Characterization and Determination of the Electrochemical Parameters of EC_{irr} Process Via Convolutive Voltammetry Combined with Digital Simulation Method

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Convolution - deconvolution voltammetry was applied to provide a simple and accurate method for characterization the nature of electrode reaction as well as determination of the homogeneous chemical rate constant k_c, *and the standard reduction potential* E^0 *of the* EC_{irr} *mechanism. The experimental data were combined with digital simulation to confirm the nature of electrode reaction and verification of the experimental electrochemical parameters.*

Keywords: electrochemical parameters, convolution-deconvolution, EC_{irr} *system, digital simulation*

Convolution-deconvolution voltammetry treatments were considered to overcome the limitation arising from the cyclic voltammetry measurements irrespective of the rate of electron transferr [1-7]. The convolution theorem finds use in the situation where it is required to perform the inverse transformation on a function which is the product of two functions of the Laplace variable each of which individually had known inverse transformations. In such a situation, the convolution theorem gives [8]

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

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

$$Ox + ne \rightleftharpoons R$$

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 [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]

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

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

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

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

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

and I_{lim} is the limiting value of I_1 at 'extreme' potentials 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 decomposition equation (3)

$$Ox + ne^- \underset{\alpha,\ D,\ E^o}{\overset{k^o}{\rightleftharpoons}} R \underset{k_{-1}}{\overset{k_1}{\longrightarrow}} P \qquad (3)$$

$$(k_1 >> k_{-1}),\ (k_c = k_1 + k_{-1})$$

where k^o, α, D, E^o, k_1, k_{-1} and k_c are defined as following [10]:
k^o is the standard heterogeneous rate constant
α - the transfer coefficient
D - the diffusion coefficient
E^o - reduction potential
k_1 - the forward homogeneous chemical rate constant
k_{-1} - the backward homogeneous chemical rate constant
k_c - the homogeneous chemical rate constant.

The species here are produced by electron transfer at a planar electrode and decomposed in the bulk via a first order chemical reaction of rate constant k_c. The Fick's Second Law expression is now [9, 10]

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

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

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

where the 'kinetic' convolution I_2 is given by [10]

$$I_2(t) = \pi^{-1/2}\int_0^t [\,i(u).\exp(-k_c(t-u))]/(t-u)^{1/2}du. \qquad (4)$$

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.

Several algorithms have been proposed for the evaluation of the convolution integral I(t). The following one was used in this work: [11-15]

$$I(t) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{j=k} \frac{\Gamma(k-j + 1/2)}{(k-j)!} . \Delta t^{1/2} i(j\,\Delta t) \quad (5)$$

in which k is the index of the discrete convoluted current being calculated ($I(k\Delta t)$), j is the series counter to the discrete current data points 0 .. .k., Δt is the time interval between successive data points, and Γ (f) is the gamma function of f.

The present work aimed to characterize the nature of the EC_{irr} scheme (electron transfer followed by fast chemical step) via $I_{1\,(end)}$ (convoluted current at the end of the backward sweeps), and the ratio of the height of the forward sweep to the backward one of deconvoluted current $(dI_1/dt)_f/(dI_1/dt)_b$ vs the square root of scan speed $(v)^{1/2}$ plots. The determination of E^0 and k_c via accurate and simple convolutive method was carried out and discussed. The selected experimental example for EC_{irr} is the electroreduction of N,N\-propylene-bis-(salicylideniminato)Mn(III) complex in phosphate buffer solution at mercury electrode. Digital simulation was combined with experimental work to verify our proposed method for calculating the electrochemical parameters as well as the identification of the nature of the electrode reaction.

Experimental part

Materials and apparatus

The investigated N,N\-Propylene-bis-(salicylideniminato)-Mn(III) complex was prepared according to the method described in the literature [6]. An alcoholic (40% v/v) of the complex in phosphate buffer as supporting electrolyte was tested. The reagents were generally of laboratory grade. Triply distilled mercury was employed. The complex was dissolved in alcoholic phosphate buffer solution (*p*H = 7.4) as supporting electrolyte which proceed at the mercury electrode as EC_{irr} process [16].

The exprimental data were obtained using an electrochemical cell connected to a potentiostate Model 264 PAR (from EG&G). The electrode assembly with a hanging mercury drop electrode (surface area 2.6×10^{-4} m^2) as a working electrode, a platinum wire as auxiliary electrode and a Ag/AgCl as a reference electrode was used. The auxiliary and reference electrodes were platinium and Ag/ACl respectively. The sweep rate in the range from 0.05 to 5 V s^{-1} were used. Working solutions were degassed thoroughly with oxygen free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the course of measurements.

Convolution-deconvolution voltammetry were performed by Condecon software based on the method established in literature [17, 18]. The digital simulation of the generated cyclic voltammograms was carried out on PC computer using EG & G Condesim package.

Results and discussion

Characterization of $EC_{irr\,system}$

Figure 1a represent the experimental cyclic voltammogram of N,N\-propylene-*bis*-(salicylideniminato) Mn(III) complex in phosphate buffer solution at mercury electrode, scan speed 5V/s and temperature 298 K, while figure 1b shows the simulated cyclic voltammogram of EC_{irr} system at scan speed 0.2 V/s, T = 298 K using the following electrochemical parameters: diffusion coefficient (D) = 5×10^{-9} m^2 s^{-1}, standard heterogeneous rate constant (k_s) = 2×10^{-5} m s^{-1}, standard reoduction potential (E^0) 0.5 V, transfer coefficient (α) = 0.5, homogeneous chemical rate constant (k_c) = 19 s^{-1}, surface electrode area (S) = 2.6×10^{-4} m^2.

The I_1 convolution of Mn(III) – complex in phosphate buffer solution at sweep rates of 0.5 V/s is shown in figure 2. The convoluted current indicates a distinct separation between the forward and reverse sweep and clearly indicates the sluggishness of electron transfer of the electrode process as well as the presence of a fast chemical reaction following the charge transfer. Also it was found that the magnitude of $I_{1\,(end)}$ decreases with increasing the sweep rate (i.e. decreasing the duration time of the experiment).

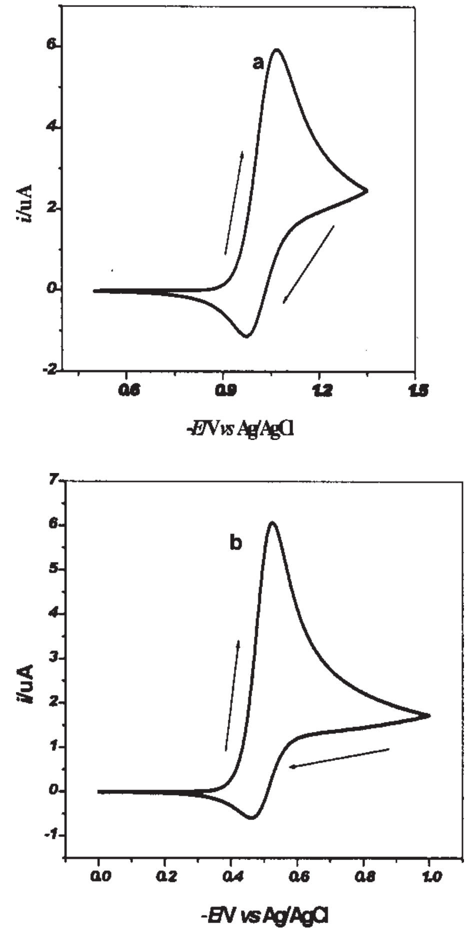

Fig. 1 experimental (a) and Simulated (b) cyclic voltammograms of ECirr system

The deconvolution of current can be expressed as the differential of the I_1 convolution. In more grneral terms deconvolution is akin to semi- differentiation in a similar manner to considering $t^{-1/2}$ convolution as semi-integration.

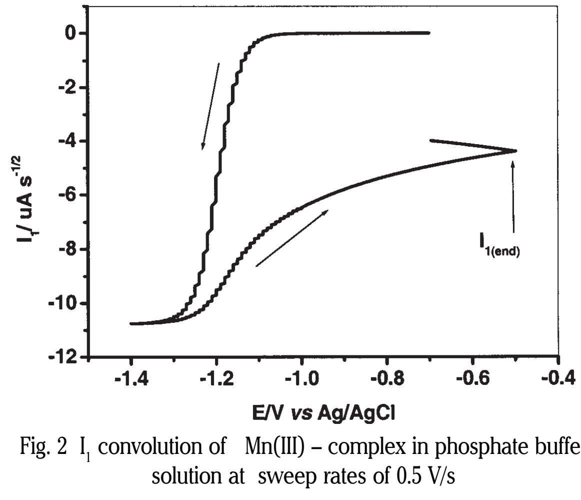

Fig. 2 I_1 convolution of Mn(III) – complex in phosphate buffer solution at sweep rates of 0.5 V/s

The relationship between $t^{-1/2}$ convolutions and deconvolutions is indicated in the following scheme [10].

$$\begin{tikzcd}
dI_1/dt \arrow[r, shift left, "\text{convolution}"] & i \arrow[l, shift left, "\text{deconvolution}"] \arrow[r, shift left, "\text{convolution}"] & I_1(t) \arrow[l, shift left, "\text{deconvolution}"]
\end{tikzcd}$$

The semiderivative (e) of current I is defined as [19]:

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

which consist of two mirror – 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 mV in case of rapid electron transfer and T = 298 K. Figure 3 indicates an example of deconvoluted current (dI_1 / dt) of Mn(III) – complex at sweep rate of 0.5 V s^{-1} which indicate the non symmetry of the forward and backward sweep confirming the existence of EC_{irr} nature of the electrode mechanism. It was found that with increasing the sweep rate, the homogeneous chemical rate constant decreases due to the decreasing of the time of the experiment, i.e. the $(dI_1/dt)_f$ /$(dI_1/dt)_b$ decrease with increasing the sweep rate.

The plots of the simulated convoluted current at the end of the return sweep, $I_{1(end)}$, and the ratio of the simulated forward to backward heights of deconvoluted current $(dI_1/dt)_f/(dI_1/dt)_b$ versus square root of scan speed $(v)^{1/2}$ are shown in figure 4 The curves in the plot exhibited that for generated EC_{irr} the values of $I_{1(end)}$ and $(dI_1/dt)_f/(dI_1/dt)_b$ decrease on increasing the square root of sweep rate. The plot of the experimental $I_{1(end)}$ and $(dI_1/dt)_f/(dI_1/dt)_b$ versus the square root of sweep rate $(v)^{1/2}$ are shown in figure 5 which compare well with the trend obtained in figure 4.

Estimation of the homogeneous chemical rate constant (k_c) and the reduction potential (E^0) of the EC_{irr} mechanism

Equation (3) of EC_{irr} reaction scheme was treated to give equation (6) [20, 22]:

$$\frac{i(D_{Ox})^{1/2}e^{-\xi}}{k^0} = I_{lima} - I_1 - I_2\left(\frac{D_{Ox}}{D_R}\right)^{1/2}e^{-\xi} \qquad (6)$$

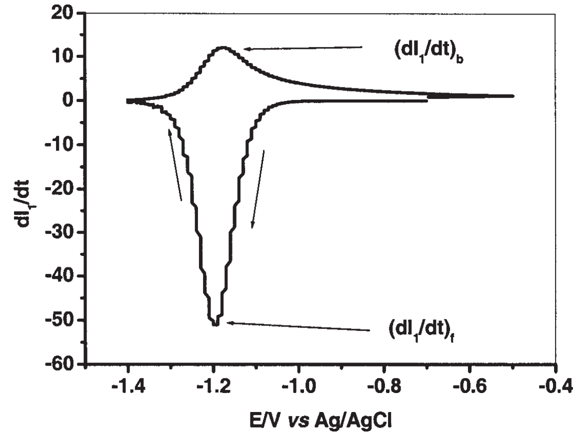

Fig. 3. Deconvolution voltammogram (dI_1/dt) of Mn(III) – complex in phosphate buffer solution at sweep rates of 0.5 Vs^{-1}

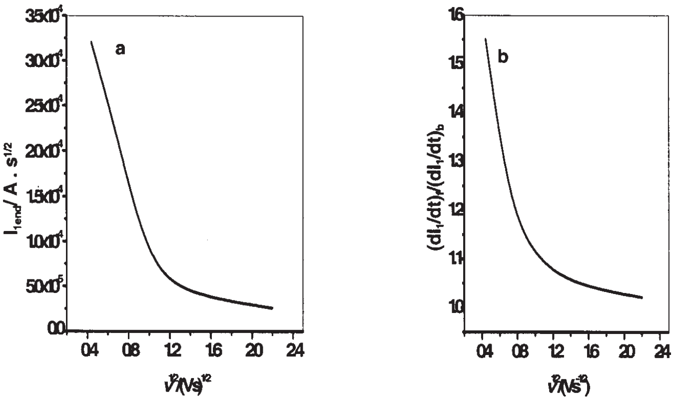

Fig. 4. Simulated I_1(end) (a) and $(dI_1/dt)_f/(dI_1/dt)_b$ (b) versus square root of sweep rate of EC_{irr} system

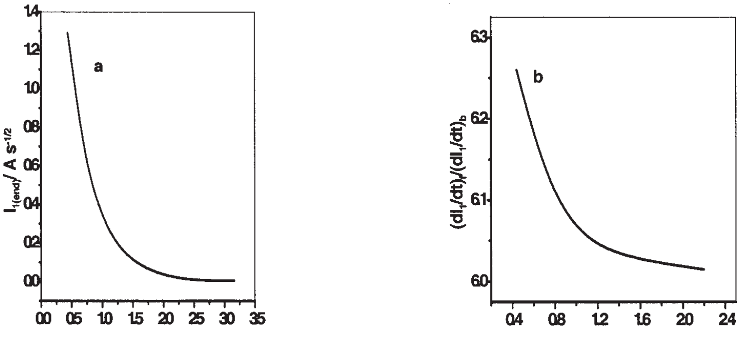

Fig. 5. Experimental I_1(end) (a) and $(dI_1/dt)_f/(dI_1/dt)_b$ (b) of EC_{irr} system versus square root of sweep rate

Table 1
EXPERIMENTAL DATA OF I_1 CONVOLUTION, KINETIC CONVOLUTION (I_2) AND I_{lim} - I_1 AT VARIOUS VALUES OF POTENTIAL FOR EC_{irr} SYSTEM (Mn-COMPLEX), at k_c = 19 s^{-1} AND υ = 5 Vs^{-1}

-E/V	I_1/A $s^{-1/2}$	I_2/A $s^{-1/2}$	(I_{lim}-I_1)/A $s^{-1/2}$
0.928	9.607E-8	5.137E-6	2.241E-7
0.979	8.326E-7	4.531E-6	9.607E-7
0.984	9.927E-7	4.426E-6	1.088E-6
1.005	1.665E-6	3.899-6	1.729E-6
1.020	2.657E-6	**2.921E-6**	**2.921E-6**
1.040	3.394E-6	2.188E-6	3.810E-6
1.066	4.570E-6	1.554E-6	4.579E-6
1.080	5.440E-6	9.748E-7	5.280E-6
1.107	5.860E-6	4.470E-7	5.924E-6

where I_{lima} , and ζ are defined as following [7, 19]:
I_{lima} is the limiting convoluted current
$\xi = (E - E^0)nF/RT$

So, on the region i = 0 equation (6) yields
$I_{lim} = I_1 + I_2(D_A/D_B)^{1/2}\exp\text{-}\xi$

assuming $(D_A) = (D_B)$ then
$I_{lim} = I_1 + I_2 \exp\text{-}((E - E^0)(nF/RT))$
$$I_{lim} - I_1 = I_2 \exp\text{-}((E - E^0)(nF/RT)) \qquad (7)$$

So, from equation (7) we can calculate the true value of k_c and E^0 simultaneously. Example of the computed numerical values of I_1, I_2 convolution and I_{lim} -I_1 at various potentials of Mn – complex (EC_{irr} system) under consideration are listed in table 1, indicating the equality of I_{lim} - I_1 and I_2 at E^0 (-1.02 V) when the value of k_c true is (19 s^{-1}). Figure 6a shows the plot of I_{lim} – I_1 and I_2 *vs* E of N,N\-Propylene-bis-(salicylideniminato)-Mn(III) complex which proceed as EC_{irr} mechanism indicates that the curves intersect at standard reduction potential (E^0)when k_c is true. Figure 6b gives example response of I_{lim} - I_1 and I_2 *vs* E of theoretical EC_{irr}.

Conclusions

In present article we succeeded in applying convolution – deconvolution voltammetry combined with digital simulation method for the characterization and the determination of the relevant chemical and electrochemical parameters of EC_{irr} scheme. The application of this methods provides the opportunity for obtaining accurate kinetic parameters very precisely irrespective to the rate of charge transfer. The test of the validity of our method is carried out by applying it to the electroreduction of N,N\-Propylene-bis-(salicylideniminato)-Mn(III) complex in phosphate buffer solution at the hanging mercury drop electrode, and is found to give good result confirming the accuracy of the proposed method.

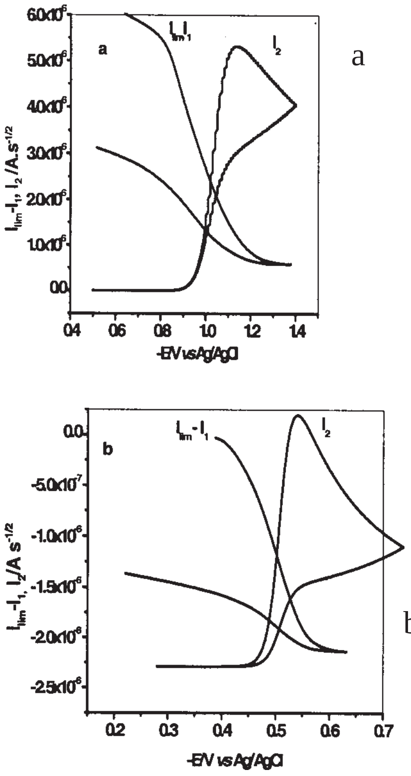

Fig. 6 Experimental I_{lim}-I_1 and I_2 versus the applied potential of the investigated system (a), simulated (b)

References

1. A. J. BARD, L. R. FAULKNER, Electrochemical Methods. Wiley, New York. 1980
2. R. S. NICHOLSON, I. SHAIN, Anal. Chem. , 1964. **36,** p. 706
3. R. M. CROOKS, A. J. BARD, J. Electroanal Chem., 1988. **243**, p. 117
4. J. M. SAVEANT AND D. TESSIER, J. Electroanal Chem Interfacial Electrochem., 1975, p. 65, 57 -66
5. K. B. OLDHAM, J. Electroanal Chem., 1983, **145**, p. 9
6. I. S. EL-HALLAG AND M. M GHONEIM, (1996). Monatsh fur Chemie., 1996, **127**, p. 487
7. P. DALRYMPLE-ALFORD, M. GOTO , K. B. OLDHAM, J. electroanal. Chem., 1977, **49**, p. 1390
8. A. BLAGG, A., S. W. CARR, G. R. COOPER, I. D. DOBSON, J. B. GILL, , D. C. GOODAL, B. L. SHAW, N. TAYLOR., T. BODDINGTON, J. Chem Soc Dalton Trans., 1985, p. 1213
9. G. DOETSCH, Laplace Transformation, Dover, New York 1953
10. I. S. EL-HALLAG,; Electrochemical studies of some metallo borane and carbonyl phosphine complexes in non-aqueous medium, ph. D Thesis, Tanta University, Egypt , 1991
11. F. E. WOODARD, R. D. GOODIN, P. J KINLEN , Anal. Chem., . 1984, **56** , p. 1920
12. H. W. VANDENBORN, D. H. EVANS, Anal. Chem., 1974, **46**, p. 643
13. L. NADJO, J. M. SAVEANT, J. Electroanal. Chem., 1973, **48**, p. 113
14. J. LEDDY, A. J. BARD, J. Electroanal. Chem., 1985, **189**, p. 203
15. K. B. OLDHAM, J. Electroanal. Chem., 1983, **9**, p. 145
16. F. AMMAR, J. M. SAVEANT, J. Electroanal. Chem., 1973, **47**, p. 215
17. K. B. OLDHAM, R. A. OSTERYOUNG, J. Electroanal Chem., 1966, **11**, p. 397
18. K. B. OLDHAM, J. SPANIER, The Fractional Calculus.Academic Press, 1974
19. I.S. EL-HALLAG, M. M. GHONEIM AND E. HAMMAM, Anal. Chim. Acta., 2000, **414**, p. 173
20. I. S. EL-HALLAG., A. M. HASSANIEN, (1999). Collect. Czech. Chem. Commun., 1999, **64**, p. 1953
21. Y. I. MOHARRAM, J. Electroanal. Chem., 2006, **587**, p. 115
22. S. A. EL-DALY, I. S. EL-HALLAG, E. M. EBEID, M.M. GHONEIM, Chin J Chem, 2009, **27**, p. 241

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