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Voltammetric current–potential calculations using infinite series solution

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Abstract

Highly accurate analytical solution contributing to the theory of linear sweep voltammetry for single scan experiments is given by application of exponential infinite series. The cases of reversible or irreversible charge transfer with or without coupled chemical reaction are treated and calculated results are compared with the customary solution of Nicholson and Shain. Problems with partial divergence of the series were overcome by the series transformation and the use of arbitrary precision arithmetic. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The theory of linear sweep voltammetry is based mainly on the work of Nicholson and Shain [1] where current–potential, *I–E*, curves were computed by means of numerical solution of integral equations obtained for a given mechanism. Even though an analytical solution using infinite series was also obtained a long time ago [2–5], the main way of the theoretical *I–E* computation is based on solving integral equations (e.g., [6,7]) or digital simulation (e.g., [8,9]), which is also a numerical technique. The reason why the infinite series solution has not been applied to a greater extent is the series' divergence at and beyond the curve maximum. The series for simple reversible case was successfully computed in a broad potential region [10], other successful results in a narrower potential range were achieved for quasi-reversible [11,12] and reversible [13] charge transfer. More complicated cases, involving some kind of chemical reaction, have not been treated, except for chemical reaction following reversible charge transfer, derived but not calculated in [3].

We have tried to apply transformations of infinite series to sequences enabling us [14] to achieve summable sequences by means of different techniques [15,16]. Recently we succeeded in calculating all cases described in [1] but with a better accuracy (up to 12 valid figures even in the region beyond the peak) and generally in a much wider potential region. However, our calculations are only for the single scan voltammetric mode. The way of using infinite series for cyclic voltammetry has so far been found only for the reversible case [17], otherwise numerical solution is necessary [1,6,7].

The purpose of this communication is to exemplify without delay accurate values of the theoretical dimensionless current functions $\chi(at)$ and $\chi(bt)$ at relevant potentials for various cases of reversible and irreversible charge transfer in voltammetry with or without a coupled chemical reaction of different kind, presented in [1]. Our results, obtained in a rather laborious way, can help electrochemists employing digital simulation or other kind of fast numerical computing to check the magnitude of the computational error and optimise the given numerical technique.

2. Formulation of the problem

Eight studied electrochemical mechamisms are described in Table 1. They are compatible with cases I–VIII solved numerically in [1], however, electrochemical

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Table 1
Infinite series solution for different mechanisms in stationary electrode voltammetry

Type of reaction	Mechanism	Case
Reversible el. reaction	$R - ze^- \Longleftrightarrow O$	I
Irreversible el. reaction	$R - ze^- \overset{k}{\Rightarrow} O$	II
Chem. reaction preceding reversible el. reaction	$Z \overset{k_f}{\rightleftarrows} R$ $R \overset{k_b}{-} ze^- \Longleftrightarrow O$	III
Chem. reaction preceding irreversible el. reaction	$Z \overset{k_f}{\rightleftarrows} R$ $R \overset{k_b}{-} ze^- \overset{k}{\Rightarrow} O$	IV
Reversible chem. reaction following rev. el. reaction	$R - ze^- \Longleftrightarrow O$ $O \underset{k_b}{\overset{k_f}{\rightleftarrows}} Z$	V
Irreversible chem. reaction following rev. el. reaction	$R - ze^- \Longleftrightarrow O$ $O \xrightarrow{k_f} Z$	VI
Catalytic reaction with reversible el. reaction	$R - ze^- \Longleftrightarrow O$ $O + Z \xrightarrow{k_f} R$	VII
Catalytic reaction with irrev. el. reaction	$R - ze^- \overset{k}{\Rightarrow} O$ $O + Z \xrightarrow{k_f} R$	VIII

oxidation is supposed in our work. Series solution presented in [1] was therefore re-written for electrochemical oxidation using the same symbols as defined in [1] and the resulting series are summarised in Table 2.

3. Results and discussion

3.1. Ways of calculation

The term *RT*/*F* is included in all current function calculations if a real potential scale, e.g., in millivolts, is desired. Consequently, its most accurate value is needed, which is given by the combination of the currently best values of R and F with the preset value of T, $T = 298.15$ K in this work. Using contemporary NIST values and respecting the combined standard uncertainty of this term [18], the value $RT/F = 25.692606$ mV ensues and is used in all results calculation in this work.

Our success in using infinite series solution in a broad potential range, including also the potentials where the series are wildly divergent, has been determined by three factors: (1) Effective implementation of the transform techniques converting the series into summable sequences, mainly Epsilon and Eta transformations [15,16]. (2) The use of arbitrary precision arithmetic (APA) by implementation of UBASIC [19] or MATHEMATICA [20]; the necessity of using APA for calculations with the series was stressed also by Cope [12]. (3) Optimisation of the summation step of the algorithm especially when the current function is calculated at the potential far beyond the voltammetric peak. Fulfilment of two latter factors helps in preventing the loss of significant digits in internal computer operations.

ε-Transformation is a nonlinear lozenge algorithm utilising the partial sums of the original series $\varepsilon_0^{(0)} = s_0, \varepsilon_0^{(1)} = s_1, \ldots, \varepsilon_0^{(n)} = s_n$, and it is defined by the equations [15]:

$$\varepsilon_{-1}^{(n)} = 0, \ \varepsilon_0^{(n)} = s_n, \quad n \geqslant 0, \tag{1}$$

$$\varepsilon_k^{(n)} = \varepsilon_{k-2}^{(n+1)} + 1/\Delta\varepsilon_{k-1}^{(n)}, \quad k > 0, \tag{2}$$

where the forward difference operator Δ is applied to superscripts:

Table 2
Infinite series for eight cases shown in Table 1

I.	$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{j} \exp[jnF/RT)(E - E_{1/2})]$
II.	$\chi(bt) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}} \exp\left[\left(\frac{j\beta n_a F}{RT}\right)\left(E - E^0 + \frac{RT}{\beta n_a F} \ln \frac{\sqrt{\pi D_0 b}}{k_s}\right)\right]$
III.	$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[\sqrt{j} \prod_{i=1}^{j-1} \left(1 + \frac{\sqrt{i}}{K\sqrt{(l/b) + i}}\right)\right] \exp\left[\frac{jnF}{RT}\left(E - E_{1/2} - \frac{RT}{nF} \ln \frac{K}{1+K}\right)\right]$
IV.	$\chi(bt) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[\frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}} \prod_{i=1}^{j-1} \left(1 + \frac{\sqrt{i}}{K\sqrt{(l/b) + i}}\right)\right] \exp\left[\frac{j\beta n_a F}{RT}\left(E - E^0 + \frac{RT}{\beta n_a F} \ln \frac{\sqrt{\pi D b}}{k_s} - \frac{RT}{\beta n_a F} \ln \frac{K}{1+K}\right)\right]$
V.	$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[\sqrt{j} \Big/ \prod_{i=1}^{j-1} \left(1 + \frac{K\sqrt{i}}{\sqrt{(l/a) + i}}\right)\right] \exp\left[\frac{jnF}{RT}\left(E - E_{1/2} - \frac{RT}{nF} \ln(1+K)\right)\right]$
VI.	$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[\frac{1}{\sqrt{(j-1)!}} \prod_{i=1}^{j} \sqrt{(k_f/a) + i}\right] \exp\left[\frac{jnF}{RT}(E - E_{1/2})\right]$
VII.	$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{(k_f/a) + j} \exp\left[\frac{jnF}{RT}(E - E_{1/2})\right]$
VIII.	$\chi(bt) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[(\sqrt{\pi})^j \Big/ \prod_{i=1}^{j-1} \sqrt{(k_f/b) + i}\right] \exp\left[\frac{j\beta n_a F}{RT}\left(E - E^0 + \frac{RT}{\beta n_a F} \ln \frac{\sqrt{\pi D b}}{k_s}\right)\right]$

All series were derived in [1] and then transformed for electrochemical oxidation. $a = nFv/(RT)$, $b = \beta n_a Fv/(RT)$, $K = k_f/k_b$, $l = k_f + k_b$.

Table 3
Comparison of calculated current function $\pi^{1/2}\chi(at)$ by [1] (N–S), [13] (B–S)[a], and [8] (Oldham)[b] with our results (inf. series)

E^* (mV)	I^* (N–S)	I^* (B–S)	I^* (Oldham)	I^* (inf. series)	E^* (mV)	I^* (N–S)	I^* (B–S)	I^* (Oldham)	I^* (inf. series)
−120	0.009		0.009 243 948	0.009 243 941	25	0.445	0.445 4	0.445 402 715	0.445 402 714
−100	0.020		0.019 826 795	0.019 826 790	28.5	0.4463	0.4463		
−80	0.042	0.041 8	0.041 786 884	0.041 786 881	28.493 1			0.446 29	
−60	0.084	0.084 9	0.084 946 670	0.084 946 669	28.491 796				0.446 294 695
−50	0.117	0.118 3	0.118 310 310	0.118 310 309	30	0.446	0.446 1	0.446 135 903	0.446 135 902
−45	0.138	0.138 4	0.138 469 122	0.138 469 121	35	0.443	0.443 5	0.443 491 462	0.443 491 461
−40	0.160	0.160 9	0.160 985 410	0.160 985 410	40	0.438	0.438 1	0.438 031 319	0.438 031 317
−35	0.185	0.185 7	0.185 748 099	0.185 748 098	45			0.430 338 397	0.430 338 395
−30	0.211	0.212 5	0.212 498 303	0.212 498 302	50	0.421	0.421 2	0.420 972 452	0.420 972 450
−25	0.240	0.240 8	0.240 808 267	0.240 808 266	60	0.399	0.399 7	0.399 177 424	0.399 177 421
−20	0.269	0.270 0	0.270 075 288	0.270 075 287	80	0.353		0.352 959 075	0.352 959 070
−15	0.298	0.299 5	0.299 537 230	0.299 537 230	100	0.312		0.312 422 930	0.312 422 923
−10	0.328	0.328 3	0.328 313 538	0.328 313 538	120	0.280		0.280 211 978	0.280 211 969
−5	0.355	0.355 4	0.355 470 694	0.355 470 693	150	0.245		0.244 875 940	0.244 875 926
0	0.380	0.380 1	0.380 104 813	0.380 104 813	200			0.207 358 837	0.207 358 813
5	0.400	0.401 4	0.401 428 451	0.401 428 451	250			0.183 584 028	0.183 583 991
10	0.418	0.418 8	0.418 846 013	0.418 846 013	300				0.166 746 096
15	0.432	0.432 0	0.432 003 878	0.432 003 877	350				0.153 943 061
20	0.441	0.440 8	0.440 807 134	0.440 807 133	400				0.143 750 173

I^* is used in the table headings instead of $\pi^{1/2}\chi(at)$ for the sake of space.

[a] Calculations were made by means of Padé approximants.

[b] Current functions were calculated by our program in UBASIC based on the "hastened" algorithm and all constants published by Oldham [8]. The current function at the peak was taken from [8] and the dimensionless peak potential 1.1090 reported there was transformed into millivolt scale using the multiplication factor of 25.692606 mV.

Table 4
Current functions for cases III–VIII and kinetic parameter $p_x = 1$ (x = III–VIII) compared with those in [1]

E^* (mV)	Case III, $p_{\mathrm{III}} = 1$		Case IV, $p_{\mathrm{IV}} = 1$		Case V, $p_{\mathrm{V}} = 1$		Case VI, $p_{\mathrm{VI}} = 1$		Case VII, $p_{\mathrm{VII}} = 1$		Case VIII, $p_{\mathrm{VIII}} = 1$	
	[1]	Our results	[1]	Our results	[1]	Our results	[1]	Our results	[1]	Our results	[1]	Our results
−120	0.009	0.00912513	0.016	0.01606586	0.005	0.00465771	0.013	0.01303429	0.013	0.01309605	0.016	0.01640884
−100	0.019	0.01929056	0.034	0.03369749	0.010	0.01007971	0.027	0.02786058	0.028	0.02814712	0.035	0.03525426
−80	0.039	0.03949420	0.067	0.06783527	0.021	0.02165034	0.057	0.05829107	0.059	0.05958738	0.074	0.07456408
−60	0.075	0.07611632	0.126	0.12621923	0.046	0.04576193	0.116	0.11671553	0.121	0.12228156	0.152	0.15262955
−50	0.100	0.10203048	0.164	0.16439132	0.066	0.06580331	0.160	0.16053425	0.170	0.17168286	0.213	0.21371530
−45	0.116	0.11681541	–	0.18485384	0.079	0.07858298	0.185	0.18639860	0.201	0.20198770	–	0.25094083
−40	0.131	0.13263417	0.205	0.20559639	0.093	0.09351987	0.213	0.21470692	0.234	0.23629477	0.291	0.29280677
−35	0.149	0.14926200	0.226	0.22602654	0.110	0.11083887	0.244	0.24508600	0.273	0.27465234	0.339	0.33920804
−30	0.164	0.16640962	0.244	0.24551105	0.129	0.13072799	0.276	0.27694613	0.315	0.31693835	0.388	0.38977301
−25	0.183	0.18373566	0.263	0.26343398	0.152	0.15330791	0.308	0.30947568	0.361	0.36282545	0.444	0.44381781
−20	0.199	0.20086580	0.279	0.27925830	0.177	0.17859404	0.340	0.34166604	0.409	0.41176011	0.498	0.50033031
−15	0.216	0.21741682	0.292	0.29257926	0.205	0.20645338	0.371	0.37237279	0.461	0.46296446	0.556	0.55799975
−10	0.232	0.23302260	0.302	0.30315881	0.235	0.23656097	0.400	0.40041197	0.512	0.51546673	0.612	0.61530310
−5	0.246	0.24735856	0.310	0.31093516	0.265	0.26836415	0.424	0.42468031	0.566	0.56816165	0.666	0.67064695
0	0.259	0.26016154	0.315	0.31600785	0.300	0.30106606	0.443	0.44427915	0.617	0.61989519	0.719	0.72253803
5	0.271	0.27124281	0.318	0.31860437	0.332	0.33364111	0.458	0.45861713	0.668	0.66956142	0.766	0.76976692
10	0.280	0.28049345	0.318	0.31903746	0.363	0.36489282	0.467	0.46746938	0.715	0.71619531	0.809	0.81152701
15	0.288	0.28788217	0.317	0.31766212	0.391	0.39355700	0.471	0.47098148	0.757	0.75904529	0.844	0.84747167
20	0.293	0.29344716	0.314	0.31483895	0.416	0.41843992	0.470	0.46962006	0.796	0.79761469	0.875	0.87768095
25	0.297	0.29728389	0.310	0.31090724	0.436	0.43856759	0.464	0.46408523	0.829	0.83166833	0.900	0.90256446
30	0.299	0.29953073	0.306	0.30616841	0.452	0.45331180	0.456	0.45520630	0.861	0.86120854	0.921	0.92273551
35	0.300	0.30035446	0.301	0.30087815	0.461	0.46246085	0.444	0.44384227	0.885	0.88643005	0.937	0.93889183
40	0.300	0.29993688	0.295	0.29524519	0.465	0.46621708	0.431	0.43080209	0.907	0.90766509	0.951	0.95172491
45	0.298	0.29846356	–	0.28943433	0.464	0.46512583	0.417	0.41679193	0.924	0.92532875	–	0.96186432
50	0.296	0.29611500	0.283	0.28357167	0.459	0.45996035	0.403	0.40238892	0.939	0.93987160	0.969	0.96985201
60	0.289	0.28945296	0.272	0.27203870	0.441	0.44089825	0.375	0.37405445	0.961	0.96136712	0.980	0.98108329
80	0.272	0.27194408	–	0.25098394	0.389	0.38851315	0.325	0.32495958	0.984	0.98431640	0.988	0.99240132
100	0.253	0.25337808	–	0.23325973	0.340	0.33902157	–	0.28797839	0.994	0.99362625	0.992	0.99687017
120	0.236	0.23632944	–	0.21856074	–	0.29988201	–	0.26060893	0.997	0.99737536	0.997	0.99868561
140	0.222	0.221517	–	0.20629121	–	0.27014719	–	0.23985415	0.999	0.99890243	0.999	0.99944009

$$\Delta\varepsilon_{k-1}^{(n)} = \varepsilon_{k-1}^{(n+1)} - \varepsilon_{k-1}^{(n)} \tag{3}$$

η-transformation represents further nonlinear lozenge algorithm, utilising the terms of the original series $\eta_0^{(0)} = a_0, \eta_0^{(1)} = a_1, \ldots, \eta_0^{(n)} = a_n$, and defined by the equations [15]:

$$1/\eta_{-1}^{(n)} = 0, \quad \eta_0^{(n)} = a_n, \quad n \geqslant 0, \tag{4}$$

$$1/\eta_{2k+1}^{(n)} = 1/\eta_{2k-1}^{(n+1)} + 1/\eta_{2k}^{(n+1)} - 1/\eta_{2k}^{(n)}, \quad n,k \geqslant 0, \tag{5}$$

$$\eta_{2k}^{(n)} = \eta_{2k-2}^{(n+1)} + \eta_{2k-1}^{(n+1)} - \eta_{2k-1}^{(n)}, \quad n,k \geqslant 0, \tag{6}$$

where $\varepsilon_{-1}^{(n)}$ and $1/\eta_{-1}^{(n)}$ are the starting values of the respective algorithms. The η-algorithm has separate formulae for odd and even indices k. For both algorithms, the rate of convergence increases with the increasing index k; in case of ε-algorithm the best convergence is supposed for the sequence $\varepsilon_{2k}^{(0)}$, i.e., for the upper diagonal terms with even indices [15]. In η-algorithm, each upper diagonal term $\eta_k^{(0)}$ (with $k = 0, 1, 2, \ldots$) is used for summation.

3.2. Simple reversible electrode reaction

The comparison of the current function values $\pi^{1/2}\chi(at)$ (denoted shortly as I^*), related to planar diffusion, is demonstrated in Table 3 where our results acquired by means of infinite series are shown together with the results published in [1] (denoted by N–S), those in [13] utilising Padé approximants (B–S), and our computations based on the "hastened" formula of Oldham [10] but utilising arbitrary precision arithmetic.

Calculation of spherical correction for reversible case, $\Phi(at)$, and irreversible case, $\Phi(bt)$, is principally different. It can be evaluated quite easily and independently from the planar diffusion term only for reversible case [1,21]. However, even in reversible case, when trying to calculate spherical correction to more valid digits, there is a problem with setting a proper starting potential. Nicholson and Shain assumed to start voltammetric experiment at potential E_i (well before the current rise) regulated by the u-value, $u = (E_{1/2} - E_i)nF/(RT)$ [1]. We have found in our preliminary calculations that the value $u = 6.5$, recommended in [1], is fair only when $\Phi(at)$ is given to 3 decimal digits. For the results accurate at least to 5 decimal digits in the whole potential range, the parameter $u \approx 12$ is required.

3.3. Reversible or irreversible electrode reaction with a coupled chemical reaction

In this study, we have evaluated current functions $\pi^{1/2}\chi(at)$ or $\pi^{1/2}\chi(bt)$ for each studied mechanism and all values of the corresponding dimensionless parameter p_x accounted for kinetics and thermodynamics of the chemical reaction coupled to the charge transfer step and defined in the headings of tables VII–X, XII–XIII of [1]. Normalised potentials E^* in our Tables 3 and 4, are defined by the potential scales indicated below the earlier mentioned tables in [1].

For cases III–VIII (Table 1) seven to nine different p_x values were used in calculations (with $x = \mathrm{III, IV, V, VI, VII}$, and VIII), corresponding to the case. Exhibited current functions in Table 4 are limited to $p_x = 1$, all other results will be summarised elsewhere [18]. Except the last two $\pi^{1/2}\chi(at)$ values for case III, at least 12 valid decimal figures were verified by thorough inspection of the obtained results. This was based on comparing the differences in the current function, corresponding to the given and the previous summation loop index, with the preselected maximum error, $\varepsilon_{\max}$. If this condition was fulfilled successively four times, the calculation was automatically terminated. In most difficult cases this procedure was made personally using output current function values at each summation loop index. Notwithstanding the potential range used in this comparison study, compatible with [1], we have calculated most of current functions up to 10 dimensionless potential units (cca 257 mV).

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