

Numerical modelling and simulation of Laviron treatment for poly-phenothiazine derivative-modified glassy carbon electrodes

Delia Maria Gligor · Mihaela Ligia Ungureşan

Published online: 19 November 2009
© Springer Science+Business Media, LLC 2009

Abstract Electropolymerization of a new phenothiazine derivative (bis-phenothiazin-3-yl methane, BPhM) on glassy carbon electrodes leads to electroactive and conducting layers of poly-BPhM. Based on the Laviron method, the kinetic parameters (the heterogeneous electron transfer rate constants k_s and transfer coefficients α) were calculated out of the experimental and theoretical data. The theoretical data have been obtained by using the analogical modelling and numerical simulating method. The modified electrodes present high values of k_s ($\sim 50 \text{ s}^{-1}$) in phosphate buffer solutions of different pH values. A good correlation of mathematical and numerical simulated kinetic parameters has been obtained, with the experimental values and the norm of residuals being very close to zero.

Keywords Electropolymerization · Heterogeneous electron transfer rate constant · Numerical modelling · Simulation

1 Introduction

Chemically modified electrodes (CMEs) are attracting a great deal of attention in various fields of science and technology [1]. Among these, CMEs containing an immobilized surface layer of redox-active and/or electrocatalytically active organic species seem to be of a great and fast-growing interest.

The electropolymerization of various organic compounds has been one of the most popular and fruitful procedures of the recent years, used in obtaining redox-active and electrocatalytically active CMEs for the potential use in electrosynthesis

D. M. Gligor (✉)
Department of Physical Chemistry, “Babes Bolyai” University, 400028 Cluj-Napoca, Romania
e-mail: ddicu@chem.ubbcluj.ro

M. L. Ungureşan
Chemical Department, Technical University of Cluj-Napoca, 400641 Cluj-Napoca, Romania

and electroanalysis [2]. This can be explained by the fact that the permselective electropolymerized film covers the whole electrode surface, improving the selectivity and the stability of the modified electrodes [3].

One of the most important applications of CMEs with electropolymerized films is NADH oxidation [4–7]. For this application, a number of phenoxazine and phenothiazine derivatives have been electropolymerized into conventional electrodes.

Within this frame, this paper presents the electropolymerization of a new phenothiazine derivative (bis-phenothiazin-3-yl methane, BPhM) on glassy carbon electrodes (GCE). Following the cyclic voltammetric (CV) measurements realized at different potential scan rates, the heterogeneous electron transfer rate constant (k_s) and transfer coefficients (α) were determined using the Laviron treatment, at different pH values of the supporting electrolyte.

The aim of this paper is to calculate the kinetic parameters by analogical modelling and numerical simulation, using the MATLAB program. The final goal of this work is to check the proposed mathematical model and to obtain the kinetic parameters, comparing the experimental results with the numerically simulated data. It is desired that the calculated errors are as low as possible.

2 Experimental

2.1 Materials

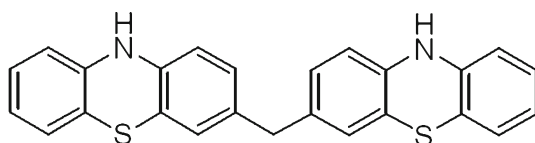
Bis-phenothiazin-3-yl methane (BPhM) was a gift from Assoc. Prof. Castelia Cristea from the Department of Organic Chemistry, “Babes-Bolyai” University Cluj-Napoca, (Romania). Its structure is shown in Scheme 1.

The supporting electrolyte used in the electrochemical cell was a solution of 0.1 M sodium phosphate (Merck). The pH of the solution was adjusted to the desired value by adding H_3PO_4 (Riedel) or NaOH (Merck). All other reagents were of analytical grade and used as received.

2.2 Electrode preparation

The GCE was mechanically polished with alumina (Al_2O_3 , 1 μm) to a mirror finish and then cleaned by sonicating in Millipore water. Poly-BPhM modified electrodes were prepared by cycling sweeping (20 scans) the GCE from $-1,000$ to $+1,200$ mV *versus* SCE, at 50 mV s^{-1} , in DMSO containing 0.1 M TFB and 1 mM BPhM, according to [8,9]. The monomer concentration in the “growing solution” was selected to 1 mM, which was previously found to be optimal for obtaining graphite modified

Scheme 1 Structural formula of bis-phenothiazin-3-yl methane



electrodes through adsorption [10]. The modified electrodes were rinsed with Millipore water.

Prior to all electropolymerization experiments, the solutions containing the TFB/BPhM were de-oxygenated with nitrogen gas for 10 min. All presented results are the average of at least 3 identically prepared electrodes, if not otherwise mentioned.

2.3 Electrochemical measurements

Cyclic voltammetric experiments were carried out in a conventional three-electrode electrochemical cell. The mediator modified GCE (3 mm diameter) was used as the working electrode, a platinum ring as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetric studies were performed using an electrochemical analyzer (BAS 50W, Bioanalytical Systems, West Lafayette, IN, USA) connected to a PC microcomputer for potential control and data acquisition. The pH of the buffer solution was adjusted using a Radiometer PHM210 Standard pH-meter with a combined glass electrode.

3 Results and discussions

Because of the strong adsorption behavior of the poly-BPhM modified GCE redox processes, the following Laviron's equation [11, 12] may be used to calculate the heterogeneous electron transfer rate constants (k_s, s^{-1}).

$$E_{pc} - E^{0'} = \frac{RT}{\alpha nF} \cdot 2.3 \lg \frac{\alpha nF}{RTk_s} + \frac{2.3RT}{\alpha nF} \lg v \quad (1)$$

$$E_{pa} - E^{0'} = \frac{RT}{(1 - \alpha)nF} \cdot 2.3 \lg \frac{(1 - \alpha)nF}{RTk_s} + \frac{2.3RT}{(1 - \alpha)nF} \lg v \quad (2)$$

where: $k_s[s^{-1}]$ is the heterogeneous electron transfer rate constant; α is the electron transfer coefficient; n is the number of transferred electrons (which is considering to be 1) [10]; $v[V s^{-1}]$ the scan rate and $E^{0'}$ [V] the formal standard potential, $E^{0'} = (E_{pa} + E_{pc})/2$ [13]. The temperature is being maintained constant during the kinetic study, at the value $T = 298$ K; the universal constant of the perfect gases is $R = 0.082l \cdot atm mol^{-1} \cdot K^{-1}$; Faraday's constant is $F = 96500$ C.

According to the equation that has been presented above, if $E^{0'}$ is known, from the dependence of E_p versus $\lg v$, α and k_s values can be calculated for the poly-BPhM modified GCE. The kinetic equations have been implemented for the anodic and cathodic processes.

The values that resulted from the experimental data have been graphically represented and the numerical calculus and the graphic representation has been achieved in the MATLAB program.

Based on the experimental graph, $E_{pa} - E^{0'}$, respectively, $E_{pc} - E^{0'}$ versus $\lg v$ have been represented, and it is possible to approximate these data according to a polynomial function of different orders: $y = a + bx + cx^2 + dx^3 + \dots$. The unknown coefficients

Table 1 The experimental and numerically simulated values for peak potential at different potential scan rates, corresponding to poly-BPhM modified GCE, in phosphate buffer, pH 3

v (V s ⁻¹)	E_{pa} (V) exp.	E_{pa} (V) simulated	E_{pc} (V) exp.	E_{pc} (V) simulated
0.01	0.21386	0.2292	0.1215	0.1010
0.02	0.21551	0.2294	0.1215	0.1009
0.04	0.22981	0.2298	0.11985	0.1005
0.05	0.22816	0.2300	0.1116	0.1004
0.08	0.22981	0.2306	0.10857	0.0999
0.1	0.22981	0.2310	0.10335	0.0996
0.16	0.2452	0.2321	0.10445	0.0987
0.2	0.23805	0.2329	0.10171	0.0981
0.32	0.2609	0.2353	0.09621	0.0962
0.4	0.26347	0.2369	0.08356	0.0950
0.64	0.27874	0.2417	0.08741	0.0912
0.8	0.28863	0.2449	0.06927	0.0888
1.28	0.30403	0.2544	0.06927	0.0813
1.6	0.31667	0.2607	0.04563	0.0764
2.56	0.33097	0.2798	0.01869	0.0615
3.2	0.3543	0.2925	0.00458	0.0516
5.4	0.38943	0.3362	-0.02901	0.0175
6.4	0.41463	0.3561	-0.04047	0.0020
10.52	0.45968	0.4379	-0.10232	-0.0618
12.8	0.49251	0.4832	-0.13744	-0.0972
21.04	0.5704	0.6469	-0.21991	-0.2248
25.6	0.59789	0.7374	-0.28991	-0.2955
42.08	0.75916	1.0647	-0.38737	-0.5509
51.2	0.79391	1.2459	-0.42047	-0.6922

(a, b, c, \dots) have been determined using the method of the smallest squares, which minimizes the sum of the model deviation squares from the experiment.

The matrix equation is being solved
$$\begin{bmatrix} y_1 \\ \vdots \\ y_n \end{bmatrix} = \begin{bmatrix} 1 & x_1 & \dots & x_1^n \\ \vdots & \vdots & \vdots & \vdots \\ 1 & x_n & \dots & x_n^n \end{bmatrix} \begin{bmatrix} a \\ b \\ \vdots \end{bmatrix}$$
, thus obtain-

ing the values of the coefficients a, b, c, \dots [14].

The calculated values (a, b, c, \dots) have been introduced in the implemented equations, obtaining the values of E_{pa} and E_{pc} . Table 1 presents the obtained experimentally and analogically values of E_{pa} and E_{pc} , at different potential scan rates v , in phosphate buffer, pH 3.

The rigorous correspondence between the numerically simulated data and the experimental values can be observed. The experimental and theoretical values from Table 1 have been graphically represented with respect to $\lg v$ and a good overlap of these data has been obtained (Fig. 1).

All the kinetic parameters were listed and compared in Table 2.

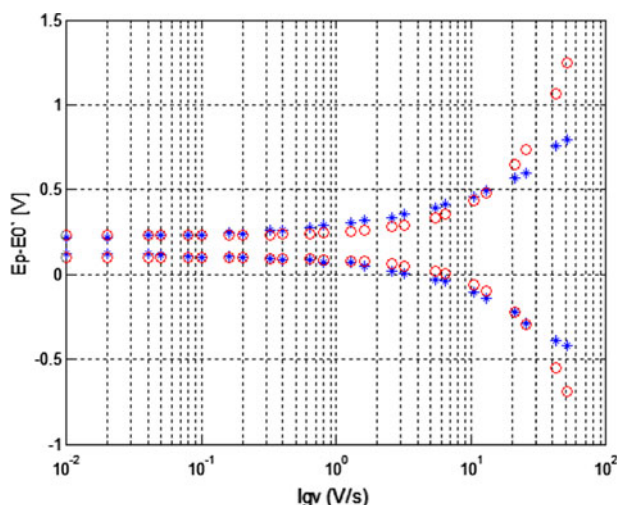


Fig. 1 Semilogarithmic dependence of the peak potential on the potential scan rate. Superposition of the experimental data (*asterisk*) with the modelled ones (*open circle*) for poly-BPhM modified GCE. Experimental conditions: supporting electrolyte, phosphate buffer (pH 3)

Table 2 The experimental and simulated kinetic parameters obtained by Laviron treatment, for poly-BPhM modified GCE, in supporting electrolytes with different pH values

pH	k_s (s^{-1})		α		R / no of exp. points	
	Exp.	Simulated	Exp.	Simulated	Oxidation	Reduction
3	56.0	55.8	0.50	0.49	0.9863/6	0.9967/6
5	45.4	45.1	0.38	0.36	0.9904/6	0.9863/6
6	51.8	51.3	0.42	0.40	0.9754/6	0.9800/6
7	50.4	50.1	0.47	0.46	0.9854/6	0.9874/6
9	18.7	18.4	0.45	0.44	0.9852/8	0.9902/8

It can be seen that the values of k_s and α obtained using the experimental and simulated methods, are almost similar. For different pH values, the transfer coefficient (α) is close to 0.5 and k_s constants have values around $50 s^{-1}$ (except the value obtained at pH 9, $18.7 s^{-1}$) being one of the highest values reported in literature [15]. These results are important, because modified electrodes which present high values of k_s constants present a very good electrocatalytic activity (in the case of this electrode type for NADH electrocatalytic oxidation). These modified electrodes can be used as efficient amperometric biosensors by using a NAD^+ -dependent dehydrogenase, for detection of analytes used in environmental and biomedical applications (i. e. ethanol, lactate, etc).

The calculated errors, representing the difference between the experimental values and the ones resulted from the model, present values in admitted limits. There have been some attempts to design a numerical method which is efficient and numerically stable. The efficiency is ensured through the development of some algorithms that involve a smaller number of elementary arithmetic operations.

Table 3 Comparison between the norm of residuals for the experimental and simulated data, corresponding to poly-BPhM modified GCE

Norm of residuals	$E_{pa} - E^{0'}$	$E_{pc} - E^{0'}$
Experimental data	0.10074	0.062549
Simulated data	3.6082×10^{-6}	3.6082×10^{-6}

The stability of a numerical algorithm stands in the sensitiveness with respect to rounding errors or other numerical uncertainties which can appear during the calculus process.

If all calculations are based on convex combinations, all the intermediate results and even the final results will be of the size of the original data, ensuring the stability of the algorithm.

The issue is to solve an undersized system of algebraic equations, i.e. the number of equations is less than the unknown number [16].

The idea is to “solve” the system by minimizing the Euclidian norm of residuals. Because the norm of residuals can't be made equal to zero, it should be made as short as possible to a certain standard residue, called norm of residuals.

The norm of the residuals is a measure of the goodness of the fit, i.e. a lower norm signifies a better fit, and this is defined in Matlab as:

$$\text{norm}(d, 2) \equiv \text{sum}(\text{abs}(d).^2)^{(1/2)} = \sqrt{\sum_{i=1}^n d_i^2} \quad (3)$$

As it can be observed from Table 3, the norm of residuals for theoretical data resulted by numerical simulation is extremely low (very close to zero), in comparison with the norm of residuals calculated for the obtained experimental data. Thus, it can be concluded that the selected mathematical model is optimum, with the minimal norm of residuals and with the best overlap of the experimental data with those numerically simulated.

4 Conclusions

The kinetic parameters (the heterogeneous electron transfer rate constants, k_s and transfer coefficients, α) for poly-BPhM modified GCE, have been obtained through Laviron treatment, from cyclic voltammetric measurements realized at different potential scan rates.

The proposed mathematical model, which is based on the Laviron equation determined in accordance with the obtained experimental results, allows the calculation of the kinetic parameters by numerical simulation.

It has been shown that the experimentally obtained data overlaps almost perfectly with the mathematical and numerical simulated data and the norm of residuals are very close to zero, so the validity of the model has been proved.

Acknowledgments Financial support from CNCIS (Project ID_512) is gratefully acknowledged. The authors thank Assoc. Prof. Castelia Cristea (Department of Organic Chemistry, “Babeş-Bolyai” University Cluj-Napoca, Romania) for providing the phenothiazine derivative.

References

1. R.W. Murray, *Molecular Design of Electrode Surfaces* (Wiley, New York, 1992)
2. A. Malinauskas, *Synth. Met* **107**, 75 (1999)
3. B. Prieto-Simón, E. Fàbregas, *Biosens. Bioelectron* **19**, 1131 (2004)
4. F. Pariente, E. Lorenzo, F. Tobalina, H.D. Abruna, *Anal. Chem.* **67**, 3936 (1995)
5. M.J. Lobo, A.J. Miranda, J.M. Lopez-Fonseca, P. Tunon, *Anal. Chim. Acta* **325**, 33 (1996)
6. P.N. Bartlett, P.R. Birkin, E.N.K. Wallace, *J. Chem. Soc., Faraday Trans* **93**, 1951 (1997)
7. Y. Sha, Q. Gao, X. Qi, B. Yang, *Microchim. Acta* **148**, 335 (2004)
8. A.A. Karyakin, E.E. Karyakina, H.L. Schmidt, *Electroanalysis* **11**, 553 (1999)
9. Y. Dilgin, L. Gorton, G. Nisli, *Electroanalysis* **19**, 286 (2007)
10. M.L. Ungureşan, D. Gligor, F. Dulf, IEEE Catalog Number: CFP08AQT-PRT **16**, 238 (2008)
11. E. Laviron, *J. Electroanal. Chem.* **52**, 355 (1974)
12. E. Laviron, *J. Electroanal. Chem.* **101**, 19 (1979)
13. R.W. Murray, in: *Electroanalytical Chemistry*, eds. A.J. Bard (Marcel Dekker, New York, 1984), pp. 191–368
14. T. Colosi, M. Abrudean, E. Dulf, M.L. Ungureşan, *Numerical Modelling and Simulation Method for Lumped and Distributed Parameters Processes with Taylor Series and Local Iterative Linearization* (Mediamira Publishing House, Cluj-Napoca, 2008)
15. D. Dicu, L. Mureşan, I.C. Popescu, C. Cristea, I.A. Silberg, P. Brouant, *Electrochim. Acta* **45**, 3951 (2000)
16. Y. Saad, M. Schultz, *SIAM J. Sci. Statist. Comput* **7**, 856 (1986)