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Fernando Garay

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Although square-wave voltammetry (SWV) is a technique mostly used for analytical purposes, its intrinsic sensitivity to the kind of electrode reaction merges facts related to fundamental studies with those expected from analytical applications. In this regard, analytical studies could be significantly improved with adequate knowledge about the reaction mechanism. On the other hand, it might be difficult to explain some anomalous behaviors such as the lack of linearity between the peak current and concentration if some mechanistic aspects were not considered.

This book provides a wide collection of data for the description of diverse tendencies that characterize several electrochemical reactions analyzed by SWV. Numerous experimental conditions are suggested for determining the kind of mechanism involved and thus, the most suitable SW parameters for the analyses of that sample. Theoretical frameworks are used to support and explain the characteristics of each mechanism. In all cases, solutions are reached by employing Laplace transforms and numerical integration methods. Several SW voltammograms, including the forward, backward, and net currents, are shown. They are useful to understand the behavior of variables such as the net peak current (ΔI_p) on parameters like frequency (f) or SW amplitude (E_{sw}). The chapters are organized into three parts: introduction to SWV, electrode mechanisms, and applications.

The introduction encloses experimental, theoretical, and instrumental facts about SWV that help to understand the further discussion. In SWV, a rather reversible redox species that is close to the electrode surface can change

its redox state several times during a single scan, since the oxidizing and reducing steps are separated by the few milliseconds of a single SW period. This is a significant difference between SWV and cyclic voltammetry, which is the major reason for complementing the results of both techniques. On the other hand, a detailed mathematical resolution for the case of kinetically controlled heterogeneous charge transfer reactions is provided in this chapter. This example shows how Laplace transforms and numerical integration methods can be used to find solutions of a given electrochemical system. Another full resolution is given at the end of the book for the case of a thin-layer cell.

The topic related to electrode mechanisms is presented through a significant set of reaction schemes that involve more than 120 pages of the book. The reactions are organized in two big groups depending on the possibility of adsorption of electroactive species.

In the first group, the discussion is focused on reaction mechanisms where species are exclusively in solution. Systems under linear, spherical, or limited diffusion are analyzed. Hanging mercury drop electrodes (HMDE) and thin-film electrodes are extensively used in analyses of anodic stripping SWV. In this regard, only microelectrodes with $r_o < 50 \mu\text{m}$ would show spherical effects in SWV, and standard HMDE will not exhibit this effect. On the other hand, even though factors of preconcentration are higher for the thinner mercury films, analytes with reversible redox reactions are oxidized at the very beginning of the pulses, and relatively minor oxidative currents can then be recorded. The authors discuss quite a lot about these counterbalanced effects and how ΔI_p would behave depending on the film thickness and f .

Electrode reactions coupled with homogeneous chemical reactions are also considered in this group. Several metal complexes can be described as CE or EC reactions, while

F. Garay (✉)
Department of Biomedical Engineering, 330 Engineering
Technology, The University of Memphis,
Memphis, TN 38152, USA
e-mail: fgaray@fcq.unc.edu.ar

the presence of some reagents can provide catalytic effects that could be described by an EC' reaction mechanism. The authors offer several dependencies that could be useful for a qualitative analysis of these systems. Unfortunately, it is practically impossible to include quantitative results for systems where the chemical reaction and the electrode kinetics are quasireversible. In such cases, the fitting of experimental curves is required, since there is no simple expression to relate the dependence of ΔI_p or E_p on experimental available parameters such as f or E_{sw} .

The second big group involves reaction schemes with adsorbed species. Usually, symmetrical bell-shaped peaks are associated with a reversible charge transfer reaction where both electroactive species are adsorbed. Nevertheless, a negligible faradaic current should be observed if SWV were used for measuring this kind of electrochemical system. This is a very important difference between the responses of techniques such as normal cyclic voltammetry and those where the current sampling is performed at the end of potential pulses. Therefore, the maximal current responses will be mostly related to electrochemical reactions with quasireversible kinetics if adsorbed species are involved. In order to study some kinetic properties of these reactions, it is suggested to evaluate the dependence of $\Delta I_p/f$ on f . If such dependence shows a maximum, then the value of f at the *quasireversible maximum* can be used to estimate the charge transfer rate constant (k_s) of this reaction. Moreover, the presence of the quasireversible maximum can be used to estimate k_s of diverse reaction mechanisms that involve adsorbed species and have quasireversible charge transfer.

The authors describe two particular kinds of surface electrode reactions. The simplest situation is for reactions in which both electroactive species are adsorbed at the electrode but are not in the solution. There are several tendencies such as the quasireversible maximum or the splitting of peaks of the net current that are useful to predict and describe thermodynamic properties of reactions involving this electrode mechanism. Many organic molecules can be extracted as adsorbed species and then analyzed in aqueous solution where those species cannot dissolve. Under these boundary conditions, it is even possible to go further with the mathematical equations and to evaluate other reaction schemes, in which the influence of different adsorption isotherms or coupled chemical or electrochemical reactions are present. Unfortunately, there is no precise dependence between ΔI_p or E_p and experimentally controlled parameters to characterize these last systems. Consequently, simulation and fit of experimental curves are required to determine the thermodynamic constants that would characterize the more complex mechanisms.

The second kind of surface electrode reactions is related to systems where the redox species can be adsorbed at the

electrode as well as be present in solution. Since adsorption properties can be associated with one or both reagents, there are several experimental situations that can be described by this sort of model. The models presented in this part can be used for simulating systems where only a submonolayer of electroactive species is present, i.e., controlled by linear adsorption isotherms. Accordingly, numerous reaction schemes normally found in trace analysis fulfill these boundary conditions. Under such circumstances, it is possible to study some thermodynamic properties by using relatively simple strategies, like the quasireversible maximum or the split of net peak current. However, in order to simplify the study of experimental results, it is valuable to include an accumulation step that involves the adsorption of one reagent. Other more complicated reaction schemes involving different kinds of coupled chemical reactions are described in the book. The authors include different tendencies that would be useful for qualitative analysis of experimental systems. However, a more quantitative approach would require the simulation and fit of experimental curves.

Around 250 references have been selected for the chapter of applications; however, there are many others included as examples in previous chapters. The applications might be divided in four parts: quantitative analysis in diverse media, qualitative identification of insoluble compounds, mechanistic studies, and evaluation of ion transfer across liquid–liquid interfaces. The last subject is an amazing application of SWV that, at the same time, merges all the other uses. Interfaces between two immiscible electrolyte solutions (ITIES) represent a very wide and novel field to study by pulsed techniques like SWV. Commonly, the very resistive solutions can be a significant problem to deal with when the potential changes too fast or, in other words, when potential pulses are applied. Nevertheless, this inconvenience can be minimized if the organic solution of liquid–liquid interfaces is limited to a thin film that covers the electrode surface. In this way, the experimental setup is significantly simpler, and the interface becomes more stable than for the typical four-electrode arrangement. Moreover, the responses of backward scans can be more simply analyzed than for some cyclic voltammetric studies, and thus, complementary information can be obtained. Qualitative identification and quantitative analysis can be performed from the values of E_p and ΔI_p . However, since the value of E_p is usually not well known, mechanistic examination is usually required for these systems. Experimental curves can also be simulated to estimate kinetic parameters of a system. In this regard, an outcome equivalent to the previously described quasireversible maximum can be observed for the case of thin-film electrodes, and a simpler kinetic determination can be achieved.

In summary, the book is highly recommended for researchers and research students who are interested in working with SWV. The authors are some of the foremost experts on the computation and experimental studies about this technique, and the readers will find a significant number of expected behaviors that will simplify the

understanding and characterization of different experimental systems. On the other hand, although some computational skills could be required to resolve the included equations, the authors provide an excellent introduction for anybody interested in the simulation of voltammetric curves.