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(Accepted, 24 April 1992)

Digital Simulation of Cyclic Voltammetry - Influence of the Space Discretization Technique

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ABSTRACT. The application of unequal space grid discretization to the solution of the diffusion equations in cyclic voltammetry by the line method (semi-discretization) is subjected to a preliminary analysis. It is shown that a carefully chosen exponentially expanding space grid can improve the accuracy of digital simulations by this method, although a significant improvement is only obtained for moderate values of the expanding parameter (larger values for this parameter result in performance degradation).

1. Introduction

Digital simulation techniques have been gaining popularity, even among experimental chemists, due to the current availability of inexpensive and fast computation means. The development of new programming techniques, leading to user-friendly programs, is also favouring the widespread use of digital simulation.

Electrochemistry, and in particular cyclic voltammetry, has been a very active field for digital simulation, and the quest for an "universally efficient" method still attracts a lot of attention.

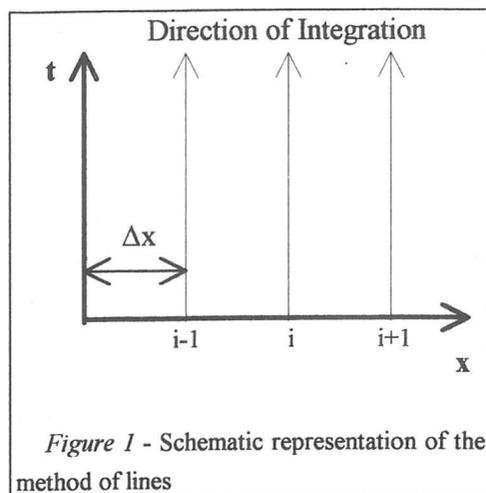
In the present work we are concerned with the space discretization technique, and its effect on the accuracy of the computed voltammograms. The interest of this type of investigation has already been recognized by Britz [1] who suggested that it would be worthwhile to study the improvement of the space discretization, in order to make the

Runge-Kutta integration method more efficient. The author pointed out that, as an explicit technique, this method was more efficient than the classical finite-differences and required a minimum effort to implement and modify.

The method applies to the set of ordinary first-order differential equations (equations 2, where C_i^j is the concentration of species j in box i , D^j is the diffusivity of this species and Δx is the box width) which are obtained by discretizing only the spatial derivatives of the second order partial differential equations that describe the electrochemical system (equations 1, where x is the spatial dimension).

$$\frac{\partial C^j}{\partial t} = D^j \frac{\partial^2 C^j}{\partial x^2} \quad (1)$$

$$\frac{dC_i^j}{dt} = D^j \frac{C_{i+1}^j - 2C_i^j + C_{i-1}^j}{\Delta x^2} \quad (2)$$



This procedure, which Fox [2] suggested, back in the sixties, to solve the parabolic type partial differential equations (1), is called the "method of lines", whereas the process of discretization in space, using finite differences, is known as the "semi-discretization" process.

One way of improving the space discretization is considering a non-uniform space grid, where the thicknesses of volume elements, Δx , decreases towards the electrode surface, as required by the large

changes in concentration occurring therein. Thus, any concentration profile will be described in greater detail close to the electrode surface than farther from it, where the concentration evolves less drastically. The exponentially expanding space grid was first suggested by Joslin and Pletcher [3] and refined later by Feldberg [4]. As defined in their paper, the ratio between two consecutive volume elements is a constant, greater than

unity and up to $e^{0.5}$. This upper limit was determined empirically as the largest value that maintains reasonable accuracy [3]. When the ratio equals unity a uniform grid is generated. The exponentially expanding space grid was used with explicit finite difference methods [5,6], the implicit finite difference method [7], and as an essential ingredient of the so-called fast quasi-explicit finite difference method [8]. It was demonstrated the time saving virtues of using such a non-uniform grid, and the advantage of this approximation when multiple kinetic processes originate a stiff differential equation system [9].

However, as far as we know, the exponentially expanding grid has not been previously applied to the "method of lines" and its application to this method is the object of our study. This follows our previous investigation of several Runge-Kutta integration schemes and some predictor-corrector methods, such as the Adams-Moulton multistep method, applied to an ECECE type mechanism [10], which shows how an improved time integration technique affects the error surface and the stability regions for that process. In that study a uniform space grid was always employed. In the present work we wish to report the influence of improved space discretization on the performance of the "method of lines" to integrate the parabolic equations describing cyclic voltammetry experiments.

2. Digital Simulation

A simple E mechanism was simulated, so that it could easily be compared to known published data [11]. A conventional model for the solution was built, considering that the continuous solution could be represented by perfectly homogeneous "boxes", having a width of Δx . The way this width varied with the position of the box inside the solution depended on the particular method used. The "method of lines" was applied to solve the necessary equations, and several numerical integration schemes were used to solve the set of ordinary differential equations resulting from the space discretization [12]. These methods included the 2nd order Runge-Kutta (or modified Euler), the fourth order Runge-Kutta and the Adams-Moulton multistep predictor-corrector. The step size was chosen to be sufficiently small (0.1 mV), so that no significant errors resulted from time discretization.

The program to compute all the voltammograms was written in Turbo Pascal Version 6 (from Borland Int.) and run on a 386SX/25MHz based IBM compatible personal computer, equipped with a Fasmath Cyrix math co-processor.

The error was computed comparing the simulated voltammograms with the theoretical one (for an infinite diffusion layer) published by Nicholson and Shain [11]. For all available points the relative error was computed and these were then averaged according to the expression (3).

$$\overline{Error(\%)} = \sum \frac{(Cf_{NS} - Cf_{Sim})/Cf_{NS}}{N} \times 100 \quad (3)$$

where Cf_{Sim} represents the current function obtained by the simulation, Cf_{NS} the current function obtained from the indicated reference and N the number of data points being compared.

3. Results and Discussion

The first set of simulations was carried out using a fixed and an expanding space discretization grid. The sizes of the solution "boxes" were computed according to the following expression:

$$\Delta x_i = \Delta x_0 e^{\beta i} \quad i = 0, 1, \dots, n \quad (4)$$

where Δx_0 represents the width of the first box, β the expansion parameter and n the number of boxes.

Both β and the width of the first box (Δx_0) were varied, the former changed from 0 (fixed width) to 1, and the latter from 1 μm to 8 μm . As an example, the box distribution obtained as a function of β (from 0 to 0.6) is depicted in figure 2. For this space discretization, equation 1 becomes:

$$\frac{dC_i^j}{dt} = \frac{2D^j}{\Delta x_i} \left(\frac{C_{i+1}^j - C_i^j}{\Delta x_{i+1} + \Delta x_i} - \frac{C_i^j - C_{i-1}^j}{\Delta x_i + \Delta x_{i-1}} \right) \quad (5)$$

For this comparison, a low number of solution elements (10 plus the electrode box) was purposely chosen, corresponding to a diffusion layer thickness (Δ) given by:

$$\Delta = \sum_{i=0}^{10} \Delta x_i \quad (6)$$

Although for the fixed box size, this number of boxes corresponds to a value of Δ which is much smaller than that estimated (0.02 cm) for the semi-infinite solution approximation*, the latter diffusion layer thickness is already obtained for sufficiently high β values. The limitation of the number of boxes also serves the purpose of testing the ability of this scheme to achieve a reasonable accuracy with a limited amount of computation. In fact, a relevant goal of this work is to open the way to a general and fast simulation program. If, in a simulation, we can keep the number of elements to compute at a low level, the computation time will decrease significantly.

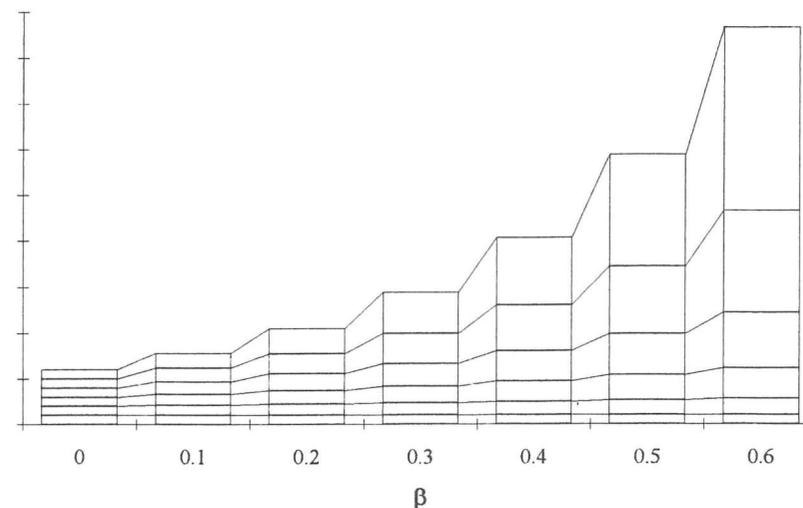


Figure 2 - Representation of the division of the solution into unequal boxes as a function of β . For clarity only six boxes are shown ($i=0$ to 5 , ordered from the bottom to the top).

*It has been proposed [6] that the extent to which an infinite solution is affected by an experiment with the duration τ can be estimated by $\Delta \approx 6 \sqrt{D \tau}$ [6], which, in our case ($D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $v = 200 \text{ mV s}^{-1}$) is about 0.02 cm.

Figure 3 represents the average error, computed as indicated above, as a function of both Δx_0 and β .

One can observe that, if the box width (Δx_0) is small, an accuracy gain results from the use of an exponentially expanding grid ($\beta > 0$) relatively to a fixed grid ($\beta = 0$), in agreement with the increase of the width of the simulated diffusion layer. However, the expansion parameter (β) should not be increased too much, since beyond a certain limit an increase of the error is observed (see figure 4), on account of excessive box width. Moreover if a relatively large element is used to start with (higher Δx_0), the exponential grid does not improve the accuracy, but on the contrary induces a growth of the error.

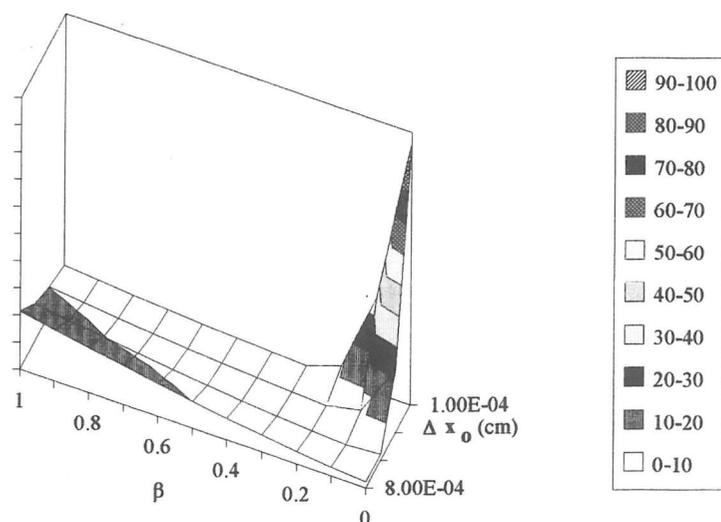


Figure 3 - Representation of the average error (percentage) of the computed voltammograms as a function of the width of the first box (Δx_0 /cm) and the expansion parameter (β).

In fact, if Δx_0 is large enough, the expansion of the space grid results in an increase of the discretization error, by unnecessarily increasing the apparent diffusion layer.

Another important conclusion that can be drawn from figure 4 is that it is feasible to obtain reasonably good simulations (at 1 % average error) even with such a low number of solution elements as that used in this work.

It is also important to see how the error is distributed along the voltammogram. This is shown in figure 5, which reveals that these simulations appear to be adequate for the purpose of dealing with the experimental data (the error relative to the theoretical Nicholson and Shain values is commonly ca. 1 %, except for very low currents, i.e., lies below the usual experimental error).

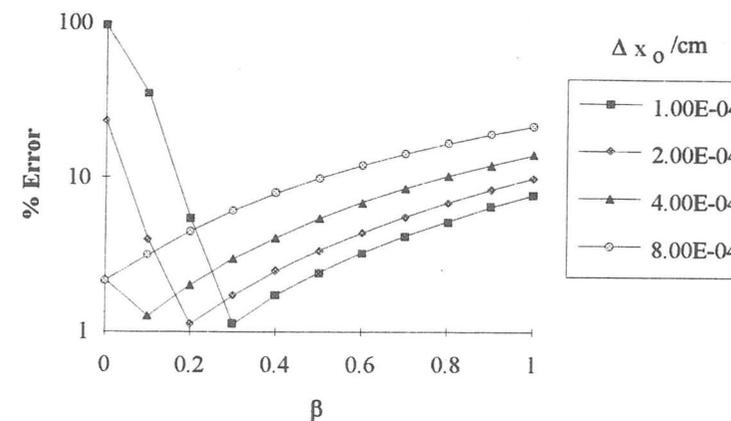


Figure 4 - Evolution of the average error (in percentage) as a function of β , for various values of Δx_0 (cm).

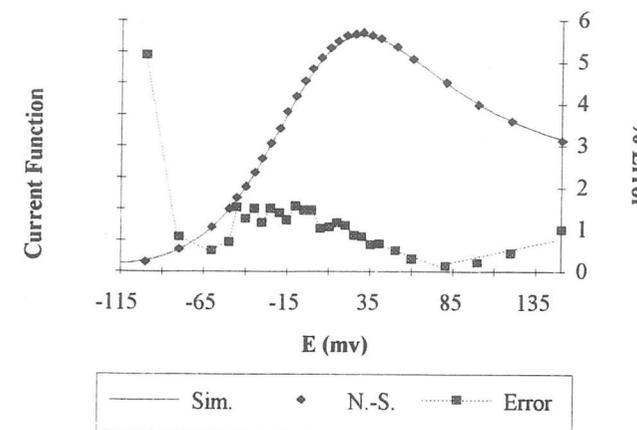


Figure 5 - Comparison of the simulated voltammogram (curve) and data (\blacklozenge) from ref. [11] (Nicholson and Shain, N.-S.). The distribution of relative (\blacksquare) error along the voltammogram is also included.

However, as expected, the increase of the number of boxes clearly improves the accuracy of the simulation (all other parameters remaining constant), as can be seen in figures 6 and 7, which show the decrease of the average error with the increase of the number of boxes, for the same total width of the diffusion layer (Δ).

This last assumption (fixed finite diffusion layer) was made considering that, although the theoretical description of the phenomena that occur during a cyclic voltammetry experiment implies that one considers a perfectly stationary solution, where the transport processes are exclusively diffusional (in the presence of a supporting electrolyte) and the diffusion layer is infinite, a practical experiment necessarily deviates from this model, not because of the finite size of the electrochemistry cell itself (since its dimensions are far larger than that of the diffusion layer), but as a result of natural convection processes which tend to homogenize the solution from a certain distance to the electrode.

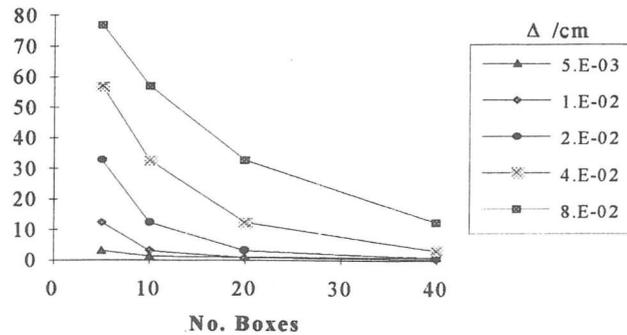


Figure 6 - Average error (in percentage) as a function of the number of boxes (n) for different widths of the diffusional layer (Δ /cm). Simulations were done with evenly spaced boxes.

In the case of figure 6 equal boxes were used. For a fixed total width, the error decreases as the number of boxes increases, as it would be expected from the decrease in the discretization error. However, an increase in the total width of the diffusion layer usually leads to a poorer accuracy. In the range used in this study, the error is mainly dependent on the width of each individual box (Δx_0) as can be seen if we rearrange the data from figure 6. Figure 7 represents the average error as a function of Δx_0 for various

numbers of boxes, showing that only for very small values of this parameter do the results present a dependence on the number of boxes used (for $\Delta x_0 \geq 0.001$ cm the average error is independent of the number of boxes).

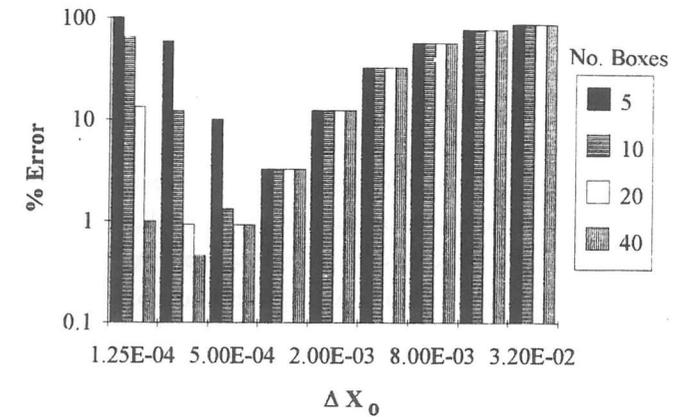


Figure 7 - Average error (in percentage) as a function of the box width (Δx_0 /cm) for various numbers of boxes. Simulations were done with evenly spaced boxes.

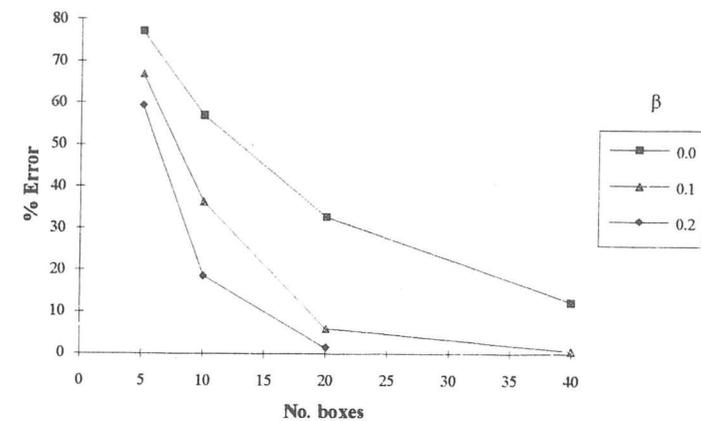


Figure 8 - Average relative error as a function of the number of boxes for various values of β (0, for uniformly spaced, 0.1 and 0.2). The total width of the diffusion layer under calculation was kept constant at 0.08 cm.

The use of unevenly spaced boxes also brings benefits in this case, rapidly decreasing the error as can be seen in figure 8. However, since the total width of the diffusion layer is kept fixed, the increase in the value of β induces a marked decrease in the first box width, leading to the need of decreasing the time increment, thus enlarging the computation time.

4. Conclusions

This work indicates that, even with a small number of solution elements (boxes), it is feasible to obtain simulations that would suit comparison purposes with experimental data. In this case the simulations are easily handled in any small personal computer.

The step size used in this work was quite small (see above); however this would not be required, since we have shown previously [10] that the use of the fourth-order Runge-Kutta integration method or even of the Adams-Moulton scheme can produce simulations with a negligible error level, even with relatively large time integration steps.

The use of exponentially expanding space grids can improve the accuracy of the simulations, provided that both Δx_0 (width of the first box) and β (expansion parameter) are carefully chosen. However, a balance between the gain in computation time due to improved space discretization should be weighed against the possible opposite effect due to the need of using smaller time step size (which is related to the width of the first box). Careful use of this expanding grid technique enables the experimental chemist to have fast simulations near the laboratory workbench.

The use of the expanding grid allows the use of smaller boxes near the electrode and larger ones away from it, and this can also be important in cases where electrogenerated species suffer fast homogeneous reactions, occurring very near the electrode.

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Acknowledgement - This work has been partially supported by JNICT and INIC.

(Received 8 Juni 1992)