Review

Analytical solutions for fast and straightforward study of the effect of the electrode geometry in transient and steady state voltammetries: Single- and multi-electron transfers, coupled chemical reactions and electrode kinetics

A. Molina [a,*], J. González [a], E. Laborda [a], R.G. Compton [b,*]

[a] Departamento de Química Física, Facultad de Química, Regional Campus of International Excellence "Campus Mare Nostrum", Universidad de Murcia, 30100 Murcia, Spain
[b] Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

ARTICLE INFO

ABSTRACT

We survey recently-reported, analytical solutions for the study of simple and complicated charge transfer reactions by means of any voltammetric technique with electrodes of very different geometries under conditions where the mass transfer takes place only by diffusion, that is, in fully-supported media where migration can be neglected. Under transient conditions, expressions are reported for one-electron and multi-electron reversible transfers, electrode reactions coupled to homogeneous chemical equilibria and the first-order catalytic mechanisms with electrodes of any geometry.

The steady-state voltammetric response of the above systems will also be considered at submicro- and nanoelectrodes of very different shapes and arrays. Also, a universal approach to the steady-state voltammetry of sluggish electron transfer processes is presented. Finally, solutions for ion transfer processes across (sub)micrometric liquid|liquid interfaces is discussed.

© 2015 Elsevier B.V. All rights reserved.

Contents

* Corresponding authors.
    E-mail addresses: amolina@um.es (A. Molina), richard.compton@chem.ox.ac.uk (R.G. Compton).

1. Introduction

Having at our disposal mathematically analytical equations and solutions for physico-chemical and electrochemical problems is essential for multiple reasons. First, once no approximations are employed for their deduction, analytical solutions provide us with rigorous description of the system in the full range of values of experimental variables. Also, the behavior of the system can be analyzed and predicted directly from closed-form expressions. This enables the identification of the key variables and their influence on the electrochemical response as well as of particular and limit cases and the conditions under which these can be attained (such as steady state conditions). Finally, generally speaking, analytical expressions are easier to compute than numerical methods and the calculations are less time-consuming and computer-demanding. Indeed, analytical solutions are employed to test the accuracy of numerical simulations [1–7].

In recent years we have reported analytical expressions for the response of fundamental electron transfer processes in multipulse voltammetric techniques under transient and steady state regimes [8–17]. Particular attention has been paid to the most widely employed methods (namely, cyclic voltammetry [18,19] and square wave voltammetry [20]) and to the use of disk and hemispherical microelectrodes. The former are ubiquitous in experimental studies given their easy fabrication and cleaning and the reduction of distorting effects with respect to macroelectrodes [18,19,21–26]. However, the modeling of the electrochemical response at microdisks is not straightforward and it has been almost exclusively performed by means of sophisticated numerical methods.

Within the above context, the aim of this work is to review simple, analytical solutions such that any electrochemist can get insight into the voltammetry of fundamental systems that can also act as starting point of more complex situations, as well as to predict and characterize the influence of major factors. In order to define the physico-chemical problem clearly, as well as the conditions under which the theoretical solutions apply, the differential equation system and boundary value problem of each system will also be analyzed in detail. This leads to suitable procedures and simplifications to tackle the original mathematical problem more easily. The results presented can also be employed to test numerical methods.

First, the voltammetry of one-electron reversible electron transfers in one- and two-dimensional systems will be considered under transient conditions. These cases enable us to obtain the electrochemical response at electrodes of different geometries, from macroelectrodes, where diffusion is linear, to microelectrodes where convergent diffusion is significant. Also, the situation where the diffusivity of the electroactive species differs significantly will be tackled at macroelectrodes.

Next, more complex cases will be addressed where the reactivity and transport of more than two electroactive species must be considered, such as reversible multi-electron transfers (Section 2.2) and electrode reactions complicated by homogeneous chemical equilibria (Section 2.3). The voltammetric response is affected by the relative stability of the different chemical species resulting from (electro)chemical transformations either at the electrode surface or in solution. The first-order catalytic mechanism (Section 2.4) will introduce the issue of coupled, chemical-diffusive equation systems that can be challenging in numerical simulations in terms of problem-solving methodology as well as of run-time when very fast reactions take place [1,27].

Finally, the steady state response at micro- and submicroelectrodes of very different geometries and their arrays will be studied. Apart from the electrochemical systems above-mentioned, a general and accurate theoretical approach for sluggish electrode processes under steady state conditions will be discussed.

2. Voltammetric response under transient conditions

2.1. Nernstian one-electron transfers

2.1.1. Equal diffusion coefficients

Let us consider the case of a fast one-electron transfer where both electroactive species are stable within the timescale of the measurements and they do not take part in chemical reactions in solution (the so-called E mechanism):

$$O + e^- \rightleftharpoons R \quad E^{0'} \qquad \text{(Scheme I)}$$

where $E^{0'}$ is the formal potential of the redox couple O/R. Taking into account that in most electrochemical experiments,[1] semi-infinite diffusion is the only active mass transport mechanism and that in conventional solvents the diffusion coefficients of O and R are usually very similar ($D_O = D_R = D$), the variation of the species concentrations when applying a potential-controlled perturbation ($E(t)$) is described by Fick's second law:

$$\begin{aligned} \hat{\delta} c_O = 0 \\ \hat{\delta} c_R = 0 \end{aligned} \qquad (1)$$

with the following boundary value problem corresponding to a reversible electrode reaction:

$$\left. \begin{array}{l} t = 0, \ q \geq q_{\text{surface}} \\ t > 0, \ q \to \infty \end{array} \right\} \quad c_O(q,t) = c_O^*, \quad c_R(q,t) = c_R^* \qquad (2)$$

$$t > 0, \ q = q_{\text{surface}} : D\left(\frac{\partial c_O}{\partial q_N}\right)_{q=q_{\text{surface}}} + D\left(\frac{\partial c_R}{\partial q_N}\right)_{q=q_{\text{surface}}} = 0 \qquad (3)$$

$$c_O(q_{\text{surface}}) = c_R(q_{\text{surface}}) \exp\left(\frac{F}{RT}\left(E - E^{0'}\right)\right) \qquad (4)$$

where $\hat{\delta}$ is the diffusion operator given in Table 1, q_{surface} refers to the values of the spatial coordinates (q) at the surface of the electrode and q_N is the spatial coordinate normal to the electrode surface.

From Eqs. (1)–(3), it is concluded that when the diffusion coefficients of the participating species are equal, the total concentration of electroactive species does not vary with time and it is the same at any point in solution:

$$c_O(q,t) + c_R(q,t) = c_O^* + c_R^* \quad \forall q, \ t. \qquad (5)$$

Note that Eq. (5) holds *independently of* the reversibility of the electron transfer process and the geometry of the electrode (i.e., the form of the diffusion operator $\hat{\delta}$). Furthermore, when the electrode reaction is reversible, it can be deduced from Eqs. (4) and (5) that the surface concentrations are time-independent and their values are defined by the value of the applied potential, E_k, as follows:

$$\begin{aligned} c_O(q_{\text{surface}}) = c_O^{(k),s} = \frac{e^{\eta_k}\left(c_O^* + c_R^*\right)}{1 + e^{\eta_k}} \\ c_R(q_{\text{surface}}) = c_R^{(k),s} = \frac{c_O^* + c_R^*}{1 + e^{\eta_k}} \end{aligned} \qquad (6)$$

where:

$$\eta_k = \frac{F\left(E_k - E^{0'}\right)}{RT}. \qquad (7)$$

---

[1] This is valid for typical time-scales of the perturbation (<10 s) and volume of electrochemical cells (much larger than the depletion layer). Otherwise, mass transport by convection in very long experiments and thin layer effects must be considered, respectively.