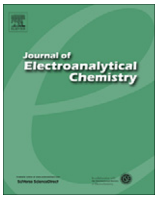
Journal of Electroanalytical Chemistry 683 (2012) 1–13

Contents lists available at SciVerse ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem



Cyclic voltammetry in the absence of excess supporting electrolyte: The effect of analyte charge

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ARTICLE INFO

Article history:
Received 5 June 2012
Received in revised form 12 July 2012
Accepted 17 July 2012
Available online 31 July 2012

Keywords:
Hemisphere
Microelectrode
Migration
Self support
Simulation
Weak support

ABSTRACT

The cyclic voltammetry of the simple electrochemically reversible reduction, $A^{Z_A} + ne^- \rightleftharpoons B^{Z_B}$, is modelled using numerical simulations. The effect of adding different concentrations of supporting electrolyte is studied as a function of the scan rate, the diffusion coefficients of species A and B and the diffusion coefficients of the ions in the supporting electrolyte. These studies cover the following Z_A/Z_B redox couples: 2/1, −1/−2, 8/7, and −7/−8. The supporting information contains a table listing the minimum concentration of supporting electrolyte required to achieve fully supported voltammetry pertaining to a range of scan rates ($10^{-1} \leqslant \frac{Fvr_e^2}{D_A RT} \leqslant 10^5$); a wide range of charges of the electroactive species ($-7 \leqslant Z_A \leqslant 8$) and includes both one and two electron transfer. This allows experimental conditions to be defined so that any particular Nernstian electrochemical system may be studied under diffusion-only conditions without the need for additional experiments and/or simulations.

1. Introduction

Since the publication of Nicholson and Shain's landmark paper of 1964 [1], cyclic voltammetry has evolved into one of the most widely used and useful techniques in analytical chemistry. The experiments are relatively simple yet can provide fundamental information for a spectrum of chemical systems. Diverse applications have been found and range from chemical sensors [2–5] to the use as an experimental probe with which to investigate the electrocatalytic properties of nanoparticles [6] or the various theories of electron transfer [7].

Two modes of mass transport operate in a quiescent solution: diffusion and migration [8,9]. Although it is possible, and in some cases necessary [10,11], to conduct voltammetry in the presence of both, so-called 'diffusion-only' conditions are generally preferred because the experiments are easily reproducible and can be quantified by fast, accurate numerical modelling [12].

When the potential applied at the working electrode is changed, electrolysis occurs and a net charge is formed in solution. The charge is dissipated by migration between the working and counter electrodes. Resistance to this flow of current leads to the establishment of a potential gradient across the solution. The potential available to drive electrolysis at the working electrode is correspondingly diminished: the difference is called 'ohmic drop'. Electrolysis therefore establishes concentration and potential gradients along which chemical species diffuse and migrate respectively. The potential gradient leads to two main qualitative differences in the voltammetry compared to diffusion-only conditions: first, the peak to peak separation is greater because the applied potential at which the electrode kinetics outrun mass transport is offset by ohmic drop; secondly, the peak heights are distorted because mass transport is augmented (either positively or negatively) by the migration of ions along the potential gradient.

Diffusion-only conditions must be attained by adding a large quantity of inert salt, so-called 'supporting electrolyte', to the solution [13–18]. As the resistivity of the solution decreases, the potential gradient decreases and becomes increasingly confined to the surface of the working electrode. In practice, experimentalists need only add sufficient supporting electrolyte to compress the potential gradient to within *ca* 20 Åof the working electrode [9,19]. In this situation, voltammetry is purely diffusional because the electrons "bypass" the potential gradient by quantum mechanical tunneling [9,20].

In cases where diffusion-only conditions are assumed, it is imperative that sufficient supporting electrolyte be present. For example, if the potential gradient was naively ignored, a large peak to peak separation, derived from an appreciable ohmic drop, might erroneously be ascribed to a low electrochemical rate constant. As a general rule, voltammetric experiments can be considered purely diffusional when the concentration of supporting electrolyte exceeds 100 times that of the electroactive species [21]. However, this value, often called the 'support ratio', is known to vary according to the experimental conditions. For example, the support ratio required to

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http://dx.doi.org/10.1016/j.jelechem.2012.07.023

achieve purely diffusional steady-state voltammetry is known to be more forgiving than in the corresponding transient cases [22].

In this paper, the cyclic voltammetry of the reduction, $A^{Z_A} + ne^- \rightleftharpoons B^{Z_B}$ $(1 \leqslant n \leqslant 2)$, assumed to be electrochemically reversible, is studied using numerical simulations. The effect of adding different concentrations of supporting electrolyte is studied as a function of the scan rate, the diffusion coefficient of species B and the diffusion coefficients of the ions in the supporting electrolyte. These studies cover the following Z_A/Z_B redox couples: 2/1, −1/−2, 8/7, and −7/−8. This paper extends Dickinson's et al. [21] work on unsupported systems of relatively low ion charge ($A^{3+} + e^- \rightleftharpoons B^{2+}$ and $A^+ + e^- \rightleftharpoons B^0$) in three ways. First, a fuller range of charges of the electroactive species are considered (see Section 2.1 for a definition of the charge range used). Secondly, both one and two electron transfers are studied. Thirdly, a comprehensive supporting information is included which tabulates the minimum concentration of supporting electrolyte required to achieve fully supported voltammetry. The data is pertaining to a range of scan rates $(10^{-1} \leqslant \frac{F v r_e^2}{D_A RT} \leqslant 10^5)$ and a range of charges of the electroactive species (see Section 2.1 for a definition of the charge range used) and for both one electron and concurrent two electron transfer ($n = 1$or2 respectively). This allows experimental conditions to be defined so that any particular Nernstian electrochemical system may be studied under diffusion-only conditions without the need for additional experiments or simulations.

2. Theory

In this section, the type of experiment studied is explained and cast in mathematical form. The method of numerical simulation is also described. All symbols are defined in Tables 1 and 2.

2.1. Reaction mechanism

We consider a solution containing an electroactive species, A, of charge Z_A, which is capable of undergoing a n electron reduction to form species B, of charge Z_B. The process is entirely heterogeneous and takes place at an inert hemispherical electrode.

$$A^{z_A} + ne^- \rightleftharpoons B^{z_A - n} \tag{1}$$

Species A is accompanied by an inert, monovalent, counterion, X^-, and the solution is supported by a monovalent 1:1 inert salt, M^+X^-. Three further assumptions are made: first, the magnitude of the highest charge, Z_A, is 8; secondly, the maximum number of electrons transferred in the electrochemical process is 2; finally, ion pairing is completely absent. This leads to 16 permissible combinations of Z_A, Z_B and n. Note that ions of high charge, such as dendrimers, can exist without substantial ion pairing [19].

Table 1
List of parameters.

Real parameter	Definition
c_A	Concentration of species A (mol m^{-3})
$c_{A,0}$	Surface concentration of species A (mol m^{-3})
c_A^*	Bulk concentration of species A (mol m^{-3})
D_A	Diffusion coefficient of species A (m^2 s^{-1})
ϵ_0	Permittivity of free space ($= 8.85 \times 10^{-12}$) (F m^{-1})
ϵ_r	Relative permittivity (unitless)
E	Applied potential (V)
$E^0_{f,A/B}$	Formal reduction potential of A/B redox couple (V)
i	Current (A)
j	Flux (mol m^{-2} s^{-1})
ϕ	Potential (V)
$\Delta\phi$	Loss in driving force for the electrochemical reaction (V)
r	Radial coordinate (m)
r_e	Radius of the electrode (m)
r_{max}	Maximum value of r (m)
t	Time (s)
v	Scan rate ($= \lvert\frac{\partial E}{\partial t}\rvert$) (V s^{-1})
z_A	Charge of species A (unitless)

Table 2
List of normalised parameters.

Normalised parameter	Definition
C_A	$\frac{c_A}{c_A^*}$
$C_{A,0}$	$\frac{c_{A,0}}{c_A^*}$
J	$\frac{i}{2\pi F c_A^* D_A r_e}$
θ	$\frac{FE}{RT}$
θ_f	$\frac{FE_f^0}{RT}$
$\Delta\theta$	$\frac{F\Delta\phi}{RT}$
R	$\frac{r}{r_e}$
R_e	$r_e\sqrt{\frac{F^2 c_A^*}{RT\epsilon_s\epsilon_0}}$
σ	$\frac{r_e^2 F}{D_A RT}\lvert\frac{\partial E}{\partial t}\rvert$
τ	$\frac{D_A t}{r_e^2}$

2.2. Experiment

The reaction described in Section 2.1 is studied using cyclic voltammetry. The applied potential, E, varies as a function of time, t, according to:

$$E = \lvert -vt + E_{start} - E_{vertex}\rvert + E_{vertex} \tag{2}$$

where E_{start} and E_{vertex} are the starting and vertex potentials respectively.

2.3. Mathematical formulation

The concentration of each species varies in space and time according to the Nernst–Planck (NP) equation for mass transport in a hemispherical coordinate system:

$$\frac{\partial c_A}{\partial t} = D_A\left(\frac{\partial^2 c_A}{\partial r^2} + \frac{2}{r}\frac{\partial c_A}{\partial r}\right) + D_A z_A\left(\frac{\partial c_A}{\partial r}\frac{\partial \phi}{\partial r} + c_A\frac{\partial^2 \phi}{\partial r^2} + c_A\frac{2}{r}\frac{\partial \phi}{\partial r}\right)$$

$$\frac{\partial c_B}{\partial t} = D_B\left(\frac{\partial^2 c_B}{\partial r^2} + \frac{2}{r}\frac{\partial c_B}{\partial r}\right) + D_B(z_A - n)\left(\frac{\partial c_B}{\partial r}\frac{\partial \phi}{\partial r} + c_B\frac{\partial^2 \phi}{\partial r^2} + c_B\frac{2}{r}\frac{\partial \phi}{\partial r}\right)$$

$$\frac{\partial c_M}{\partial t} = D_M\left(\frac{\partial^2 c_M}{\partial r^2} + \frac{2}{r}\frac{\partial c_M}{\partial r}\right) + D_M z_M\left(\frac{\partial c_M}{\partial r}\frac{\partial \phi}{\partial r} + c_M\frac{\partial^2 \phi}{\partial r^2} + c_M\frac{2}{r}\frac{\partial \phi}{\partial r}\right)$$

$$\frac{\partial c_X}{\partial t} = D_X\left(\frac{\partial^2 c_X}{\partial r^2} + \frac{2}{r}\frac{\partial c_X}{\partial r}\right) + D_X z_X\left(\frac{\partial c_X}{\partial r}\frac{\partial \phi}{\partial r} + c_X\frac{\partial^2 \phi}{\partial r^2} + c_X\frac{2}{r}\frac{\partial \phi}{\partial r}\right)$$

Each equation consists of two terms: the first quantifies diffusion while the second quantifies migration. This system of four independent equations contains five unknowns: the concentration for the each of the four species (c_A, c_B, c_M and c_X) and an additional term for the potential (ϕ). Consequently, the description of the problem is incomplete and a further relationship must be introduced. For this purpose, the Poisson equation is invoked:

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r}\frac{\partial \phi}{\partial r} = -\frac{F}{\epsilon_r\epsilon_0}\sum_s z_s c_s \tag{3}$$

This relationship follows from Maxwell's equations; however, many workers have attempted to simplify the problem by invoking, instead, the electroneutrality approximation

$$0 = -\frac{F}{\epsilon_r\epsilon_0}\sum_s z_s c_s \tag{4}$$

The electroneutrality equation is well obeyed because the Gibb's energy of the heterogeneous process is insufficient to overcome