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Task No. NR 359-718

TECHNICAL REPORT NO. 9

Simulation of Edge Effects in Electroanalytical Experiments. Part II. The Theory for Cyclic Voltammetry by Collocation.

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Prepared for Publication In

Canadian Journal of Chemistry

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August 18, 1982

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: 9	2. GOVT ACCESSION NO.: AD-A118709
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): Simulation of Edge Effects in Electroanalytical Experiments. II The theory for cyclic Voltammetry by Collocation.	5. TYPE OF REPORT & PERIOD COVERED: Technical Report # 9
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Bernd Speiser and Stanley Pons	8. CONTRACT OR GRANT NUMBER(s): N00014-82-G-0017
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Task No. NR 359-718
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Chemistry Program - Chemistry Code 472, Arlington, Virginia 22217	12. REPORT DATE: August 18, 1982
	13. NUMBER OF PAGES: 41
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electrochemistry, Simulation, Cyclic voltammetry, Orthogonal Collocation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The procedure and theory for simulation of currents perturbed by edge effects at disc electrodes in cyclic voltammetric experiments is presented. The results are obtained rapidly and accurately.

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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SIMULATION OF EDGE EFFECTS IN ELECTROANALYTICAL EXPERIMENTS BY ORTHOGONAL COLLOCATION. PART 3. THEORY FOR CYCLIC VOLTAMMETRY

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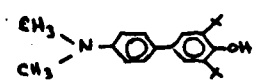
INTRODUCTION

We have shown (1,2) that orthogonal collocation is suitable not only for the solution of linear diffusion problems but also for simulation of two-dimensional models. Thus, it is possible to simulate edge effects on electroanalytical experiments using this fast and flexible numerical technique.

Cyclic voltammetry is one of the most commonly used electroanalytical methods and it might be of considerable interest to calculate the effects caused by edge diffusion on the i/E-curves. Lines and Parker (3) have observed an increase of ΔE_p when using microelectrodes and attributed this to edge effects, a conclusion which was confirmed by theoretical calculations by Heinze (4). Speiser and Rieker (5) found dramatic changes in cyclic voltammograms of 2,6-Di-tert butyl-4[4-dimethylaminophenyl]-phenol I in unbuffered, neutral acetonitrile when decreasing the electrode area from 0.29 cm^2 to 0.0022 cm^2. These experiments have also been explained in terms of edge diffusion. Up to now, however, it was not possible to simulate the complex mechanism describing the oxidation of I under the conditions of a finite circular disc electrode.



This paper expands the theory of two-dimensional orthogonal collocation to cyclic voltammetry and mechanisms as complex as the oxidation of I. It will only deal with the mathematics of the method, while a complete numerical analysis showing the usefulness of the derived equations will be given in part 4.

This partition has been used because the analysis (which has to be done to validate the new two-dimensional collocation method) requires the discussion of many parameters. We point out, however, that this has to be done only once, while extension to more complicated mechanisms is obvious. Also, research on a comparison of the experimental results with I and numerical simulations is under way.

INITIAL AND BOUNDARY CONDITIONS

The initial and boundary conditions have been given by Nicholson and Shain (6) and used by Speiser and Rieker (7) in the context of orthogonal collocation for linear diffusion. Pons (8) simulated cyclic voltammograms under spherical diffusion conditions using orthogonal collocation.

For simulation of edge effects we employ our two-dimensional model of a finite, circular electrode of radius r_0 imbedded into an insulator body (1). The radius of the insulator may go to infinity.

We assume an EC mechanism:

$$A \underset{+ne^-}{\overset{-ne^-}{\rightleftharpoons}} B \qquad E^\circ, n \qquad (1)$$

$$B \longrightarrow C \qquad k \qquad (2)$$

where the diffusion controlled electron transfer is described by the formal potential, E°, and the number of transferred electrons, n. The chemical step (2) proceeds with a rate constant k.

Fick's second law for the substrate A takes the form

$$\frac{\partial c_A}{\partial t} = D\left[\frac{\partial^2 c_A}{\partial x^2} + \frac{1}{r}\frac{\partial c_A}{\partial r} + \frac{\partial^2 c_A}{\partial r^2}\right] \qquad (3)$$

where t is time and x and r are the distance coordinate perpendicular to the electrode and the radial coordinate respectively. The total diffusion is expressed as superimposition of a linear and a cylindrical term.

For species B and C equations (4) and (5) hold:

$$\frac{\partial c_B}{\partial t} = D\left[\frac{\partial^2 c_B}{\partial x^2} + \frac{1}{r}\frac{\partial c_B}{\partial r} + \frac{\partial^2 c_B}{\partial r^2}\right] - k c_B \qquad (4)$$

$$\frac{\partial c_C}{\partial t} = D\left[\frac{\partial^2 c_C}{\partial x^2} + \frac{1}{r}\frac{\partial c_C}{\partial r} + \frac{\partial^2 c_C}{\partial r^2}\right] + k c_B \qquad (5)$$

For convenience the diffusion coefficient of all species is set equal to D.

We assume that A is the only species present in the solution at the beginning of the experiment, its concentration being c_A°. Thus, the initial conditions are

$$t=0,\ x \geq 0,\ r \geq 0: \quad c_A(x,r,0) = c_A^\circ \qquad (6)$$

$$c_B(x,r,0) = c_C(x,r,0) = 0 \qquad (7)$$

At a distance far from the electrode no concentration changes take place during the experiment. This yields the boundary conditions at $x \to \infty$ and $r \to \infty$

$$t>0,\ x \to \infty,\ r \geq 0: \quad c_A(\infty,r,t) \to c_A^\circ \qquad (8)$$

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$$c_B(\infty,r,t) = c_C(\infty,r,t) = 0 \tag{9}$$

$t > 0, x \geq 0, r \to \infty$:

$$c_A(x,\infty,t) \longrightarrow c_A^{\circ} \tag{10}$$

$$c_B(x,\infty,t) = c_C(x,\infty,t) = 0 \tag{11}$$

At the electrode surface the concentrations of A and B are given by (12) and (13), while (14) holds for species C:

$t > 0, x = 0, 0 \leq r \leq r_0$:

$$\left(\frac{\partial c_A}{\partial x}\right)_{x=0} = -\left(\frac{\partial c_B}{\partial x}\right)_{x=0} \tag{12}$$

$$\frac{c_A(0,r,t)}{c_B(0,r,t)} = \exp\left[\frac{nF}{RT}(E^{\circ}-E)\right] = \Theta_{A/B}\, S_\lambda(t) \tag{13}$$

$$\left(\frac{\partial c_C}{\partial x}\right)_{x=0} = 0 \tag{14}$$

Equation (13) reflects the special features of cyclic voltammetry if

$$\Theta_{A/B} = \exp\left[\frac{nF}{RT}(E^{\circ}-E_{start})\right] \tag{15}$$

and

$$S_\lambda(t) = \begin{cases} \exp[2(m-1)at_\lambda - at] & \text{for } 2(m-1)t_\lambda \leq t \leq (2m-1)t_\lambda \\ & m = 1,2,\ldots \\ \exp[at - 2m\,at_\lambda] & \text{for } (2m-1)t_\lambda \leq t \leq 2m\,t_\lambda \end{cases} \tag{16}$$

Here F, R and T have their usual meaning, E_{start} is the starting potential of the scan, t the time when the scan is reversed, m the number of the present scan. A cycle consists of two scans. Finally a is given by

$$a = \frac{nF}{RT}\, v \tag{17}$$

where v is the scan rate, dE/dt.

There is no redox reaction at the insulator and hence no flux through this surface. Thus

$t > 0, x = 0, r \gg r_0$:

$$\left(\frac{\partial c_A}{\partial x}\right)_{x=0} = \left(\frac{\partial c_B}{\partial x}\right)_{x=0} = \left(\frac{\partial c_C}{\partial x}\right)_{x=0} = 0 \tag{18}$$

At r = 0 there must be no flux in r-direction because our model is symmetric around r = 0:

$t > 0, x \geq 0, r = 0$:

$$\left(\frac{\partial c_A}{\partial r}\right)_{r=0} = \left(\frac{\partial c_B}{\partial r}\right)_{r=0} = \left(\frac{\partial c_C}{\partial r}\right)_{r=0} = 0 \tag{19}$$

It is convenient [1] to divide the space in the r-direction into two parts, inside and outside of r_0. The concentration may be described by c_1 and c_2, respectively. The two concentration

functions have to fulfill the conditions (20) and (21) at $r = r_0$ for all species.

$t > 0, x \geq 0, r = r_0$:

$$c_1(x, r_0, t) = c_2(x, r_0, t) \tag{20}$$

$$\left(\frac{\partial c_1}{\partial r}\right)_{r=r_0} = \left(\frac{\partial c_2}{\partial r}\right)_{r=r_0} \tag{21}$$

TRANSFORMATION TO A DIMENSIONLESS PROBLEM

Equations (3)-(22) are transformed into a dimensionless problem by

$$X = x/L \tag{22}$$

$$c^*_{A1} = c_{A1}/c_A^0 \tag{23}$$

$$c^*_{A2} = c_{A2}/c_A^0 \tag{24}$$

$$c^*_{B1} = c_{B1}/c_A^0 \tag{25}$$

$$c^*_{B2} = c_{B2}/c_A^0 \tag{26}$$

$$c^*_{C1} = c_{C1}/c_A^0 \tag{27}$$

$$c^*_{C2} = c_{C2}/c_A^0 \tag{28}$$

$$R = r/r_0 \quad \text{for } 0 \leq r \leq r_0 \tag{29a}$$

$$R = (r - r_0)/(M - r_0) \quad \text{for } r \geq r_0 \tag{29b}$$

$$T' = at \tag{30}$$

$$\alpha = kD/r_0^2 \tag{31}$$

Here X is a dimensionless distance perpendicular to the electrode, L is a distance from the electrode defined such that diffusion effects are negligible at all times the c^* are dimensionless concentrations, R and R' are dimensionless coordinates in r-direction for the inner and outer functions respectively, while M is defined as L except it is a radial distance from the center of the electrode. The symbols T' and a *denote* the dimensionless simulation time and rate constant respectively.

Thus, we get the dimensionless differential equations:

$$\frac{\partial c^*_{A1}}{\partial T'} = \beta \frac{\partial^2 c^*_{A1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c^*_{A1}}{\partial R} + \beta' \frac{\partial^2 c^*_{A1}}{\partial R^2} \tag{32}$$

$$\frac{\partial c^*_{B1}}{\partial T'} = \beta \frac{\partial^2 c^*_{B1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c^*_{B1}}{\partial R} + \beta' \frac{\partial^2 c^*_{B1}}{\partial R^2} - \alpha c^*_{B1} \tag{33}$$

$$\frac{\partial c^{*}_{A1}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{A1}}{\partial X^2} + \frac{\beta'}{R}\frac{\partial c^{*}_{A1}}{\partial R} + \beta' \frac{\partial^2 c^{*}_{A1}}{\partial R^2} + \alpha c^{*}_{B1} \tag{34}$$

$$\frac{\partial c^{*}_{A2}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{A2}}{\partial X^2} + \frac{\sqrt{\beta'}\,\beta''}{\sqrt{\beta''}+\sqrt{\beta'}\,R'}\frac{\partial c^{*}_{A2}}{\partial R} + \beta'' \frac{\partial^2 c^{*}_{A2}}{\partial R^2} \tag{35}$$

$$\frac{\partial c^{*}_{B2}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{B2}}{\partial X^2} + \frac{\sqrt{\beta'}\,\beta''}{\sqrt{\beta''}+\sqrt{\beta'}\,R'}\frac{\partial c^{*}_{B2}}{\partial R} + \beta'' \frac{\partial^2 c^{*}_{B2}}{\partial R^2} - \alpha c^{*}_{B2} \tag{36}$$

$$\frac{\partial c^{*}_{C2}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{C2}}{\partial X^2} + \frac{\sqrt{\beta'}\,\beta''}{\sqrt{\beta''}+\sqrt{\beta'}\,R'}\frac{\partial c^{*}_{C2}}{\partial R} + \beta'' \frac{\partial^2 c^{*}_{C2}}{\partial R^2} + \alpha c^{*}_{C2} \tag{37}$$

where β is given by

$$\beta = D/a L^2 \tag{38}$$

β' contains only experimental parameters

$$\beta' = D/a r_0^2 \tag{39}$$

and

$$\beta'' = D/a(R-r_0)^2 \tag{40}$$

As in the case of the chronoamperometric simulations [1] we have

two dimensionless parameters, here β and β''. The parameter β' is given by experimental parameters and thus the simulations will depend on β' as e.g. on a.

The transformed initial and boundary conditions are given by

$T'=0, 0 \le X \le 1, 0 \le R \le 1, 0 \le R' \le 1$:

$$c^{*}_{A1}(X,R,0) = c^{*}_{A2}(X,R',0) = 1 \tag{41}$$

$$c^{*}_{B1}(X,R,0) = c^{*}_{B2}(X,R',0) = c^{*}_{C1}(X,R,0) = c^{*}_{C2}(X,R',0) = 0 \tag{42}$$

$T'>0, X=1, 0 \le R \le 1$;

$$c^{*}_{A1}(1,R,T') = 1 \tag{43}$$

$$c^{*}_{B1}(1,R,T') = c^{*}_{C1}(1,R,T') = 0 \tag{44}$$

$T'>0, X=1, 0 \le R' \le 1$:

$$c^{*}_{A2}(1,R',T') = 1 \tag{45}$$

$$c^{*}_{B2}(1,R',T') = c^{*}_{C2}(1,R',T') = 0 \tag{46}$$

$T'>0, 0 \le X \le 1, R'=1$:

$$c^{*}_{A2}(X,1,T') = 1 \tag{47}$$

$$c^{*}_{B2}(X,1,T') = c^{*}_{C2}(X,1,T') = 0 \tag{48}$$

$T'>0, X=0, 0 \le R \le 1$:

$$\left(\frac{\partial c^{*}_{A1}}{\partial X}\right)_{X=0} = -\left(\frac{\partial c^{*}_{B1}}{\partial X}\right)_{X=0} \tag{49}$$

$$\frac{c^*_{B_1}(0,R,T')}{c^*_{A_1}(0,R,T')} = \Theta_{A/B}\, S_\lambda(T') \tag{50}$$

with

$$S_\lambda(T') = \begin{cases} \exp\left[2(m-1)T'_\lambda - T'\right] \\ \exp\left[T' - 2mT'_\lambda\right] \end{cases} \qquad m = 1, 2, \cdots \tag{51}$$

where

$$T'_\lambda = a t_\lambda \tag{52}$$

$$\left(\frac{\partial c^*_{d_1}}{\partial X}\right)_{X=0} = 0 \tag{53}$$

$T'>0, X=0, 0<R'<1$:

$$\left(\frac{\partial c^*_{A_2}}{\partial X}\right)_{X=0} = \left(\frac{\partial c^*_{B_2}}{\partial X}\right)_{X=0} = \left(\frac{\partial c^*_{d_2}}{\partial X}\right)_{X=0} = 0 \tag{54}$$

$T'>0, 0<X<1, R=0$:

$$\left(\frac{\partial c^*_{A_1}}{\partial R}\right)_{R=0} = \left(\frac{\partial c^*_{B_1}}{\partial R}\right)_{R=0} = \left(\frac{\partial c^*_{d_1}}{\partial R}\right)_{R=0} = 0 \tag{55}$$

$T'>0, 0\le X\le 1, R=1 (R'=0)$:

$$c^*_{A_1}(X,1,T') = c^*_{A_2}(X,0,T') \tag{56}$$

$$c^*_{B_1}(X,1,T') = c^*_{B_2}(X,0,T') \tag{57}$$

$$c^*_{d_1}(X,1,T') = c^*_{d_2}(X,0,T') \tag{58}$$

$$\left(\frac{\partial c^*_{A_1}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta^*}{\beta'}}\left(\frac{\partial c^*_{A_2}}{\partial R'}\right)_{R'=0} \tag{59}$$

$$\left(\frac{\partial c^*_{B_1}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta^*}{\beta'}}\left(\frac{\partial c^*_{B_2}}{\partial R'}\right)_{R'=0} \tag{60}$$

$$\left(\frac{\partial c^*_{d_1}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta^*}{\beta'}}\left(\frac{\partial c^*_{d_2}}{\partial R'}\right)_{R'=0} \tag{61}$$

APPLICATION OF TWO-DIMENSIONAL COLLOCATION

As in the case of chronoamperometry [1] we have to solve the system of second order partial differential equations (32)-(37) under the conditions (41)-(61) to get the dimensionless concentrations of species A, B and C as functions of X, R (R') and T'. We use the two-dimensional collocation method outlined in part 1 of this series [1] to discretise equations (32)-(37) with respect to the grid of collocation points (X_i, R_k) in the X/R-space.

We have shown [1] that the first and second derivatives of the concentration with respect to x and r respectively at a collocation point (X_i, R_k) may be expressed as

$$\left(\frac{\partial c}{\partial x}\right)_{X_i, r_k} = \sum_{j=4}^{N_x+2} A_{ij}\, c(x_j, r_k, t) \tag{62}$$

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_{x_i, r_k} = \sum_{j=1}^{N_x+2} B_{i,j}\, c(x_j, r_k, t) \tag{63}$$

$$\left(\frac{\partial c}{\partial r}\right)_{x_i, r_k} = \sum_{\ell=1}^{N_r+2} C_{\ell,k}\, c(x_i, r_\ell, t) \tag{64}$$

$$\left(\frac{\partial^2 c}{\partial r^2}\right)_{x_i, r_k} = \sum_{\ell=1}^{N_r+2} D_{\ell,k}\, c(x_i, r_\ell, t) \tag{65}$$

where N_x and N_r are the numbers of interior collocation points (chosen as the roots of an orthogonal polynomial [9]) in the x and r direction respectively and $A_{i,j}$, $B_{i,j}$, $C_{l,k}$ and $D_{l,k}$ are elements of matrices. The numerical values of those elements depend only on the degree and kind of the polynomial chosen for collocation [10]. Thus, if the matrix elements have once been calculated they may be used for any problem. The degree of the polynomial used depends on the desired accuracy of the simulation.

Using equations (62)-(65) we may discretize the partial differential equations (32)-(37) in terms of the concentrations at the collocation points. If we introduce the boundary conditions (43)-(48) we arrive at equations (66)-(71).

$$\left.\frac{dc^*_{A1}}{dT'}\right|_{X_i, R_k} = \beta\left\{B_{i,1}\, c^*_{A1}(0, R_k, T') + B_{i,N_x+2} + \sum_{j=2}^{N_x+1} B_{i,j}\, c^*_{A1}(X_j, R_k, T')\right\} \tag{66}$$
$$+ \beta'\left\{E_{1,k}\, c^*_{A1}(X_i, 0, T') + E_{N_r+2,k}\, c^*_{A1}(X_i, 1, T') + \sum_{\ell=2}^{N_r+1} E_{\ell,k}\, c^*_{A1}(X_i, R_\ell, T')\right\}$$

$$\left.\frac{dc^*_{B1}}{dT'}\right|_{X_i, R_k} = \beta\left\{B_{i,1}\, c^*_{B1}(0, R_k, T') + \sum_{j=2}^{N_x+1} B_{i,j}\, c^*_{B1}(X_j, R_k, T')\right\} \tag{67}$$
$$+ \beta'\left\{E_{1,k}\, c^*_{B1}(X_i, 0, T') + E_{N_r+2,k}\, c^*_{B1}(X_i, 1, T') + \sum_{\ell=2}^{N_r+1} E_{\ell,k}\, c^*_{B1}(X_i, R_\ell, T')\right\} - \alpha c^*_{B1}$$

$$\left.\frac{dc^*_{C1}}{dT'}\right|_{X_i, R_k} = \beta\left\{B_{i,1}\, c^*_{C1}(0, R_k, T') + \sum_{j=2}^{N_x+1} B_{i,j}\, c^*_{C1}(X_j, R_k, T')\right\} \tag{68}$$
$$+ \beta'\left\{E_{1,k}\, c^*_{C1}(X_i, 0, T') + E_{N_r+2,k}\, c^*_{C1}(X_i, 1, T') + \sum_{\ell=2}^{N_r+1} E_{\ell,k}\, c^*_{C1}(X_i, R_\ell, T')\right\} + \alpha c^*_{B1}$$

$$\left.\frac{dc^*_{A2}}{dT'}\right|_{X_i, R_k} = \beta\left\{B_{i,1}\, c^*_{A2}(0, R'_k, T') + B_{i,N_x+2} + \sum_{j=2}^{N_x+1} B_{i,j}\, c^*_{A2}(X_j, R'_k, T')\right\} \tag{69}$$
$$+ \beta'\left\{F'_{1,k}\, c^*_{A2}(X_i, 0, T') + F'_{N_r+2,k} + \sum_{\ell=2}^{N_r+1} F'_{\ell,k}\, c^*_{A2}(X_i, R'_\ell, T')\right\}$$

$$\left.\frac{dc^*_{B2}}{dT'}\right|_{X_i, R_k} = \beta\left\{B_{i,1}\, c^*_{B2}(0, R'_k, T') + \sum_{j=2}^{N_x+1} B_{i,j}\, c^*_{B2}(X_j, R'_k, T')\right\} \tag{70}$$
$$+ \beta'\left\{F'_{1,k}\, c^*_{B2}(X_i, 0, T') + \sum_{\ell=2}^{N_r+1} F'_{\ell,k}\, c^*_{B2}(X_i, R'_\ell, T')\right\} - \alpha c^*_{B2}$$

$$\left.\frac{dc^*_{C2}}{dT'}\right|_{X_i,R_k} = \beta\left\{B_{i,1}c^*_{C2}(0,R'_k,T') + \sum_{j=2}^{M_x+1} B_{i,j}\,c^*_{C2}(X_j,R_k',T')\right\} \tag{71}$$
$$+\beta''\left\{F'_{1,k}\,c^*_{C2}(X_i,0,T') + \sum_{\ell=2}^{M_R+1} F'_{\ell,k}\,c^*_{C2}(X_i,R_\ell',T')\right\} + \alpha\, c^*_{B2}$$

with

$$E_{\ell,k} = \frac{C_{\ell,k} + R_k D_{\ell,k}}{R_k} \tag{72}$$

and

$$F'_{\ell,k} = \frac{\sqrt{\beta'}}{\sqrt{\beta''}+\sqrt{\beta'}\,R'_k}\,C'_{\ell,k} + D'_{\ell,k} \tag{73}$$

Primed matrix elements correspond to the outer discretization function. As in the case of chronoamperometry we have to substitute implicit equations for the unknown concentrations at the boundaries. The calculations of the $c^*_1(X_i,0,T')$, $c^*_1(X_i,1,T')$, $c^*_2(X_i,0,T')$ $c^*_1(0,R_k,T')$ and $c^*_2(0,R_k,T')$ is essentially the same as for chronoamperometric simulations and we refer to part 1 of this series [1] for the derivations.

They are [1]:

$$c^*_{A1}(X_i,0,T') = -\frac{1}{G_1}\left\{\sum_{\ell=2}^{M_R+1} G_\ell\, c^*_{A1}(X_i,R_\ell,T') + \sum_{\ell=2}^{M_R+1} C_{M_R+2,1}\,C'_{\ell,1}\,c^*_{A2}(X_i,R_\ell',T') + C_{M_R+2,1}\,C'_{M_R+2,1}\right\} \tag{74}$$

$$c^*_{B1}(X_i,0,T') = -\frac{1}{G_1}\left\{\sum_{\ell=2}^{M_R+1} G_\ell\, c^*_{B1}(X_i,R_\ell,T') + \sum_{\ell=2}^{M_R+1} C_{M_R+2,1}\,C'_{\ell,1}\,c^*_{B2}(X_i,R_\ell',T')\right\} \tag{75}$$

$$c^*_{C1}(X_i,0,T') = -\frac{1}{G_1}\left\{\sum_{\ell=2}^{M_R+1} G_\ell\, c^*_{C1}(X_i,R_\ell,T') + \sum_{\ell=2}^{M_R+1} C_{M_R+2,1}\,C_{\ell,1}\,c^*_{C2}(X_i,R_\ell',T')\right\} \tag{76}$$

$$c^*_{A1}(X_i,1,T') = c^*_{A2}(X_i,0,T') = \frac{1}{G_1}\left\{\sum_{\ell=2}^{M_R+1} H_\ell\, c^*_{A1}(X_i,R_\ell,T') + \sum_{\ell=2}^{M_R+1} C_{1,1}\,C'_{\ell,1}\,c^*_{A2}(X_i,R_\ell',T') + C_{1,1}\,C'_{M_R+2,1}\right\} \tag{77}$$

$$c^*_{B1}(X_i,1,T') = c^*_{B2}(X_i,0,T') = \frac{1}{G_1}\left\{\sum_{\ell=2}^{M_R+1} H_\ell\, c^*_{B1}(X_i,R_\ell,T') + \sum_{\ell=2}^{M_R+1} C_{1,1}\,C'_{\ell,1}\,c^*_{B2}(X_i,R_\ell',T')\right\} \tag{78}$$

$$c^*_{C1}(X_i,1,T') = c^*_{C2}(X_i,0,T') = \frac{1}{G_1}\left\{\sum_{\ell=2}^{\mu_B+1} H_\ell\, c^*_{C1}(X_i,R_\ell,T') + \sum_{\ell=2}^{\mu_B+1} C_{\ell,1}\, C'_{\ell,1}\, c^*_{C2}(X_i,R'_\ell,T')\right\} \tag{79}$$

$$c^*_{C1}(0,R_k,T') = -\frac{1}{A_{1,1}} \sum_{j=2}^{\mu_B+1} A_{1,j}\, c^*_{C1}(X_j,R_k,T') \tag{80}$$

$$c^*_{A2}(0,R'_k,T') = -\frac{1}{A_{1,1}}\left\{A_{1,\mu_B+2} + \sum_{j=2}^{\mu_B+1} A_{1,j}\, c^*_{A2}(X_j,R'_k,T')\right\} \tag{81}$$

$$c^*_{B2}(0,R'_k,T') = -\frac{1}{A_{1,1}} \sum_{j=2}^{\mu_B+1} A_{1,j}\, c^*_{B2}(X_j,R'_k,T') \tag{82}$$

$$c^*_{C2}(0,R'_k,T') = -\frac{1}{A_{1,1}} \sum_{j=2}^{\mu_B+1} A_{1,j}\, c^*_{C2}(X_j,R'_k,T') \tag{83}$$

with

$$G_\ell = \left(C_{\mu_B+2,\mu_B+2} - C'_{1,1}\right) C_{\ell,1} - C_{\ell,\mu_B+2}\, C_{\mu_B+2,1} \tag{84}$$

and

$$H_\ell = C_{1,\mu_B+2}\, C_{\ell,1} - C_{1,1}\, C_{\ell,\mu_B+2} \tag{85}$$

The values of $c^*_{A1}(0,R_k,T')$ and $c^*_{B1}(0,R_k,T')$ may be calculated from equations (49) and (50), yielding

$$c^*_{A1}(0,R_k,T') = -\frac{\Theta_{A/B}\, S_A(T')}{A_{1,1}\left[1+\Theta_{A/B}\, S_A(T')\right]} \times \left\{A_{1,\mu_B+2} + \sum_{j=2}^{\mu_B+1} A_{1,j}\left[c^*_{A1}(X_j,R_k,T') + c^*_{B1}(X_j,R_k,T')\right]\right\} \tag{86}$$

and

$$c^*_{B1}(0,R_k,T') = -\frac{1}{A_{1,1}\left[1+\Theta_{A/B}\, S_A(T')\right]} \times \left\{A_{1,\mu_B+2} + \sum_{j=2}^{\mu_B+1} A_{1,j}\left[c^*_{A1}(X_j,R_k,T') + c^*_{B1}(X_j,R_k,T')\right]\right\} \tag{87}$$

Now we may substitute (74)-(87) into equations (66)-(71) which gives us finally the discretized equations describing the time dependence of the concentration of all three species A, B and C at the collocation points.

From (66) it follows using (74) (77) and (86)

$$\left.\frac{dc^*_{A1}}{dT'}\right|_{X_i,R_\ell} = \beta\Bigg\{-\frac{B_{i,1}\,\Theta_{A/B}\,S_A(T')}{A_{1,1}[1+\Theta_{A/B}S_A(T')]}\Big[A_{1,M_B+2}+\sum_{j=2}^{M_B+4}A_{1,j}[c^*_{A1}(X_j,R_\ell,T')$$

$$+c^*_{B1}(X_j,R_\ell,T')]\Big]+B_{i,M_B+2}+\sum_{j=2}^{M_B+4}B_{i,j}\,c^*_{A1}(X_j,R_\ell,T')$$

$$+\frac{\beta'}{G_1}\Big\{I_{1,A}C'_{M_B+1,1}+\sum_{\ell=2}^{M_B+4}[\gamma_{\ell,A}(C'_{1,1}-C_{M_B+1,M_B+2})-I_{1,A}C_{\ell,M_B+2}-I_{\ell,A}C_{1,M_B+2}]$$

$$\cdot c^*_{A1}(X_i,R_\ell,T')+\sum_{\ell=2}^{M_B+4}I_{1,A}C'_{\ell,1}\,c^*_{A2}(X_i,R'_\ell,T')\Big\} \tag{88}$$

where

$$I_{\ell,A} = E_{M_B+2,A}\,C_{\ell,1}-E_{\ell,A}\,C_{M_B+2,1} \tag{89}$$

and

$$\gamma_{\ell,A} = E_{1,A}\,C_{\ell,1}-E_{\ell,A}\,C_{1,1} \tag{90}$$

If we combine (67) with (75), (78) and (87), we get

$$\left.\frac{dc^*_{B1}}{dT'}\right|_{X_i,R_\ell} = \beta\Big\{-\frac{B_{i,1}}{A_{1,1}[1+\Theta_{A/B}S_A(T')]}\Big[A_{1,M_B+2}+\sum_{j=2}^{M_B+4}A_{1,j}[c^*_{A1}(X_j,R_\ell,T')+c^*_{B1}(X_j,R_\ell,T')]\Big]$$

$$+\sum_{j=2}^{M_B+4}B_{i,j}\,c^*_{B1}(X_j,R_\ell,T')\Big\}+\frac{\beta'}{G_1}\Big\{\sum_{\ell=2}^{M_B+4}[\gamma_{\ell,A}(C'_{1,1}-C_{M_B+1,M_B+2})-I_{1,A}C_{\ell,M_B+2}$$

$$-I_{\ell,A}C_{1,M_B+2}]c^*_{B1}(X_i,R_\ell,T')+\sum_{\ell=2}^{M_B+4}I_{1,A}C'_{\ell,1}\,c^*_{B2}(X_i,R'_\ell,T')\Big\}-\alpha\,c^*_{B1} \tag{91}$$

similarly (68) gives with (76), (79) and (80)

$$\left.\frac{dc^*_{C1}}{dT'}\right|_{X_i,R_\ell} = \frac{\beta}{A_{1,1}}\sum_{j=2}^{M_B+4}K_{i,j}\,c^*_{C1}(X_j,R_\ell,T')$$

$$+\frac{\beta'}{G_1}\Big\{\sum_{\ell=2}^{M_B+4}[\gamma_{\ell,A}(C'_{1,1}-C_{M_B+1,M_B+2})-I_{1,A}C_{\ell,M_B+2}-I_{\ell,A}C_{1,M_B+2}]c^*_{C1}(X_i,R_\ell,T')$$

$$+\sum_{\ell=2}^{M_B+4}I_{1,A}C'_{\ell,1}\,c^*_{C2}(X_i,R'_\ell,T')\Big\}+\alpha\,c^*_{B1} \tag{92}$$

For the outer function describing the concentration species A it holds from (69), (77), and (81)

$$\left.\frac{dc^*_{A2}}{dT'}\right|_{X_i,R'_\ell} = \frac{\beta}{A_{1,1}}\Big\{K_{i,M_B+2}+\sum_{j=2}^{M_B+4}K_{i,j}\,c^*_{A2}(X_j,R'_\ell,T')\Big\}$$

$$+\frac{\beta''}{G_1}\Big\{L'_{M_B+1,\ell}+\sum_{\ell=2}^{M_B+4}F'_{1,A}H_\ell\,c^*_{A1}(X_i,R_\ell,T')+\sum_{\ell=2}^{M_B+4}L'_{\ell,A}c^*_{A2}(X_i,R'_\ell,T')\Big\} \tag{93}$$

Equations (70), (78), and (82) combine to give

$$\left.\frac{dc^*_{B2}}{dT'}\right|_{X_i,R'_\ell} = \frac{\beta}{A_{1,1}}\sum_{j=2}^{M_B+4}K_{i,j}\,c^*_{B2}(X_j,R'_\ell,T')$$

$$+\frac{\beta''}{G_1}\Big\{\sum_{\ell=2}^{M_B+4}F'_{1,A}H_\ell\,c^*_{B1}(X_i,R_\ell,T')+\sum_{\ell=2}^{M_B+4}L'_{\ell,A}c^*_{B2}(X_i,R'_\ell,T')\Big\}-\alpha\,c^*_{B2} \tag{94}$$

Finally (71), (79), and (83) yield

$$\left.\frac{dc^*_{C2}}{dT'}\right|_{X_i,R'_k} = \frac{\beta}{A_{4,4}}\sum_{j=2}^{N_X+1} K_{i,j}\, c^*_{C2}(X_j,R'_k,T') + \frac{\beta^*}{G_4}\left\{\sum_{\ell=2}^{N_R+1} F'_{4,k}\, He\, c^*_{C4}(X_i,R_\ell,T') + \sum_{\ell=2}^{N_R+1} L'_{\ell,k}\, c^*_{C2}(X_i,R'_\ell,T')\right\} + \alpha c^*_{B2} \tag{95}$$

where we used

$$K_{i,j} = B_{i,j} A_{4,4} - B_{i,4} A_{4,j} \tag{96}$$

and

$$L'_{\ell,k} = F'_{\ell,k} G_4 + C_{4,4} C'_{\ell,4} F'_{4,k} \tag{97}$$

Thus, the system of 6 second order partial differential equations (32)-(37) has been converted into a set of $3N_X(N_R + N_{R'})$ simultaneous ordinary differential equations, (88) and (91)-(95). After integrating this set we get the concentrations of species A, B and C at the collocation points (X_i, R_k) and (X_i, R_k') as a function of the simulation time T'.

One of the distinctive features of the orthogonal collocation approach can be seen from a comparison of equations (88) and (91)-(95). Those formulae are very similar from a structural point of view. Furthermore, compared to the expressions describing the model of a chronoamperometric experiment [1], there are only few changes in the inner

functions, while the outer functions are the same both for the models of cyclic voltammetry and chronoamperometry.

CALCULATION OF THE CURRENT

Also, the calculation of the current is fully analogous to that performed for the chronoamperometric model. Again we have to integrate the flux over the part between 0 and r_0 on the r-axis

$$i = nFD\int_0^{r_0} 2\pi r \left(\frac{\partial c_A}{\partial x}\right)_{x=0} dr \tag{98}$$

Transforming the right hand side of equation (98) into a dimensionless form we get

$$i = nFAc^*_A\sqrt{Da\pi}\sqrt{\frac{\beta}{\pi}}\cdot 2\cdot\int_0^1 R\left(\frac{\partial c^*_{A4}}{\partial X}\right)_{X=0} dR \tag{99}$$

or, using Nicholson and Shain's current function [6]

$$\chi = \frac{i}{nFAc^*_A\sqrt{Da\pi}} = 2\sqrt{\frac{\beta}{\pi}}\int_0^1 R\left(\frac{\partial c^*_{A4}}{\partial X}\right)_{X=0} dR \tag{100}$$

The integration may be performed exactly by a quadrature method [11], for we know the derivative $(\partial c^*_A/\partial X)_{X=0}$ at all collocation points

$$\chi = 2\sqrt{\frac{\beta}{\pi}} \sum_{\ell=1}^{N_p+2} Q_\ell R_\ell \frac{1}{1+\Theta_{A/B} S_A(T')} \Big[A_{1,N_p+2}{}^{*} \sum_{j=2}^{N_p+1} A_{1,j}\, c^{*}_{A1}(X_j, R_\ell, T') - \Theta_{A/B} S_A(T') \sum_{j=2}^{N_p+1} A_{1,j}\, c^{*}_{B1}(X_j, R_\ell, T') \Big] \tag{101}$$

where the elements of the vector Q depend only on the degree and kind of the trial function in r-direction.

MODEL MECHANISM FOR OXIDATION OF I

It has been shown [12,13] that the oxidation of I (denoted as A) may be described by an ECE-type mechanism, where protons released after the oxidation step are picked up by unoxidized phenol molecules giving the protonated form of I, HA^+. The latter is oxidized at more positive potentials releasing two protons during reaction. The end product of both reactions is the stable phenoxenium cation, E, which is most probably formed from the neutral phenoxy radical, C, in a homogeneous redox reaction between C and the primary radical cation B [13]. The intermediate D was not oxidized further. The observation of changes in voltammograms of I with electrode size has been attributed to the protonation reaction $A \rightarrow HA^+$ which causes a phenol-free layer in front of the electrode [5]. The time after which phenol again reaches the electrode surface is decreased if more substrate diffuses into this layer dueto edge effects.

$$A \underset{+e^{\ominus}}{\overset{-e^{\ominus}}{\rightleftharpoons}} B \qquad E^{\circ}_{A/B},\ n_A = 1$$

$$B \longrightarrow H^{\oplus} + C \qquad k_1$$

$$H^{\oplus} + A \longrightarrow HA^{\oplus} \qquad k_2$$

$$HA^{\oplus} \underset{+e^{\ominus}}{\overset{-e^{\ominus}}{\rightleftharpoons}} D \qquad E^{\circ}_{HA^{\oplus}/D},\ n_D = 1$$

$$D \longrightarrow 2H^{\oplus} + C \qquad k_3$$

$$B + C \rightleftharpoons A + E \qquad K_4 \gg 1,\ k_4/k_{-4} = K_4$$

$$C \underset{+e^{\ominus}}{\overset{-e^{\ominus}}{\rightleftharpoons}} E \qquad E^{\circ}_{C/E},\ n_E = 1$$

With our two-dimensional simulation model it is now possible to include the effects of a finite disc into the calculations. This may also serve as a further example for the application of orthogonal collocation to electroanalytical problems. In this paper we show the derivation of the expressions for dc^*/dT' for the species involved, while the comparison with experimental results will be reported in part 4 of this series.

The kinetic diffusion equations for the above model mechanism in dimensionless form are

$$\frac{\partial c^*_{A1}}{\partial T'} = \beta \frac{\partial^2 c^*_{A1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c^*_{A1}}{\partial R} + \beta' \frac{\partial^2 c^*_{A1}}{\partial R^2} - \alpha_2 c^*_{H\oplus_1} c^*_{A1} - \alpha_{-4} c^*_{A1} c^*_{E1} + \alpha_4 c^*_{B1} c^*_{C1} \tag{102}$$

$$\frac{\partial c^*_{B1}}{\partial T'} = \beta \frac{\partial^2 c^*_{B1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c^*_{B1}}{\partial R} + \beta' \frac{\partial^2 c^*_{B1}}{\partial R^2} - \alpha_1 c^*_{B1} - \alpha_4 c^*_{B1} c^*_{C1} + \alpha_{-4} c^*_{A1} c^*_{E1} \tag{103}$$

$$\frac{\partial c^*_{C1}}{\partial T'} = \beta \frac{\partial^2 c^*_{C1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c^*_{C1}}{\partial R} + \beta' \frac{\partial^2 c^*_{C1}}{\partial R^2} + \alpha_1 c^*_{B1} + \alpha_3 c^*_{D1} - \alpha_4 c^*_{B1} c^*_{C1} + \alpha_{-4} c^*_{A1} c^*_{E1} \tag{104}$$

$$\frac{\partial c^*_{H\oplus_1}}{\partial T'} = \beta \frac{\partial^2 c^*_{H\oplus_1}}{\partial X^2} + \frac{\beta'}{R} \frac{\partial c^*_{H\oplus_1}}{\partial R} + \beta' \frac{\partial^2 c^*_{H\oplus_1}}{\partial R^2} + \alpha_1 c^*_{B1} + 2\alpha_3 c^*_{D1} - \alpha_2 c^*_{A1} c^*_{H\oplus_1} \tag{105}$$

$$\frac{\partial c^{*}_{\omega\omega_1}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\omega\omega_1}}{\partial X^2} + \frac{\beta'}{R}\frac{\partial c^{*}_{\omega\omega_1}}{\partial R} + \beta' \frac{\partial^2 c^{*}_{\omega\omega_1}}{\partial R^2} + \alpha_2 c^{*}_{A1} c^{*}_{\omega\omega_1} \tag{106}$$

$$\frac{\partial c^{*}_{\beta_{21}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\beta_{21}}}{\partial X^2} + \frac{\beta'}{R}\frac{\partial c^{*}_{\beta_{21}}}{\partial R} + \beta' \frac{\partial^2 c^{*}_{\beta_{21}}}{\partial R^2} - \alpha_3 c^{*}_{\beta_{21}} \tag{107}$$

$$\frac{\partial c^{*}_{\beta_{41}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\beta_{41}}}{\partial X^2} + \frac{\beta'}{R}\frac{\partial c^{*}_{\beta_{41}}}{\partial R} + \beta' \frac{\partial^2 c^{*}_{\beta_{41}}}{\partial R^2} + \alpha_4 c^{*}_{\beta_{41}} c^{*}_{\alpha_{41}} - \alpha_{-4} c^{*}_{A1} c^{*}_{\beta_{41}} \tag{108}$$

$$\frac{\partial c^{*}_{A_{12}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{A_{12}}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{A_{12}}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{A_{12}}}{\partial R'^2} - \alpha_2 c^{*}_{\omega\omega_2} c^{*}_{A_{12}} - \alpha_{-4} c^{*}_{A_{12}} c^{*}_{\beta_{12}} + \alpha_4 c^{*}_{\beta_{12}} c^{*}_{\alpha_{12}} \tag{109}$$

$$\frac{\partial c^{*}_{\beta_{12}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\beta_{12}}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{\beta_{12}}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{\beta_{12}}}{\partial R'^2} - \alpha_4 c^{*}_{\beta_{12}} - \alpha_4 c^{*}_{\beta_{12}} c^{*}_{\alpha_{12}} + \alpha_{-4} c^{*}_{A_{12}} c^{*}_{\beta_{12}} \tag{110}$$

$$\frac{\partial c^{*}_{\alpha_{12}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\alpha_{12}}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{\alpha_{12}}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{\alpha_{12}}}{\partial R'^2} + \alpha_4 c^{*}_{\beta_{12}} + \alpha_3 c^{*}_{\beta_{12}} - \alpha_4 c^{*}_{\beta_{12}} c^{*}_{\alpha_{12}} + \alpha_{-4} c^{*}_{A_{12}} c^{*}_{\beta_{12}} \tag{111}$$

$$\frac{\partial c^{*}_{\omega\omega_2}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\omega\omega_2}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{\omega\omega_2}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{\omega\omega_2}}{\partial R'^2} + \alpha_4 c^{*}_{\beta_{12}} + 2\alpha_3 c^{*}_{\beta_{12}} - \alpha_4 c^{*}_{A_{12}} c^{*}_{\omega\omega_2} \tag{112}$$

$$\frac{\partial c^{*}_{\omega\omega_{12}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\omega\omega_{12}}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{\omega\omega_{12}}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{\omega\omega_{12}}}{\partial R'^2} + \alpha_2 c^{*}_{A_{12}} c^{*}_{\omega\omega_2} \tag{113}$$

$$\frac{\partial c^{*}_{\beta_{12}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\beta_{12}}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{\beta_{12}}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{\beta_{12}}}{\partial R'^2} - \alpha_3 c^{*}_{\beta_{12}} \tag{114}$$

$$\frac{\partial c^{*}_{\beta_{12}}}{\partial T'} = \beta \frac{\partial^2 c^{*}_{\beta_{12}}}{\partial X^2} + \frac{\beta''\sqrt{\beta''}}{\sqrt{\beta''}+\sqrt{\beta'}R'}\frac{\partial c^{*}_{\beta_{12}}}{\partial R'} + \beta'' \frac{\partial^2 c^{*}_{\beta_{12}}}{\partial R'^2} + \alpha_4 c^{*}_{\alpha_{12}} c^{*}_{\beta_{12}} - \alpha_{-4} c^{*}_{A_{12}} c^{*}_{\beta_{12}} \tag{115}$$

where

$$\alpha_j = k_j/a \quad , \quad j = 4,3 \tag{116}$$

$$\alpha_2 = k_2 c^{*}_{A} / a \tag{117}$$

and

$$\alpha_4 = k_4 c^{*}_{A} / a \tag{118a}$$

$$\alpha_{-4} = k_{-4} c^{*}_{A} / a \tag{118b}$$

In addition to the initial conditions (41) and (42) we assume

$T'=0, 0 \le X \le 1, 0 \le R \le 1, 0 \le R' \le 1$:

$$c^*_{HA\Theta_1}(X,R,0) = c^*_{HA\Theta_2}(X,R',0) = c^*_{HA\Theta_1}(X,R,0) = c^*_{HA\Theta_2}(X,R',0) =$$

$$c^*_{D1}(X,R,0) = c^*_{D2}(X,R',0) = c^*_{E1}(X,R,0) = c^*_{E2}(X,R',0) = 0 \tag{119}$$

The boundary conditions include now

$T'>0, X=1, 0 \le R \le 1$:

$$c^*_{HA\Theta_1}(1,R,T') = c^*_{HA\Theta_1}(1,R,T') = c^*_{D1}(1,R,T') = c^*_{E1}(1,R,T') = 0 \tag{120}$$

$T'>0, X=1, 0 \le R' \le 1$:

$$c^*_{HA\Theta_2}(1,R',T') = c^*_{HA\Theta_2}(1,R',T') = c^*_{D2}(1,R',T') = c^*_{E2}(1,R',T') = 0 \tag{121}$$

$T'>0, 0 \le X \le 1, R'=1$:

$$c^*_{HA\Theta_2}(X,1,T') = c^*_{HA\Theta_2}(X,1,T') = c^*_{D2}(X,1,T') = c^*_{E2}(X,1,T') = 0 \tag{122}$$

$T'>0, X=0, 0 \le R \le 1$:

$$\left(\frac{\partial c^*_{HA\Theta_1}}{\partial X}\right)_{X=0} = -\left(\frac{\partial c^*_{D1}}{\partial X}\right)_{X=0} \tag{123}$$

$$\frac{c^*_{HA\Theta_1}(0,R,T')}{c^*_{D1}(0,R,T')} = \Theta_{HA\Theta/D}\, S_1(T') \tag{124}$$

(where $\Theta_{HA^+/D}$ is defined in analogy to $\Theta_{A/B}$)

$$\left(\frac{\partial c^*_{HA\Theta_1}}{\partial X}\right)_{X=0} = 0 \tag{125}$$

$$\left(\frac{\partial c^*_{D1}}{\partial X}\right)_{X=0} = -\left(\frac{\partial c^*_{E1}}{\partial X}\right)_{X=0} \tag{126}$$

$$\frac{c^*_{C1}(0,R,T')}{c^*_{E1}(0,R,T')} = \Theta_{C/E}\, S_1(T') \tag{127}$$

$T'>0, X=0, 0 < R' \le 1$

$$\left(\frac{\partial c^*_{HA\Theta_2}}{\partial X}\right)_{X=0} = \left(\frac{\partial c^*_{HA\Theta_2}}{\partial X}\right)_{X=0} = \left(\frac{\partial c^*_{D2}}{\partial X}\right)_{X=0} = \left(\frac{\partial c^*_{E2}}{\partial X}\right)_{X=0} \tag{128}$$

$T'>0, X \ge 0, R=1 (R'=0)$:

$$c^*_{HA}(X,0,T') = c^*_{HA\Theta_1}(X,1,T') \tag{129}$$

$$c^*_{HA\Theta_2}(X,0,T') = c^*_{HA\Theta_1}(X,1,T') \tag{130}$$

$$c^*_{D2}(X,0,T') = c^*_{D1}(X,1,T') \tag{131}$$

$$c^*_{E2}(X,0,T') = c^*_{E1}(X,1,T') \tag{132}$$

$$\left(\frac{\partial c^*_{H\Theta_1}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta''}{\beta'}}\left(\frac{\partial c^*_{H\Theta_2}}{\partial R'}\right)_{R'=0} \tag{133}$$

$$\left(\frac{\partial c^*_{HA\Theta_1}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta''}{\beta'}}\left(\frac{\partial c^*_{HA\Theta_2}}{\partial R'}\right)_{R'=0} \tag{134}$$

$$\left(\frac{\partial c^*_{D1}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta''}{\beta'}}\left(\frac{\partial c^*_{D2}}{\partial R'}\right)_{R'=0} \tag{135}$$

$$\left(\frac{\partial c^*_{E2}}{\partial R}\right)_{R=1} = \sqrt{\frac{\beta''}{\beta'}}\left(\frac{\partial c^*_{E2}}{\partial R'}\right)_{R'=0} \tag{136}$$

$T'>0,\ X\geq 0,\ R=0$:

$$\left(\frac{\partial c^*_{H\Theta_1}}{\partial R}\right)_{R=0} = \left(\frac{\partial c^*_{HA\Theta_1}}{\partial R}\right)_{R=0} = \left(\frac{\partial c^*_{D1}}{\partial R}\right)_{R=0} = \left(\frac{\partial c^*_{E1}}{\partial R}\right)_{R=0} = 0 \tag{137}$$

Now, the set of equations (102)-(115) in connection with the

initial conditions (41), (42) and (119) and the boundary conditions (43)-(50), (54)-(61) and (120)-(137) has to be solved.

After proceeding in the same manner as for the EC mechanism we arrive at

$$\left.\frac{dc^*_{A1}}{dT'}\right/_{X_i,R_R} = \mathrm{RHS}(88) - \alpha_2 c^*_{H\Theta_1} c^*_{A1} - \alpha_{-4} c^*_{A1} c^*_{E1} + \alpha_4 c^*_{B1} c^*_{C1} \tag{138}$$

$$\left.\frac{dc^*_{B1}}{dT'}\right/_{X_i,R_R} = [\mathrm{RHS}(91)\ \text{without kinetic term}] - \alpha_1 c^*_{B1} - \alpha_4 c^*_{B1} c^*_{C1} + \alpha_{-4} c^*_{A1} c^*_{E1} \tag{139}$$

$$\left.\frac{dc^*_{C1}}{dT'}\right/_{X_i,R_R} = \beta\Big\{-\frac{B_{i,1}\Theta_{C/E} S_1(T')}{A_{1,1}[1+\Theta_{C/E} S_1(T')]}\sum_{j=2}^{M_2+1} A_{1,j}\left[c^*_{C1}(X_j,R_R,T') + c^*_{E1}(X_j,R_R,T')\right] + \sum_{j=2}^{M_2+1} B_{i,j}\, c^*_{C1}(X_j,R_R,T')\Big\} + \frac{\beta'}{G_1}\Big\{\sum_{\ell=2}^{M_R+1}\left[J_{\ell,R}(C'_{1,1} - C_{M_2+1,M_R+1}) - I_{1,R} C_{\ell,M_R+2} - I_{\ell,R} C_{1,M_R+1}\right]\cdot c^*_{C1}(X_i,R_\ell,T') + \sum_{\ell=2}^{M_R+1} I_{1,R}\, C'_{\ell,1}\, c^*_{C2}(X_i,R'_\ell,T')\Big\} + \alpha_1 c^*_{B1} + \alpha_3 c^*_{D1} - \alpha_4 c^*_{B1} c^*_{C1} + \alpha_{-4} c^*_{A1} c^*_{E1} \tag{140}$$

$$\left.\frac{dc^*_{H\Theta_1}}{dT'}\right/_{X_i,R_R} = [\mathrm{RHS}(92)\ \text{without kinetic term and } c^*_{H\Theta_1} \text{ substituted for } c^*_{C1}] + \alpha_1 c^*_{B1} + 2\alpha_3 c^*_{D1} - \alpha_2 c^*_{A1} c^*_{H\Theta_1} \tag{141}$$

$$\left.\frac{dc^*_{HA\Theta_1}}{dT'}\right/_{X_i,R_R} = [\mathrm{RHS}(140)\ \text{without kinetic terms and } c^*_{HA\Theta_1} \text{ substituted for } c^*_{C1},\ c^*_{D1} \text{ substituted for } c^*_{E} \text{ and } \Theta_{HA\Theta/D} \text{ substituted for } \Theta_{C/E}] +$$

$$+\alpha_2 c^*_{A1} c^*_{HO_1} \tag{142}$$

$$\left.\frac{dc^*_{D1}}{dT'}\right|_{X_i', R_k} = [\text{RHS}(91) \text{ without kinetic term and } c^*_{D1} \text{ substituted for } c^*_{B1}, c^*_{HA} \text{ substituted for } c^*_A \text{ and } \Theta_{HA\Theta/D} \text{ substituted for } \Theta_{A/B}] - \alpha_3 c^*_{D1} \tag{143}$$

$$\left.\frac{dc^*_{E1}}{dT'}\right|_{X_i', R_k} = [\text{RHS}(91) \text{ without kinetic term and } c^*_{E1} \text{ substituted for } c^*_{B1}, c^*_{C1} \text{ substituted for } c^*_{A1} \text{ and } \Theta_{C/E} \text{ substituted for } \Theta_{A/B}] + \alpha_4 c^*_{B1} c^*_{C1} - \alpha_{-4} c^*_{A1} c^*_{E1} \tag{144}$$

$$\left.\frac{dc^*_{A2}}{dT'}\right|_{X_i', R_k'} = \text{RHS}(93) - \alpha_2 c^*_{HO_2} c^*_{A2} - \alpha_{-4} c^*_{A2} c^*_{E2} + \alpha_4 c^*_{B2} c^*_{C2} \tag{145}$$

$$\left.\frac{dc^*_{B2}}{dT'}\right|_{X_i', R_k'} = [\text{RHS}(94) \text{ without kinetic term}] - \alpha_1 c^*_{B2} - \alpha_4 c^*_{B2} c^*_{C2} + \alpha_{-4} c^*_{A2} c^*_{E2} \tag{146}$$

$$\left.\frac{dc^*_{C2}}{dT'}\right|_{X_i', R_k'} = [\text{RHS}(95) \text{ without kinetic term}] + \alpha_1 c^*_{B2} + \alpha_3 c^*_{D2} - \alpha_4 c^*_{B2} c^*_{C2} + \alpha_{-4} c^*_{A2} c^*_{E2} \tag{147}$$

$$\left.\frac{dc^*_{HO_2}}{dT'}\right|_{X_i', R_k'} = [\text{RHS}(95) \text{ without kinetic term and } c^*_{HO_2} \text{ substituted for } c^*_{C2}] + \alpha_1 c^*_{B2} + 2\alpha_3 c^*_{D2} - \alpha_2 c^*_{A2} c^*_{HO_2} \tag{148}$$

$$\left.\frac{dc^*_{HA\Theta_2}}{dT'}\right|_{X_i', R_k'} = [\text{RHS}(95) \text{ without kinetic term and } c^*_{HA\Theta_2} \text{ substituted for } c^*_{C2}] + \alpha_2 c^*_{A2} c^*_{HO_2} \tag{149}$$

$$\left.\frac{dc^*_{D2}}{dT'}\right|_{X_i', R_k'} = [\text{RHS}(95) \text{ without kinetic term and } c^*_{D2} \text{ substituted for } c^*_{C2}] - \alpha_3 c^*_{D2} \tag{150}$$

$$\left.\frac{dc^*_{E2}}{dT'}\right|_{X_i', R_k'} = [\text{RHS}(95) \text{ without kinetic terms and } c^*_{E2} \text{ substituted for } c^*_{C2}] + \alpha_4 c^*_{B2} c^*_{C2} - \alpha_{-4} c^*_{A2} c^*_{E2} \tag{151}$$

Again, the close resemblance of all expressions may be noted. The current function in this model is determined by the fluxes of A, HA^+ and C to the electrode

$$\begin{aligned}
\chi = {} & 2\sqrt{\frac{\beta}{\pi}} \int_0^1 R\left[\left(\frac{\partial c^*_{HA}}{\partial X}\right)_{X=0} + \left(\frac{\partial c^*_{HA\Theta_1}}{\partial X}\right)_{X=0} + \left(\frac{\partial c^*_{C1}}{\partial X}\right)_{X=0}\right] dR \\
= {} & 2\sqrt{\frac{\beta}{\pi}} \sum_{\ell=1}^{N_R+2} Q_\ell R_\ell \left[\frac{1}{1+\Theta_{A/B} S_A(T')} \left\{A_{1,N_R+2} + \sum_{j=2}^{N_R+1} A_{1,j} c^*_{A1}(X_j, R_k, T') - \Theta_{A/B} S_A(T') \sum_{j=2}^{N_R+1} A_{1,j} c^*_{B1}(X_j, R_k, T')\right\} + \frac{n_2}{n_1} \frac{1}{1+\Theta_{HA\Theta/D} S_A(T')} \right. \\
& \left[\sum_{j=2}^{N_R+1} A_{1,j} c^*_{HA\Theta_1}(X_j, R_k, T') - \Theta_{HA\Theta/D} S_A(T') \sum_{j=2}^{N_R+1} A_{1,j} c^*_D(X_j, R_k, T')\right\} \\
& \left. + \frac{n_3}{n_1} \frac{1}{1+\Theta_{C/E} S_A(T')} \left\{\sum_{j=2}^{N_R+1} A_{1,j} c^*_{C1}(X_j, R_k, T') - \Theta_{C/E} S_A(T') \sum_{j=2}^{N_R+1} A_{1,j} c^*_E(X_j, R_k, T')\right\}\right]
\end{aligned} \tag{152}$$

CONCLUSION

We showed in this paper the use of two-dimensional collocation to spatially discretize partial differential equations describing a model of cyclic voltammetric experiments under the influence of edge effects. The formal similarity of descretized equations for even very complicated mechanisms has been demonstrated by considering the oxidation scheme of phenol I. This similarity simplifies the writing and testing of computer programs used to calculate numerical simulation results. In fact, a change in mechanism normally only requires the exchange of a few FORTRAN statements while the main body of the program is untouched. We see this as one of the great advantages of our method which outweighs the difficulties encountered while assessing the features and behavior of a new type of a model, as this two-dimensional one. A thorough discussion of the numerical results for cyclic voltammetry simulations is given in part 4.

ACKNOWLEDGEMENT

We thank the Office of Naval Research, Washington, D.C., for support of this work.

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