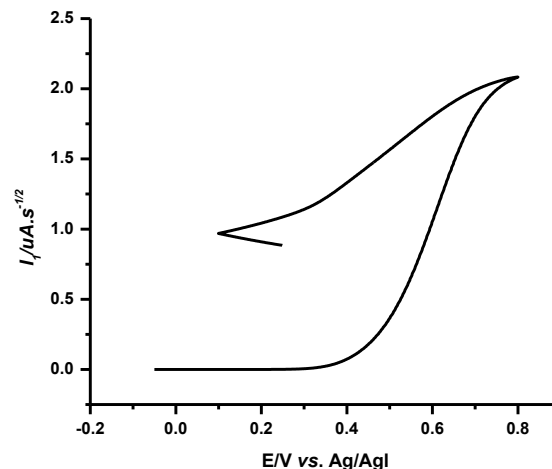

Figure 3. I$_1$ convolution of the investigated compound in 0.1 mol.L^{-1} tetraethyl-ammonium perchlorate (TEAP) in acetonitrile solvent at a platinum electrode and sweep rate of 0.2 V.s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Figure 1 gives an example of the cyclic voltammogram response of the investigated compound in 0.1 mol.L^{-1} tetraethyl-ammonium perchlorate (TEAP) in acetonitrile solvent at a platinum electrode at sweep rate of 0.08 V.s^{-1}. The scan rates used in this study was in the range of 0.02 – 1.0 mV.s^{-1}. It was found that the compound under consideration exhibit well defined three oxidative waves (A + F), (B+ E) & (C + D). Also, extension of the potential to more negative value lead to the appearance of associated two peaks (G & H) which may be due to the reduction of the original compound.

Figure 2 represents the cyclic voltammograms of the compound under consideration at various scan rates. As shown, the height of backward peaks increase with increasing in the sweep rate confirming the existence of moderate rapid chemical reaction following the electron exchange at the first and third peaks.

The change of anodic peak position (E$_p$) to more positive potential by increasing the sweep rate and the magnitude of half peak width (E$_p$ - E$_{p/2}$), confirm the irreversible and/ or slow electrode process [19].

Table 1. Values of kinetic parameters of investigated compound

Peak number	α	E^0,V	k$_s$, m.s^{-1}
1st	0.34	0.375	6e-5
2nd	0.29	0.900	3e-5
3rd	0.41	1.330	8e-5

Table 2. Variation of the peak characteristic of the investigated compound at various scan rates.

Peak number	v, mV.s^{-1}	Ep, mV	i$_p$, mA	Ep –Ep/2, mV	ΔEp, mV
1st peak	20	500	0.08	130	250
	40	550	0.09	158	290
	60	610	0.12	180	360
	80	665	0.14	198	377
	200	698	0.15	205	390
	400	730	0.17	240	405
	600	763	0.19	269	430

The symmetry coefficient values (α) was calculated using equation (9) and listed in Table 1 confirming the irreversible character of the anodic step [21]:

$$Ep = E_{p/2} + 1.857 \ (RT/\alpha_{na}F) \tag{9}$$

For irreversible charge transfer [22], the peak current (i$_p$) can be expressed by the following equation:

$$i_p = 2.99 \times 10^5 \ n \ (\alpha n_a)^{1/2} \ AD^{1/2}Cv^{1/2} \tag{10}$$

where i$_p$ denotes the peak current in amp, and C denotes concentration of the reactants species or groups which equals 2×10^{-4} M in the recent study, and the other parameters have their normal definition. On drawing of the i$_p$ versus $v^{1/2}$ straight line passing through the origin is obtained and reveals how the current diffuses. The second Table revealed that the half peak width (E$_p$ – E$_{p/2}$) grows directly on increasing the scan rate, indicates increasing of irreversibility of the electrode process as the scan rate increases [22]. The standard rate constant (k$_s$) value was calculated through ΔE_p, values *versus* rate constants (k$_s$) [23, 24] (Table 1).

In the case of simple charge transfer or EC scheme, the I$_1$ convolution [25] determines the magnitude of diffusion coefficient (D) of the species from Eq. (11):

$$I_{lim} = nFAC\sqrt{D} \tag{11}$$

where I$_{lim}$ denotes the limiting convoluted current, the remaining symbols have their usual definition. The diffusion coefficients (D)

Table 3 Diffusion coefficient (m2.s^{-1}) of the investigated compound via different methods

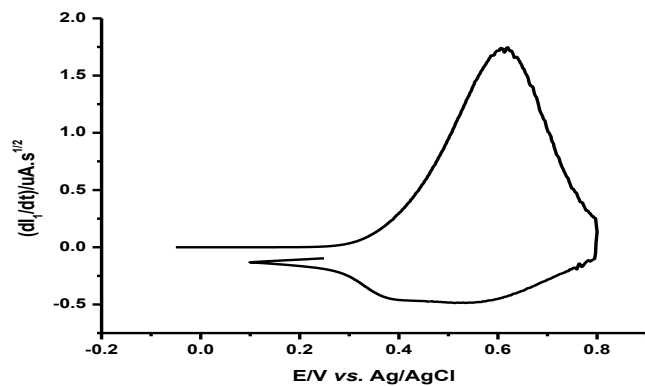| Peak number	CV DxE^{10}	I$_{lim}$ DxE^{10}	Eq. (12) DxE^{10}	Eq.(13) DxE^{10}	Simulation DxE^{10}
1st	6.2	6.7	6.9	6.8	6.6
2nd	5.6	5.2	5.4	5.6	5.8
3rd	4.5	4.1	4.4	4.3	4.2

Figure 4. Deconvolution voltammogram of the investigated compound in 0.1 mol.L^{-1} tetraethyl-ammonium perchlorate (TEAP) in acetonitrile solvent at a platinum electrode and sweep rate of 0.2 V.s^{-1}.

of the investigated compounds were determined using Eq. (11) and cited in Table 3. The semi integration of current (I_1) at a scan speed of of 0.2 V.s^{-1} is displayed in Figure 3. The I_1 exhibits a wide distance 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.

Also, the following equation (12) was used for determination of the "D" value of the investigated compound [22]:

$$I_{lim} = ip/3.099(\alpha n_a \nu)^{1/2} \tag{12}$$

For moderate fast charge transfer, the D value of the compound under consideration was extracted from deconvolution transform (Fig.4) via the ratio $[(dI_1/dt)_f]/i_p$:

$$[(dI_1/dt)_f]/i_p = 3.73(\alpha/n_a)^{1/2}n\nu^{1/2} \tag{13}$$

where $[(dI_1/dt)_f] = \alpha n^2 F^2 SCD^{1/2}\nu/3.367RT$ is the height of the deconvoluted peak and the other symbols have their normal definition. Hence from relationship (13), the values of $[(dI_1/dt)_f]$ can be used as a simple and accurate tool for determination the diffusion coefficient. The values of (D) calculated via various equations are indicated in Table 3, and shows an agreement between the D values calculated via different equations.

3.2. Digital simulation in electrochemistry

Dynamic simulation is defined as the imitation of the behavior of a system with respect to time [26]. Digital simulation has become a very useful tool to researchers of theoretical and experimental electrochemistry [27]. Digital simulation of electrochemical experiments was pioneered by Stephen Feldberg [28 - 30] who is still at work developing the field till date.

In this work digital simulation method was used for generating the first peak of theoretical cyclic voltammogram of the inspected compound. The verification of the parameters was carried out by good agreement between the generated voltammograms and the experimental one, using the mean values of the experimental parameters [24].

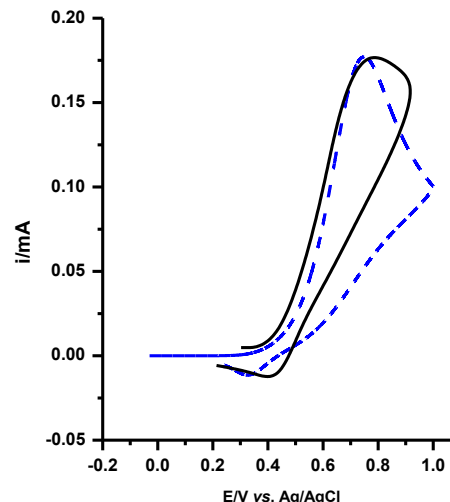The electrochemical parameters used in simulated cyclic voltammograms were:

Figure 5. Matching between captured (—) and generated **(-----)** cyclic voltammograms of the investigated compound at sweep rate of 0.1 V.s^{-1}.

i- D values (diffusivity) of the investigated compound ; ii- the standard redox potential (E^0); iii- bulk solution concentration (C mol.l^{-1}); iv- standard heterogeneous rate constant (k_s, cm.s^{-1}); v- scan speed (V.s^{-1}); vi- temperature (T. K); vii- rate constant of the forward homogeneous chemical step (k_f s^{-1}); viii- rate constant of the backward homogeneous chemical step (k_b s^{-1}) and symmetry factor (α).

Figure 5 indicates the matching of the captured against simulated voltammograms of E_qC_{irr} model for first peak with its semi-integration and semi-differentiation of current of investigated compound at scan speed of 200 mV.s^{-1}. The values of kinetic parameters and k_c for chemical steps were determined via theoretical treatment and its value was found to 8.9 s^{-1}. The agreement between theoretical and experimental data confirms the accuracy of the electrochemical parameters calculated from the experimental techniques as well as the proposed mechanism.
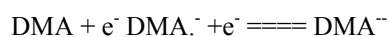
The kinetic convolution I_2 was used for determination of the homogeneous chemical rate constant (kc). The procedure was done via introducing various test values of k_c until a value is found that returning I_2 to zero at the end of the reverse sweep. The true k_c value of the chemical step following the electron transfer is found to be 8.9 s^{-1} for the compound under investigation.

According to obtained results the electrode pathway of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione can be summarized as follows:

Oxidation process

$$DMA - e ==== DMA^+ - e ==== DMA^{++} - e^- === DMA^{+++}$$

↓ rearrangement   ↓ rearrangement

Product   Product
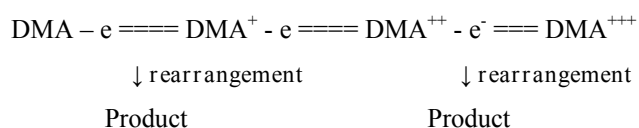
Reduction Process

$$DMA + e^- \ DMA^{.-} + e^- ==== DMA^{--}$$

4. CONCLUSION

In 0.1 mol/L tetra-ethylammonium perchlorate (TEAP) and acetonitrile solvent, the electrochemical behavior of 5-(4-Dimethylamino-benylidene)-1,3-diethyl-2-thioxo-dihydro-pyrimidine-4,6-dione at a platinum electrode was studied by cyclic voltammetry, semi-integration, semi differentiation of current, and digital simulation methods. Cyclic voltammetric investigation revealed that the overall oxidative electrode process is ECEEC scheme. On going to negative potential there are two unidirectional reductive peaks associated with the oxidative peaks. The calculated electrochemical parameters and the nature of the electrode reaction were established & confirmed via digital simulation method.

5. ACKNOWLEDGEMENT

REFERENCES

[1] M.M. Labes; P. Love; F.L. Nichols, Chem. Rev., 79, 1 (1979).

[2] A.J. Banister; I.B. Gorrell., Adv. Mater., 10, 1415 (1998).

[3] J.M. Rawson; J.J. Longridge., Chem. Soc. Rev., 26, 53 (.).

[4] J.-P. Lang; H. Kawaguchi; K. Tatsumi, J. Chem. Soc., Dalton Trans., 2573 (2002).

[5] T. Chivers., Sulfur–Nitrogen Compounds. In Encyclopedia of Inorganic Chemistry, John Wiley & Sons, Ltd: 2006.

[6] W. Ji; S. Shi; H. J. Du; P. Ge; S. H. Tang; X. Q. Xin., J. Phys. Chem., 99, 17297 (1995).

[7] R.T. Oakley., Cyclic and Heterocyclic Thiazenes. In Prog. Inorg. Chem., John Wiley & Sons, Inc., p299-391, 2007.

[8] M.–H. Whangbo; R. Hoffmann; R.B. Woodward., Proc. Royal Soc. London A. Math. Phy. Sci., 366, 23 (1979).

[9] J.M. Rawson; G.D. McManus., Coord. Chem. Rev., 189, 135 (1999).

[10] A.W. Cordes; R.C. Haddon; R.T. Oakley., Adv. Mater., 6, 798 (1994).

[11] S. Al-Ahmad; B. Boje; J. Magull; T.B. Rauchfuss; Y. Zheng; J. Am. Chem. Soc., 117, 1145 (1995).

[12] K. Krumova; G. Cosa ; J. Am. Chem. Soc., 132, 17560 (2010).

[13] F. Pop; A. Amacher; N. Avarvari; J. Ding; L.M.L. Daku; A. Hauser; M. Koch; J. Hauser; S.-X. Liu; S. Decurtins; Chem. A. Eur. J., 19, 2504 (2013).

[14] K. Bechgaard; V.D. Parker; C.T. Pedersen; J. Am. Chem. Soc., 95, 4373 (1973).

[15] R.T. Boeré; K.H. Moock; M.Z. Parvez, M; Anorg., Allg. Chem., 620, 1589 (1994).

[16] J. Geue Rodney; V. Hanna John; A. Höhn; C.J. Qin; F. Ralph Stephen; M. Sargeson Alan; C.Willis Anthony; In Electron Transfer Reactions, American Chemical Society, 253, 137 (1997).

[17] P. Bullock; A.M. Bond; R.T. Boeré; T.M. Gietz; T.L. Roemmele; S.D. Seagrave; J.D. Masuda; M. Parvez; J. Am. Chem. Soc., 135, 11205 (2013).

[18] V.Y. Lee; A. Sekiguchi; Acc. Chem. Res., 40, 410 (2007).

[19] J.C. Imbeaux and J.M. Saveant, J. Electroanal. Chem., 44, 169 (1970).

[20] K.B. Oldham, G.D. Zoski, Anal. Chem., 52, 2116 (1980).

[21] A. Neudeck and J. Dittrich, J. Electroanal. Chem., 264, 91 (1989).

[22] I.S. El-Hallag, Ph.D. Thesis, Tanta University, Egypt, 1991.

[23] R.S. Nichlson, Anal. Chem., 37, 1351 (1965).

[24] A.A. Al-Owais, I.S. El-Hallag, L.M. Al-Harbi, E.H. El-Mossalamy and H.A. Qar., J. New Mat. for Electrochem. Systems, 17, 17 (2014).

[25] Ammar, J.M. Saveant, J. Electroanal. Chem., 47, 215 (1973).

[26] J. Banks; Discrete-event system simulation. Prentice Hall: 2001.

[27] D. Britz; Digital Simulation in Electrochemistry, Springer: 2005.

[28] A.B. Bard; L.R. Faulkner; Electrochemical Methods: Fundamentals and Applications, 2001.

[29] S.W. Feldberg; C. Auerbach; Anal. Chem., 36, 505 (1964).

[30] Z.-X. Deng; X.-Q. Lin; Z.-H. Tong; Chin. J. Chem., 22, 719 (2004).