DATA ANALYSIS AND EVALUATION OF THE ELECTROCHEMICAL PARAMETERS FOR THE ET PROCESS VIA CONVOLUTIVE VOLTAMMETRY AND DIGITAL SIMULATION

I.S. EL-HALLAG¹, A.M. ASIRI² AND E.H. EL-MOSSALAMY²

¹Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

² Chemistry Department, Faculty of Science, King Abdulaziz University, P. O. Box. 80203, Jeddah 21589 Saudi Arabia

(Received: December 21, 2012 - Accepted: April 18, 2013)

ABSTRACT

Data treatment and determination of the standard heterogeneous rate constant of simple ET process (simple electron transfer) & number of electrons consumed in electrode reaction were carried out via convolution-deconvolution voltammetry and digital simulation methods. The working curves required for determination of the standard heterogeneous rate constant, k_s , were constructed and discussed. The number of electrons, n , consumed in electrode reaction was calculated via simple method. The electro-reduction of Pb^{2+} was carried out at hanging mercury drop electrode while the redox behaviour of Fe^{3+}/Fe^{2+} couple was performed at glassy carbon electrode to confirm the validity of the reported method in calculation of k_s and n in case of simple ET.

Keywords: ET process; convolutive voltammetry; digital simulation; electroactive species; working curves.

1. INTRODUCTION

It was established that when the dimensionless parameter $\Psi \geq 7$, the heterogeneous rate constant of electron, k_s , of the electrode reaction is fast, while in case of $\Psi < 0.001$ the rate of electron transfer of electrode reaction is slow. In the region of Ψ between 0.001 and 7.0 is that of so-called moderate fast electron transfer.¹ The correlation between Ψ and k_s is indicated in the following equation:¹

$$\Psi = \frac{k_s}{(\pi D n F \nu / RT)^{1/2}} \quad (1)$$

As shown Ψ is a function of heterogeneous rate constant of electron, k_s , and scan rate, ν , i.e. Ψ increase with increasing k_s and decrease with increasing ν .

The exact peak separation (ΔE_p) as a function of Ψ is given in the working curve established by Nicholson.¹ It was found that when $\Delta E_p > 250$ mV/n, the calculation of standard heterogeneous rate constant, k_s , is inaccurate. This means that the useful range of the working curve for the determination of k_s is $59 \leq \Delta E_p \leq 250$ mV/n.

The present work gives an alternative accurate method for data analysis via construction of the working curves for determination of the heterogeneous rate constant (k_s) of the simple electron transfer scheme in the range 10 to 1×10^6 cm.s⁻¹. It was found that, our proposed method minimize the error arising in calculation of the standard heterogeneous rate constant (k_s) determined from tabulation method especially when $\Delta E_p > 250$ mV/n. The electro-reduction of Pb^{2+} ion in 0.1 M KNO_3 at HMDE and the redox behaviour of Fe^{3+}/Fe^{2+} system in 1M HCl at glassy carbon electrode (GCE) were taken as an experimental examples of simple ET. The heterogeneous rate constant of these ions was determined via the constructed working curves in the present article. Also, this work provide a simple and accurate method for determination of the number of electrons consumed in electrode reaction.

The convolution transforms I_1 is defined as following:

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

where $i(u)$ is the current at time u and t is the total elapsed time.^{2,7}

The electrochemical parameters used for generating the theoretical cyclic voltammograms of the electrochemical reaction

(A + ne ↔ B) are:

$D_A = D_B$ (diffusion coefficient of species A and B)
 E^0 (standard reduction potential)
 α (transfer coefficient)
 E_s (switching potential)

t (duration of experiment)
 S (Surface electrode area)
 C_A^b (bulk concentration of the electroactive species A)
 C_B^b (bulk concentration of the electroactive species B)
 k_s (standard heterogeneous rate constant)
 ν (sweep rate)
 T (absolute temperature)

2. EXPERIMENTAL

Hydrates salts of the "laboratory grade" $Pb(NO_3)_2$ was used as solute and a source of Pb^{2+} ion. Solution of Pb^{2+} ion (2×10^{-4} M) in triple distilled water containing 0.1M KNO_3 solution were investigated. Also hydrates salts of $FeCl_3/FeCl_2$ was the solute and the source of Fe^{3+}/Fe^{2+} pair (5×10^{-4} M) in 1M HCl. A hanging mercury drop electrode (Model 303 A) working electrode (area = 2.61×10^{-2} cm²) and GCE (area = 1.2×10^{-2} cm²) were used as working electrodes for Pb^{2+} and Fe^{3+}/Fe^{2+} ions respectively, Ag/AgCl reference electrode and Pt wire as counter electrode were used. Prior to the electrochemical experiments, solutions were deoxygenated by passage of N_2 gas.

A model 264 A Polarographic Analyzer (from EG & G) was coupled with the cell for CV experiments. Scan rates used ranged from 0.05 – 5 Vs⁻¹.

The simulation and convolutive voltammetry were performed using finite differences techniques.^{8,9} Algorithms were coded and implemented into condosim software package supplied by EG & G.

3. RESULTS AND DISCUSSION

Fig. 1A shows an example response of the cyclic voltammogram of Pb^{2+} ion and theoretical cyclic voltammograms of fast and slow ET at sweep rate of 1.0 V.s⁻¹ and $T = 296$ K.

In order to evaluate the heterogeneous rate constant of electron transfer (k_s), the simulated electrochemical system consists of the reduction of electroactive species proceeds as simple ET was carried out. The arbitrary standard reduction potential (E^0) was 0.5 V and the diffusion coefficient (D) was equal to 5×10^{-9} m².s⁻¹. The potential was usually scanned between 0.0 V (initial value) and -1.0 V (switching value at fast ET); while for totally irreversible charge transfer, i.e. for $\Psi < 1 \times 10^{-3}$, the voltage window of the voltammogram was between 0.0 and -1.2 V. From the values of peak characteristics of the generated cyclic voltammograms ($E_p - E_{p/2}$, $E_p - E^0$, $E_{p/2} - E^0$ and ΔE_p) as a function of Ψ , working curves were constructed with unprecedented treatment of the investigated simple ET scheme. The values of $E_p - E^0$ used for preparing the working curves was in the range 28.3 to 629 mV, while Ψ values ranging from 572.9 to 4×10^{-6} for peak separation, ΔE_p , 57.0 – 1257.0 mV/n at $\alpha = 0.5$. Fig. 2 shows the constructed working curve of the plot $E_p - E^0$ vs. $\log \Psi$ scale. On the other hand, when $\alpha = 0.3$ the values of Ψ cover the range $0.130 - 4.04 \times 10^{-5}$ in case of variation ΔE_p from 217.4 to 1205.0 mV/n. From the measured values of wave characteristics, the corresponding values of Ψ can be calculated, which consider accurate and simple way for determination of the true value of k_s .

Inspection of Table 1 revealed that, there is an agreement between the values of k_s evaluated from working curves established in this work and from tabulation method¹ when ΔE_p in the range 59 – 250 mV/n. On the other hand, when $\Delta E_p > 250$ mV/n, there is a disagreement between the values of k_s calculated from tabulation curve and k_s calculated in this article indicate the inaccuracy of the tabulation method established in literature.¹

Fig.1. Cyclic voltammograms for Pb^{2+} ion in 0.1M KNO_3 (A), theoretical fast ET, $k_s = 10 \text{ cm.s}^{-1}$ (B) and theoretical slow ET, $k_s = 10^{-6} \text{ cm.s}^{-1}$ (C) at sweep rate of 1 V.s^{-1} .

Table 1: Values of Ψ and k_s determined from this work and from other methods.

Ψ			$k_s, \text{cm.s}^{-1}$		
this work	ref.[1]	(A)	this work	ref.[1]	(B)
572.9	---	100.0	10.000	---	10.0
127.0	---	99.00	9.990	---	10.0
57.0	---	99.99	0.990	---	1.0
18.1	21.30	99.96	0.990	1.170	1.0
5.72	6.00	100.0	1.000	1.049	1.0
4.04	5.40	99.80	0.990	1.133	1.0
1.28	2.00	100.0	1.000	1.111	1.0
0.91	1.07	100.00	1.000	0.084	1.0
0.57	0.67	100.0	0.100	0.092	0.1
0.404	0.53	99.7	0.090	0.093	0.1
0.046	0.036	99.9	0.091	0.089	0.1
0.018	0.017	100.0	1.00E-3	1.68E-3	1E-3
0.013	---	99.0	0.99E-3	---	1E-3
5.70E-3	---	100.0	1.00E-3	---	1E-3
4.04E-3	---	99.0	0.99E-3	---	1E-3
4.04E-4	---	99.9	0.99E-3	---	1E-3
5.70E-5	---	100.0	1.00E-4	---	1E-4
1.20E-5	---	100.0	1.00E-4	---	1E-4
9.00E-6	---	99.9	0.994E-5	---	1E-5
5.70E-6	---	99.5	0.995E-5	---	1E-5
4.00E-6	---	99.9	0.999E-5	---	1E-5
$\alpha = 0.3$					
0.127	---	99.8	9.97E-3	---	1E-2
0.090	---	99.7	9.95E-3	---	1E-2
0.040	---	99.5	9.95E-3	---	1E-2
0.028	---	99.5	9.98E-3	---	1E-2
0.018	---	99.8	1.00E-3	---	1E-3
0.012	---	100.0	9.98E-4	---	1E-3
5.72E-3	---	99.8	9.99E-4	---	1E-3
4.04E-3	---	99.9	9.99E-4	---	1E-3
1.80E-4	---	99.9	9.99E-5	---	1E-4
5.72E-5	---	99.9	9.98E-5	---	1E-4
4.04E-5	---	99.8	9.95E-6	---	1E-5

(A) percentage of accuracy of the k_s value extracted from working curve established in this work to the value of k_s used in simulated CV, (B) Values of k_s used for generating cyclic voltammograms.

It was found that the value of the heterogeneous rate constant (k_s) of Pb^{2+} ion in 0.1M KNO_3 calculated from the working curve established in this work equals $(2.25 \times 10^{-2} \text{ cm.s}^{-1})$ which compare well with the value $(2.10 \times 10^{-2} \text{ cm.s}^{-1})$ reported in literature¹⁰ confirming the accuracy of our method. Also the value of k_s for the system Fe^{3+}/Fe^{2+} calculated in this work $(3.41 \times 10^{-4} \text{ cm.s}^{-1})$ compare well with the value established in literature $(3.0 \times 10^{-4} \text{ cm.s}^{-1})$.²

It was found that deconvolution voltammetry^{7, 11-18} is a particular efficient tools in qualitative and quantitative electroanalysis. The action of semi differentiation operator 'e' on a current is to generate a quantity defined by

$$dI_f/dt = d^{1/2}i/dt^{1/2} \quad (3)$$

which is defined as the deconvolution of the current with respect to time.⁷ The ratio of the forward $(dI_f/dt)_f$ and backward $(dI_f/dt)_b$ peak height of deconvolution voltammetry¹⁹ is taken as a simple and accurate tool for testing and verifying the simple ET of the electrode process similar to the ratio of peak current (i_{pb}/i_{pf}) measured from cyclic voltammogram. It was found that, the ratio $(dI_f/dt)_f / (dI_f/dt)_b$ equals 1.0 and independent on the value of scan rate in the case of rapid and slow charge transfer (Table 2).

The values of the most significant quantities of wave characteristics of cyclic and deconvolution voltammetry at arbitrary values of Ψ and transfer coefficient ($\alpha = 0.3$ & 0.5) are listed in Table 3. The plots of $\log \Psi$ versus peak width of the deconvoluted current (W^p) and the separation between the forward and backward peak potentials of the deconvoluted current (ΔE_p) of the generating cyclic voltammograms shown in Fig.3 allow the evaluation of standard heterogeneous rate constant in the range 10 to $1 \times 10^{-6} \text{ cm.s}^{-1}$.

Also, the number of electrons consumed in electrode reaction can be calculated from combination between the limiting convoluted current (I_{lim}), and the peak current (i_p) for fast and slow ET as following:^{7,17}

$$(i_p)_{\text{rev}} = (2.69 \times 10^5) n^{3/2} S D^{1/2} \nu^{1/2} C^b$$

$$= 2.788 I_{\text{lim}} (n\nu)^{1/2} \quad (4)$$

and

$$(i_p)_{\text{irr}} = 2.99 \times 10^5 n (a n_a)^{1/2} S C^b D^{1/2} \nu^{1/2}$$

$$= 3.099 I_{\text{lim}} (a n_a)^{1/2} \nu^{1/2} \quad (5)$$

where $I_{\text{lim}} = n F S C^b D^{1/2}$, α is the transfer coefficient, n_a is the number of electrons exchanged in the rate determining step, and the other terms have their usual meanings. Eqs (4) & (5) can be write in the following forms:

$$(i_p)_{\text{rev}} / I_{\text{lim}} = 2.788 (n\nu)^{1/2}$$

$$(n)^{1/2} = (i_p)_{\text{rev}} / 2.778 I_{\text{lim}} (\nu)^{1/2} \quad (6)$$

and

$$(i_p)_{\text{irr}} / I_{\text{lim}} = 3.099 (a n_a)^{1/2} \nu^{1/2}$$

$$(a n_a)^{1/2} = (i_p)_{\text{irr}} / 3.099 I_{\text{lim}} (\nu)^{1/2} \quad (7)$$

Table 2: The dependence of the ratio of the forward peak height to the backward peak height ($e_{\text{pf}}/e_{\text{pb}}$) of deconvolution voltammetry on the sweep rate at $k_s = 0.1 \text{ cm.s}^{-1}$ and $k_s = 10^{-6} \text{ cm.s}^{-1}$.

Scan rate V.s ⁻¹	k_s cm.s ⁻¹	$e_{\text{pf}}/e_{\text{pb}}$
0.05	0.1	1.00
0.10		1.00
0.20		1.00
0.50		1.00
1.00		1.00
2.00		1.00
5.00		1.02
0.05	10 ⁻⁶	1.01
0.10		1.02
0.20		1.01
0.50		1.03
1.00		1.04
2.00		1.02
5.00		1.01

Fig. 2. Working curve of $E_p - E^0$ vs $\log \Psi$ for simple ET, $\alpha = 0.5$ and $T = 298 \text{ K}$.

Also, in the same manner, the ratios $((dI_1/dt)_f / i_p)$ and $((dI_1/dt)_f / I_{\text{lim}})$ for reversible and irreversible electrode processes can be written in the following form:

$$((dI_1/dt)_f / I_{\text{lim}})_{\text{rev}} = \frac{n F I_{\text{lim}} \nu}{4 I_{\text{lim}} R T} = 9.736 n \nu$$

$$n = \frac{(dI_1/dt)_f}{9.736 I_{\text{lim}} \nu} \quad (8)$$

$$((dI_1/dt)_f / i_p)_{\text{rev}} = \frac{n F I_{\text{lim}} \nu^{1/2}}{11.152 n^{1/2} I_{\text{lim}} \nu}$$

$$= 3.492 n^{1/2} \nu^{1/2}$$

$$(n)^{1/2} = \frac{(dI_1/dt)_f}{3.492 (i_p)_{\text{rev}} (\nu)^{1/2}} \quad (9)$$

$$((dI_1/dt)_f / I_{\text{lim}})_{\text{irr}} = \frac{a n F I_{\text{lim}} \nu}{3.367 R T I_{\text{lim}}} = 11.566 a n \nu$$

$$a n = \frac{(dI_1/dt)_f}{11.566 I_{\text{lim}} \nu} \quad (10)$$

$$((dI_1/dt)_f / i_p)_{\text{irr}} = \frac{a n F I_{\text{lim}} \nu}{10.434 (a n_a)^{1/2} I_{\text{lim}} R T \nu^{1/2}}$$

$$= 3.73 (a / n_a)^{1/2} n \nu^{1/2}$$

$$\left(\frac{a}{n_a} \right)^{1/2} = \frac{((dI_1/dt)_f)_{\text{irr}}}{3.73 n i_{\text{p,irr}} \nu^{1/2}} \quad (11)$$

where $(e_{\text{pf}})_{\text{rev}} = (dI_1/dt)_f = n^2 F^2 S C^b D^{1/2} \nu / 4 R T$
and $(e_{\text{pf}})_{\text{irr}} = (dI_1/dt)_f = (a n^2 F^2 S C^b D^{1/2} \nu / 3.367 R T)$

Fig. 3. Working curves for Simple ET: W_p vs $\log \Psi$ (A) and Δe_p vs $\log \Psi$ (B)

Fig.4. Convolution voltammogram (A) and deconvolution voltammogram (B) of fast ET.

Table 3: The values of peak characteristics and Ψ obtained from theoretical cyclic voltammograms and their deconvolution voltammetry at $\alpha = 0.5$ & 0.3 .

ΔE_p	$E_p - E_{p/2}$	$E_p - E^0$	$E_{p/2} - E^0$	W_p	e_{pt}, e_{pb}	Δe_p	Ψ
$\alpha = 0.5$							
57.0	57.1	28.3	-30.4	90.3	1.0	0.0	572.9
57.0	57.1	28.3	-30.4	90.3	1.0	0.0	127.9
58.2	57.8	29.3	-30.3	90.3	1.0	0.0	57.2
58.5	58.2	29.8	-30.4	91.0	1.0	0.0	18.1
62.0	60.1	32.6	-28.3	91.3	1.0	0.0	5.7
65.2	60.1	32.6	-23.9	92.5	1.0	4.0	4.04
66.0	63.0	32.9	-26.1	93.0	1.0	8.0	2.90
71.8	64.0	34.8	-26.1	95.7	1.0	9.0	1.81
78.2	65.2	39.1	-26.1	104.2	1.0	13.0	1.28
87.0	69.6	43.5	-26.1	113.0	1.0	17.0	0.91
100.0	73.9	52.2	-26.1	117.4	1.01	30.4	0.57
117.4	78.3	60.9	-17.4	117.9	1.02	39.1	0.40
195.7	87.0	100.0	13.0	139.6	1.11	113.1	0.128
226.1	89.2	119.6	30.4	143.4	1.06	139.1	0.090
275.0	90.5	142.0	46.9	144.0	1.04	182.7	0.060
311.0	100.1	162.0	60.0	148.0	1.01	217.3	0.050
391.0	101.0	200.0	100.0	151.0	1.05	304.3	0.020
424.0	101.1	217.0	119.6	152.0	1.09	339.1	0.013
506.0	106.1	256.0	160.9	152.0	1.09	416.0	5.7E-3
543.0	109.0	274.0	180.4	152.0	1.06	456.0	4.04E-3
628.3	115.8	317.0	219.0	152.2	1.06	539.1	1.81E-3
667.4	120.9	334.0	239.0	153.0	1.07	578.3	1.28E-3
702.1	124.3	354.0	256.0	157.0	1.19	608.7	9.04E-4
785.0	130.4	378.0	299.0	158.0	1.03	699.0	4.04E-4
817.4	132.0	413.0	315.0	159.0	1.05	730.5	2.86E-4
877.4	139.1	434.0	337.0	159.0	1.01	778.3	1.81E-4
902.3	141.0	451.0	357.0	160.0	1.09	807.0	1.28E-4
988.0	142.3	497.0	395.0	161.0	1.04	900.0	5.70E-5
1008.0	143.9	503.0	397.0	160.0	1.09	935.0	1.81E-5
1170.0	145.0	591.0	493.0	161.0	1.02	1000.0	9.00E-6
1223.0	148.0	612.0	514.0	161.0	1.01	1000.0	5.70E-6
1257.0	151.1	629.0	538.0	161.0	1.09	1008.0	4.04E-6
$\alpha = 0.3$							
217.0	134.8	139.1	4.0	208.7	1.09	108.7	0.130
256.6	147.9	169.6	21.0	239.1	1.07	147.0	0.090
354.3	158.7	239.1	80.4	241.2	1.00	247.8	0.040
400.0	159.6	269.6	113.0	256.6	1.03	291.4	0.028
416.0	159.0	285.0	175.7	164.0	1.09	346.9	0.021
452.2	160.9	308.7	177.8	248.0	1.06	356.5	0.018
495.6	160.8	339.1	178.3	248.0	1.07	391.3	0.013
632.0	161.0	434.0	278.3	256.0	1.01	530.0	4.04E-3
879.9	162.0	605.0	443.5	269.0	1.03	773.0	5.72E-4
921.9	164.0	638.0	473.9	276.0	1.07	818.0	4.04E-4
1023.0	167.0	706.0	549.0	276.0	1.05	914.7	1.80E-4
1159.0	171.0	803.0	642.0	282.0	1.01	1062.0	5.72E-5
1205.0	173.0	833.0	672.0	286.0	1.03	1095.0	4.04E-5

Table 4: The numerical values of the ratios of peak current height of cyclic voltammograms, deconvolution voltammetry, limiting current and the number of electrons calculated via these ratio in case of fast and slow electron transfer for theoretical and experimental work.

Scan rate V.s ⁻¹	$(i_p)_{rev}/I_{lim}$	$(i_p)_{irr}/I_{lim}$	$(e_{pt})_{rev}/I_{lim}$	$(e_{pt})_{irr}/I_{lim}$	$(e_{pt})_{rev}/(i_p)_{rev}$	$(e_{pt})_{irr}/(i_p)_{irr}$	<i>n</i>
Theoretical work							
						(a)	(b)
0.05	0.625	0.491	0.488	0.292	0.782	0.491	1.005
0.10	0.885	0.695	0.973	0.582	1.107	0.695	1.007
0.20	1.252	0.984	1.947	1.165	1.567	0.984	1.008
0.50	1.965	1.554	4.853	2.917	2.740	1.554	0.994
1.0	2.781	2.199	9.683	5.820	3.877	2.199	1.008
2.0	2.800	2.200	19.393	11.657	4.654	2.640	0.987
5.0	6.17	4.912	47.800	29.179	8.680	4.912	0.996
10.0	8.729	6.950	95.359	58.211	11.060	6.950	0.985
Experimental work							
Pb ²⁺ ion							
0.1	1.245		1.947		1.564	2.005	2.0
0.2	1.764		3.889		2.204	2.001	2.0
0.5	2.783		9.712		3.488	2.000	2.0
1.0	3.938		19.375		12.633	1.995	2.0
Fe ³⁺ /Fe ²⁺ pair							
0.05		0.142		0.0242		0.9999	1.0
0.10		0.288		0.0971		0.9995	1.0

(a) Average values of *n* calculated via Eqs. 6 - 11 established in this work.(b) Values of *n* used in generating cyclic voltammograms.

Hence, Eqs. (6-11) can be used as a simple route for determination of *n*, α , n_p of the electroactive species without knowing the electrode surface area and without knowing the bulk concentration of the electroactive species. Fig. 4 indicates an example response of convoluted and deconvoluted current of fast ET system.

Table 4 includes the computed values of the ratios and *n* obtained from Eqs 6- 11. It was found that, the values of *n* calculated in this article agree well with that used in generating the cyclic voltammograms in case of theoretical work (Table 4). On the other hand, in case of electrode reaction of Pb(NO₃)₂ and Fe³⁺/Fe²⁺ systems in aqueous media, the value of *n* calculated from Eqs. 6 – 11 is equal to 1 ± 005 in case of the electrode reaction of Fe³⁺/ Fe²⁺ pair and 2 ± 0.005 in case of electro-reduction of Pb²⁺ ion which agree with the values of *n* reported in literature.^{2,10}

4. CONCLUSION

A simple and accurate method for evaluating the heterogeneous rate constant *k_s*, via cyclic voltammetric data and convolution deconvolution procedures for simple ET systems has been developed. From the above discussion it is clear that the most applications of theoretical data established in the present work are the tabulation and plotting of the dimensionless parameters, Ψ , vs. $E_p - E^0$, W^p , Δe_p for elucidation of the experimental phenomena as well as the estimation of the number of electrons involved in the electrode reaction.

REFERENCES

- 1.- RS. Nicholson, *Anal. Chem.* **37**, 1351, (1965).
- 2.- YI. Moharram, *Monat. Fur. Chem.* **128**, 1208, (1997).
- 3.- KB. Oldham, *J. Electroanal. Chem.* **145**, 9, (1983).
- 4.- A. Blagg, SW. Carr, GR. Cooper, ID. Dobson, JB. Gill, DC. Goodall, BL. Shaw, N. Taylor, T. Boddington, *J. Chem. Soc. Dalton Trans.* 1213, (1985).
- 5.- DD. Macdonald, *Transient Techniques in Electrochemistry*. Plenum Press, New York, 1977.
- 6.- KB. Oldham, J. Spanien, *The Fractional Calculus*, Academic Press, New York, 1974.
- 7.- ID. Dobson, N. Taylor, LRH. Tipping, *Electrochemistry Sensors and Analysis*. Elsevier. Amsterdam, 61, 1986.
- 8.- SW. Feldberg, *Digital simulation in electrochemistry in* AB. Bard, *Electroanalytical chemistry*, Vol. 3. Dekker, New York, 1969.
- 9.- D. Britz, *Digital simulation in electrochemistry*, Springer-Verlag, Berlin, 1981.

- 10.- IS. El-Hallag, *B. Electrochem.* **14**, 44, 1998.
- 11.- PD. Alford, M. Goto, KB. Oldham, *J. Electroanal. Chem.* **85**, 1, 1977.
- 12.- IS. El-Hallag, AM. Hassanien, MM. Ghoneim, *Monat. Fur. Chem.* **126**, 1075, 1995.
- 13.- IS. El-Hallag, *Annali di Chimica.* **84**, 443, 1994.
- 14.- M. Goto, D. Ishii, *J. Electroanal. Chem.* **61**, 361, 1975.
- 15.- PD. Alford, M. Goto, KB. Oldham, *Anal. Chem.* **49**, 1390, 1977.
- 16.- JJ. Toman, SD. Brown, *Anal. Chem.* **53**, 1497, 1981.
- 17.- RS. Nicholson, I. Shain, *Anal. Chem.* **36**, 706, 1964.
- 18.- AM. Asiri, SA. Khan, IS. El-Hallag, *J. New. Mater. Electrochem.* **14**, 251, 2011.
- 19.- HM. Al-Bishri, EH. El-Mossalamy, IS. El-Hallag, S. El-Daly, *J. Korean Chem. Soc.* **55**, 169, 2011.