

Short communication

# Diffusion coefficient (or concentration) determination of ascorbic acid using carbon paste electrodes in Fredholm alternative

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## 1. Introduction

In this paper, using as starting point an ordinary differential equation of the first order (previously deduced), whose solutions give with sufficient accuracy the explicit equations of the voltammograms obtained by voltammetry with linear scanning of the potential, an analysis of the reversible electrode reactions  $O + ne \rightleftharpoons R$  has been carried out for the particular case  $c_O = c_R = c$  and  $D_O \approx D_R \approx D$ . Further, the resulting explicit equation of the voltammograms has permitted the grounding of a new method of determining either the diffusion coefficient  $D$  (when  $c$  is known), or

the concentration  $c$  (when  $D$  is known). The method has been successfully applied to the ascorbic acid oxidation, and the results obtained proves its validity as an electroanalytical method for studying the electrode redox reactions.

In a series of recent papers [1–5] it has been shown that the faradaic current density  $j_F$  of an electrode redox reaction  $O + e \rightleftharpoons R$ , occurring with combined overpotential of charge transfer and non-stationary, linear, semiinfinite diffusion of the species  $O$ ,  $R$  is the solution of an integral equation (of Volterra type), namely:

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

where:

$$N^*(t) = \frac{\exp[-\beta f \eta(t)]}{F \sqrt{D_O c_O}} + \frac{\exp[(1-\beta) f \eta(t)]}{F \sqrt{D_R c_R}} \quad (2)$$

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$$f(t) = j^0 (\exp[-\beta f \eta(t)] - \exp[(1 - \beta) f \eta(t)])$$

$$(\lambda = -1; \quad f = F/RT) \quad (3)$$

$\eta(t)$  represents the overpotential at the moment of time  $t$ , and depends on the experimental non-stationary method chosen for studying the reaction  $O + e \rightleftharpoons R$ . The other quantities have the usual meanings:  $\beta$  is the symmetry factor,  $j^0$  is the exchange current density,  $D_O$ ,  $D_R$  are the diffusion coefficients and  $c_O$ ,  $c_R$  are the concentrations. Of course, for the general electrode redox reaction  $O + ne \rightleftharpoons R$ , suffices to replace  $F$  by  $nF$  in Eqs. (1)–(3).

The integral equation (Eq. (1)) is a particular case of a Fredholm integral equation [6–8] in the sense that it satisfies the first case of Fredholm alternative, i.e. it has a unique solution, given by the series:

$$j_F(t) = j_0(t) + \lambda j_1(t) + \lambda^2 j_2(t) + \dots + \lambda^k j_k(t) + \dots \quad (4)$$

where:

$$j_0(t) = f(t); \quad j_{k+1} = \frac{j^0 N^*(t)}{\pi^{1/2}} \int_0^t \frac{j_k(u)}{(t-u)^{1/2}} du \quad (5)$$

In a recent doctoral thesis [9], an analysis of the voltammetry with linear scanning of the potential, for the particular case  $D_O = D_R = D$ ;  $c_O = c_R = c$ , has been carried out, and an ordinary differential equation of the first order, whose solutions  $j_F(t)$  express with sufficient accuracy the experimental voltammograms has been deduced. Of course, this differential equation is not a rigorous one as it is the Volterra type integral equation (Eq. (1)), because the solving of an integral equation may not be rigorously reduced to the solving of an ordinary differential equation of the first order. However, what it is important to be underlined is the fact that, on the basis of this differential equation, it has been possible to get the first explicit equation of the voltammograms in the case of reversible reactions, and by applying it to the particular case of redox electrode (in molten salts)  $C|CrCl_3/CrCl_2$ ,  $LiCl-KCl$ , results in perfect agreement with those given in the literature, by using other mathematical approaches, have been obtained. Further, the same differential equation

has been used to study by voltammetry with linear scanning of the potential the high temperature supraconductor/redox electrolyte interface [10].

In this paper we shall use the same differential equation as theoretical support for a new method of studying the oxidation of ascorbic acid in the aim of grounding a new method of determining the diffusion coefficient (or the concentration) of ascorbic acid, and for this reason we give here this equation:

$$\frac{1}{(j^0 \bar{N})^2} \left\{ \frac{d|j(t)|}{dt} - \frac{1 - \beta + \beta \exp(-f|v|t)}{1 - \exp(-f|v|t)} f|v| |j(t)| \right\} = \left\{ 1 + 2 \left[ 1 - \beta - \frac{\exp(-f|v|t)}{1 + \exp(-f|v|t)} \right] f|v|t \right\} \exp[2(1 - \beta)f|v|t] [1 + \exp(-f|v|t)] \left\{ [1 + \exp(-f|v|t)] |j(t)| - [1 - \exp(-f|v|t)] \frac{1}{\pi^{1/2} \bar{N} t^{1/2}} \right\} \quad (6)$$

In Eq. (6),  $|j(t)|$  is the magnitude of the anodic current density (as registered in the external circuit, because our supposes that the capacitive current may be neglected) and  $\bar{N}$  has the expression  $\bar{N} = 1/F\sqrt{D}c$ , where  $c = c_O = c_R$ , respectively  $D \cong D_O \cong D_R$ .

Let's apply Eq. (6) to the case of reversible electrode redox reactions, when the exchange current density  $j^0$  tends to infinity. Then, the first member of Eq. (6) tends to zero, and the differential equation transforms in the explicit equation of the voltammograms:

$$j(t) = \frac{1 - \exp(-f|v|t) F\sqrt{D}c}{1 + \exp(-f|v|t) \pi^{1/2} t^{1/2}} \quad (7)$$

From Eq. (7) it follows, for the great values of  $t$ :

$$j(t) \rightarrow \frac{F\sqrt{D}c}{\pi^{1/2} t^{1/2}} \quad (8)$$

which is the well known Cottrell equation [11], deduced earlier of course, by a totally different approach. The novelty brought up by Eq. (7)

consists in the fact that it describes the entire voltammogram and, consequently, may be used irrespective of the value of the anodic overpotential  $\eta = |v|t$ .

Passing from the variable  $t$  to the overpotential  $\eta = |v|t$ , Eq. (7) writes:

$$\eta^{1/2} j(\eta) = \frac{1 - \exp(-f\eta)}{1 + \exp(-f\eta)} \frac{F\sqrt{D}|v|^{1/2}c}{\pi^{1/2}} \quad (9)$$

or, using the hyperbolic function:

$$\frac{\pi^{1/2}}{F|v|^{1/2}} \frac{\eta^{1/2} j}{th\left(-\frac{f}{2}\eta\right)} = \sqrt{D}c \quad (10)$$

where  $j$  is the current density at the overpotential  $\eta$ .

Eq. (10) holds true for the particular reaction  $O + e \leftrightarrow R$ . For the general case  $O + ne \leftrightarrow R$ , one must replace  $F$  by  $nF$ , and therefore:

$$\frac{\pi^{1/2}}{nF|v|^{1/2}} \frac{\eta^{1/2} j}{th\left(-\frac{nf}{2}\eta\right)} = \sqrt{D}c \quad (11)$$

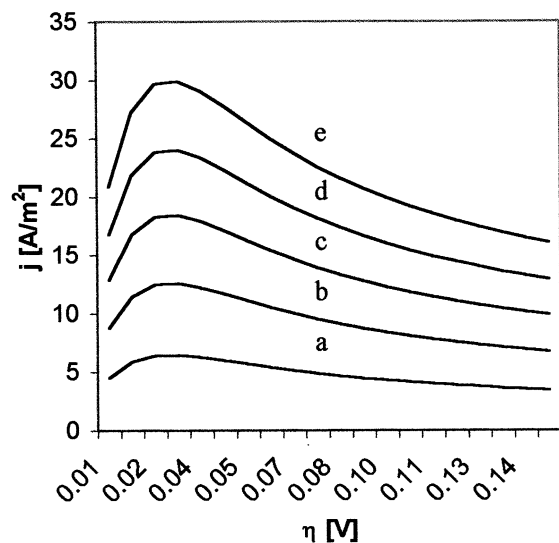


Fig. 1. Direct voltammograms of ascorbic acid in phosphate buffer at pH 7 for  $c = 2.35$  mM/l (a),  $c = 4.58$  mM/l (b),  $c = 6.71$  mM/l (c),  $c = 8.75$  mM/l (d),  $c = 10.69$  mM/l (e); scanning rate 0.05 V/s.

## 2. Experimental

The carbon paste electrode (CPE) was prepared by using the 'solid carbon paste' [12,13]. The solid paraffin was melted in a porcelain capsule at a temperature close to its melting point (46–48°C), and the graphite particles were added and mixed with a glassy spatula for the homogenization. The final 'solid carbon paste' was obtained by thoroughly mixing and crushing the mixture in a mortar with a pestle.

All chemicals were of analytical grade (Merck or Reactivul Bucuresti). The phosphate buffer pH 7 was prepared using 39 ml solution of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  0.067 M/l with 61 ml solution of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  0.2 M/l. Ascorbic acid was of pharmaceutical grade (FR X Romanian Pharmacopoeia Xth edition).

A BAS-100 system was used for electrochemical measurements, performed in a cell with Ag/AgCl reference electrode and Pt counter electrode. Numerical estimations were performed by using a computer software application. All experiments were conducted at 291 K.

## 3. Results and discussion

The  $\text{H}_2\text{A}$  is a weak acid in aqueous solution and in phosphate buffer appear an anionic form ( $\text{HA}^-$ ) because a proton dissociation.

A typical voltammograms in oxidation branch of ascorbic acid in phosphate buffer at pH 7, for 2–11 mM domain concentration is presented in Fig. 1.

Despite the rapid hydration of DHA [14] in our experiment, we found evidence of a reversible form, for direct voltammogram in accord with theoretical description. Consequently, the problem is to determine if the electrochemical process involves one or two electrons.

Let the functions representing the first members of Eqs. (10) and (11) be denoted by  $\Phi_1(\eta, |v|)$ ,  $\Phi_n(\eta, |v|)$ . Then, the performing of the experimental data in order to estimate the diffusion coefficient  $D$ , may be made in two ways. Indeed, suppose that one does not know if the electrode reaction occurs with one electron, or with two

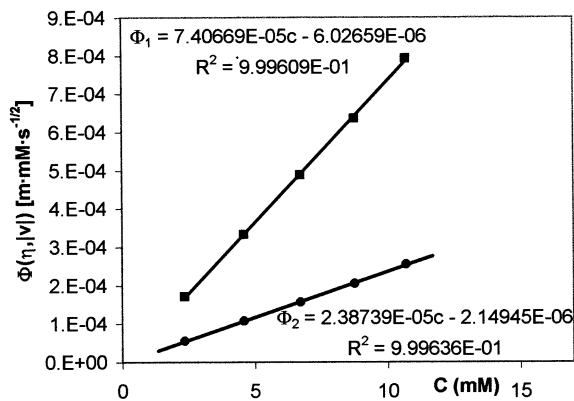


Fig. 2.  $\Phi(\eta, |v|)$  parameter versus  $c$  for peak currents.

electrons (when  $n = 2$ ). To decide, one applies the linear regression analysis to the plots  $\Phi_1(\eta, |v|)$  versus  $c$ , respectively  $\Phi_2(\eta, |v|)$  versus  $c$ , and one compares the correlation coefficients of the two linear dependences; then, the straight line with the best correlation coefficient will decide the value of  $n$  (and thus about the mechanism of the electrode reaction) and its slope will be taken as an estimate of the square root of the diffusion coefficient  $D$ .

The  $\Phi(\eta, |v|)$  plots versus  $c$  for peak currents was represented in Fig. 2.

From the slope of  $\Phi_2(\eta, |v|)$  versus  $c$  results a diffusion coefficient  $D = 5.7 \times 10^{-10} \text{ m}^2/\text{s}$  in good agreement with those reported in the literature [15,16]. All the numerical estimations underline the fact that electron transfer number is  $n = 2$ , generally accepted for the electrooxidation of ( $\text{HA}^-$ ). In these conditions, despite the presumptions found in references, the reversibility mechanism remain to be studied.

Another way of estimating the diffusion coefficient  $D$  is based on the observation that the quotients  $\Phi_1(\eta, |v|)/c$  and  $\Phi_n(\eta, |v|)/c$ , represent two invariants whose mean values estimate  $\sqrt{D}$ ; then, by comparing the standard deviations of this two mean values, one may derive the values of  $n$  and  $\sqrt{D}$  (the criterion being the smallest standard deviation).

As for estimating an unknown concentration  $c$ , one uses the calibration line  $\Phi_n(\eta, |v|)$  versus  $c$ , obtained by the procedure indicated above; from the experimental voltammogram one chooses a pair

of values  $(\eta, j)$  and because  $n$  and  $|v|$  are known, one calculates the value of  $\Phi_n(\eta, |v|)$ , and by using the calibration line will result an estimate of  $c$ .

#### 4. Conclusions

We have proposed a new method of voltammetry with linear scanning of the potential whose theoretical support satisfies the first case of Fredholm alternative. The resulted explicit equation of voltammograms is in a good agreement with the experimental data and permitted the determination of the diffusion coefficient, or concentration.

The numerical estimations underline the fact that electron transfer number in electrooxidation is  $n = 2$  and the diffusion coefficient  $D = 5.7 \times 10^{-10} \text{ m}^2/\text{s}$ .

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