



New methods for the determination of the redox potential of $E_q C_{irr}$ system via cyclic voltammetry, convolutive voltammetry and digital simulation techniques

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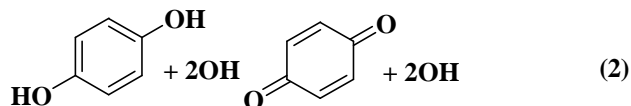
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INTRODUCTION

In general, The redox potential (E^0) of the electroactive species is determined from cyclic voltammetry by taking the average values of the forward and backward peak potentials i.e $(E_p^f + E_p^b)/2$. But in the case of EC mechanism when chemical step is fast the backward peak disappear and in this situation the redox potential (E^0) of the couple can not determine from the average peak potentials. So, in this case, we will use the potential where the current is the half of the peak current ($E_{p/2}$) to evaluate the value of $E_p - E_{p/2}$ for the determination of the value of E^0 . Also, convolutive voltammetry can be used for the extraction of E^0 via new method in the case of $E_q C_{irr}$ from the backward scan. It was found that the redox potential gives information on the ability of a redox couple to be oxidized or reduced^[1]. Although the redox potential is generally recognized to be an important hurdle for extending the shelf-life of foods, it is mainly used in microbiological area, for instance, to follow the evolution of fermentation processes or to estimate whether aerobic or anaerobic micro-organisms will grow in a given food-stuff^[2,3]. As is well known, any compound able to promote an electron transfer to a radical, can be considered an antioxidant. In general terms, the antioxidant activity may be displayed through the transfer of electron from a reducing substance to the oxidizing radical species (Reaction 1 and 2).



In other words, redox potential measurements are suitable to evaluate the ability of reducing compounds to promote electron transfer. Also, a redox potential value gives information about the real oxidation/reduction ability of a molecule and its prevalent form (oxidized or reduced) in the system. Thus, the measurement of the redox potential is an interesting way of estimating the antioxidant capacity of the product. On the basis of these discussion, the redox potential may be an interesting indicator of the antioxidant efficiency of food products and may allow a better estimate of the antioxidant efficiency of food products and the influence of possible oxidative damage by processing^[4].

This work illustrate the method of extraction of the redox potential (E^0) of $E_q C_{irr}$ mechanism via peak potential (E_p) and half-peak potential ($E_{p/2}$) of the forward scan. In the convolutive voltammetry we used the backward sweep for determination of the redox potential. These methods were demonstrated, discussed and verified using digital simulation.

EXPERIMENTAL

The selected compound for this communication is

N,N'-propylene-bis-(salicylideneiminato)Mn(III) complex [Mn(III)LH₂O]ClO₄.2H₂O) which proceed electrochemically as E_qC_{irr} SCHEME^[5]. The complex was chosen to test the validity of our derived methods. The complex was prepared according to the method described in the literature^[6,7]. An alcoholic solution (40% v/v) of the complex in phosphate buffer as supporting electrolyte was investigated. The reagents were generally of laboratory grade. Triply distilled mercury was employed. Cyclic and convolutive voltammetry experiments were carried out at sweep rates ranging from 0.05-5V/s at 23 + 2^oC using a Princeton Applied Research (PAR) potentiostat Model 264A (from EG and G). The electrode used were a hanging mercury drop electrode (HMDE) with an area of 2.61×10⁻² cm² as working electrode and Ag/AgCl and Pt-wire as reference and counter electrodes, respectively. Simulation of the data was performed using the EG and G condosim package. Air was removed from the cell solution by passing nitrogen through the solution for twenty minutes; the measurements were performed in an N₂ atmosphere.

RESULTS AND DISCUSSION

In the present communication the redox potential (E⁰) of E_qC_{irr} scheme was extracted from cyclic voltammetry by measurements of peak potential (E_p) and half peak potential (E_{p/2}) of the forward sweep of cyclic voltammogram. This procedure is very simple and a new route for the E_qC_{irr} where E_q refer to the quasireversible electron transfer and C_{irr} refer to the fast chemical step. The derivation is indicated as following:

If we suppose the magnitude of half-peak width is (E_p - E_{p/2}) = A, mV, (1)

The difference between peak potential and redox potential (E⁰) is

(E_p - E⁰) = B, mV (2)

and

(A/B) = C, (3)

then

(A/B) = (E_p - E_{p/2}) / (E_p - E⁰) = C (4)

This led to

(E_p - E_{p/2}) / C = (E_p - E⁰) (5)

TABLE 1: Values of peak potential E_p, and half peak width (E_p - E_{p/2}) of the Mn(III)-complex and simulated cyclic voltammogram at various sweep rates at pH 7.4

| Sweep rate | -E _p | | E _p -E _{p/2} , mV | | a b c-E ⁰ , V | | |
|------------|-----------------|-------|---------------------------------------|------|--------------------------|-------|-------|
| | exp | sim | exp | sim | | | |
| 0.1 | 1.06 | 1.058 | 63 | 63.1 | 1.03 | 1.021 | 1.025 |
| 0.2 | 1.08 | 1.081 | 65 | 65.2 | --- | 1.022 | --- |
| 0.5 | 1.10 | 1.102 | 69 | 69.1 | --- | 1.020 | --- |
| 1.0 | 1.12 | 1.121 | 74 | 74.1 | --- | 1.019 | --- |
| 2.0 | 1.14 | 1.142 | 78 | 78.2 | --- | 1.024 | --- |

^aValues of E⁰ determined from the intercept of the experimental data, ^bValues of E⁰ determined from cyclic voltammogram and II convolution of the experimental data, ^cValues of E⁰ determined from the intercept of the simulated values of E_p vs (E_p - E_{p/2}).

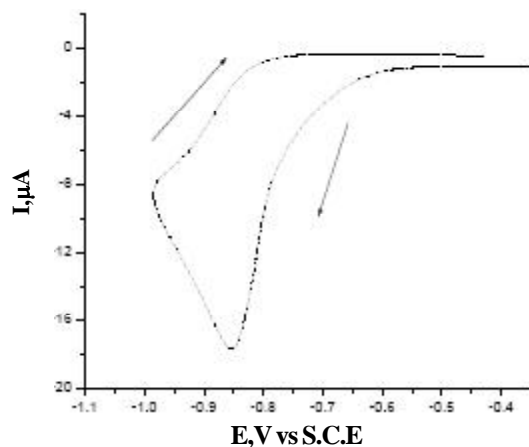


Figure 1: Cyclic voltammogram of Mn(III)-complex in phosphate buffer solution at 0.2V/s and pH 7.4

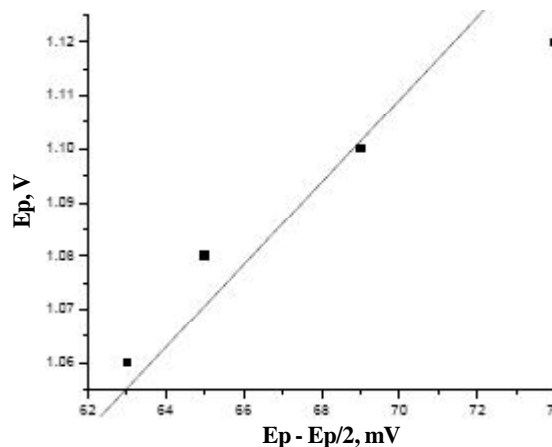


Figure 2: E_p vs (E_p - E_{p/2}) plot of Mn(III)-complex

or

(E_p - E_{p/2}) / C + E⁰ = E_p (6)

i.e E_p = E⁰ + (E_p - E_{p/2}) / C (7)

So, from the intercept of the E_p vs (E_p - E_{p/2}) plot, the redox potential (E⁰) of the electrochemical system will be determine.

Full Paper

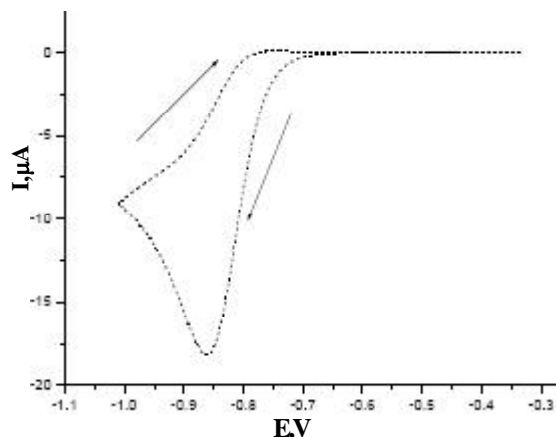


Figure 3: Simulated cyclic voltammogram of Mn(III)-complex at 0.2 V/s

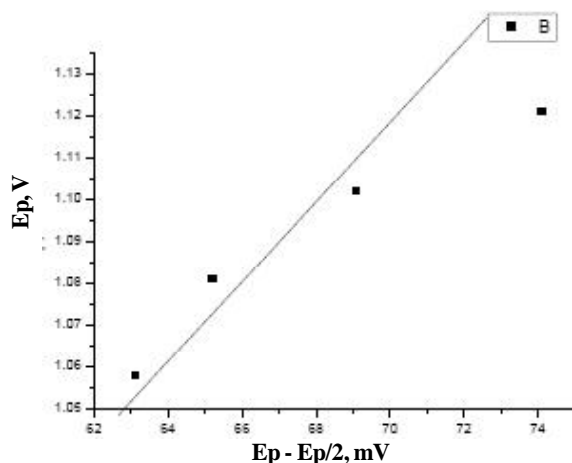


Figure 4: E_p vs $(E_p - E_{p/2})$ plot of simulated cyclic voltammogram of Mn(III)-complex

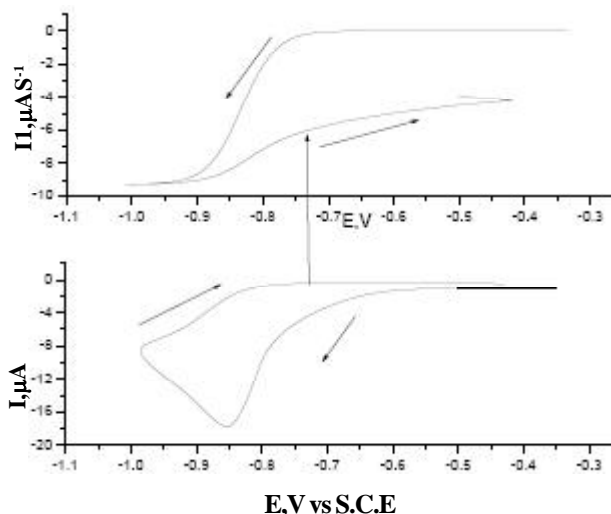


Figure 5: Cyclic voltammogram of Mn(III)-complex with II convolution

The experimental cyclic voltammogram of the selected complex in phosphated buffer solution at HMDE, pH 7.4 and sweep rate 0.2 V/s is shown in figure 1. The values of E_p and $E_p - E_{p/2}$ at various sweep rates are listed in TABLE 1. Figure 2 shows an example of the E_p vs $E_p - E_{p/2}$ plot for $E_q C_{irr}$ system. The obtained value of E^0 determined from the intercept of the previous plot is cited in TABLE 1.

The validation of our method was confirmed by generating a theoretical cyclic voltammogram of the selected complex at sweep rate 0.2 V/s using the extracted redox potential (E^0). Figures 3 and 4 give an example of the simulated cyclic voltammogram and E_p vs $E_p - E_{p/2}$ plot of theoretical data respectively. TABLE 1 shows that the value of redox potential used in generating the simulated voltammogram agree well with that extracted from the intercept of plot in figure 2.

Convulsive voltammetry combined with cyclic voltammetry was used as a simple new method for the extraction of E^0 of $E_q C_{irr}$ system.

For the electrode reaction :



which proceed as moderate fast (quasireversible) electron transfer, the current response can be described via Butler-Volmer equation as following^[8]:

$$i = nFsk_f^0 \{ [A]_{(0,t)} \exp \alpha_A nF\eta/RT - [B]_{(0,t)} \exp i - \alpha_C nF\eta/RT \} \quad (9)$$

Where k_f^0 is the standard forward heterogeneous rate constant, η is the overpotential and the other terms have their usual definition.

Substitution for $[A]_{(0,t)}$ and $[B]_{(0,t)}$ by their respective $\sqrt{\pi t}$ convoluted current allows us to express the potential dependent rate constant for the forward reaction as:

$$\ln k_f(E) = \ln \sqrt{D_A} - \ln \{ I_{lim} - I_1 (1 + \exp(\alpha nF/RT) \eta) / i \} \quad (10)$$

$$\text{where } [A]_{(0,t)} = [A]_{initial} - I_1 / nFS \sqrt{D} \quad (11)$$

$$[B]_{(0,t)} = I_1 / nFS \sqrt{D} \quad (12)$$

I_{lim} is the limiting convoluted current and is defined as^[9-13]

$$I_{lim} = nFAC\sqrt{D} \quad (13)$$

I_1 is the convoluted current and defined as^[10,11]:

$$I_1 = 1/\sqrt{\pi} \int_0^t i(u)/\sqrt{(t-u)} du \quad (14)$$

where t is the total elapsed time. At zero current point of the reverse sweep of the voltammogram, at a potential $E_{(i=0)}$ the convoluted current is given by $I_{i=0}$. At this zero current point the convolution relationship reduce to the following form:

$$I_{lim} - I_1 \left\{ 1 + \exp \frac{\alpha n F \eta}{RT} \right\} = 0 \quad (15)$$

Where $\eta = E - E^0$, this led to

$$E^0 = E_{i=0} + \frac{RT}{\alpha n F} \ln \frac{I_{lim} - I_1}{I_1} \quad (16)$$

Figure 5 shows the cyclic voltammogram of the investigated complex with its convoluted current which illustrate the extraction of E^0 at $E_{i=0}$, $I_{i=0}$ of the reverse sweep of cyclic and convolutive voltammograms using Eq. 16. Value of E^0 extracted from convolutive voltammetry are listed in TABLE 1 which compare well with the value extracted from cyclic voltammetry method and generated cyclic voltammograms.

In this work, as indicated we successes in the determination of the redox potential (E^0) of the $E_q C_{irr}$ system when the backward peak is absent due to the large value of homogeneous chemical rate constant (k_c) via cyclic voltammetry and convolutive voltammetry. The extracted E^0 was verified and confirmed via simulation technique.

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