

Short communication

Direct voltammetry for vitamin B₂ determination in aqueous solution by using glassy carbon electrode

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1. Introduction

In a series of recent papers [1–7], it has been shown that the faradaic current density $j_F(t)$ of an electrode redox reaction $O + e \rightleftharpoons R$, occurring with combined over-tension of charge transfer and non-stationary, linear, semi-infinite diffusion of the species O, R, is the solution of an integral equation of Volterra type, which in the case of the voltammetry with linear scanning of the potential in the cathodic sense gives

$$j_F(t) = \lambda \frac{j^0 N^*(t)}{\pi^{1/2}} \int_0^t \frac{j_F(u)}{(t-u)^{1/2}} du + f(t), \quad (1)$$

where

$$N^*(t) = \bar{N} [1/r + \exp(-f|v|t)] \exp(\beta f|v|t), \quad (1a)$$

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$$f(t) = j^0 [1 - \exp(-f|v|t)] \exp(\beta f|v|t), \quad (1b)$$

$$\lambda = -1, \quad f = F/RT, \quad \bar{N} = \frac{1}{F\sqrt{D_R a_R}},$$
$$r = \sqrt{\frac{D_O a_O}{D_R a_R}}, \quad (1c)$$

$|v|$ is the magnitude of the scanning rate (and thus $\eta(t) = -|v|t$ represents the over-tension at the moment of time t), and the other quantities have the usual meanings: β is the symmetry factor; j^0 is the exchange current density; D_O , D_R are the diffusion coefficients; and a_O , a_R are the activities.

Although a rigorous description of the experimental voltammograms is given only by the solution $j_F(t)$ of the integral equation (1), it has been shown [7] that a sufficient accurate description of the voltammograms may be obtained by solving the following ordinary differential equation of first-order:

$$\frac{1}{A(j^0\bar{N})^2} \left\{ \frac{dI(t)}{dt} - \left[\beta + \frac{\exp(-f|v|t)}{1 - \exp(-f|v|t)} \right] f|v|I(t) \right\} \\ = \left\{ 1 + 2 \left[\beta - \frac{\exp(-f|v|t)}{1/r + \exp(-f|v|t)} \right] f|v|t \right\} \\ \left[\exp(2\beta f|v|t) [1/r + \exp(-f|v|t)] \right. \\ \left. \left\{ [1/r + \exp(-f|v|t)] \frac{I(t)}{A} \right. \right. \\ \left. \left. - \frac{1 - \exp(-f|v|t)}{\pi^{1/2}\bar{N}t^{1/2}} \right\} \right\}, \quad (2)$$

where A is the electrode area and $I(t) = Aj(t)$ the current intensity as measured in the external circuit (i.e., one supposes that the capacity current may be neglected).

On the basis of Eq. (2), it was possible to elaborate new direct-voltammetry methods for determining the diffusion coefficients D_O , D_R [8,9], the standard exchange current densities j^{00} [10] and the symmetry factors β [11], of the electrode redox reactions, as well as for studying the high temperature superconductor/redox electrolyte interface [12].

In this paper, the ordinary differential equation (2) has been used to analyse the quasi-reversible electrode redox reactions $O + e \rightleftharpoons R$, and a direct-voltammetry method of determining the value of r (Eq. (1c)) has been theoretically and experimentally elaborated. Because, generally, the diffusion coefficients D_O , D_R have very close values, it follows that the value of r estimates the value of the ratio c_O/c_R with sufficient accuracy. Consequently, if an aqueous solution of the oxidized species O is used as a medicine, the reduced species R having no therapeutic properties, the method permits to estimate the percent of the medical active species O in the respective aqueous solution. The method has been applied to control the quality of an aqueous solution of Riboflavin-5'-phosphate (sodium salt) (containing NaCl as indifferent electrolyte).

2. The principle of the method

It is easy to prove that Eq. (2) leads to correct equations for the two extreme cases, i.e., irreversible and reversible electrode redox reactions.

In the first case, $j^0 \rightarrow 0$ and the big bracket in the first member of Eq. (2) must cancel, irrespective of the value of the time t

$$\frac{dI(t)}{dt} = \left(\beta + \frac{\exp(-f|v|t)}{1 - \exp(-f|v|t)} \right) f|v|I(t), \quad (3)$$

i.e.,

$$I(t) = C[\exp(\beta f|v|t)][1 - \exp(-f|v|t)], \quad (3a)$$

which is an equivalent form of the well-known Butler equation [13], C being the exchange current intensity $C = I^0 = Aj^0$. In the second case, $j^0 \rightarrow \infty$ and the first member of Eq. (2) cancels. Consequently, the second member of Eq. (2) must cancel too, and this irrespective of the value of t , which is possible only if the last bracket on the right-hand side of Eq. (2) is equal to zero, and thus,

$$j(t) = \frac{1 - \exp(-f|v|t) \frac{F\sqrt{D_R}a_R}{\pi^{1/2}t^{1/2}}}{\frac{1}{r} + \exp(-f|v|t)} \\ = \frac{1 - \exp(-f|v|t) \frac{F\sqrt{D_O}a_O}{\pi^{1/2}t^{1/2}}}{1 + r \exp(-f|v|t)}. \quad (4)$$

For greater values of t , Eq. (4) tends to the well-known Cottrell equation [14]

$$j(t) \rightarrow \frac{F\sqrt{D_O}a_O}{\pi^{1/2}t^{1/2}}. \quad (4a)$$

Therefore, in spite of the fact that Eq. (2) is not a rigorous equation, it leads to correct equations for the two extreme cases. Of course Eqs. (3a) and (4a) must result as particular cases, for $j^0 \rightarrow 0$, respective $j^0 \rightarrow \infty$, if instead of Eq. (2) we would use a rigorous equation. But, because Eq. (3) must hold true irrespective of the value of t , and Eq. (4a) for great values of t , it follows that this rigorous equation differs from Eq. (2) only concerning the last bracket on its right-hand side, which must have the form:

$$\left\{ [1/r + \exp(-f|v|t)] \alpha_1(t) \frac{I(t)}{A} \right. \\ \left. - \frac{1 - \exp(-f|v|t)}{\pi^{1/2}\bar{N}t^{1/2}} \alpha_2(t) \right\}, \quad (5)$$

where $\alpha_1(t)$ and $\alpha_2(t)$ are two functions that must satisfy the condition $\alpha_2(t)/\alpha_1(t) \rightarrow 1$ for great values of t .

In conclusion, this rigorous equation has its first member and the first three factors of the second member identical with those of Eq. (2). Fortunately, as we shall see, for grounding the method of estimating the value of r it is not necessary to know the correct expression of the bracket (5), and for this reason we shall use Eq. (2) as the basic equation.

Let us analyze the sign of the first member of Eq. (2). For very small values of t , the bracket tends to the function $dI/dt - I/t$, whose sign depends on the shape of the curve I vs. t in the vicinity of $t = 0$. For instance, if the curve is convex (i.e., the second derivative is negative) the sign of the first member of Eq. (2) will be negative. Further, suppose that the experimental voltammogram passes from the initial convex shape to a linear increase of I with t and, later, to a non-linear increase of I towards the cathodic peak value I_p . However, these are the shapes of the experimental voltammograms, which we are interested in.

Therefore, the first member of Eq. (2) passes from a negative sign to a positive one, existing an intermediate time τ , in-between the two intervals, where the first member cancels because both dI/dt and I must be positive for this value of time, the point $P[\tau, I(\tau)]$ must be before the point where the linear increase of I with t begins, but where I already increases with t . It follows that before the point $P[\tau, I(\tau)]$, the curve presents, if not a veritable “hump” (i.e., a local maximum, followed by a local minimum), at least a “shoulder” and for the over-tension $|\eta| = |v|\tau$ the first bracket on the right-hand side of Eq. (2) cancels

$$1 + 2 \left[\beta - \frac{\exp(-f|\eta|)}{1/r + \exp(-f|\eta|)} \right] f|\eta| = 0. \quad (6)$$

The value of $|\eta(\tau)|$ is taken from the experimental voltammogram and then, because the value of the symmetry factor β is practically equal to 1/2 [15], Eq. (6) permits to obtain the value of r .

3. Experimental

A glassy carbon (GC) was used as working electrode. It was polished and cleaned ultrasoni-

cally. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire as the counter electrode. Electrochemical cell was held in a dark compartment. In order to avoid reductions, the substance (vitamin B₂ 5'-phosphate mono-sodium salt) was quickly dissolved to make a standard 5.4×10^{-4} M/l, solution in 0.1 M NaCl supporting electrolyte and carefully purged of dissolved oxygen by bubbling with pure argon. All chemicals were of analytical grade (Merck).

A BAS-100 system was used for electrochemical measurements. Because our domain of interest from experimental voltammograms is between 25 and 45 mV, it is necessarily for an additional representation. This representation result from Eq. (6), which may be written in the form:

$$\log r = 2.303f|\eta| + \log \frac{1+f|\eta|}{1-f|\eta|}. \quad (7)$$

This equation has been used to numerically calculate the curve $\log r$ vs. η for over-tensions between 26 and 43 mV (step 1 mV). Numerical estimations were performed using a computer software application. All experiments were conducted at 291 K.

4. Results and discussion

All measurements were performed immediately after the preparation of solutions. In this way, the concentration of reduced species is negligible in the volume of standard solution.

Of course, a complete analysis must also estimate the concentrations c_O , c_R . For this, a second direct voltammetry is needed using a solution containing equal volumes of the test solution and of standard solution (having the concentration $c_O^* = 5.4 \times 10^{-4}$ M/l respective $c_R^* \cong 0$ and the same indifferent electrolyte). If this second direct voltammetry leads to a value r^* , it is easy to see that the unknown concentrations c_O , c_R are given by

$$c_O = \frac{r}{r^* - r} c_O^*, \quad c_R = \frac{1}{r^* - r} c_O^*.$$

From the experimental voltammograms (Fig. 1) have resulted the values $|\eta(\tau)| = 35$ mV and

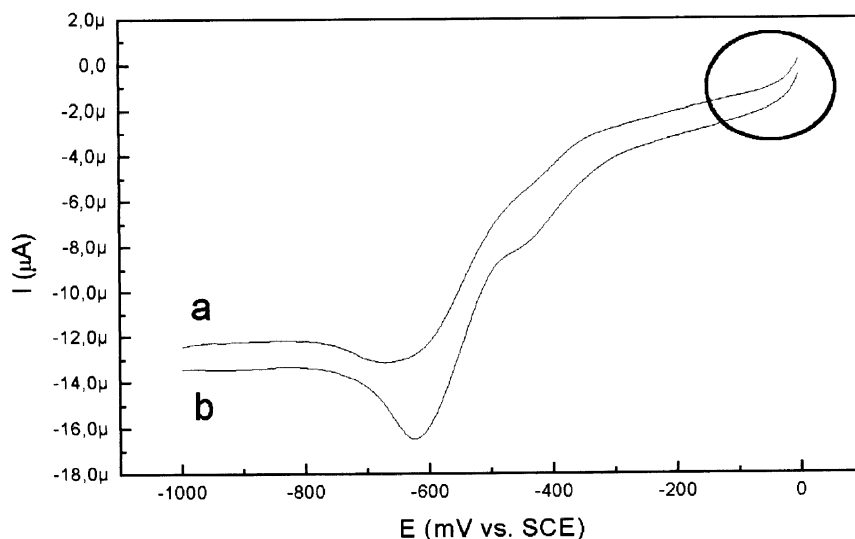


Fig. 1. Experimental voltammograms: (a) test solution and (b) solution with intern standard.

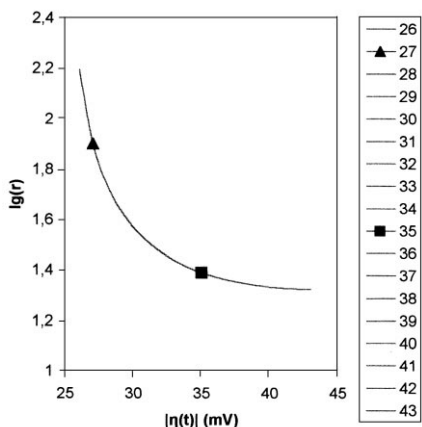


Fig. 2. The dependence $\log r$ vs. $\eta(t)$ calculated by Eq. (6) for $\beta = 0.5$.

$|\eta(\tau^*)| = 27$ mV by numerical computation applied for “shoulder domain” (see circle).

More precisely, by comparing the experimental values $I(t)$ in this domain, one gets the moment of time τ (and in this way the over-tension $|\eta(\tau)|$), when I starts to increase linearly with t . In Fig. 2, is given the dependence of $\log r$ on the over-tension $|\eta(t)|$, calculated by means of Eq. (6), considering $\beta = 0.5$, which plays the role of a calibration curve.

In this conditions after numerical computation result $r = 24.45$, $r^* = 79.47$. In consequence the concentrations for the test solution are $c_O = 2.39 \times 10^{-4}$ M/l and $c_R = 0.09 \times 10^{-4}$ M/l.

The advantage of the method consists in the fact that it does not necessitate the knowledge of the diffusion coefficients D_O , D_R .

5. Conclusions

The direct-voltammetry method elaborated has proved to be a very simple method to check the quality of the aqueous solution of Riboflavin-5'-phosphate (sodium salt), by estimating the value of the ratio $r \cong c_O/c_R$, i.e., the percent of the medical active component O. The method is very useful in controlling such solutions, in the sense that it gives a criterion for accepting only those solutions that leads to a value r greater than an initial fixed lower value.

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