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Integral equation-based simulation of transient experiments for an EC_2 mechanism: beyond the steady state simplification

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Abstract

Transient electrochemical experiments are usually described theoretically by systems of reaction-diffusion partial differential equations. Converting them to integral equations is a classical and valuable modelling approach. Unfortunately, if any reaction-diffusion equation contains nonlinear reaction rate terms, up to now such a conversion has only been possible by assuming a steady state for the equation. Consequently, only sufficiently fast homogeneous reactions could be handled. In this work a novel integral equation-based modelling approach is described. The steady state assumption is replaced by a two-term singular perturbation expansion of the concentration-flux relationship, recently published by the authors. The expansion is valid for homogeneous reactions of (integer) order $m \geq 1$, occurring at planar electrodes. An example simulation of cyclic voltammetry for an EC₂ reaction mechanism involving a second order dimerization reaction is performed. It is found that in this way the voltammograms can be satisfactorily simulated for homogeneous reaction rate constants smaller by about one order of magnitude than was previously possible.

Keywords: nonlinear reaction-diffusion; cyclic voltammetry; integral equations; singular perturbation; computational electrochemistry

1. Introduction

Transient electrochemical experiments [1] are usually described theoretically by systems of reaction-diffusion partial differential equations (PDEs), which may be either linear or nonlinear. For the solution of such equations a variety of modelling and simulation methods has been proposed over the past decades [2, 3].

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The improvement and further development of these methods becomes especially urgent in the era of computerization and automation of scientific investigations. Therefore, a relevant long-term research programme was initiated, that might be described under the general heading "computational electrochemistry" [4]. The present work is a continuation of this research programme.

A classical method of solving the reaction-diffusion PDEs in electrochemistry, applicable mostly to controlled-potential experiments [1], is known as the integral equation (IE) method [3]. It relies on determining concentration-flux relationships analytically for all chemical species of interest. The relationships are subsequently combined with boundary conditions at working electrodes, to yield IEs for the unknown fluxes (and/or the flux-related Faradaic current) at the electrodes. The IEs are then solved, usually numerically. The IE method is often more insightful, and also more efficient and more accurate than direct numerical solution methods for PDEs.

Consider, as a particularly important example, a spatially one-dimensional model of a planar working electrode immersed in a semi-infinite electrolytic solution, and located at the Cartesian coordinate x = 0. Let S be a chemical species subject to diffusion, and to an *m*th order irreversible homogeneous reaction in this electrolyte:

$$mS \xrightarrow{k} products.$$
 (1)

The concentration $c_{\rm S}(x,t)$ of S depends on the distance x from the electrode and on time t, and it obeys the PDE

$$\frac{\partial c_{\rm S}(x,t)}{\partial t} = D_{\rm S} \frac{\partial^2 c_{\rm S}(x,t)}{\partial x^2} - k \, c_{\rm S}(x,t)^m,\tag{2}$$

where $D_{\rm S}$ is the diffusion coefficient of S, and k is the rate constant of the reaction (1). If S is initially absent in the system, the initial condition is:

$$c_{\rm S}(x,0) = 0,$$
 (3)

and the boundary condition in the electrolyte bulk is

$$c_{\rm S}(\infty, t) = 0. \tag{4}$$

In a typical controlled-potential experiment the above initial equilibrium state is perturbed at t = 0, by applying some potential-time waveform to the working electrode. The resulting Faradaic current-time response is monitored and analysed. Conditions (3) and (4) imply that during such an experiment species S must be created at the electrode from other chemical species. Hence, apart from reaction (1), other (in particular heterogeneous electrochemical) reactions must occur within the system.

The IE method is relatively easily applied when the reaction-diffusion PDEs describing such experiments are linear. In the case of PDE (2) the linearity occurs only when reaction (1) is a (pseudo-)first order reaction, i.e. when m = 1. The concentration-flux relationship at the electrode is then obtainable in a straightforward way, by employing Laplace transforms (cf. Chapter 8.4 and

 $\mathbf{2}$

Appendix E.1 in [3] and references cited therein). The relationship obtained is of convolution type:

$$c_{\rm S}(0,t) = \int_0^t \frac{\exp\left[-k\left(t-\tau\right)\right]}{\left[D_{\rm S}\pi\left(t-\tau\right)\right]^{1/2}} \left[-D_{\rm S}\left.\frac{\partial c_{\rm S}(x,\tau)}{\partial x}\right|_{x=0}\right] \,\mathrm{d}\tau.$$
 (5)

The situation becomes much more difficult when the reaction (1) is of higher order (m > 1), in which case the PDE (2) is nonlinear. The Laplace transformation cannot be used in such cases. Thus far, the only way of tackling such nonlinearities in the IE method was to assume that (2) was in steady state. Under this assumption the concentration-flux relationship takes the form of a nonlinear algebraic equation (AE) (cf. Chapter 8.5 and Appendix E.4 in [3] and the references cited therein):

$$c_{\rm S}(0,t) = \left[\frac{m+1}{2} \left(kD_{\rm S}\right)^{-1}\right]^{\frac{1}{m+1}} \left[-D_{\rm S} \left.\frac{\partial c_{\rm S}(x,t)}{\partial x}\right|_{x=0}\right]^{\frac{2}{m+1}}.$$
 (6)

The assumption of the steady state relationship (6) is valid only when the rate constant k is sufficiently large, or (at least in some cases) when a sufficiently long time t has elapsed since the beginning of the experiment. The question of how the concentration-flux relationship for m > 1 looks when k is arbitrary (and especially when it is small), remains unanswered. However, in our recent study [5] we have shown that (6) can be interpreted as the first term of a singular perturbation expansion of such a general relationship, in the limit of large k, and we have presented a more general, two-term expansion:

$$\begin{bmatrix} -D_{\rm S} \left. \frac{\partial c_{\rm S}(x,t)}{\partial x} \right|_{x=0} \end{bmatrix} = (D_{\rm S}k)^{1/2} c_{\rm S}(0,t)^{\frac{m+1}{2}} \times \\ \left\{ \left(\frac{2}{m+1} \right)^{1/2} + \frac{1}{k c_{\rm S}(0,t)^m} \frac{\left[2 \left(m+1 \right) \right]^{1/2}}{m+3} \frac{\partial c_{\rm S}(0,t)}{\partial t} \right\}.$$
(7)

As is seen, in the limit of $k \to \infty$ the second term in braces in (7) vanishes, in comparison with the first term, so that (7) reduces to (6). The second term offers insights into the quantitative effect of large, but finite k, on the flux at x = 0. We see that at large finite k there is a departure from steady state, and the related correction to the flux at x = 0 is proportional to $(D_{\rm S}/k)^{1/2} c_{\rm S}(0,t)^{\frac{1-m}{2}} \partial c_{\rm S}(0,t)/\partial t$. As one might have expected, the correction involves $\partial c_{\rm S}(0,t)/\partial t$: in the steady state limit there should be $\partial c_{\rm S}(x,t)/\partial t = 0$.

In the present study we investigate the performance of the formula (7), when applied to an example IE-based model of an electroanalytical experiment, involving a nonlinear PDE (2). We also compare such simulations with those using (6). The example considered is the model of cyclic voltammetry (CV) [1] at a planar working electrode, for the EC_2 reaction mechanism:

$$\mathbf{A} + \mathbf{n}\mathbf{e}^{-} \rightleftharpoons \mathbf{B},\tag{8}$$

$$2B \xrightarrow{\kappa} P$$
 (9)

involving a heterogeneous electrochemical (E) reaction (8) and a follow-up irreversible homogeneous chemical (C) dimerization reaction (9). Mechanism (8) and (9) is probably the simplest one on which (7) can be tested. However, it is of considerable interest to organic electrochemistry, since dimerization often accompanies free radical formation [6]. Examples of studies where this mechanism (and its somewhat more general variant involving a reversible dimerization) was identified, are in [7–13]. This list of references is not intended to form an exhaustive review. Many more references could be added, describing electrochemical systems in which reactions (8) and (9) are accompanied by additional electrochemical and homogeneous chemical reactions.

To avoid potential misunderstandings, we stress that our study has a theoretical and partially mathematical and computational character. We focus on the goal clearly specified above. We do not strive to obtain and discuss complete numerical solutions for CV responses for the mechanism (8) and (9), in the entire conceivable ranges of model parameter values. We also do not aim to obtain theoretical procedures that might serve for parameter estimation utilizing experimental results. A Reader interested in such issues can be directed to former studies of CV for the EC₂ mechanism [8, 14, 15].

2. Theory

We assume that the reaction (8) is quasi-reversible and subject to the Butler-Volmer model of electrochemical reaction rates [1], whereas reaction (9) is irreversible and of second order (m = 2). Species A and B are subject to diffusional transport in an electrolyte. Following the frequent simplification, their diffusion coefficients are assumed to be equal. The product P of reaction (9) is electroinactive and in view of the irreversibility of reaction (9) its specific behaviour has no effect on the concentrations of A and B, and on the Faradaic current.

A theoretical IE-based model of linear potential sweep voltammetry (LSV) for reactions (8) and (9), satisfying the above assumptions, was earlier considered by Nadjo and Savéant [16], by employing the IE formalism combined with the steady state relationship (6). In addition, IE-based models of LSV for a reversible reaction (8) followed by reaction (1) with arbitrary m, or with m = 2, were considered by Savéant and Vianello [17, 18] and Nicholson [19], also using the steady state relationship (6). In the present work we prefer not to assume the reversibility of reaction (8), since in such a case a singularity of the Faradaic current is expected at the initial time moment, which is an unwanted (although not insurmountable, see e.g. [20]) complication for the numerical solution of IEs. In [17–19] a single (forward) potential sweep was considered only, and we are not aware of any IE-based modelling studies of CV for the above system. Owing to the nonlinearity of the governing PDEs, other investigators resorted to direct numerical PDE solution methods [2] while modelling CV experiments for this system [8, 14, 15, 21].

The electroanalytical experiment to be considered is described by the following initial-boundary value problem, where all variables and parameters are in a suitable dimensionless form. Specifically, concentrations are normalized by the initial concentration c^* of species A. Time is normalized by $t_{\text{norm}} = \frac{RT}{nFv}$, where F is the Faraday constant, R is the gas constant, T is the absolute temperature, and v is the rate of the potential sweep. The space coordinate is normalized by $(Dt_{\text{norm}})^{1/2}$, where D is the common diffusion coefficient. The rate constant k of reaction (9) is normalized by $(c^*t_{\text{norm}})^{-1}$, and rate constants of reaction (8) are normalized by $(D/t_{\text{norm}})^{1/2}$.

With such normalizations, the partial differential equations are:

$$\frac{\partial c_{\rm A}(x,t)}{\partial t} = \frac{\partial^2 c_{\rm A}(x,t)}{\partial x^2},\tag{10}$$

$$\frac{\partial c_{\rm B}(x,t)}{\partial t} = \frac{\partial^2 c_{\rm B}(x,t)}{\partial x^2} - \kappa \, c_{\rm B}(x,t)^2. \tag{11}$$

where x and t now denote the dimensionless spatial and time coordinates, respectively, $c_{\rm A}(x,t)$ and $c_{\rm B}(x,t)$ are unknown dimensionless concentrations of species A and B and κ is the dimensionless rate constant k. Comparison of (2) and (11) reveals that species B is now an instance of species S in (1)-(7).

Initial conditions corresponding to t = 0 are:

$$c_{\rm A}(x,0) = 1,$$
 (12)

$$c_{\rm B}(x,0) = 0,$$
 (13)

whereas boundary conditions in the electrolyte bulk and at the electrode surface are:

$$c_{\mathcal{A}}(\infty, t) = 1, \tag{14}$$

$$c_{\rm B}(\infty, t) = 0, \tag{15}$$

$$\frac{\partial c_{\rm A}(x,t)}{\partial x}\Big|_{x=0} + \left. \frac{\partial c_{\rm B}(x,t)}{\partial x} \right|_{x=0} = 0, \tag{16}$$

$$\kappa_{\rm f} c_{\rm A}(0,t) - \kappa_{\rm b} c_{\rm B}(0,t) = \left. \frac{\partial c_{\rm A}(x,t)}{\partial x} \right|_{x=0}.$$
(17)

In (17) $\kappa_{\rm f}$ and $\kappa_{\rm b}$ are the dimensionless rate constants of the heterogeneous charge transfer reaction (8), obeying the Butler-Volmer equation. In the case of CV $\kappa_{\rm f}$ and $\kappa_{\rm b}$ depend on time:

$$\kappa_{\rm f} = \kappa^0 \exp\left\{-\alpha \left[u - \sigma \left(t, t_{\rm s}\right)\right]\right\} \tag{18}$$

$$\kappa_{\rm b} = \kappa^0 \exp\left\{ (1 - \alpha) \left[u - \sigma \left(t, t_{\rm s} \right) \right] \right\},\tag{19}$$

where κ^0 is the dimensionless conditional rate constant, α is the charge transfer coefficient,

$$u = \frac{\mathrm{n}F}{RT} \left(E_{\mathrm{start}} - E^0 \right), \qquad (20)$$

and $\sigma(t, t_s)$ denotes a single cycle of the saw-tooth function:

$$\sigma\left(t, t_{\rm s}\right) = \begin{cases} t & \text{for } t \le t_{\rm s} \\ 2t_{\rm s} - t & \text{for } t > t_{\rm s} \end{cases}$$
(21)

In (20) and (21) $E_{\rm start}$ denotes the starting potential of the potential sweep, E^0 is the conditional potential of reaction (8), and $t_{\rm s}$ is the dimensionless time at which the direction of the potential sweep is reversed. The quantity $u - \sigma(t, t_{\rm s})$ can be perceived as a dimensionless electrode potential.

One should keep in mind that the dimensionless variables $x, t, \kappa, \kappa_{\rm f}, \kappa_{\rm b}, \kappa^0$ and $t_{\rm s}$ all depend on the potential sweep rate v, through the normalizing factor $t_{\rm norm}$.

The dimensionless Faradaic current associated with the reaction (8) is defined here as

$$i(t) = \left. \frac{\partial c_{\rm A}(x,t)}{\partial x} \right|_{x=0}.$$
 (22)

In view of the normalizations adopted, this definition is equivalent to the standard definition [22] of the voltammetric current function $\pi^{1/2}\chi(t)$ for reversible and quasi-reversible charge transfers. Theoretical determination of the current is of primary interest in electrochemistry, since the current is measured experimentally, whereas concentrations cannot normally be measured. However, since in the present work we are interested in testing the theoretical relationships between i(t) and the boundary concentration $c_{\rm B}(0, t)$, we shall pay attention to both variables.

2.1. Reference solutions

Reference solutions for i(t) and $c_{\rm B}(0,t)$, enabling a validation of IE models are needed. Analytical solutions are not available. Therefore, (10)-(17) were solved numerically by the finite-difference method of lines, using uniform temporal and spatial grids. For the temporal integration the third order accurate Rosenbrock ROWDA3 scheme of Roche [23] for differential-algebraic equations was used, except for the first time step, where the second order accurate extrapolated implicit Euler method was applied (see [21, 24] for details and more references). The spatial discretization was performed using the fourth order accurate Numerov scheme [25] (see also [26] for more details and references), and the current (22) was evaluated by the fourth order accurate three-point compact formula for the first spatial derivative [27]. The semi-infinite interval of x was replaced by a finite interval, according to the usual rules [2].

Reference CV responses were obtained for $\kappa^0 = 0.1$, 1 and 10, $\alpha = 0.5$, u = 8and $\kappa = 0$, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 10^2 , 2×10^2 , and 5×10^2 , assuming that $t \in [0, 32]$, $t_s = 16$, and $x \in [0, 60]$. This maximum value of x corresponds to about 10.6 $(2t_s)^{1/2}$, so that it is larger than the recommended 6 $(2t_s)^{1/2}$ [2]. This choice was made because high accuracy was required, so that the error resulting from replacing the semi-infinite interval of x by a finite one, had to be minimised.

Discrete temporal and spatial steps were, respectively, $\delta t = 10^{-3}$ and $h = 1.875 \times 10^{-3}$. These steps were chosen based on previous experience with finite difference solutions of the present model [21]. Comparisons with the results obtained by doubling the above step sizes (both spatial and temporal) suggest that the moduli of the relative errors of the reference current values obtained

are smaller than about 10^{-6} when $t \leq t_s$, and close to about 10^{-4} when $t > t_s$. Note, however, that the current may pass through zero when $t > t_s$, and in such cases it is impossible to obtain small relative errors. Relative errors of the reference $c_{\rm B}(0,t)$ values obtained are estimated to be between 10^{-10} and 10^{-4} .

The above calculations required rather intensive runs on a computational server with an Intel Xeon Gold 6230 processor, operating at 2.10 GHz, under control of the Windows Server 2016 Datacenter operational system. Typical computational time was about nine hours per a single cyclic voltammogram. It is likely that shorter computing times would be achieved by using judiciously designed nonuniform fixed spatial grids, or adaptive grids [2], but the above uniform grids were preferred for their simplicity. Another reason for not using nonuniform grids was that the reaction layer for reaction (9) is quite extended in space, which calls for an increased grid density away from the electrode [21]. There is also evidence that some variants of nonuniform grids can lead to inaccuracies [28].

2.2. Integral equation-based models

In order to represent the problem (10)-(17) using the IE formalism [3], one makes use of the relationships between concentrations and their fluxes (and/or the electric current) at the electrode. For species A such a relationship, resulting from (10) and (22) is [3]:

$$c_{\rm A}(0,t) = 1 - \pi^{-1/2} \int_0^t (t-\tau)^{-1/2} i(\tau) \,\mathrm{d}\tau.$$
(23)

For species B, we employed two approximate approaches valid in the limit of large κ , as already mentioned in the introduction.

Approach 1 utilized the steady state relationship (6), which for (11) (with m = 2) and (22) yields

$$c_{\rm B}(0,t) = \left(\frac{3}{2\kappa}\right)^{1/3} i\left(t\right)^{2/3}.$$
 (24)

By substituting (23) and (24) into the boundary condition (17) one obtains a nonlinear Volterra IE of the second kind, to be solved for i(t). By denoting $U_0(t) = i(t)$ and $Y_0(t) = \int_0^t (t-\tau)^{-1/2} U_0(\tau) d\tau$, this Volterra IE takes the form:

$$U_0(t) + \kappa_{\rm b} \left(\frac{3}{2\kappa}\right)^{1/3} U_0(t)^{2/3} - \kappa_{\rm f} \left[1 - \pi^{-1/2} Y_0(t)\right] = 0.$$
(25)

However, since $c_{\rm B}(0, t)$ is also of theoretical interest, and in order to facilitate comparisons with the Approach 2 below, we prefer to obtain and solve an equivalent integro-algebraic (IAE) system (comprising one IE and one AE) with two unknowns: $U_0(t) = i(t)$ and $U_1(t) = c_{\rm B}(0, t)$. This IAE system, to be solved in approach 1, can be written, in a form convenient for numerical computations, as: $U_0(t) + \kappa_{\rm b}U_1(t) - \kappa_{\rm f} \left[1 - \pi^{-1/2}Y_0(t)\right] = 0$

$$\left. \begin{array}{c} V_0(t) + \kappa_{\rm b} U_1(t) - \kappa_{\rm f} \left[1 - \pi^{-1/2} Y_0(t) \right] = 0 \\ U_0(t)^2 - \frac{2}{3} \kappa U_1(t)^3 = 0 \end{array} \right\}.$$
 (26)

Approach 2 utilized the concentration-flux relationship (7) that for (11) (with m = 2) and (22) yields

$$\frac{\partial c_{\rm B}(0,t)}{\partial t} = \left(\frac{25\kappa}{6}\right)^{1/2} \left[c_{\rm B}(0,t)^{\frac{1}{2}} i(t) - \left(\frac{2\kappa}{3}\right)^{1/2} c_{\rm B}(0,t)^2 \right]$$
(27)

Formula (27) does not provide $c_{\rm B}(0,t)$ as an explicit function of i(t). However, it can be interpreted either as an ordinary differential equation (ODE) for $c_{\rm B}(0,t)$ (apparently not solvable analytically), or it can be reformulated as an equivalent IE. The second possibility appears easier to handle, as it does not require a solution of a nonlinear integro-differential equation system, but only a nonlinear IAE system.

In order to convert the ODE (27) to an IE, one is tempted to simply integrate (27) over the interval [0, t], which gives

$$c_{\rm B}(0,t) = \left(\frac{25\kappa}{6}\right)^{1/2} \int_0^t \left[c_{\rm B}(0,\tau)^{\frac{1}{2}} i(\tau) - \left(\frac{2\kappa}{3}\right)^{1/2} c_{\rm B}(0,\tau)^2 \right] \,\mathrm{d}\tau.$$
(28)

However, this straightforward conversion leads to an IE that is somewhat difficult to solve numerically, due to the nature of nonlinearities involved. The solution process becomes easier, if (27) is rewritten as an ODE for $c_{\rm B}(0,t)^{1/2}$ rather than for $c_{\rm B}(0,t)$:

$$\frac{d\left[c_{\rm B}(0,t)^{1/2}\right]}{dt} = \left(\frac{25\kappa}{24}\right)^{1/2} \left\{i(t) - \left(\frac{2\kappa}{3}\right)^{1/2} \left[c_{\rm B}(0,t)^{1/2}\right]^3\right\}.$$
 (29)

A subsequent integration of both sides of (29), over the interval [0, t], gives

$$c_{\rm B}(0,t)^{1/2} = \left(\frac{25\kappa}{24}\right)^{1/2} \int_0^t \left\{ i(\tau) - \left(\frac{2\kappa}{3}\right)^{1/2} \left[c_{\rm B}(0,\tau)^{1/2} \right]^3 \right\} \,\mathrm{d}\tau. \tag{30}$$

Let the unknown functions be: $U_0(t) = i(t)$, $U_1(t) = c_{\rm B}(0, t)$, $U_2(t) = U_1(t)^{1/2}$ and $U_3(t) = U_0(t) - \left(\frac{2\kappa}{3}\right)^{1/2} U_2(t)^3$. Apart from the integral $Y_0(t) = \int_0^t (t-\tau)^{-1/2} U_0(\tau) d\tau$, introduce also an additional integral $Y_1(t) = \int_0^t U_3(\tau) d\tau$, present in (30). The following IAE system of four equations (two IEs and two AEs) with four unknowns $(U_0(t), U_1(t), U_2(t), U_3(t))$ is then obtained:

$$\left. \begin{array}{l}
 U_{0}(t) + \kappa_{\rm b}U_{1}(t) - \kappa_{\rm f} \left[1 - \pi^{-1/2}Y_{0}(t) \right] = 0 \\
 U_{2}(t) - \left(\frac{25\kappa}{24} \right)^{1/2}Y_{1}(t) = 0 \\
 U_{1}(t) - U_{2}(t)^{2} = 0 \\
 U_{0}(t) - \left(\frac{2\kappa}{3} \right)^{1/2}U_{2}(t)^{3} - U_{3}(t) = 0
 \end{array} \right\}.$$
(31)

2.3. Numerical solution of integral equations

Systems (26) and (31) were solved by the adaptive Huber method [29–32] based on the classical product-integration method of Huber [33]. In this method

all integrals are replaced by finite sums, using appropriate quadratures on (generally nonuniform) discrete time grids, in which the consecutive step sizes may be selected adaptively based on local error estimates. Thus, the solution proceeds stepwise, in a way similar to many methods for solving ordinary differential equations with initial conditions. However, the initial values of the solutions need not be supplied separately: they can be calculated from the IEs. The adaptive Huber method requires, in the case of nonlinear IEs, an intensive use of Newton's iterative method, at every discrete time level.

Early numerical experiments revealed that the Newton method sometimes fails to converge, especially while determining initial solutions (see Ref. [30] for details of the initialization procedure). For example, negative concentrations or currents appeared. In order to eliminate these failings in practice, the following modifications of (26) and (31) were used in the limit of small time t (specifically for $t \leq 10^{-10}$).

In the case of system (26), if t is small, one can assume that $Y_0(t) \approx 0$ since the current must be bounded for a quasi-reversible reaction (8). By denoting $w = \frac{\kappa_{\rm b}}{\kappa_{\rm f}} U_1(t)$ and $\lambda = \frac{2\kappa\kappa_{\rm f}}{3\kappa_{\rm s}^2} > 0$, one then obtains from (26):

$$\lambda w^3 - (1 - w)^2 = 0. \tag{32}$$

Plotting λw^3 vs. w and $(1-w)^2$ vs. w it is evident that (32) will always have one real root w^* , such that $0 < w^* < 1$. For this root, both $c_{\rm B}(0,t) = U_1(t) = \frac{\kappa_f}{\kappa_{\rm b}} w^*$ and $i(t) = U_0(t) = \kappa_f (1-w^*)$ will be positive. There may be two more real roots (for which, however, $w^* > 1$ implying a physically incorrect negative current), or two complex, nonphysical roots. The correct root w^* of (32) can be determined easily and infallibly by the bisection method, which subsequently allows one to replace (26) by the linear system (valid when t is sufficiently small; the condition $t \leq 10^{-10}$ was assumed):

$$\begin{array}{c} U_0(t) - \kappa_{\rm f} \left(1 - w^{\star} \right) = 0 \\ U_1(t) - \frac{\kappa_{\rm f}}{\kappa_{\rm b}} w^{\star} = 0 \end{array} \right\}.$$
 (33)

In the case of system (31), as both the current and concentrations must be bounded, one can assume that $Y_0(t) \approx 0$ and $Y_1(t) \approx 0$ if t is sufficiently small. Hence, (31) then reduces simply to the linear system:

$$\begin{array}{c}
U_0(t) - \kappa_{\rm f} = 0 \\
U_1(t) = 0 \\
U_2(t) = 0 \\
U_3(t) - \kappa_{\rm f} = 0
\end{array}$$
(34)

The results shown below were calculated using the following essential parameters of the adaptive Huber method: initial (tentative) time step $\delta t_{\text{start}} = 10^{-10}$, maximum time step $\delta t_{\text{max}} = 0.01$, absolute error tolerance $tol = 10^{-8}$. The actual initial time step adaptively selected by the method reached values as small as 4.5×10^{-11} . A typical simulation time was about 12-30 seconds (per single

cyclic voltammogram), on a laptop computer with an Intel Centrino 2 processor operating at 2.4 GHz, under the control of Windows Vista. Note that this simulation time is orders of magnitude smaller than the time required to obtain reference solutions by direct numerical integration of the PDEs, despite a demanding absolute error tolerance *tol*. But, of course, the IAE solutions will contain errors resulting from the approximate concentration-flux relationships for the species B.

3. Results and discussion

Figures 1 and 2 compare CV currents and boundary concentrations of the species B, resulting from solving systems (26) and (31), with reference solutions, at four different κ values, assuming $\kappa^0 = 1$. Results obtained for other κ^0 values were qualitatively similar, giving analogous conclusions. It is seen that good agreement between the solutions of (31) and reference solutions is achieved at smaller κ than is possible in the case of system (26). In particular, in Figs 1b and 1c one observes a fairly good visual agreement between the predictions of (31) and reference currents for $\kappa = 5$ and $\kappa = 10$, for most of the time (except for the initial t interval), whereas the predictions of (26) clearly differ from the reference currents; these differences vanish only for larger $\kappa = 10^2$ (cf. Fig. 1d). Similar observations result from the inspection of Fig. 2: here a fairly good agreement between the predictions of (31) and reference $c_{\rm B}(0,t)$ values occurs even for small $\kappa = 1$ (cf. Fig. 2a).

For a proper understanding of the dependencies on κ , one should remember that κ can be varied experimentally by changing the potential sweep rate v, which results from the normalizations used (cf. section 2). However, in such a case, the heterogeneous rate constant κ^0 would be varied, too, for the same reason. Therefore, the dependencies on κ , obtained at a constant κ^0 , are not equivalent to the dependencies resulting from varying v at constant k and k^0 .

A typical characteristic of CV responses is the presence of current extrema or peaks. In the modelling of such responses it is usually of particular interest to accurately calculate the values of these peak currents, since these values can be used for experimental data analysis. In the present case, there always occurs a forward peak (a maximum) in the interval $0 < t < t_s$. A distinct backward peak (a minimum) is observed for $t > t_s$, but only when κ is relatively small (cf. Fig. 1). For large κ the backward peak is almost undetectable. Figure 3 presents the dependencies of the modulus of the relative error rerror of the forward and backward peak currents on κ , obtainable by using approaches 1 and 2. As can be seen, for $\kappa \gtrsim 1$ approach 2 is always more accurate than approach 1, for a given κ . By choosing a target error at $|rerror| = 10^{-3}$ (which is normally sufficient for modelling purposes, in view of the typical experimental errors that are about 1%), it is also seen in Fig. 3a that approach 2 allows one to calculate forward peak currents with such a target error for κ smaller by about one order of magnitude, compared to approach 1. Specifically, if we assume that approach 1 is acceptable for $\kappa \gtrsim 500$, then approach 2 is satisfactory for $\kappa \gtrsim 50$. Approach 1 is generally incapable of reproducing the backward peak,

so that the peak current errors for this approach exceed 100% in Fig. 3b, and even increase with increasing κ . Approach 2 is more successful in reproducing the backward peak, and its accuracy improves with increasing κ . Relative peak current errors in this approach are visibly larger for the backward peak than for the forward peak, which is understandable as the backward peak currents are close to zero.

In preparing Fig. 3 it was assumed that the peak locations coincided with discrete time values at which extrema of reference currents were observed. These values represent peak locations accurate only to $\pm \delta t = \pm 10^{-3}$. Hence, we cannot present an analogous figure with dependencies of the peak location errors on κ . Much more densely tabulated reference currents would be needed.

The results obtained indicate also that the worst agreement between solutions of (26) and (31), and reference solutions, occurs at small times, and that in this limit none of the approaches 1 and 2 is advantageous. This is understandable since for both approaches it is assumed that the system being considered is close to the steady state: the larger κ , the faster this state will be reached.

Although the algorithm described presents a definite improvement of the IE-based modelling of systems involving second order homogeneous reactions, it is still limited to rather large κ values. Therefore, further work is needed to determine concentration-flux relationships that would be adequate for slow second order homogeneous reactions. Hence, the present IE-based simulations cannot yet be used for estimating arbitrary κ values from experimental voltammograms. The issues of estimating κ^0 and α parameters are beyond the scope of this study, but approach 2 does not introduce any limitations in this respect, as long as the condition $\kappa \gtrsim 50$ is satisfied. Therefore, the formerly determined rules and limitations [8, 14, 15], should be applicable. Alternatively (and preferably) modern robust data analysis techniques such as automated multiresponse fitting, Bayesian inference techniques, or even machine learning-based mechanism identification [34–36] can be recommended. These techniques are superior to the simple data analysis employing peak characteristics (used in [8, 14, 15]), since they utilize the entire information content of multiple voltammograms, and not just single current-potential data points. A detailed examination, of how to simultaneously estimate κ , κ^0 and α using these methods, would require a separate study.

4. Conclusions

The present work together with our former results given in [5], represents a first step towards developing effective IE-based algorithms for simulating electroanalytical experiments described by nonlinear reaction-diffusion PDEs associated with homogeneous reactions of order greater than one. We have described a novel IE-based model of CV for an EC_2 reaction mechanism involving a second order homogeneous dimerization reaction. In the model, the classical steady state assumption for the reaction-diffusion PDE is replaced by a more general, two-term singular perturbation expansion of the concentration-flux relationship. This leads to an IAE system to be solved numerically for the Faradaic current.

By solving this system, satisfactory simulation results can be obtained for homogeneous reaction rate constants smaller by about one order of magnitude than was thus far possible while adopting the steady state assumption. Further work should concentrate on attempts to determine theoretical concentrationflux relationships valid for still slower homogeneous reactions (and/or for small times).

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Figure 1: Dimensionless CV current responses i(t), with i(t) equivalent to the voltammetric current function $\pi^{1/2}\chi(t)$, as functions of the dimensionless potential, corresponding to $\kappa = 1$ (a), 5 (b), 10 (c), and 10^2 (d). Other model parameters are: $\kappa^0 = 1$, $\alpha = 0.5$, u = 8 and $t_s = 16$. Reference responses are denoted by solid lines. Dashed lines represent solutions of the IAE system (26) in Approach 1. Dotted lines denote solutions of the IAE system (31) in Approach 2. Arrows indicate the direction of the time flow



Figure 2: Dimensionless boundary concentrations $c_B(0,t)$ in CV, corresponding to $\kappa = 1$ (a), 5 (b), 10 (c) and 10^2 (d). Other parameters and notations as in Fig. 1.



Figure 3: Modulus of the relative error rerror of the forward (a) and backward (b) peak current (relative to the reference currents), as a function of the dimensionless homogeneous reaction rate constant κ , in the case of approach 1 (\circ) and 2 (\bullet). Other model parameters are: $\kappa^0 = 1$, $\alpha = 0.5$, u = 8 and $t_s = 16$.

Credit Author Statement for EA22-2099

- L.K. Bieniasz: Conceptualization, Methodology, Software, Investigation, Writing-Original Draft
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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

 \Box The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: