Journal of Electroanalytical Chemistry 705 (2013) 44–51

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Automatic solution of integral equations describing electrochemical transients at dropping mercury electrodes

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A R T I C L E I N F O

Article history:
Received 10 May 2013
Received in revised form 2 July 2013
Accepted 19 July 2013
Available online 29 July 2013

Keywords:
Computational electrochemistry
Laboratory automation
Digital simulation
Transient methods
Volterra integral equations
Expanding plane DME model

A B S T R A C T

Polarographic experiments at dropping mercury electrodes belong to the classics of electroanalytical techniques. Theoretical modelling and computer simulation of such experiments is often based on the expanding plane model, which in the absence of homogeneous reactions is represented by one-dimensional convection–diffusion partial differential equations. The latter equations can be converted to integral equations involving a specific kernel function. In the present study, the adaptive Huber method, recently elaborated by the present author, has been extended to handle such a kernel function. The resulting simulation technique has been tested on examples of integral equations representing simple models of D.C. and A.C. polarography. The method is shown to provide automatic solutions, with a user-selected target accuracy. Errors corresponding to the range from about 10^{-2} of the maximum solution value, down to about 10^{-7} or even smaller, can be easily achieved at a modest computational cost.

1. Introduction

Trends to automate methods of scientific research with the help of computers are noticeable in various areas of natural sciences, including electroanalytical chemistry [1]. By following these trends, in the series of papers by the present author [2–18] an automatic method has been described, of solving integral equations (IEs) arising in the theory of transient electroanalytical experiments [19]. The IE-based digital simulation [20,21] is one of the approaches to the theoretical modelling in electrochemistry. The method of Refs. [2–18] makes use of the classical Huber discretisation [22], which has been popular among electrochemists (see, in particular, Refs. [20,23–36]). However, it has been supplemented with an algorithm for the adaptive selection of discrete integration steps. It therefore allows one to obtain solutions with a prescribed accuracy, thereby releasing the method user from the troubles of selecting computational grids and other details of the procedure.

The integrals occurring in the IEs of electroanalytical chemistry usually involve products of unknown functions (which are to be determined by solving the IEs), and diverse known functions, termed kernel functions (for the introduction to IEs and related terminology, see, for example, Ref. [37]). The adaptive Huber method of Refs. [2–18] works most satisfactorily when kernel-dependent coefficients of the method are calculated analytically or by using highly accurate approximations (preferably accurate at the level of machine accuracy). This makes the resulting algorithm more robust and less expensive computationally, compared to algorithms in which the method coefficients are computed by employing numerical quadratures or by solving auxiliary IEs (see, for example, the methods proposed by Mirčeski et al. [38,39]). Relevant formulae or approximations to the coefficients of the adaptive Huber method have already been developed for a number of most frequently encountered kernel functions [2–18]. However, there are still a few kernels that have not been incorporated into the method. One of them is the kernel representing the convection–diffusion transport in the electrolytic solution at dropping mercury electrodes (DMEs), in the absence of homogeneous reactions:

$$\mathcal{K}(t,\tau) = \tau^{2/3}\left(t^{7/3} - \tau^{7/3}\right)^{-1/2}, \qquad (1)$$

where t denotes time, and τ is an integration variable (see next section for further details, especially Eq. (6)). This kernel occurs in the theory of a variety of polarographic experiments [19]. Examples of IEs involving this kernel can be found in Refs. [40–55]. Although the DMEs are currently relatively less popular than other kinds of electrodes, a search on the *Science Direct* database still reveals over 600 publications related to the subject of “dropping mercury electrode” in the period 2000–2013, and predictions can be found [56,57] about continued uses of polarographic and drop formation techniques in the future. The inclusion of the kernel (1) into the adaptive Huber method is also a matter of completeness and respect for classical polarography as one of the milestones of contem-

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http://dx.doi.org/10.1016/j.jelechem.2013.07.022

porary electrochemistry. The ultimate goal of Refs. [2–18], and of the present work, is to develop an automatic software for solving all kinds of electrochemical models, independently of their current popularity.

Electrochemical literature does not seem to contain applications of the Huber method to IEs involving the kernel (1). Lovrić [55] described a simpler discretisation, a variation of the so-called step-function method [20], by assuming that the product of the unknown function of τ, and the factor $\tau^{-2/3}$, is approximated by a piecewise constant function. In contrast, in the Huber method the unknown functions are approximated by linear splines, which is a more accurate approach. Furthermore, there have been no applications of adaptive IE methods to IEs involving kernel (1). For all the above reasons, in the present paper we describe an extension of the adaptive Huber method onto this kernel function, and demonstrate its utility using typical example IEs of interest to electrochemistry.

2. Theory

Let us consider an electrochemical system comprising an electrolytic solution and a working DME, at which a number of chemical species participates in one or more electrochemical reactions. The discussion below applies exclusively to species distributed in the electrolyte phase. Let X_j be a jth of these species. According to the standard expanding plane model of the DME (a lucid derivation of the model can be found, for example, in Section 4.4 of Ref. [58]), the flux $J_j(x, t)$ of the species X_j is given by the formula:

$$J_j(x,t) = -D_j \frac{\partial c_j(x,t)}{\partial x} - \frac{2x}{3t} c_j(x,t), \tag{2}$$

so that its transport in the electrolyte is governed by the spatially one-dimensional convection–diffusion partial differential equation (PDE):

$$\frac{\partial c_j(x,t)}{\partial t} = D_j \frac{\partial^2 c_j(x,t)}{\partial x^2} + \frac{2x}{3t} \frac{\partial c_j(x,t)}{\partial x}. \tag{3}$$

In Eqs. (2) and (3) x denotes the distance from the surface of the DME, t denotes time (from drop birth), $c_j(x, t)$ is the concentration of the species, and D_j is its diffusion coefficient. In the case of electroanalytical experiments using the DMEs, Eq. (3) is usually accompanied by the uniform initial condition:

$$c_j(x,0) = c_j^*, \tag{4}$$

and the boundary condition

$$c_j(\infty,t) = c_j^*, \tag{5}$$

where c_j^* is the concentration of X_j in the electrolyte bulk.

By solving analytically the incomplete initial boundary value problem (3)–(5) with the help of the Laplace transform method, one obtains [40–55] the following integral relationship between the concentration and flux at the electrode:

$$c_j(0,t) = c_j^* + D_j^{-1/2} \left(\frac{7}{3\pi}\right)^{1/2} \int_0^t \mathcal{K}(t,\tau)\, J_j(0,\tau) d\tau, \tag{6}$$

where $\mathcal{K}(t, \tau)$ is the aforementioned kernel function (1) of interest to the present study. Although the problem (3)–(5) is incomplete, because it does not contain boundary conditions at $x = 0$, the relationship (6) can be derived, because both the concentration and the flux of X_j depend on the same unknown integration constant. In the spirit of the IE method, Eq. (6) must be written for all distributed species occurring in a particular model of an electroanalytical experiment, and combined with the relevant boundary conditions at $x = 0$ (not explicitly provided here). In this way one obtains one or more IEs for the unknown fluxes $J_j(0, t)$ at the electrode. The fluxes, in turn, allow one to calculate the electric current.

An interesting property of the function (1) is that, unlike many other kernels pertinent to the electroanalytical modelling (and previously included into the adaptive Huber method [2–18]), the kernel (1) is not of convolution type. This means that $\mathcal{K}(t, \tau)$ does not reduce to a function of the difference $t - \tau$, but it must be considered a function of two variables. Consequently, the name "convolutive modelling", preferred by Mahon and Oldham [59] to denote the modelling approach essentially equivalent to IE solving, cannot apply to this case, although it is still perfectly correct to use the name "IE-based modelling". Despite this difference, the kernel (1) is weakly singular at $\tau = t$, similar to the well known and frequently encountered convolution kernel $(t - \tau)^{-1/2}$ representing planar diffusion in a semi-infinite spatial domain. According to the usual definition (see, for example Ref. [60]), weak singularity means that although the kernel is singular at $\tau = t$, its improper integral $\int_0^t \mathcal{K}(t,\tau)d\tau$ exists. For any fixed t value, $\mathcal{K}(t, \tau)$ is an increasing function of τ. Such a property is important for the numerical stability of the Huber method [10] (and should also be important for the stability of other similar methods). Fig. 1 depicts typical plots of $\mathcal{K}(t, \tau)$.

2.1. Coefficients of the adaptive Huber method

As was discussed in Refs. [5–8], the kernel-dependent coefficients of the adaptive Huber method are given by the formulae:

$$R_{n,l,k} = \frac{t_k Q_{0,n,l,k} - Q_{1,n,l,k}}{t_k - t_l}, \tag{7}$$

$$S_{n,l,k} = \frac{Q_{1,n,l,k} - t_l Q_{0,n,l,k}}{t_k - t_l}, \tag{8}$$

$$V_n = \frac{1}{2} h_n^{-2} \left[(t_{n-1}^2 + h_n t_{n-1}) Q_{0,n,n-1,n} - (2t_{n-1} + h_n) Q_{1,n,n-1,n} + Q_{2,n,n-1,n} \right], \tag{9}$$

and

$$W_{1/2} = \frac{1}{2} h_1^{-2} (Q_{2,1/2,0,1/2} - h_1 Q_{1,1/2,0,1/2}), \tag{10}$$

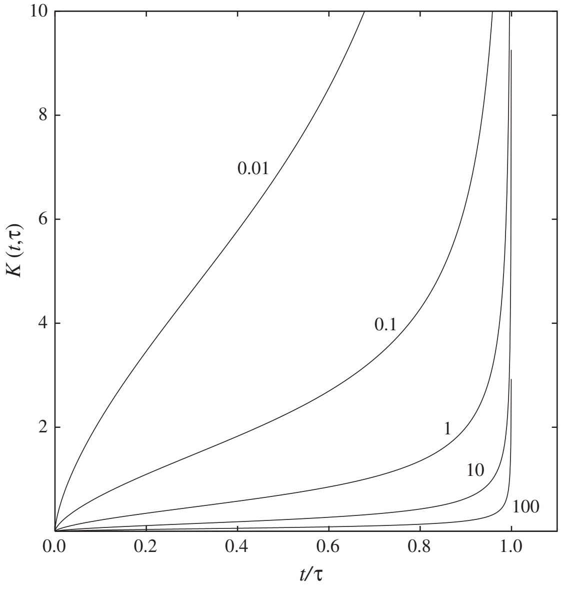

Fig. 1. Kernel function (1), plotted as a function of t/τ, assuming various values of t indicated in the figure.