CYCLIC VOLTAMMETRY SIMULATION USING ORTHOGONAL COLLOCATION: COMPARISON WITH EXPERIMENTAL DATA AND MEASURING THE ELECTROCHEMICAL RATE CONSTANT

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Prezenta lucrare estimează constanta de viteză pentru cuplul redox $Co(bpy)_3^{2+/3+}$ folosind metoda propusă de Nicholson. Valoarea acesteia a fost verificată prin simularea digitală a experimentelor de voltametrie ciclică. Metoda numerică utilizată în simulare se bazează pe metoda colocației ortogonale și include căderea ohmică necompensată din experimente.

The electrochemical rate constant for the redox couple $Co(bpy)_3^{2+/3+}$ was estimated using the Nicholson method. The value was checked by digital simulation of a cyclic voltammetry experiment. The simulation procedure is based on the orthogonal collocation method and includes the uncompensated ohmic drop during experiments.

Keywords: electrochemical rate constant, digital simulation, cyclic voltammetry, ohmic drop.

1. Introduction

The measurement of electrochemical rate constants has never been an easy task. Thus, it was often necessary to combine high-precision equipment or rather elaborate and carefully executed experimental procedures with advanced calculus. The method proposed by Nicholson [1], though not considered generally a reliable method for electrochemical rate constant measurement, is nevertheless still widely employed, despite its shortcomings. The method will be used in this paper showing the advantages of numerical simulation of experimental work. Even if the digital simulation in electrochemistry has a long history [2], the practical use of these methods is not as widely implemented as one might expect.

The simulation used in this study is based on orthogonal collocation: this procedure was intensively studied by Speiser [3 - 5] and also by other authors [6,

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7]. We have already proposed a simple but efficient numerical simulation scheme: a detailed description of procedures associated with Jacobi polynomials is given in [8].

An efficient method for describing the ohmic drop in the circuit was previously presented in [9] and was included in the numerical procedure in order to evaluate its influence. We have checked the simulated data against experimental ones, using $Co(bpy)_3^{2+/3+}$-acetonitrile as a redox couple, since it offers several advantages: it is a simple, moderately fast, outer-sphere electrode reaction and experimental data for this couple are available in literature [10, 11].

2. Derivation of electrochemical rate constants using Fick's laws:

A typical cyclic voltammetry experiment is mathematically described by the following equations system, written for the following electrochemical process:

$O + e^- \rightarrow R$

$$\begin{cases} \dfrac{\partial c_O(x,t)}{\partial t} = D_O \cdot \dfrac{\partial^2 c_O(x,t)}{\partial x^2}; \quad J_O(x,t) = -D_O \cdot \dfrac{\partial c_O(x,t)}{\partial x} \\ \dfrac{\partial c_R(x,t)}{\partial t} = D_R \cdot \dfrac{\partial^2 c_R(x,t)}{\partial x^2}; \quad J_R(x,t) = -D_R \cdot \dfrac{\partial c_R(x,t)}{\partial x}; \\ J_O(0,t) = -J_R(0,t); \\ J_O(0,t) = k_1 \cdot c_O(0,t) - k_2 \cdot c_R(0,t); \\ k_1 = k^0 \cdot \exp\left(-\alpha \cdot \dfrac{n_e F}{RT} \cdot (E(t) - E^{0'})\right); \\ k_2 = k^0 \cdot \exp\left((1-\alpha) \cdot \dfrac{n_e F}{RT} \cdot (E(t) - E^{0'})\right); \end{cases} \tag{1}$$

where c_O, c_R – concentrations of oxidized (O) and reduced (R), species, respectively, depending on both distance and time; x – distance from electrode surface; v – potential scan rate; t – time; D_O, D_R – diffusion coefficient for O and R, respectively; J_O, J_R – flux for O and R, respectively; k^0 – standard electrochemical rate constant; k_1,k_2 – electrochemical rate constant for forward and backward reaction, respectively; α – charge transfer coefficient; F – Faraday constant; R – ideal gas constant; n_e – number of electrons transferred; T – temperature; E – applied potential; $E^{0'}$ – formal potential.

In these conditions the Faradaic current, I_f, is given by (2)

$$I_f = nFA(k_1 \cdot c_O - k_2 \cdot c_R)\,. \tag{2}$$

where A is surface area of electrode.

To avoid the time dependence, a potential grid is employed instead, by dividing the whole potential scan domain in N_P points, where N_P has a convenient user-chosen value. The above system (1) thus becomes:

$$\begin{cases} \dfrac{\Delta c_O(x)}{\Delta t} = D_O \cdot \dfrac{\partial^2 c_O(x)}{\partial x^2}; \quad J_O(x) = -D_O \cdot \dfrac{\partial c_O(x)}{\partial x}; \\ \dfrac{\Delta c_R(x)}{\Delta t} = D_R \cdot \dfrac{\partial^2 c_R(x)}{\partial x^2}; \quad J_R(x) = -D_R \cdot \dfrac{\partial c_R(x)}{\partial x}; \\ J_O(0) = -J_R(0); \\ J_O(0) = k_1 \cdot c_O(0) - k_2 \cdot c_R(0); \\ k_1 = k^0 \cdot \exp\left(-\alpha \cdot \dfrac{n_e F}{RT} \cdot (E - E^{0'})\right); \\ k_2 = k^0 \cdot \exp\left((1-\alpha) \cdot \dfrac{n_e F}{RT} \cdot (E - E^{0'})\right); \\ E = E_i + i \cdot \Delta E, \qquad i = 1,\ldots,N_P; \\ \Delta c_{O,R}(x) = c_{O,R}(x, t+\Delta t) - c_{O,R}(x,t); \end{cases} \tag{3}$$

where E_i – is the initial potential, Δt is constant and represents the time interval in which the polarization potential is changing from $i*\Delta E$ to $(i+1)*\Delta E$.

As previously proposed [8], the method chosen for solving system (3) is based on concentration functions by an orthogonal Jacobi polynomial. When the system simulated includes also the ohmic drop, the constants k_1 and k_2 become k'_1 and k'_2 respectively (4) :

$$\begin{cases} k'_1 = k^0 \cdot \exp\left(-\alpha \cdot \dfrac{n_e F}{RT} \cdot (E - E^{0'} - I_f \cdot R)\right); \\ k'_2 = k^0 \cdot \exp\left((1-\alpha) \cdot \dfrac{n_e F}{RT} \cdot (E - E^{0'} - I_f \cdot R)\right); \end{cases} \tag{4}$$

The flowing current will thus be calculated using the corrected rate constants:

$$I_f = nFA(k'_1 \cdot c_O - k'_2 \cdot c_R). \tag{5}$$

The only unknown parameter is I_f. The above nonlinear equation is solved iteratively using the Newton-Raphson method at each potential step *i*, with the initial guess taken from the *i*-1 point [9].

3. The orthogonal collocation method

Approximating the concentration profile by an orthogonal polynomial was extensively used by Speiser [3], using Legendre polynomials, a particular case of more general Jacobi polynomials, defined in (6)

$$g(x) = \int_{-1}^{1} (1-x)^{\alpha} \cdot (1+x)^{\beta} \cdot P_n(x) \cdot P_m(x) dx = 0 . \tag{6}$$

where α, β are constants, P_m and P_n are Jacobi polynomials with m and n degree, respectively, with $n \neq m$. The roots of such polynomials are distributed in the [-1;1] interval.

Chapman [7] used a variant of Lagrange polynomials, but his method, perhaps because of its complexity, was not developed further. The method used in this paper was proposed in [8] and it has a better flexibility comparing with Speiser's Legendre polynomials.

The concentration function is approximated through the polynomial $P_{n+2}(x)$:

$$c(x) \approx P(x) = \sum_{j=0}^{n+1} a_j \cdot x^j ;$$

$$c(x)\big|_{x_i} = P(x_i) = \sum_{j=0}^{n+1} a_j \cdot x_i^{\,j} ; \tag{7}$$

Also, the first and second derivatives can be expressed as:

$$\frac{\partial c(x)}{\partial x} \approx P'(x) = \sum_{j=0}^{n+1} j \cdot a_j \cdot x^{j-1} ;$$

$$\left.\frac{\partial c(x)}{\partial x}\right|_{x_i} = P'(x_i) = \sum_{j=0}^{n+1} j \cdot a_j \cdot x_i^{\,j-1} ; \tag{8}$$

$$\frac{\partial^2 c(x)}{\partial x^2} \approx P''(x) = \sum_{j=0}^{n+1} j \cdot (j-1) \cdot a_j \cdot x^{j-2} ; \tag{9}$$

$$\left.\frac{\partial^2 c(x)}{\partial x^2}\right|_{x_i} = P''(x_i) = \sum_{j=0}^{n+1} j \cdot (j-1) \cdot a_j \cdot x_i^{\,j-2}; \tag{10}$$

where x_i are the roots of polynomial *P(x)*.

The first and second derivatives are then given by:

$$\left.\frac{\partial c(x)}{\partial x}\right|_{x_i} = A \cdot c(x_i) \;;\; \left.\frac{\partial^2 c(x)}{\partial x^2}\right|_{x_i} = B \cdot c(x_i)\,, \tag{11}$$

with i=1,...,n. A and B are the matrixes which depend on both the type and order of the polynomial equation used.

Their coefficients are calculated using the Lagrange interpolation method [12], with the roots of an orthogonal n-grade Jacobi polynomial as collocation points. Thus

$$P_n(x) = \prod_{i=1}^{n}(x - x_i)\,.$$

The n+2 order polynomial becomes $P(x) = \prod_{i=0}^{n+1}(x - x_i)$. Under these circumstances the function *c(x)* can be written as:

$$c(x) \approx \sum_{j=0}^{n+1} \frac{P(x)}{(x - x_j) \cdot P'(x_j)} \cdot c(x_j)\,. \tag{12}$$

In this case, the coefficients of A and B are explicitly calculated with:

$$\text{for i=j: } a_{i,i} = \frac{1}{2} \cdot \frac{P''(x_i)}{P'(x_i)} \quad b_{i,i} = \frac{1}{3} \cdot \frac{P'''(x_i)}{P'(x_i)} \tag{13}$$

$$\text{for i}\neq\text{j: } a_{i,j} = \frac{1}{x_i - x_j} \cdot \frac{P'(x_i)}{P'(x_j)} \quad b_{i,j} = \frac{1}{x_i - x_j} \cdot \left(\frac{P''(x_i)}{P'(x_j)} - 2 \cdot a_{i,j} \right) \tag{14}$$

where *P'''* is the third derivative of polynomial P.

4. Nicholson's method for kinetic rate constant calculation

In his classical method [1] Nicholson associated the parameter ψ with $\Delta E_{peak} * n$, where ψ is proportional with the rate constant k^0 according to

$$\psi = \frac{\gamma^{\alpha} k^{0}}{\sqrt{\pi a D_O}}; \quad \gamma = \left(\frac{D_O}{D_R}\right)^{1/2}; \quad a = \frac{nF}{RT} v . \tag{15}$$

For each ψ Nicholson associates a corresponding $\Delta E_{peak} * n$ value. Since Nicholson's tabulated values are rather difficult to use, as one needs to interpolate its values, it was thought better to use a fitted function to Nicholson's values. Several fitting functions have been employed and it was found that that the best results (correlation coefficient 0.99996 and maximum error of 0.6%.) were obtained using the function, with ΔE_{peak} expressed in mV:

$$\Delta E_{peak} = f(\Psi) = A_2 + \frac{A_1 - A_2}{1 + (\Psi / x_0)^p} , \tag{16}$$

where A_1=*432.91 mV*, A_2=*59.55 mV*, x_0=*0.0688* and *p=0.9938*. Thus:

$$\Psi = x_0 \cdot \left(\frac{A_1 - A_2}{\Delta E_{peak} - A_2} - 1\right)^{\frac{1}{p}}, \; k^0 = \frac{\Psi \sqrt{\pi \cdot a \cdot D_O}}{\gamma^{\alpha}} . \tag{17}$$

5. Experimental

The redox couple studied corresponds to the electrode process:

$$[Co(bpy)_3]^{3+} + e \rightleftharpoons Co(bpy)_3]^{2+}$$

The hydrated compound $[Co(bpy)_3](ClO_4)_3 \times 3H_2O$ was precipitated with $LiClO_4$ from a solution of $[Co(bpy)_3]Cl_3$ in water, (which was synthesized according to literature procedures [13], [14]) and recrystallized from water.

Typical experiments were performed using a 4.85 mM $[Co(bpy)_3](ClO_4)_3$ solution in acetonitrile, and 0.2M $KClO_4$ as supporting electrolyte. A Pt working electrode (0.82 cm^2) and a large platinum mesh counter electrode were used; the reference electrode was a $Ag/AgNO_3$ 0.01M in 0.1 M $KClO_4$ in acetonitrile. All measurements were performed at room temperature (25 ± 2^0C) using an AUTOLAB PGSTAT 12, electrochemical workstation.

The ohmic resistance in the cell was estimated using high-frequency (1 MHz - 100 kHz) impedance measurements; typical values were in the range of 11±2 Ω. The cyclic voltammetry experiments were performed with scan rates between 0.025 and 5 V/s, with and without ohmic drop compensation. The data presented below are in all cases corrected for the charging current: a set of cyclic

voltammograms were recorded in separate runs using only 0.2 M $KClO_4$ in acetonitrile and the resulting curves were subtracted from the corresponding curves containing the redox species.

6. Results and discussions

Using Nicholson's method an average value k^0 = 0.0416 ± 0.0044 cm/s was calculated: Table 1 shows the results obtained (the last column contains the percent error from the average value). The k^0 values for the 0.025 and 0.05 V/s were not used when calculating the average value, since for these scan rates the ΔE_{peak} values are too close to the theoretical reversible value and thus lead to large errors when calculating k^0.

Table 1

k^0 values for the electroreduction of $[Co(bpy)_3]^{3+}$ in acetonitrile calculated with Nicholson's method:

No	scan rate [mV/s]	ΔE_{peak} [mV]	ψ	k^0 [cm/s]	k^0 error[%]
1	25	65.46	4.39569	0.02418	-
2	50	69.89	2.47273	0.01923	-
3	100	67.07	3.4338	0.03778	-9
4	200	68.21	2.96964	0.04620	10
5	300	74.15	1.72668	0.03290	-21
6	400	73.85	1.76462	0.03883	-6
7	500	75.97	1.5263	0.03755	-9
8	600	75.07	1.61949	0.04364	4
9	700	76.9	1.44018	0.04192	0
10	800	77.82	1.36365	0.04243	1
11	900	77.5	1.38938	0.04585	10
12	1000	81.18	1.13962	0.03965	-4
13	2000	90.79	0.765565	0.03766	-9
14	3000	92.1	0.731733	0.04409	5
15	4000	95.06	0.664509	0.04624	11
16	5000	97.22	0.622143	0.04840	16

Our experimental data were simulated using the following data available in literature [11], $D_O = D_R = 9.9 \cdot 10^{-6}$ cm^2/s, $\alpha = 0.5$. In our simulation procedure, the formal potential was estimated as $(E_a+E_c)/2$ where E_a – peak potential for the anodic process, E_c – peak potential for the cathodic process.

Also, the rate constant used in the simulation was the above calculated value, i.e. k^0 = 0.0416 cm/s. Further, the Nicholson's method was again applied, but this time to the simulated data. The result is seen in Table 2. The errors in this case are calculated related to the average value k^0 = 0.0416 cm/s from experimental data.

These results prove that the simulated data agree very well to the experimental ones, the errors in Table 2 being quite small (except, as noted above, for the lower scan rates, where the cyclic voltammogram curves are very close to the reversible case).

Fig. 1 shows a comparison between distributions of k^0 errors obtained from experimental and simulated data.

Fig. 2 and Fig. 3 show also the good correlation between the simulated and experimental data, for both the uncorrected and ohmic drop corrected cyclic voltammograms. A small difference between corrected experimental and simulated data may however be noticed. This difference is virtually non-existent for scan rates up to 0.5 V/s, it is small for intermediate scan rates (up to 0.6V/s, Fig. 4) but it becomes quite obvious for higher scan rates, such as 5 V/s (Fig 5.).

Table 2

Rate constant k^0 values using interpolation applied to simulation data:

No	scan rate [mV/s]	ΔE_{peak} [mV]	ψ	k^0 [cm/s]	Error for k^0 [%]
1	25	61.32	14.974	0.08237	97
2	50	62.64	8.51067	0.06621	58
3	100	64.8	4.96123	0.05458	31
4	200	67.74	3.14529	0.04893	17
5	300	69.96	2.45552	0.04679	12
6	400	71.76	2.08091	0.04579	9
7	500	73.32	1.83571	0.04516	8
8	600	74.76	1.65415	0.04457	7
9	700	76.08	1.5156	0.04411	5
10	800	77.28	1.40761	0.04380	5
11	900	78.48	1.31335	0.04334	4
12	1000	79.56	1.23821	0.04308	3
13	2000	87.96	0.849346	0.04179	0
14	3000	94.08	0.685485	0.04130	0
15	4000	99.12	0.588713	0.04096	-1
16	5000	103.44	0.523512	0.04072	-2

The main reason for this behaviour is most likely due to the residual ohmic drop which has not been compensated: indeed, due to technical difficulties, the ohmic drop cannot be totally compensated, but only about 80-90%.

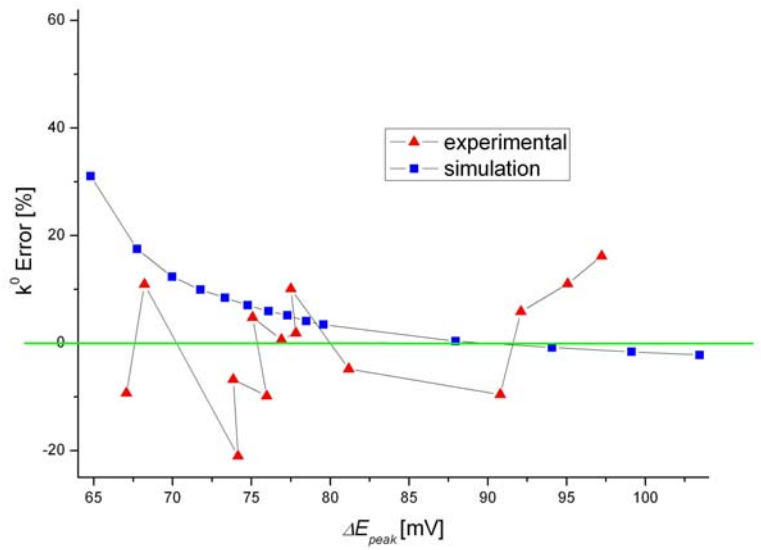

Fig. 1. Error distribution for the calculated standard rate constants against k^0=0.0416, the average value for experimental and simulated data

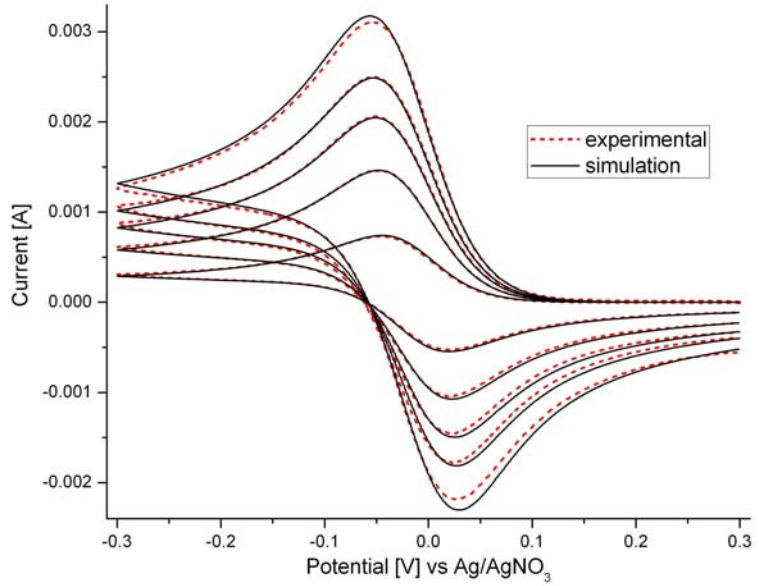

Fig. 2. Experimental and simulated voltammograms for of 0.05, 0.2, 0.4, 0.6 and 1V/s scan rates with ohmic drop compensation

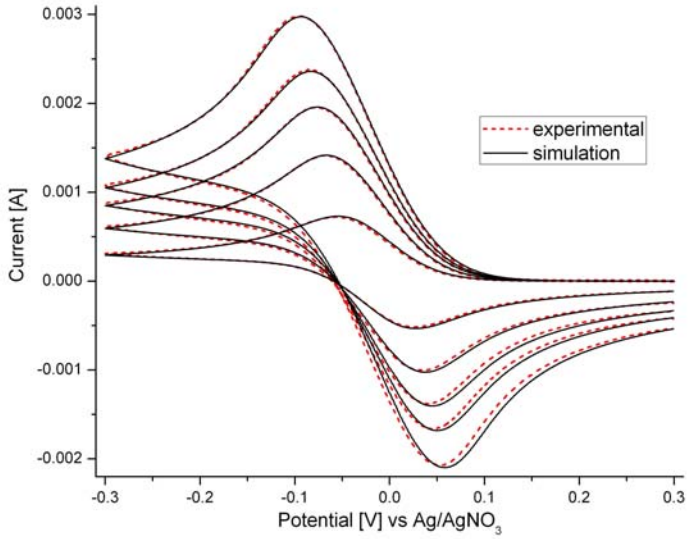

Fig. 3. Experimental and simulated voltammograms for 0.05, 0.2, 0.4, 0.6 and 1V/s scan rates without ohmic drop compensation

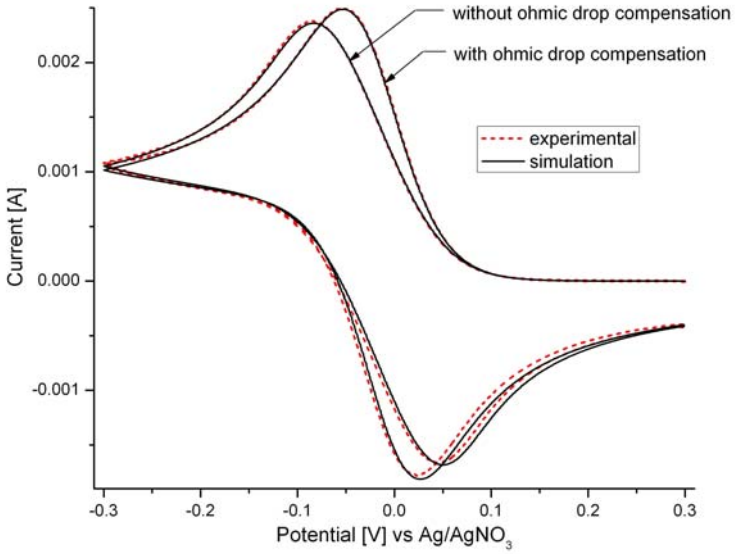

Fig. 4. Comparison between the experimental and simulated voltammograms for 0.6 V/s with and without ohmic drop compensation

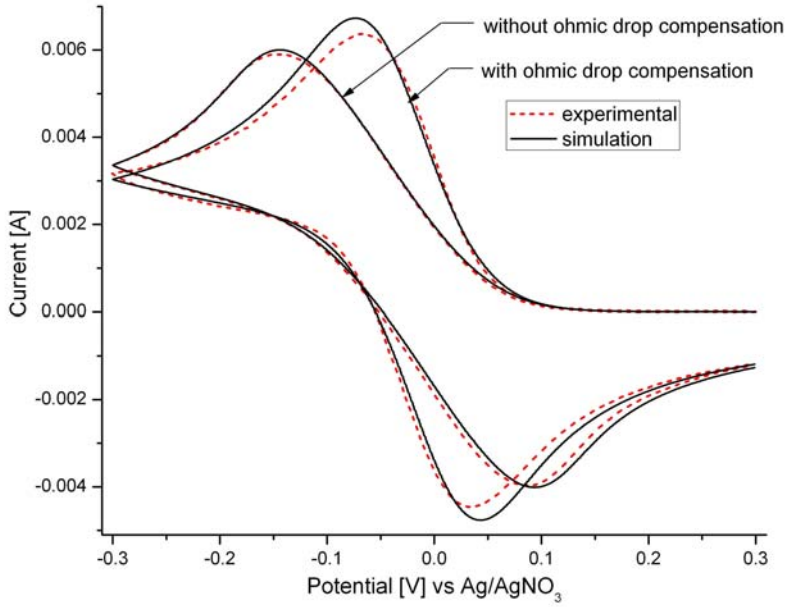

Fig. 5. Experimental and simulated voltammograms at 5 V/s for experiments with and without ohmic drop compensation

On the other hand it is clear that the standard rate constant obtained using Nicholson's method is significantly different when compared to other literature values for the same system $k^0 = 0.086$ cm/s [11] and $k^0 = 0.198$ cm/s [10]. While some small differences in experimental conditions exist between these sets of experiments, it is unlikely to account for such a rather large variation in k^0. However, the value $k^0 = 0.198$ cm/s is more credible because it was obtained by using an a.c. method, which is known to yield more reliable kinetic data than methods based on cyclic voltammetry [15]

Since the value obtained in our experiments using Nicholson's method is almost with one order of magnitude smaller than the accepted value of about 0.2 cm/s, a special attention should be paid to the correction of the ohmic drop. It has long been known that the uncompensated resistance has the same effect on the cyclic voltammograms as a lower rate constant [1].

Since it is impossible to correct entirely for the ohmic drop [15, page 243], and also because the measurement of rather low resistances (~10 Ω) usually involves errors of about 2-3%, new simulations were performed, using the accepted value for k^0 (0.198 cm/s) in order to check whether a residual uncompensated resistance of about 1-2 ohms can have a significant impact on the measured value of k^0.

This is indeed the case, as can be seen from figure 6: the simulated curve for 1 V/s using k^0 = 0.198 cm/s and an uncompensated resistance of 14 Ω, which is well within the range of about 3% compared to the value we have used for correcting our cyclic voltammetry curves (11 Ω) agrees well with the experimental curve and it is virtually indistinguishable from the curve using k^0 = 0.042 cm/s and R = 11 Ω.

Thus it is indeed obvious that the residual uncompensated resistance can have dramatic effects on the measured rate constant when using Nicholson's methods. The overall errors when comparing uncorrected experimental and simulated cyclic voltammograms do not exceed 1% for both pairs R=14 Ohm and k^0=0.198 cm/s as well as R=13 Ohm and k^0=0.086 cm/s (Fig. 7 and Fig. 8). The formula for error calculation is (18) :

$$error = \frac{I_{\exp} - I_{sim}}{I_{\exp,\max} - I_{\exp,\min}} \cdot 100\ \%. \tag{18}$$

It is thus worth noting that Nicholson's method for measuring electrochemical rate constants is quite unreliable, the rate constant values calculated using this method are almost always smaller than the ones obtained by other methods (a. c. methods especially).

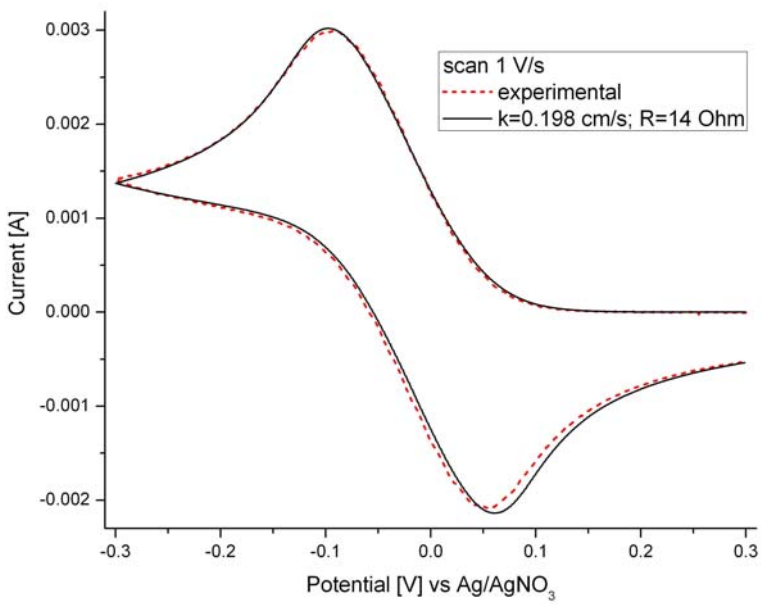

Fig. 6. Comparison between the simulated curve using $k^0 = 0.198$ cm/s and R = 14 Ω and the experimental voltammogram at 1 V/s

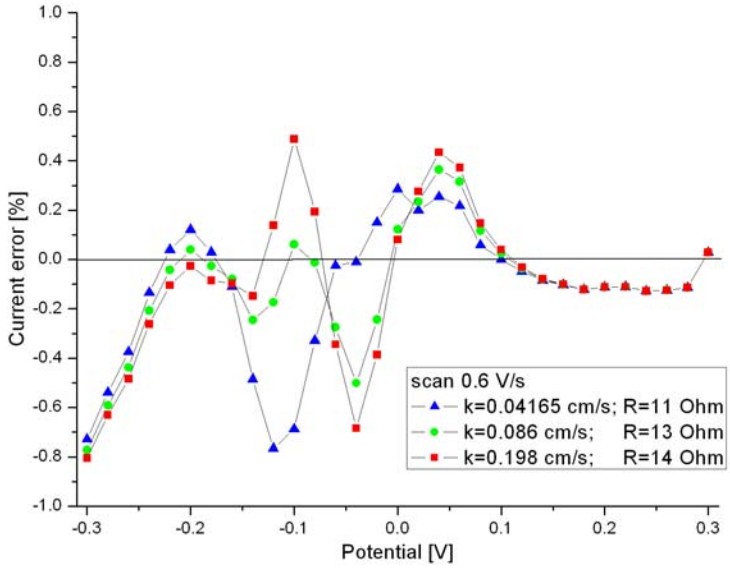

Fig. 7. Errors between experimental and simulated currents for different rate constants and ohmic resistances at 0.6 V/s

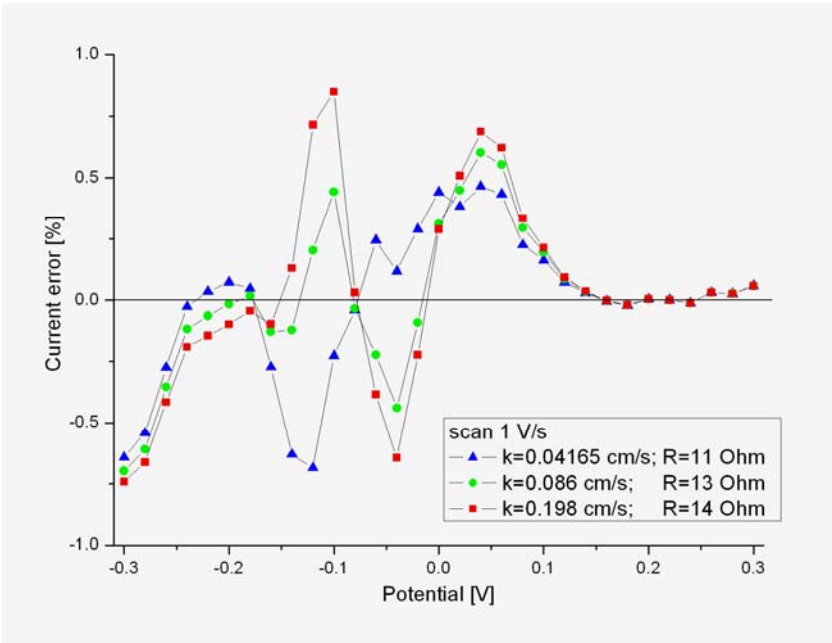

Fig. 8. Errors between experimental and simulated currents for different rate constants and ohmic drops at 1 V/s

7. Conclusions:

We have shown that the simulation of cyclic voltammetry data using orthogonal collocation is an efficient and accurate technique and the comparison with both corrected and uncorrected experimental data referring to ohmic drop compensation is excellent. The cyclic voltammetry simulation software developed so far may prove itself as an important tool in electrochemical investigations.

Also, by using more reliable simulated voltammograms, we may conclude that Nicholson's method for calculation the standard electrochemical rate constant is not well suited for fast and moderately-fast electrochemical reactions. The main reason for this inaccuracy is the presence of the residual uncompensated resistance.

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