Original Article

Theoretical analysis of temperature dependences in linear and cyclic voltammetry

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Abstract : Theoretical analysis of the temperature responses in linear and cyclic voltammetry was performed in this communication for reversible and totally irreversible electrochemical reactions. The proposed procedure of processing the experimental dependences of peak current and potential on the electrolyte temperature seems to be less tedious that the conventional method.   **© Global Scientific Inc.**

Keywords : Temperature dependences; Linear and cyclic voltammetry; Activation parameters.

INTRODUCTION

Linear and cyclic voltammetry is widely used both for analytical application and for investigating the mechanisms and kinetics of various electrochemical systems[1-4]. In order to study the electrochemical behavior of a redox couple, different parameters determined the view of voltammetric response may be changed (e.g. sweep rate, bulk concentrations, hydrodynamic conditions, geometry and size of the utilized electrode, etc.). Meanwhile, analyzing temperature responses is comparatively rarely performed in voltammetric measurements, although such experiments allow getting valuable information on the kinetics and mechanism of electrode reactions. A limited quantity of works devoted to temperature-kinetic investigations in voltammetry theory and applications, seems to be accounted for by a lack of proper formalism. Thus, this work is aimed to the development of methods for processing the temperature responses of linear voltammograms for reversible and irreversible electrochemical reactions.

THEORY AND DISCUSSION

Reversible electrochemical reactions

Let us consider a simple reversible electrochemical reaction:

$$Ox + ne^- \Leftrightarrow Red \tag{1}$$

Electrochemical reversibility presupposes that Nernstian concentrations will exist at the electrode surface because the forward and reverse electron transfers are fast and occur simultaneously, near to equilibrium. The following criterion has been suggested by Matsuda and Ayabe[5] for the confirmation of electro-

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chemical reversibility:

$$k_s^0 > 0,3(nv)^{1/2} \tag{2}$$

where k_s^0 is the standard rate constant (cm s^{-1}), v is the potential scan rate (V s^{-1}), n is the number of electrons.

It should be noted that this criterion is based upon the assumptions that the temperature is 298 K, the diffusion coefficients of *Ox* and *Red* are closed to 10^{-5} cm^2 s^{-1}, and both activity coefficients are equal to one.

The peak current for a reversible couple is given by the following equation[6]:

$$i_p = 0.446 \frac{n^{3/2}F^{3/2}}{R^{1/2}T^{1/2}} sD_{Ox}^{1/2} v^{1/2} C_{Ox}^0 \tag{3}$$

where F is the Faraday constant (96487 A s mol^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the thermodynamic temperature (K), s is the electrode surface area, D_{Ox} is the diffusion coefficient, C_{Ox}^0 is the depolarizer concentration in the bulk solution. Note that i_p in Equation (3) will have units of A when D is in cm^2 s^{-1}, C_{Ox}^0 is in mol cm^{-3}, s is in cm^2, and v is in V s^{-1}.

At T = 298 K, Equation (3) is transformed into the following form:

$$i_p = 2.69 \cdot 10^5 n^{3/2} sD_{Ox}^{1/2} v^{1/2} C_{Ox}^0 \tag{4}$$

The latter formula is often named as Randles-Ševčik equation.

Assuming that the diffusion coefficients of the oxidized and reduced species are equal, we may write expression for the peak potential in case of a reversible electrochemical reaction in the form[2]:

$$E_p = E^\circ - 1.109 \frac{RT}{nF} \tag{5}$$

where E^0 is the standard potential.

Let us examine further what information on electrochemical system may be achieved from the experimental temperature dependences of peak current and peak potential. For the temperature dependences of the diffusion coefficient, we can write Arrhenius equation as follows[7]:

$$D_{Ox} = A_D exp\left[-\frac{E_D}{RT}\right] \tag{6}$$

where A_D is the corresponding pre-exponential factor; E_D is the corresponding activation energy of the diffusion mass transfer.

Combining Equations (3) and (6), we derive:

$$lni_p = lnK' - \frac{1}{2}lnT - \frac{E_D}{2RT} \tag{7}$$

where $K' = 0.446 \frac{n^{3/2}F^{3/2}}{R^{1/2}} sA_D^{1/2} v^{1/2} C_{Ox}^0$ includes terms in Equations (3) and (6) which are independent of temperature.

Denoting the sum $lni_p + \frac{1}{2}lnT$ as $h(T)$, we get:

$$h(T) = K' - \frac{E_D}{2RT} \tag{8}$$

In accordance with Equation (8), the line plotted on the coordinates $h(T)$ vs. $1/T$ can be used in order to calculate the activation energy of diffusion from the slope of this line (Figure 1). It is evident that the intersection in the ordinate gives the value of lnK', hence A_D may be easily calculated.
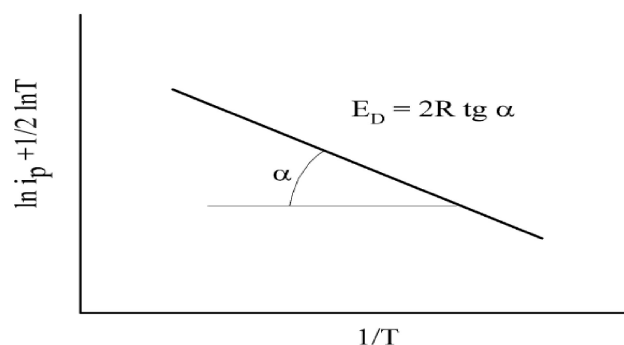
Figure 1 : Determination of the activation energy of diffusion

Naturally, the linear character of the plot $h(T)$ vs $1/T$ holds true if pre-exponential factor and activation energy in Equation (6) do not change with the temperature.

As concerns the temperature dependences of the peak potential, it should be stressed that in Equation (5) not only the last term $\left(-1.109\frac{RT}{nF}\right)$ but also the value of standard potential (E°) changes with temperature. In order to obtain E° vs. T dependence explicitly, let us employ a method described in our works[8-10]. To that end, one has to assume that the current density of the electrochemical reaction under consideration may be described by the following Butler-Volmer equations:

$$i = nF\left(\bar{k}^0 C_{Ox,S} exp\left[-\frac{\alpha FE}{RT}\right] - \bar{k}^0 C_{Red,S} exp\left[\frac{(1-\alpha)FE}{RT}\right]\right) \tag{9}$$

where $\bar{k}^0$ and $\bar{k}^0$ are the rate constants of the forward

and reverse reactions of electrochemical process when the value of the electrode potential is equal to zero (E = 0) (in the scale of the arbitrarily chosen reference electrode), respectively; α is apparent transfer coefficient; $C_{Ox,S}$ and $C_{Red,S}$ are the concentrations of the reagents Ox and Red in the near-electrode layer (i.e. its surface concentration), respectively.

For the $\vec{k}^0$ and $\overleftarrow{k}^0$ values we may write the following temperature dependences (Arrhenius equations in an integral form):

$$\vec{k}^0 = \vec{J}_0 \exp\left[-\frac{\vec{\Omega}_0}{RT}\right] \qquad (10)$$

$$\overleftarrow{k}^0 = \overleftarrow{J}_0 \exp\left[-\frac{\overleftarrow{\Omega}_0}{RT}\right] \qquad (11)$$

where $\vec{J}_0$ and $\overleftarrow{J}_0$ are the pre-exponential factors for the forward and reverse electrochemical stages, respectively; $\vec{\Omega}_0$ and $\overleftarrow{\Omega}_0$ are the corresponding values of the formal activation energies at $E = 0$.

In connection with the last two formulae, let us note that the formal activation energy Ω is determined at a constant electrode potential measured versus an arbitrary chosen reference electrode (at the same temperature, as the studied electrode)[8-11]:

$$\Omega = RT^2\left(\frac{\partial \ln i}{\partial T}\right)_E \qquad (12)$$

Assuming $C_{Ox} = C_{Red} = 1$ (standard state), we have for equilibrium established on the electrode, the following expressions:

$$i = \vec{i} - \overleftarrow{i} = 0, \; \vec{i} = \overleftarrow{i}, \; E = E^0, \; C_{Ox,S} = C_{Ox} = 1,$$
$$C_{Red,S} = C_{Red} = 1 \qquad (13)$$

Combining Equations (9)-(13), we get:

$$\vec{k}^0 \exp\left[-\frac{\alpha FE^0}{RT}\right] = \overleftarrow{k}^0 \exp\left[\frac{(1-\alpha)FE^0}{RT}\right] = k_s^0 \qquad (14)$$

$$E^0 = \frac{RT}{F}\ln\frac{\vec{k}^0}{\overleftarrow{k}^0} = \frac{RT}{F}\left(\ln\frac{\vec{J}_0}{\overleftarrow{J}_0} + \frac{\overleftarrow{\Omega}_0 - \vec{\Omega}_0}{RT}\right) \qquad (15)$$

Hence, the temperature derivative of the standard potential is given by:

$$\frac{dE^0}{dT} = \frac{R}{F}\ln\frac{\vec{J}_0}{\overleftarrow{J}_0} \qquad (16)$$

Taking into account Equation (5), we obtain:

$$\frac{dE_p}{dT} = \frac{R}{F}\ln\frac{\vec{J}_0}{\overleftarrow{J}_0} - 1.109\frac{R}{nF} \qquad (17)$$

It should be stressed that the latter two equations are valid only if the corresponding activation energies and pre-exponential factors in Equation (15) do not depend on the temperature.

As far as cyclic voltammetry is concerned, let us conventionally accept that the forward sweep is cathodic and the backward one is anodic. Then the following relationship between forward and backward peak potentials ($E_{p,f}$ and $E_{p,b}$, respectively) are valid for uncomplicated reversible electrode processes[12]:

$$E_{p,b} - E_{p,f} = 2.22\frac{RT}{nF} \qquad (18)$$

Then we get:

$$\frac{dE_{p,b} - E_{p,f}}{dT} = 2.22\frac{R}{nF} \qquad (19)$$

Consequently, the value of ($E_{p,b} - E_{p,f}$) depends linearly on the temperature.

Thus, as expected, the temperature responses of linear voltammograms in case of reversible electrochemical reactions do not allow obtaining data on kinetic characteristics of the charge transfer process; only the activation parameters (i.e. pre-exponential factor and activation energy) of the diffusion process may be calculated from the experimental dependences of peak current and peak potential on the temperature.

Irreversible electrochemical reactions

For uncomplicated totally irreversible electrode process

$$Ox + ne^- \rightarrow Red \qquad (20)$$

the following criterion has been suggested[5]:

$$k_s^0 < 2\cdot 10^{-5}(nv)^{1/2} \qquad (21)$$

where the meaning of the symbols and their units have been defined above in connection with expression (2).

Electrochemical irreversibility means that the Nernst law does not hold regarding the partners of the redox couple at the electrode surface and the recorded current is at any potential coincident with that relative to either forward or the backward electrode reaction alone.

The peak current for an irreversible electrode reaction may be given by the following equation[2,13]:

$$i_p = 0.28nFsC_{Ox}^0\sqrt{\pi D_{Ox}b} \qquad (22)$$

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where $b = \dfrac{\alpha nF}{RT}v$.

Equation (22) is transformed at T = 298 K into the form:

$$i_p = 3.00 \cdot 10^5 n\alpha^{1/2} s D_{Ox}^{1/2} v^{1/2} C_{Ox}^0 \qquad (23)$$

Expression (23) is known as Delahay equation. In formulae (22) and (23) i_p has unit of A when D_{Ox} is in $cm^2 s^{-1}$, C_{Ox}^0 is in mol cm^{-3}, s is in cm^2, and v is in V s^{-1}.

Since the electrode surface area, bulk concentration of the Ox species and the potential scan rate in the experiments are commonly kept constant, the variation of i_p with temperature is only associated with a corresponding change in the diffusion coefficient of electroactive species.

If we substitute Arrhenius expression for the diffusion coefficient (6) into Equation (23) and then perform some simple algebraic transformations, we may obtain the following temperature dependence of lni_p:

$$lni_p = lnK'' - \frac{1}{2}lnT - \frac{E_D}{2RT} \qquad (24)$$

where $K'' = 0.28 nFsc_0\sqrt{\pi A_D v \dfrac{\alpha nF}{R}}$ is independent of temperature.

Note that Equations (7) and (24) are quite analogous in their structures. Hence, acting similarly to the procedure described above, we may denote the sum $lni_p + \dfrac{1}{2}lnT$ as $f(T)$, and then obtain the following linear relationship between $f(T)$ and reciprocal temperature:

$$f(T) = lnK'' - \frac{E_D}{2RT} \qquad (25)$$

Thus, according to Equation (25), the values of E_D and A_D may be calculated from the slope of such a linear dependence (see Figure 1). Similarly to the case of reversible electrochemical processes, the intersection in the ordinate allows evaluating the quantities of lnK' and A_D.

The current flowing in the initial ascending portion of the voltammetric peak is known to be independent of the sweep rate, provided the current is equal to zero at the initial potential[6,12,14]. Then the following equation holds for currents measured at the foot of the peak where $i < 0$, li_p:

$$i = nFsC_{Ox}^0 k_s^0 exp\left[-\frac{\alpha F}{RT}\left(E - E^0\right)\right] \qquad (26)$$

On the basis of this equation the kinetics parameters of the electrode process α and k_s^0 can be evaluated by plotting lni vs. $(E - E^0)$ dependences if E^0, s, C_{Ox}^0 and n are known.

Hence, using i vs. E responses obtained at different temperatures at the foot of the current peak, the formal activation energy of the forward electrochemical reaction $\bar{\Omega}$ may be found. To this effect, lni vs. $1/T$ dependences should be plotted at $E = const$; according to Equation (12), the slopes of these lines being equal to $\vec{\Omega}/R$. It was earlier shown[10] that under kinetic control conditions the following expression is valid for the apparent (measured experimentally) formal activation energy:

$$\vec{\Omega} = \vec{\Omega}_0 + \alpha FE \qquad (27)$$

It should be stressed that these conditions are fulfilled in case of irreversible liner voltammograms at the foot of the i vs. E curves.

It is clear that the value of $\vec{\Omega}_0$ can be calculated from the intersection in the ordinate of the line plotted in coordinates $\vec{\Omega}$ vs. E, the slope of this plot giving the value of the transfer coefficient α. Performing analogous measurements and calculations for the backward scan in cyclic voltammetry allows obtaining the value $\bar{\Omega}_0$. Then the real activation energy of the electrochemical reaction under study at equilibrium potential may be evaluated by means of the following equation[10,11]:

$$A_0 = (1 - \alpha)\vec{\Omega}_0 + \alpha\bar{\Omega}_0 \qquad (28)$$

However, some difficulties arise with processing voltammograms when using the initial ascending portion of the current peak. Firstly, for large enough values of $(E_{p,b} - E_{p,f})$ (i.e. at a high degree of electrochemical irreversibility; the standard rate constant is too small in such a case), the backward peak becomes no longer detectable in the potential range which is experimentally available for the solvent employed. Secondly, the measurements of current at the foot of the voltammetric peak are not accurate enough. In addition, in many cases standard potential E^0 is not strictly known.

Therefore, we have suggested an alternative and con-

venient method for processing temperature responses in case of totally irreversible electrochemical reactions studied by linear voltammetry[15]. This procedure is grounded on the following theoretical propositions.

Apart from Equation (22), another expression for the peak current of an irreversible electrode process is valid[16]:

$$i_p = 0.227 nFsC_{Ox}^0 k_s^0 \exp\left[-\frac{\alpha nF(E_p - E^0)}{RT}\right] \qquad (29)$$

For the temperature dependences of the standard rate constant we may use Arrhenius equation as follows:

$$k_S^0 = A_a \exp\left[-\frac{E_a}{RT}\right] \qquad (30)$$

where E_A is the standard activation energy of the charge transfer; A_a is the corresponding pre-exponential factor.

Combining Equations (29) and (30), we obtain after simple transformation:

$$\ln i_p = \ln B - \frac{E_a}{RT} - \frac{\alpha nF(E_p - E^0)}{RT} \qquad (31)$$

where $B = 0.227 nFsC_{Ox}^0 A_a$.

Let us designate the sum $\ln i_p + \frac{\alpha nF(E_p - E^0)}{RT}$ as $q(T)$:

$$q(T) = \ln i_p + \frac{\alpha nF(E_p - E^0)}{RT} \qquad (32)$$

Consequently, we have:

$$q(T) = \ln B - \frac{E_a}{RT} \qquad (33)$$

Thus, there is a linear dependence $q(T)$ vs. $1/T$ (Figure 2) which enables us to calculate Arrhenius parameters – the activation energy of charge transfer (E_A) and the pre-exponential factor (A_a) from the slope and the intersection in the ordinate, correspondingly.

It should be noted that for performing calculations described above one has to know the values of E^0 for different temperatures. These values may be computed from the experimental dependences of E_P vs. v and i_P vs. v according to the procedure reported in work[17]. To this effect, the following equation for the peak potential of irreversible electrode reaction should be used:

$$E_p = E^0 - \frac{RT}{\alpha nF}\left(0.78 - \ln k_s^0 + \ln\sqrt{D_{Ox}b}\right) \qquad (34)$$

The charge transfer coefficient α is to be drawn out from Equation (34) by plotting E_p vs. $\ln v$. Then the

value of the diffusion coefficient D_{Ox} may be easily calculated on the basis of Equation (23) by linearizing the experimental data in the coordinates i_p vs. $v^{1/2}$ (at a constant value of C_{Ox}^0) and (or) i_p vs. (C_{Ox}^0 at a constant value of v). Finally, the standard rate constant k_s^0 as well as the formal standard electrode potential E^0 may be determined solving simultaneous Equations (29)-(34) using preliminarily determined values of α and D_{Ox}. In order to solve above mentioned nonlinear simultaneous equations, some commercially available software is to be applied.
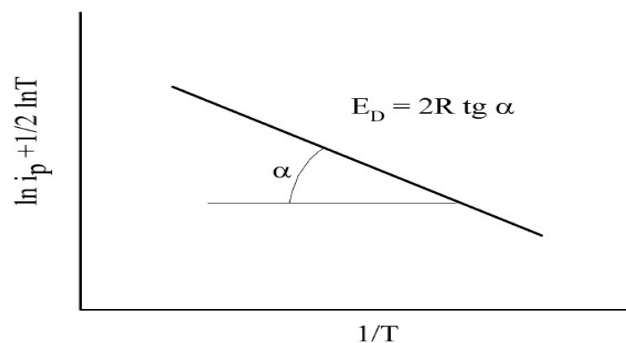

Figure 2 : Determination of the activation energy of charge transfer

Quasi-reversible electrochemical reactions

Uncomplicated quasi-reversible electrode processes in conditions of "usual" linear and cyclic voltammetry is defined by the following criterion[5]:

$$0.3(nv)^{1/2} > k_S^0 > 2 \cdot 10^{-5}(nv)^{1/2} \qquad (35)$$

The expression of the peak current for a quasi-reversible charge transfer can be written as follows[18]:

$$i_p = 0.452 \frac{n^{3/2}F^{3/2}}{R^{1/2}T^{1/2}} sD_{Ox}^{1/2} v^{1/2} C_{Ox}^0 K(\alpha, k_s^0, v) \qquad (36)$$

where $K(\alpha(k_s^0, v)$ is a suitable function depending upon transfer coefficient, standard rate constant and potential scan rate.

For the difference between peak potential and half-peak potential the following equation is valid[18]:

$$\left(E_p - E_{p/2}\right) = \frac{RT}{nF} \Delta(\alpha, k_s^0, v) \qquad (37)$$

where $\Delta(\alpha, k_s^0, v)$ is another function of transfer coefficient, standard rate constant and potential scan rate.

From our point of view, it seems to be rather inconvenient to use Equations (36) and (37) for defining the temperature responses of linear voltammograms as

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$K(\alpha(k_s^0, v))$ and $\Delta(\alpha, k_s^0, v)$ are reported in the literature as tabulated functions[18].

It is well known that the same electrode reaction can exhibit either a reversible or a totally irreversible response depending upon the scan rate employed[18,19]. With an increase in the sweep rate, a transition from a reversible to an irreversible behavior progressively occurs. Thus, the easiest way to gain information on the activation parameters of the charge transfer is that of employing suitable (i.e. increased) values of the potential scan rate where voltammograms show typical irreversible electrochemical response.

CONCLUSION

The theoretical expressions describing temperature dependences in linear and cyclic voltammetry were derived and analyzed. Convenient and accurate procedures of calculating the activation parameters were developed both for reversible electrochemical reactions and for irreversible ones. In case of reversible electrochemical processes, the temperature responses of linear voltammograms do not allow obtaining kinetic parameters of the charge transfer; only the activation parameters (i.e. pre-exponential factor and activation energy) of the diffusion mass transfer may be evaluated from the experimental dependences of peak current and peak potential on the temperature. On the contrary, in case of totally irreversible electrochemical processes, reported methods for processing the temperature responses of linear voltammograms enable calculating activation energy and corresponding pre-exponential factor both for the diffusion mass transfer and for the charge transfer. It was observed that the theoretical models become too complicated in case of quasi-reversible electrode processes; the easiest way to obtain information on the activation parameters is that of application of increased values of the sweep rate in order that voltammetric responses show typical irreversible behavior.

The theoretical procedure reported in this work has been applied to the calculation of the activation energy of the charge transfer for Cr(III)→Cr(II) irreversible cathodic reaction studied by means of linear voltammetry technique in methanesulfonate and sulfate solutions[15]. Comprehensive statement of the data concerned goes beyond the scope of this report. For more detailed inter-pretation of the issue, the reader is referred to the works[15,20].

REFERENCES

[1] C.M.A.Brett, A.M.O.Brett; Electrochemistry: Principles, Methods, and Applications, Oxford University Press, Oxford, 427 (**1993**).

[2] D.K.Gosser; Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms, VCH, New York, 154 (**1993**).

[3] A.J.Bard, L.R.Faulkner; Electrochemical Methods and Applications, John Wiley & Sons, 833 (**2001**).

[4] R.G.Compton, C.E.Banks; Understanding Voltammetry, World Scientific, Singapore, 371 (**2007**).

[5] H.Matsuda, Y.Ayabe; Z.Elektrochem., **59**, 494 (**1955**).

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

[7] A.A.Vlček; Collect.Czech.Chem.Commun., **24**, 3538 (**1959**).

[8] F.I.Danilov, V.S.Protsenko; Rus.J.Electrochem., **45**, 1105 (**2009**).

[9] F.I.Danilov, V.S.Protsenko; Rus.J.Electrochem., **46**, 188 (**2010**).

[10] V.S.Protsenko, F.I.Danilov; J.Electroanal.Chem., **651**, 105 (**2011**).

[11] F.I.Danilov, V.S.Protsenko; Rus.J.Electrochem., **45**, 1037 (**2009**).

[12] Z.Galus; Fundamentals of Electrochemical Analysis, 2nd (revised) Edition, Ellis Horwood and Polish Scientific Publishers, New York and Warsaw, 350 (**1994**).

[13] P.Delahay; J.Am.Chem.Soc., **75**, 1190 (**1953**).

[14] W.H.Reinmuth; Anal.Chem., **32**, 1891 (**1960**).

[15] A.A.Kityk, V.S.Protsenko, F.I.Danilov; J.Electroanal. Chem., **689**, 269 (**2013**).

[16] A.Ya.Gokhstein, Ya.P.Gokhstein; Dokl.Akad.Nauk SSSR, **131**, 601 (**1960**).

[17] V.S.Protsenko, A.A.Kityk, F.I.Danilov; J.Electroanal. Chem., **661**, 213 (**2011**).

[18] H.Matsuda, Y.Ayabe; Z.Elektrochem., **59**, 494 (**1955**).

[19] R.S.Nicholson; Anal.Chem., **37**, 1352 (**1965**).

[20] V.S.Protsenko, A.A.Kityk, F.I.Danilov; Voltammetry: Theory, Types and Applications, Y.Saito, T.Kikuchi, (Eds); Nova Science Publishers, Inc., New York, 319 (**2014**).