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**DETERMINATION OF THE ACTIVATION PARAMETERS OF ELECTRODE PROCESSES ON THE BASIS OF TEMPERATURE DEPENDENCES IN LINEAR VOLTAMMETRY**

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The theoretical analysis of the temperature dependences in linear voltammetry was performed in this communication for reversible and totally irreversible electrochemical processes. A new procedure of calculating the activation parameters (i.e. pre-exponential factor and activation energy) was developed both for reversible electrochemical reactions and for irreversible ones. It was stated that for the case of reversible electrochemical reactions only the activation parameters of the diffusion process may be calculated from the experimental dependences of peak current and peak potential on electrolyte temperature. In case of totally irreversible electrochemical reactions, the temperature responses of linear voltammograms allow obtaining quantitative data both on the activation parameters of the diffusion mass transfer and on the activation parameters of the charge transfer. The theoretical procedure reported in this work has been applied to the calculation of the activation energy and pre-exponential factor of the irreversible cathodic reaction  $\text{Cr(III)} + \bar{e} \rightarrow \text{Cr(II)}$  studied by means of linear voltammetry technique in sulfate solutions. The values of the activation energy for charge transfer and diffusion mass transfer were shown to be close to 61.3 and 11.6 kJ/mol, respectively.

***Introduction***

Linear 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***

***Reversible electrochemical reactions***

Let us consider a simple reversible electro-

chemical reaction:



Electrochemical reversibility presupposes that the forward and reverse electron transfers are fast and occur simultaneously, near to equilibrium and the concentrations of reagents obey the Nernst equation.

The peak current for a reversible couple is given by the following equation [5]:

$$i_p = 0.446 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} s D_{\text{Ox}}^{1/2} v^{1/2} C_{\text{Ox}}^0, \quad (2)$$

where  $F$  is the Faraday constant;  $R$  is the universal gas constant;  $T$  is the thermodynamic temperature;  $s$  is the electrode surface area;  $D_{\text{Ox}}$  is the diffusion coefficient;  $C_{\text{Ox}}^0$  is the electroactive species concentration in the bulk solution;  $n$  is the potential scan rate,  $n$  is the number of electrons.

At the temperature  $T=298$  K, Equation (2) is transformed into the following form (Randles-Ševčík equation):

$$i_p = 2.69 \cdot 10^5 n^{3/2} s D_{\text{Ox}}^{1/2} v^{1/2} C_{\text{Ox}}^0, \quad (3)$$

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]:

$$E_p = E^0 - 1.109 \frac{RT}{nF}, \quad (4)$$

where  $E^0$  is the standard electrode potential.

Let us examine further what information on an electrochemical system may be achieved from the experimental temperature dependences of peak current and peak potential. For this end, we can write the Arrhenius equation for the temperature dependences of the diffusion coefficient in the following form [6]:

$$D_{\text{Ox}} = A_D \exp\left[-\frac{E_D}{RT}\right], \quad (5)$$

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

Then combining Equations (2) and (5), we derive:

$$\ln i_p = \ln K' - \frac{1}{2} \ln T - \frac{E_D}{2RT}, \quad (6)$$

where  $K' = 0.446 \frac{n^{3/2} F^{3/2}}{R^{1/2}} s A_D^{1/2} v^{1/2} C_{\text{Ox}}^0$  includes

terms in Equations (2) and (5) which are independent of temperature.

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

$$h(T) = K' - \frac{E_D}{2RT}. \quad (7)$$

In accordance with Equation (7), 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. It is evident that the intersection in the ordinate gives the value of  $\ln K'$ , hence  $A_D$  may be easily calculated.

It should be stressed that the similar procedure for processing linear voltammograms in case of reversible electrode reactions has been proposed in works by V.S. Kublanovsky, O.L. Bersirova, and S.V. Bik [7] for the first time.

Naturally, the linear character of the plot  $h(T)$  vs.  $1/T$  holds true if pre-exponential factor and activation energy in Equation (5) do not change with the temperature.

As concerns the temperature dependences of the peak potential, it should be stressed that in

Equation (4) not only the last term  $\left(-1.109 \frac{RT}{nF}\right)$  but also the value of standard potential ( $E^0$ ) changes with temperature. In order to obtain  $E^0$  vs.  $T$  dependence explicitly, let us employ a method described in 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:

$$i = nF \left( \begin{array}{l} \bar{k}^0 C_{\text{Ox},S} \exp\left[-\frac{\alpha FE}{RT}\right] - \\ - \bar{k}^0 C_{\text{Red},S} \exp\left[\frac{(1-\alpha)FE}{RT}\right] \end{array} \right), \quad (8)$$

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;  $\alpha$  is apparent transfer coefficient;  $C_{\text{Ox},S}$  and  $C_{\text{Red},S}$  are the concentrations of the reagents Ox and Red in the near-electrode layer (i.e. its surface concentrations), respectively.

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

$$\bar{k}^0 = \bar{J}_0 \exp\left[-\frac{\bar{\Omega}_0}{RT}\right], \quad \bar{k}^0 = \bar{J}_0 \exp\left[-\frac{\bar{\Omega}_0}{RT}\right], \quad (9)$$

where  $\bar{J}_0$  and  $\bar{J}_0$  are the pre-exponential factors for the forward and reverse electrochemical stages, respectively;  $\bar{\Omega}_0$  and  $\bar{\Omega}_0$  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  $\Omega$  is determined at a constant electrode potential measured versus an arbitrary chosen reference electrode (at the same temperature, as the studied electrode) [8–11]:

$$\Omega = RT^2 \left( \frac{\partial \ln i}{\partial T} \right)_E \quad (10)$$

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

$$i = \bar{i} - \bar{i} = 0, \quad \bar{i} = \bar{i}, \quad E = E^0, \quad C_{Ox,S} = C_{Ox} = 1,$$

$$C_{Red,S} = C_{Red} = 1. \quad (11)$$

Combining Equations (8)–(11), we get:

$$\bar{k}^0 \exp \left[ -\frac{\alpha FE^0}{RT} \right] = \bar{k}^0 \exp \left[ \frac{(1-\alpha)FE^0}{RT} \right] = k_s^0, \quad (12)$$

$$E^0 = \frac{RT}{F} \ln \frac{\bar{k}^0}{k_s^0} = \frac{RT}{F} \left( \ln \frac{\bar{J}_0}{\bar{J}_0} + \frac{\bar{\Omega}_0 - \bar{\Omega}_0}{RT} \right), \quad (13)$$

where  $k_s^0$  is the standard rate constant.

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

$$\frac{dE^0}{dT} = \frac{R}{F} \ln \frac{\bar{J}_0}{\bar{J}_0}. \quad (14)$$

Taking into account Equation (4), we then obtain:

$$\frac{dE_p}{dT} = \frac{R}{F} \ln \frac{\bar{J}_0}{\bar{J}_0} - 1.109 \frac{R}{nF}. \quad (15)$$

It should be stressed that the latter two equations are valid only if the corresponding activation energies and pre-exponential factors in Equation (13) do not depend 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

Electrochemical irreversibility presupposes 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, 12]:

$$i_p = 0.28nFsC_{Ox}^0 \sqrt{\pi D_{Ox} b}, \quad (16)$$

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

Equation (16) is transformed at  $T=298$  K into the form (Delahay equation):

$$i_p = 3.00 \cdot 10^5 n \alpha^{1/2} s D_{Ox}^{1/2} v^{1/2} C_{Ox}^0. \quad (17)$$

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 (5) into Equation (17) and then perform some simple algebraic transformations, we may obtain the following temperature dependence of  $\ln i_p$ :

$$\ln i_p = \ln K'' - \frac{1}{2} \ln T - \frac{E_D}{2RT}, \quad (18)$$

where  $K'' = 0.28nFsC_{Ox}^0 \sqrt{\pi A_D v \frac{\alpha nF}{R}}$  is independent of temperature.

Note that Equations (6) and (18) are quite analogous in their structures. Hence, acting similarly to the procedure described above, we denote the

sum  $\ln i_p + \frac{1}{2} \ln T$  as  $\Phi(T)$ , and then obtain the following linear relationship between  $\Phi(T)$  and reciprocal temperature:

$$\Phi(T) = \ln K'' - \frac{E_D}{2RT}. \quad (19)$$

Thus, according to Equation (19), the values of  $E_D$  and  $A_D$  may be calculated from such a linear

dependence. Similarly to the case of reversible electrochemical processes, the intersection in the ordinate allows evaluating the quantities of  $\ln K'$  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 [5,13]. Then the following equation holds for currents measured at the foot of the peak where  $i < 0.1i_p$ :

$$i = nFsC_{Ox}^0 k_s^0 \exp\left[-\frac{\alpha F}{RT}(E - E^0)\right]. \quad (20)$$

On the basis of this equation the kinetics parameters of the electrode process  $\bar{\Omega}$  and  $k_s^0$  can be evaluated by plotting  $\ln i$  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,  $\ln i$  vs.  $1/T$  dependences should be plotted at  $E = \text{const}$ ; according to Equation (10), the slopes of these lines being equal to  $\bar{\Omega}/R$ . It was earlier shown [10] that under kinetic control conditions the following expression is valid for the apparent (measured experimentally) formal activation energy:

$$\bar{\Omega} = \bar{\Omega}_0 + \alpha FE. \quad (21)$$

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  $\bar{\Omega}_0$  can be calculated from the intersection in the ordinate of the line plotted in coordinates  $\bar{\Omega}$  vs.  $E$ , the slope of this plot giving the value of the transfer coefficient  $\alpha$ . 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]:

$$A_0 = (1 - \alpha) \cdot \bar{\Omega}_0 + \alpha \cdot \bar{\Omega}_0. \quad (22)$$

However, some difficulties arise with processing voltammograms when using the initial ascending portion of the current peak. Firstly, at a high enough degree of electrochemical irreversibility, 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 convenient method for processing temperature responses in case of totally irreversible electrochemical reactions studied by linear voltammetry [14]. This procedure is grounded on the following theoretical propositions.

Apart from Equation (16), another expression for the peak current of an irreversible electrode process is valid [15]:

$$i_p = 0.227nFsC_{Ox}^0 k_s^0 \exp\left[-\frac{\alpha nF(E_p - E^0)}{RT}\right]. \quad (23)$$

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

$$k_s^0 = A_a \exp\left[-\frac{E_a}{RT}\right], \quad (24)$$

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

Combining Equations (23) and (24), we obtain after simple transformation:

$$\ln i_p = \ln B - \frac{E_a}{RT} - \frac{\alpha nF(E_p - E^0)}{RT}, \quad (25)$$

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

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

$$\Psi(T) = \ln i_p + \frac{\alpha nF(E_p - E^0)}{RT}. \quad (26)$$

Consequently, we have:

$$\Psi(T) = \ln B - \frac{E_a}{RT}. \quad (27)$$

Thus, there is a linear dependence  $\Psi(T)$  vs.  $1/T$  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 [16]. To this effect, the following equation

for the peak potential of irreversible electrode reaction should be used:

$$E_p = E^0 - \frac{RT}{\alpha nF} \left( 0.78 - \ln k_s^0 + \ln \sqrt{D_{Ox} b} \right). \quad (28)$$

The charge transfer coefficient  $\alpha$  is to be drawn out from Equation (28) 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 (21) 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  $k_s^0$  and the formal standard electrode potential  $E^0$  may be determined solving simultaneous Equations (23)–(28) using preliminarily determined values of  $\alpha$  and  $D_{Ox}$ .

#### Experimental, results and discussion

Electrochemical couple Cr(III)/Cr(II) is a convenient object for experimental testing various theoretical models. In addition, study on electrochemical characteristics of Cr(III)/Cr(II) couple draws a special attention in view of its practical significance; the kinetics of the electrochemical system involved has been investigated in a number of publications [16–19].

In the present work, temperature responses of Cr(III)/Cr(II) electrochemical system were studied by means of linear voltammetry on the lead electrode in sulfate electrolyte. Lead was chosen as the electrode materials as the hydrogen evolution reaction (HER) on this metal occurs with a very high overvoltage and the  $i_p$ ,  $E$  wave of the Cr(III) reduction may be easily separated from that referred to the HER.

All solutions were prepared using doubly distilled water and reagent grade chemicals. Linear voltammetric curves were recorded using Potentiostat/Galvanostat Reference 3000 (Gamry). All electrochemical experiments were performed in a conventional glass three-electrode cell deaerated by blowing with electrolytic hydrogen. The cathodic and anodic compartments were separated with a porous glass diaphragm. The working electrode was an end face of a platinum cylinder embedded into glass on which a Pb-coating was deposited prior each experiment. The visible surface of the working electrode was equal to 0.28 cm<sup>2</sup>. The counter electrode was made of platinum wire. All potentials were measured with respect to the saturated Ag/AgCl-electrode and recalculated to a standard hydrogen electrode.

The linear voltammograms obtained in Cr(III) sulfate electrolyte at various temperatures are shown in Fig. 1. With an increase in temperature, the peak potential of the Cr(III) discharge shifts to more positive potentials and the peak current grows.

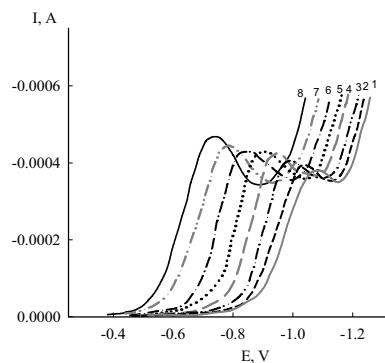


Fig. 1. Voltammograms obtained in sulfate Cr(III) solution at different temperatures, K: 298 (1), 303 (2), 308 (3), 313 (4), 318 (5), 323 (6), 328 (7), 333 (8). Potential scan rate 50 mV/s; 5·10<sup>-3</sup> M Cr(III)

According to expression (16), the change in  $i_p$  with temperature is determined by the corresponding change in the diffusion coefficient of Cr(III) ions since the electrode surface area, Cr(III) ions concentration and the potential scan rate were kept constant. As noted above, there is a linear dependence

$$\Phi(T) \equiv \ln i_p + \frac{1}{2} \ln T \text{ vs. reciprocal temperature (see$$

Eq. (19)), this experimental dependence being presented in Fig. 2 (curve 1). The values of  $E_D$  and  $A_D$  were calculated from the linear dependence

$$\ln i_p + \frac{1}{2} \ln T \text{ vs. } 1/T \text{ (Table).}$$

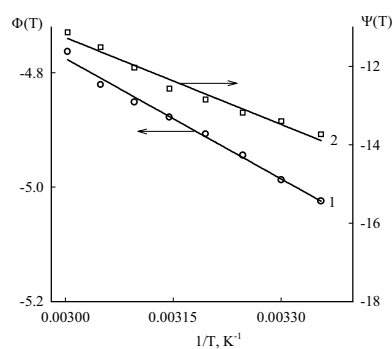


Fig. 2. Linear plots in coordinates  $\Phi(T)$  vs.  $1/T$  (1) and  $\Psi(T)$  vs.  $1/T$  (2). Potential scan rate 50 mV s<sup>-1</sup>; 5·10<sup>-3</sup> M Cr(III)

#### The calculated activation parameters

Parameter	Value
$E_{Df}$ kJ/mol	11.6
$A_D \cdot 10^3$ , cm <sup>2</sup> /s	4.97
$E_{ar}$ kJ/mol	61.3
$A_a \cdot 10^{-5}$ , cm/s	15.44

The Arrhenius parameters of the charge transfer – activation energy of electron transfer ( $E_a$ ) and pre-



exponential factor ( $A_a$ ) – were calculated by means of graphical processing the temperature responses of linear voltammograms according to Equation (27) (Fig. 2, curve 2); the values obtained are presented in Table. Let us stressed that the required values of  $E^0$  were found from the experimental dependences of  $E_p$  vs.  $n$  and  $i_p$  vs.  $n$  according to the routine procedure described in [16]. The activation parameters of the diffusion mass transfer and charge transfer calculated by the method proposed in this work are in good agreement with those given in literature [14,16–19].

### Conclusions

The theoretical expressions describing temperature dependences in linear 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.

The theoretical procedure reported in this work has been applied to the calculation of the activation energy of the charge transfer for  $\text{Cr(III)} + e^- \rightarrow \text{Cr(II)}$  irreversible cathodic reaction studied by means of linear voltammetry technique in sulfate solutions.

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**Keywords:** linear voltammetry; temperature dependence; activation parameters; electroreduction; trivalent chromium.

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