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Data analysis and determination of the electrochemical parameters of EC_{rev} mechanism via new convolutive voltammetry and digital simulation methods

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ABSTRACT

A simple and accurate method for data analysis and evaluating the relevant chemical and electrochemical parameters (homogeneous chemical rate constant k_c, the equilibrium constant K, the diffusion coefficient D,and the standard reduction potential E^0) of the EC_{rev} mechanism were done using new convolutive voltammetry and digital simulation methods. The experimental data were combined with digital simulation to ascertain the nature of electrode reaction as well as the verification of the electrochemical parameters estimated experimentally.

KEYWORDS

Electrochemical parameters;
Convolution-deconvolution;
Cyclic voltammograms;
EC_{re} mechanism;
Digital simulation.

INTRODUCTION

It is well known that values of the homogeneous chemical rate constant, k_c, and the equilibrium constant (K) of the chemical step coupled with charge transfer are usually determined from the ratio of i_{pb}/i_{pf} of a cyclic voltammogram[1]. The obtained values by this method have some errors arising from the inaccurate measurement of the ratio i_{pb}/i_{pf} in cyclic voltammetry experiments. Convolution-deconvolution voltammetric treatments[2-8] was used to overcome the limitation arising from the cyclic voltammetric measurements.

The present work aimed to analyse and characterize the nature of the electrode reaction (EC_{rev}) via I_1 convolution at the end of the backward sweeps, $I_{1(end)}$, and the ratio of the height of the forward sweep to the backward one of deconvoluted current versus the square root of scan speed. $(dI_1/dt)_f/(dI_1/dt)_b$ vs $(v)^{1/2}$ plots. The determination of E^0, k_c, K and D via new and simple convolutive method was carried out. The selected experimental example of EC_{rev} mechanism is the electrooxidation of pcym-ruthenium carborane complex [pcym-closo-1,2,4-$RuC_2B_8H_{10}$] in TBAP/CH_2Cl_2 at glassy carbon electrode. Digital simulation was combined with experimental work to verify our proposed method for calculating the electrochemical parameters as well as identification the nature of electrode reaction.

EXPERIMENTAL

The experimental data were obtained using an electrochemical cell connected to a potentiostate Model 273 PAR (from EG and G). [pcym-closo-1,2,4-$RuC_2B_8H_{10}$] in 0.1M TBAP/CH_2Cl_2 solution as supporting electrolyte at glassy carbon electrode was selected as an example of EC_{rev} scheme. Ruthenium carborane complex were prepared by and provided from Dr. J.Kennedy[9], Leeds University.

Convolution-deconvolution voltammetry were performed according to the method established in literature[10-13]. The digital simulation of the generated cyclic voltammograms was carried out on PC computer using EG and G Condesim package.

RESULTS AND DISCUSSION

Figure 1a shows the simulated cyclic voltammogram of EC_{rev} system at sweep rate of 0.2 V/s, T = 298 K, while figure 1b represent the experimental cyclic voltammogram of [pcym-closo-1,2,4- $RuC_2B_8H_{10}$] complex in 0.1M TBAP/CH_2Cl_2 solution as supporting electrolyte at glassy carbon electrode, scan speed of 0.5V/s and temperature 298K.

It was noted that, the reverse sweep of the I_1 convolution at all sweep rates does not return to the starting point. Figure 2 indicate the plots of I1(end) and (dI1/dt)f/(dI1/dt)b vs $(v)^{1/2}$ of the theoretical and experimental ECrev mechanism. Figure 3a gives an example response of I_1 convolution of [pcym-closo-1,2,4- $RuC_2B_8H_{10}$] complex at sweep rate of o.5 V/s. At extreme potential the I_1 convolution reaches the limiting value[7] $I_{lima} = nFS(D_A)^{1/2}C^b_A$. As shown the plot of $I_{1(end)}$ and $(dI_1/dt)_f/(dI_1/dt)_b$ vs $(v)^{1/2}$ was found to increase then decrease with increasing the square root of sweep rate. This behaviour can be used as a simple procedure for the diagnosis and analyse the type of the electrode process.

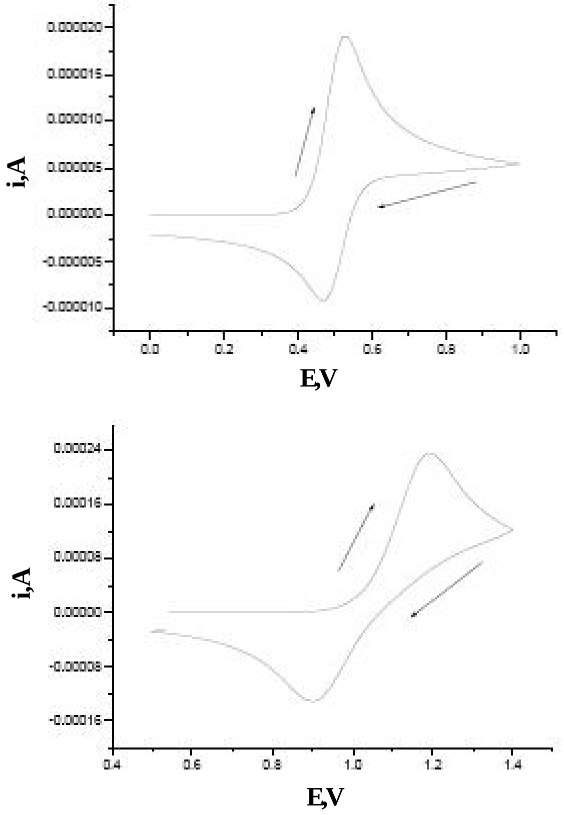

Figure 1 : (a) Simulated cyclic voltammogram of EC rev system at scan speed 0.2 V/s, n = 1.0, redox potential (E^0). 0.5V, diffusion coefficient (D) 5 × $10^{-10}m^2/s$, standard heterogeneous rate constant (ks) 1 × 10^{-2} m/s, transfer coefficient (α) 0.5, bulk concentration (C^0)1 mol/m^3, homogeneous chemical rate constant (kc) 4 per s. (b) Experimental cyclic voltammogram of of pcym-closo-1,2,4- $RuC_2B_8H_{10}$ in 0.1M TBAP/CH_2Cl_2 at glassy carbon electrode (GCE), scan speed 0.5V/s, n = 1.0, redox potential 1.04 V diffusion coefficient (D) 4.25 × 10^{-9} m2/s, standard heterogeneous rate constant (ks) 2.5 × 10^{-5} m/s, transfer coefficient (α) 0.45, bulk concentration (Co) 5 mol/ m3, homogeneous chemical rate constant (kc) 0.09 per s.

Estimation of k_c, K, and E^0

For a reversible chemical reaction following the charge transfer (EC_{rev}) the following equation is hold:

$$\text{A-ne} \underset{D}{\overset{k^0,E^0,a}{\rightleftharpoons}} B \underset{\substack{k_{-1}(k_1\sim k_1)\\(k_c=k_1+k_{-1})}}{\overset{k_1}{\rightleftharpoons}} C \qquad (1)$$

The concentration of the species A (C^s_A) & B (C^s_B), at electrode surface can be detrmined and defined as:

$$C^s_A = C^b_A - (I_1/nFS(D_A)^{1/2}) \qquad (2)$$

$$CsB = \left(\frac{I_1}{(1+K)} + \frac{I_{2.}K}{1+K} + \frac{I}{nFS(D_B)^{1/2}}\right) \qquad (3)$$

where D_A and D_B is the diffusion coefficient of the species A and B respectively, K is the equilibrium constant = k_1/k_{-1}, and the other terms have their usual meaning. By substituting the values of C^s_A, C^s_B, forward (k_f) and backward (k_b) heterogeneous rate constants of the electron transfer process in the Butler-Volmer relationships one obtains the following expression:

$$\frac{i(D_A)^{1/2}}{k^0}\exp-\alpha\xi = I_{lim} - I_1\left(\frac{I_1}{1+K} + \frac{I_{2.}K}{1+K}\right)e^{-\xi} \qquad (4)$$

The true value of homogeneous chemical rate constant (k_c), equilibrium constant (K) and the standard reduction potential (E^0) were determined via I_1 and I_2 convolution using suitable time-scale for the cyclic voltammetry experiments. So, on the return of the wave

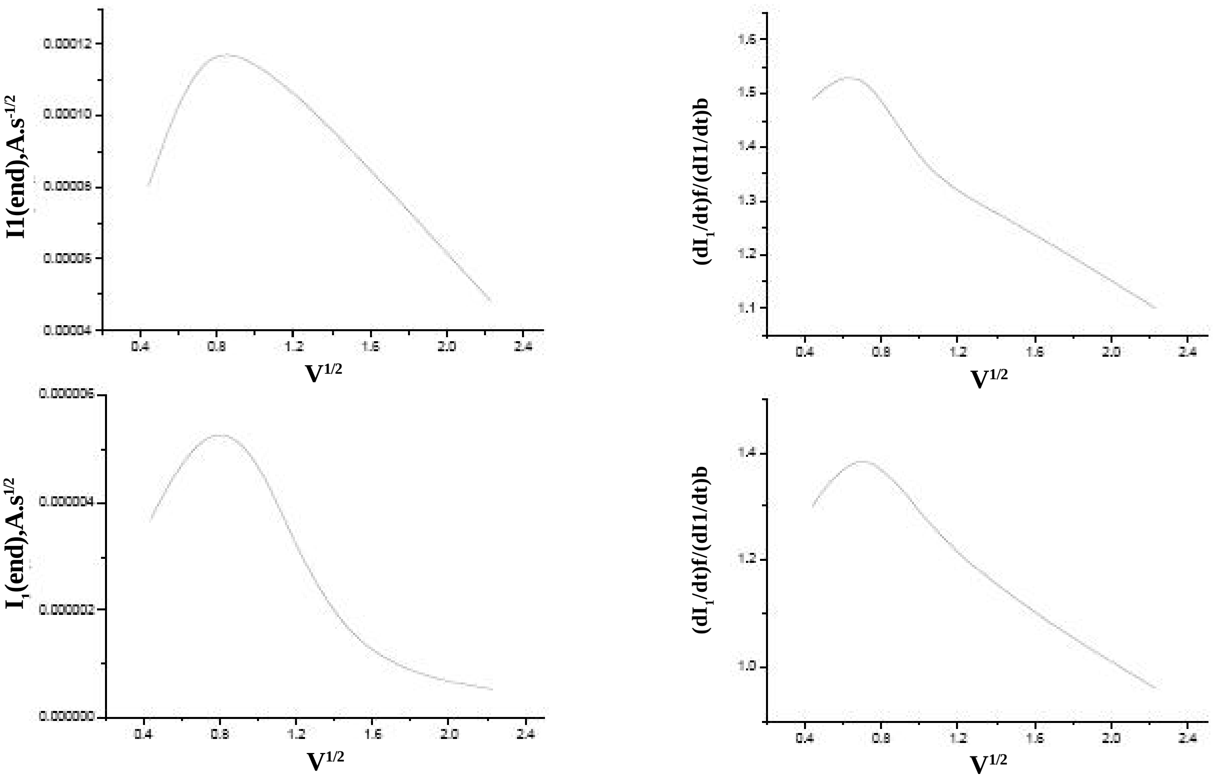

Figure 2 : I_1end and $(dI_1/dt)_f/(dI_1/dt)_b$ versus square root of scan speed of the simulated (a and b) and of the experimental (c and d) data of ECrev

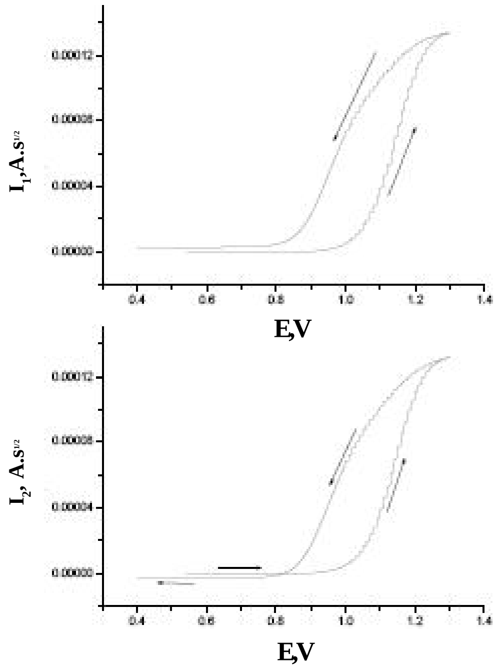

Figure 3 : (a) I_1 convolution of ECrev, (b) I_2 convolution of ECrev at true kc value

to the initial potential $\xi \rightarrow$ infinity, $I_{lim} = I_1$, and the left hand side becomes very small and can be neglected, and hence, eq(4) gives the following form:

$$\frac{I_1}{1+K} + \frac{I_{2.}K}{1+K} = 0 \qquad (5)$$

This means that $I_1 = -I_2$ K, and at this extreme, K can be calculated for the various test values of k_c from the ratio $|I_{1(end)}/I_{2(end)}|$. The I_2 convolution of Ru-Carborane complex at sweep rate of 0.5 V/s are shown in figure 3b which indicate the equality of I_1 and I_2 convolution at the end of sweep Values of k_c and K estimated from this method are found to be 0.09 s^{-1} and 1.0 respectively. Values of I_1 convolution at the end of the backward sweep $I_{1(end)}$ and I_2 convolution at the end of the backward sweep $I_{2(end)}$ at various values of k_c were reported in TABLE 1. It was found that for Ru-carborane complex $I_{1(end)} = -I_{2(end)}$ at true k_c value (0.04 s^{-1}).

Also, at potential corresponding to the formal reduction potential, i.e at $E = E^0$, the left hand side of eq. 4 is very small and can be neglected, and eq. 4 can be written as following:

$$I_{lim} - I_1 - \frac{I_1}{1+K} + \frac{I_2K}{1+K} e^{-\xi} = 0.0 \qquad (6)$$

$$I_{lim} - I_1 - \left(\frac{I_1}{1+K} + \frac{I_2K}{1+K}\right) e - nF/RT(E - E_0) = 0.0 \qquad (7)$$

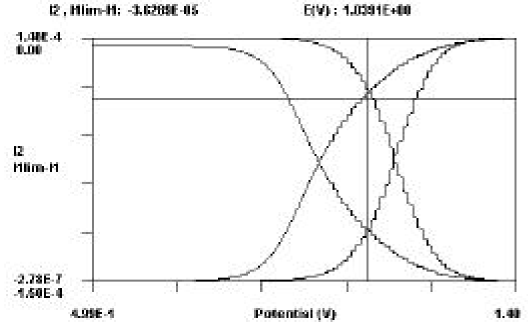

Figure 4 : Ilim - I_1 and I_2 versus the applied potential of experimental work of ECrev system

TABLE 1 : Values of k_1, k_{-1}, k_c, $I_{1(end)}$, and $I_{2(end)}$ for Ru-carborane complex at sweep rate 0.1 V/s

k_1 (s^{-1})	k_{-1} (s^{-1})	k_c (s^{-1})	$I_{1(end)}$ ($As^{1/2}$)	$I_{2(end)}$ ($As^{1/2}$)
1.000	1.000	2.000	1.242×10^{-4}	8.05×10^{-6}
0.250	0.250	0.500		1.02×10^{-5}
0.100	0.100	0.200		2.197×10^{-5}
0.050	0.050	0.100		1.419×10^{-5}
0.010	0.010	0.020		7.440×10^{-5}
0.005	0.005	0.010		9.430×10^{-5}
0.002	0.002	0.004		1.241×10^{-4}

So, at true value of k_c eq. (7) becomes

$$\mathbf{I_{lim} - I_1 - \left(\frac{I_1}{2} + \frac{I_2}{2}\right) = 0.0} \qquad \mathbf{(8)}$$

since at true k_c, $I_1 = -I_2$, eq. (8) gives

$$\mathbf{I_{lim} - I_1 - I_2 = 0.0} \qquad \mathbf{(9)}$$

$$\mathbf{i.e\ I_{lim} - I_1 = I_2} \qquad \mathbf{(10)}$$

This means that at true value of k_c and K, the plot of I_{lim} - I_1 with I_2 vs the applied potential will intersect exactly at true E^0 value. Figure 4 gives an example of the combination between I_{lim} - I_1 and I_2 vs E of Ru carborane complex that intersect at E^0 (- 1.04 V) value. This plot indicates that the accuracy and the validity of this method for evaluation of the k_c, K and E^0 for EC$_{rev}$ system via simple convolutive voltammetry from one experiment.

CONCLUSION

A simple and accurate method for estimating the chemical and electrochemical parameters and analyse the electrode mechanistic of the EC$_{rev}$ reaction via convolutive voltammetry is proposed and discussed. The kinetic convolution (I_2) appear to be an excellent tool for determining the homogeneous chemical rate constant (k_c), equilibrium constant (K) and the standard reduction potential (E^0) of the EC$_{rev}$ scheme from combination between I_2 and I_{lim} - I_1 vs. the applied potential (E). Identification of the nature of chemical step which following the charge transfer via simple method was illustrated and discussed. The application of convolution-deconvolution procedure in treating the data gives a better accuracy in the mechanism determination. The obtained data of the theoretical work were found to compare very well with those obtained in the experimental one.

REFERENCES

[1] R.S.Nicholson, I.Shain; Anal.Chem., **36**, 706 **(1964)**.

[2] J.M.Saveant, D.Tessier; J.Electroanal Chem. Interfacial Electrochem., **65**, 57 **(1975)**.

[3] Oldham K.B., J. Electroanal Chem., **145**, 9 **(1983)**.

[4] R.M.Crooks, A.J.Bard; Jelectroanal Chem., **243**, 117 **(1988)**.

[5] A.J.Bard, L.R.Faulkner; Electrochemical Methods, Wiley, New York, **(1980)**.

[6] K.B.Oldham; J.Electroanal Chem., **145**, 9 **(1985)**.

[7] A.Blagg, 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, 1213 **(1985)**.

[8] I.S.El-Hallag, M.M.Ghoneim; Monats fur Chemie, **127**, 1075 **(1996)**.

[9] J.Kennedy; University of Leeds, Private Communication.

[10] K.B.Oldham, J.Spanier; 'The Fractional Calculus', Academic Press, Inc., **(1974)**.

[11] M.Goto, K.B.Oldham; Anal.Chem., **49**, 1390 **(1977)**.

[12] G.Si Xuan, W.A.M.Andrew, S.Christine, M.B.Alan, G.W.Anthony; J.Electroanal.Chem., **591**, 7 **(2006)**.

[13] A.J.Bard, L.R.Faulkner; Electrochemical Methods: Fundamentals and Applications, 2nd ed., Wiley, New York, **(2001)**.