Journal of Mathematical Chemistry Vol. 35, No. 2, February 2004 (© 2004)

Two algorithms for computing the Randles–Sevcik function from electrochemistry

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Received 4 August 2003

We derive two expansions of the Randles–Sevcik function $\sqrt{\pi}\chi(x)$: an asymptotic expansion of $\sqrt{\pi}\chi(x)$ for $x \to \infty$ and its Taylor expansion at any $x_0 \in \mathbb{R}$. These expansions are accompanied by error bounds for the remainder at any order of the approximation.

KEY WORDS: Randles–Sevcik function, Taylor expansions, asymptotic expansions, error bounds

AMS subject classification: 41A60, 30E20

1. Introduction

The Randles–Sevcik function $\sqrt{\pi}\chi(x)$ arises in electrochemistry. This function characterizes the dependence of electric current on cell voltage under certain electrolysis conditions [1–3]. Several authors have investigated its analytical properties and different methods for computation, see for example [4–9]. Reinmouth gave a rapidly convergent series for $\sqrt{\pi}\chi(x)$ which permits its evaluation for negative values of x [9]. However, the chemically interesting region is contained in the positive real axis. The region $x \simeq 1.1$ is particularly interesting because this function has a relatively steep peak there [4,8]. In order to approximate $\sqrt{\pi}\chi(x)$ in this region, Oldham, by using Weyl fractional calculus, provided a series reformulation of the Randles–Sevcik function on

0259-9791/04/0200-0131/0

the whole real axis [8,10]:

$$\sqrt{\pi}\,\chi(x) = \left(\frac{\pi}{2}\right)^{1/2} \sum_{n=1}^{\infty} \gamma_n(x), \quad x \in \mathbb{R}, \tag{1}$$

where $\gamma_n(x) = \beta_n^{-3}(\beta_n - x)^{1/2}(\beta_n + 2x)$, $\beta_n = (x^2 + b_n^2)^{1/2}$ and $b_n = (2n-1)\pi$. But the convergence of Oldham's series is extremely slow [7]. More recently, Lether has obtained a integral representation of the Randles–Sevcik function from which he has derived a two-parameter expansion of $\sqrt{\pi}\,\chi(x)$ valid $\forall x \in \mathbb{R}$ [7]. This expansion has the form

$$\sqrt{\pi}\,\chi(x) = S_N(x) + E_{N,K}(x), \tag{2}$$

where S_N is the Nth partial sum of (1) and $E_{N,K}$ is an error correction term given by

$$E_{N,K}(x) \equiv \sum_{k=0}^{K} d_k \left(x^2 + 4N^2\pi^2\right)^{-(k+1/4)} \sin\left(\left(2k + \frac{1}{2}\right)\theta_N + \frac{\pi}{4}\right),$$

where $\theta_N \equiv \tan^{-1}(x/2N\pi)$ and the coefficients d_k are defined in terms of Bernoulli numbers and the gamma function:

$$d_k \equiv 2\left(1 - 2^{2k-1}\right) B_{2k} \pi^{2k-1} \frac{\Gamma(2k + 1/2)}{(2k)!}.$$

Moreover, Lether presents a method for selecting appropriate values of N and K for computing $\sqrt{\pi}\,\chi(x)$ to a specified number of decimal digits of accuracy.

However, complete asymptotic expansions including error bounds of $\sqrt{\pi}\,\chi(x)$ are not fully investigated. The purpose of this paper is to obtain an asymptotic expansions of $\sqrt{\pi}\,\chi(x)$ for large x and its Taylor expansion at any point $x_0 \in R$, in particular at $x_0 = 1.1$. These expansions are derived in section 2. We obtain there easy algorithms to compute the coefficients of the expansions as well as error bounds at any order of the approximation. They are derived by using the ideas of Watson's lemma [11, chapter 1]. We compare our expansion with Lether's expansion and give numerical examples in section 3.

2. A Taylor expansion and an asymptotic expansion

The starting point is the integral representation [7]:

$$\pi^{1/2}\chi(x) = \int_0^{\infty} t^{1/2} \operatorname{csch} \pi t \sin\left(xt + \frac{\pi}{4}\right) \mathrm{d}t. \tag{3}$$

Using the exponential representation of the csch and sin functions, we can write this integral as

$$\pi^{1/2}\chi(x) = 2\Im\left\{ \mathrm{e}^{\mathrm{i}\pi/4} \int_0^{\infty} \frac{t^{1/2}}{\mathrm{e}^{\pi t} - \mathrm{e}^{-\pi t}} \mathrm{e}^{\mathrm{i}tx}\, \mathrm{d}t \right\}. \tag{4}$$

Then, expansions of $\pi^{1/2}\chi(x)$ follow immediately from expansions of the Fourier transform of the function $t^{1/2}/(\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t})$:

$$\int_0^\infty \frac{t^{1/2}}{\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t}}\mathrm{e}^{\mathrm{i}tx}\,\mathrm{d}t. \tag{5}$$

Theorem 1. For $n=1,2,3,\ldots$, the Taylor expansion of the integral (5) at x_0, convergent for $|x-x_0|<\pi$, is given by

$$\int_0^\infty \frac{t^{1/2}\mathrm{e}^{\mathrm{i}tx}}{\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t}}\,\mathrm{d}t = \sum_{k=0}^{n-1}\frac{\mathrm{i}^k\Gamma(k+3/2)}{k!(2\pi)^{k+3/2}}\zeta\left(k+\frac{3}{2},\frac{1}{2}-\frac{\mathrm{i}}{2\pi}x_0\right)(x-x_0)^k + R_n(x_0,x), \tag{6}$$

where $\zeta(z,a)$ is the Hurwitz zeta-function. The remainder term is bounded by

$$\left|R_n(x_0,x)\right| \leqslant \frac{\Gamma(n+3/2)\zeta(n+3/2)}{n!\pi^{n+3/2}}|x-x_0|^n, \tag{7}$$

where $\zeta(z)$ is the Riemann zeta-function.

Proof. We write (5) in the form:

$$\int_0^\infty \frac{t^{1/2}\mathrm{e}^{\mathrm{i}tx_0}}{\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t}}\mathrm{e}^{\mathrm{i}t(x-x_0)}\,\mathrm{d}t \tag{8}$$

and consider the Taylor expansion of the exponential function at the origin:

$$\mathrm{e}^{\mathrm{i}t(x-x_0)} = \sum_{k=0}^{n-1}\frac{[\mathrm{i}t(x-x_0)]^k}{k!} + r_n(t,x-x_0). \tag{9}$$

Introducing this expansion in (8), interchanging sum and integral and using the integral representation of the Hurwitz zeta-function [12, section 2.2.1, p. 46] we obtain (6) with

$$R_n(x_0,x) \equiv \int_0^\infty \frac{t^{1/2}\mathrm{e}^{\mathrm{i}tx_0}}{\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t}} r_n(t,x-x_0)\,\mathrm{d}t.$$

To derive (7), consider the explicit expression given by the Lagrange form for the remainder $r_n(t,x-x_0)$ of the Taylor expansion (9):

$$r_n(t,x-x_0) = \frac{\mathrm{e}^{\mathrm{i}\xi}}{n!}\left[\mathrm{i}t(x-x_0)\right]^n, \quad \xi\in\left(0,t(x-x_0)\right), n=1,2,3,\ldots.$$

Therefore $|r_n(t,x-x_0)| \leqslant t^n|x-x_0|^n/n!$, and

$$\left|R_n(x_0,x)\right| \leqslant \frac{1}{n!}\int_0^\infty \frac{t^{n+1/2}}{\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t}}\,\mathrm{d}t|x-x_0|^n.$$

Using that $\mathrm{e}^{\pi t}-\mathrm{e}^{-\pi t}\geqslant \mathrm{e}^{\pi t}-1\ \forall t\geqslant 0$ and [13, equation (23.2.7)] we obtain (7). □

Corollary 1. For $|x| < \pi$,

$$\chi(x) = \frac{1}{2\pi^2}\sum_{k=0}^{\infty}\frac{(-1)^{[k/2]}}{k!(2\pi)^k}\left(2^{k+3/2}-1\right)\Gamma\left(k+\frac{3}{2}\right)\zeta\left(k+\frac{3}{2}\right)x^k. \qquad (10)$$

Proof. Set $x_0 = 0$ in (6) and use (4) and [13, equation (23.2.20)]. □

Theorem 2. For $n = 2, 3, \ldots$, an asymptotic expansion of the integral (5) for $x \to \infty$ is given by

$$\int_0^{\infty}\frac{t^{1/2}}{e^{\pi t}-e^{-\pi t}}e^{itx}\,dt = \frac{1}{2\sqrt{\pi}(\pi - ix)^{1/2}} + \frac{\sqrt{\pi}}{4(\pi - ix)^{3/2}} + \sum_{k=1}^{n-1}\frac{(2\pi)^{2k-1}B_{2k}\Gamma(2k+1/2)}{(2k)!(\pi - ix)^{2k+1/2}} + R_n(x). \qquad (11)$$

The remainder term verifies

$$\left|R_n(x)\right| \leqslant \left\{4\left(1+\frac{2}{3(2^{2n-1}-1)}\right)\left[\Gamma\left(2n+\frac{1}{2}\right) - \Gamma\left(2n+\frac{1}{2}, \pi|\pi - ix|\right)\right] + C\left(\frac{2}{\pi}\sqrt{\pi^2+x^2}\right)^{2n}\Gamma\left(2n+\frac{1}{2}, \pi|\pi - ix|\right)\right\}\frac{1}{|\pi - ix|^{2n+1/2}}, \qquad (12)$$

where C is a bound of $|w/(e^w-1)|$ in the region $W \equiv \{w \in C,\ |w - t(\pi - ix)| < \pi^2/\sqrt{\pi^2+x^2},\ 0 \leqslant t < \infty\}$ (see figure 1(a)). A possible value for C is given in [14, equation (16)].

Proof. From (5),

$$\int_0^{\infty}\frac{t^{1/2}}{e^{\pi t}-e^{-\pi t}}e^{itx}\,dt = \frac{1}{2\pi}\int_0^{\infty}t^{-1/2}\frac{(-2\pi t)}{e^{-2\pi t}-1}e^{-(\pi - ix)t}\,dt. \qquad (13)$$

Consider the Taylor expansion [13, equation (23.1.1)],

$$\frac{-2\pi t}{e^{-2\pi t}-1} = 1 + \pi t + \sum_{k=1}^{n-1}\frac{B_{2k}}{(2k)!}(2\pi t)^{2k} + r_n(t), \quad n = 1, 2, 4, 6, 8, \ldots, \qquad (14)$$

where $r_n(t) = \mathcal{O}(t^{2n})$ when $t \to 0^+$ and $n = 2, 4, 6, 8, \ldots$. Introducing this expansion into the second integral in (13) and interchanging sum and integral we obtain (11) with

$$R_n(x) \equiv \frac{1}{2\pi}\int_0^{\infty}t^{-1/2}r_n(t)e^{-(\pi - ix)t}\,dt.$$

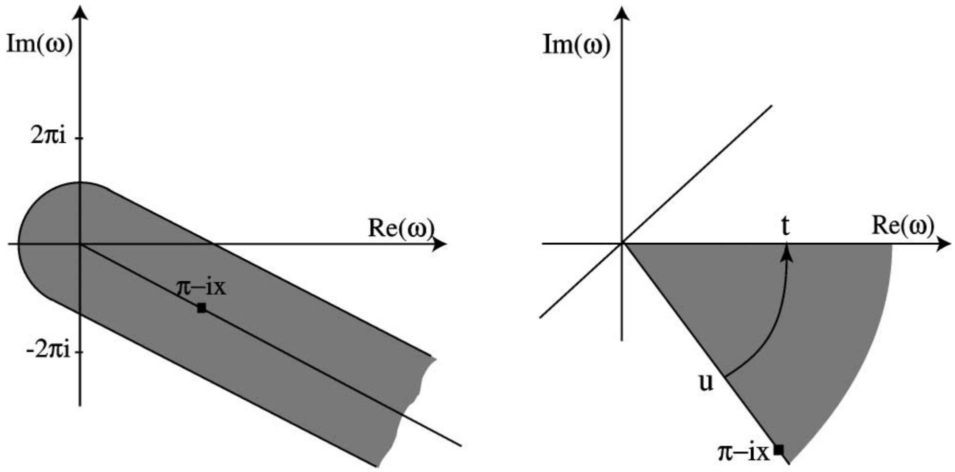

Figure 1. (a) The region W introduced in theorem 2. It is comprised by the complex points located at a distance $< \pi^2/\sqrt{\pi^2 + x^2}$ from the half straight $[0, \infty(\pi - \mathrm{i}x))$. (b) From (14), the complex function $r_n((\pi - \mathrm{i}x)^{-1}w)$ of the variable w is analytic and bounded in the half plane $|\mathrm{Arg}(w) - \mathrm{Arg}(\pi - \mathrm{i}x)| < \pi/2$, in particular in the shaded region of figure (b). Then, we can replace the integration path u by the integration path t.

After the change of variable $t \to u/(\pi - \mathrm{i}x)$ we obtain

$$R_n(x) = \frac{1}{2\pi(\pi - \mathrm{i}x)^{1/2}} \int_0^{\infty(\pi - \mathrm{i}x)} u^{-1/2} r_n\left(\frac{u}{\pi - \mathrm{i}x}\right) \mathrm{e}^{-u}\, \mathrm{d}u.$$

The integrand is an analytic function of u in the sector $|\mathrm{Arg}(u) - \mathrm{Arg}(\pi - \mathrm{i}x)| < \pi/2$ and is exponentially small when $u \to \infty$ with $\mathrm{Arg}(\pi - \mathrm{i}x) < \mathrm{Arg}(u) < 0$. Then, using the Cauchy residua theorem, we can shift the integration contour from $[0, \infty(\pi - \mathrm{i}x))$ to $[0, \infty)$ (see figure 1(b)):

$$R_n(x) = \frac{1}{2\pi(\pi - \mathrm{i}x)^{1/2}} \int_0^{\infty} t^{-1/2} r_n\left(\frac{t}{\pi - ix}\right) \mathrm{e}^{-t}\, \mathrm{d}t.$$

Therefore,

$$\left|R_n(x)\right| \leqslant \frac{1}{2\pi|\pi - \mathrm{i}x|^{1/2}} \int_0^{\infty} t^{-1/2} \left| r_n\left(\frac{t}{\pi - \mathrm{i}x}\right)\right| \mathrm{e}^{-t}\, \mathrm{d}t.$$

Dividing the above integral at the point $t = \pi|\pi - \mathrm{i}x|$ and using the bound for $r_n(w)$ given in [14, equation (14)] in the first integral, and the bound for $r_n(w)$ given in [14, equation (15)] in the second integral, we obtain (12). □

3. Numerical experiments and conclusions

Tables 1 and 2 show numerical experiments about the accuracy of the approximations and error bounds supplied by theorems 1 and 2. In these tables, the second column

Table 1
Approximation supplied by (6) at $x_0 = 1$ and error bound given by (7).

x	$\pi^{1/2}\chi(x)$	1st order approx.	Relative error	Rel. error bound	2nd order approx.	Relative error	Rel. error bound
1.1	0.446291	0.445725	0.0013	0.04	0.446784	0.001	0.0014
1.01	0.445826	0.445725	2.0 e−4	0.004	0.44583	1.0 e−5	1.4 e−5
1.001	0.445735	0.445725	2.0 e−5	0.00038	0.445735	1.3 e−7	1.4 e−7
1.0001	0.445726	0.445725	2.4 e−6	3.8 e−5	0.445726	1.0 e−9	1.4 e−9
1.00001	0.445725	0.445725	2.4 e−7	3.8 e−6	0.445725	1.0 e−11	1.4 e−11

Table 2
Approximations supplied by (11) and error bound given by (12).

x	$\pi^{1/2}\chi(x)$	1st order approx.	Relative error	Rel. error bound	2nd order approx.	Relative error	Rel. error bound
50	−7.757 e−4	7.74 e−4	0.002	0.004	−7.757 e−4	2.0 e−5	4.0 e−5
100	−1.3869 e−4	−1.386 e−4	5.7 e−4	1.0 e−3	−1.3869 e−4	1.3 e−6	2.7 e−6
500	−2.489859 e−7	−2.489802 e−7	2.3 e−5	4.7 e−5	−2.489859 e−7	2.0 e−9	4.0 e−9
1000	−4.401985 e−8	−4.4019597 e−8	5.7 e−6	1.0 e−5	−4.401985 e−8	1.3 e−10	2.7 e−10
5000	−7.874793 e−10	−7.874791 e−10	2.3 e−7	4.7 e−7	−7.874793 e−10	2. e−13	4.0 e−13

Table 3
The first three lines compare the approximations, for $x \simeq 1$, supplied by the expansion (6) with $x_0 = 1$ and $n = 2$ and the expansion (2) with $N = 2$ and $K = 0$. The last three lines compare the approximations, for large x, supplied by the expansion (11) with $n = 1$ and the expansion (2) with $N = 1$ and $K = 0$.

x	$\pi^{1/2}\chi(x)$	Theorems 1, 2 approx.	Relative error	Lether's approx.	Relative error
1.1	0.44629094	0.44678382	0.001	0.44622851	0.00014
1.01	0.4458258	0.44583082	1.0 e−5	0.44576409	0.000138
1.001	0.44573548	0.44573553	1.0 e−7	0.44567384	0.000138
100	0.05642592	0.05641896	0.0005	0.05641908	0.00012
1000	0.01784126	0.01784124	5.0 e−6	0.01784124	1.2 e−6
10000	0.00564189	0.00564189	5.0 e−8	0.00564189	1.2 e−8

represents the value of $\pi^{1/2}\chi(x)$. The third and sixth columns represent, respectively, a first and a second order approximation given by the corresponding theorem. Fourth and seventh columns represent the respective relative errors $|R_n(x_0, x)/(\pi^{1/2}\chi(x))|$ or $|R_n(x)/(\pi^{1/2}\chi(x))|$. Fifth and last columns represent the respective relative error bounds given by the corresponding theorem.

In table 3 we compare the expansions given in theorems 1 and 2 with Lether's expansions for $K = 0$. We observe that Lether's expansion and the expansions given in theorems 1 or 2 offer approximately the same accuracy for a given CPU time of computation (theorem 1 is slightly more accurate). And conversely, to get a prescribed accuracy, Lether's expansion and the expansions given in theorems 1 or 2 needs approximately the same CPU time. The advantages of the expansions given in theorems 1 or 2 are more analytical than computational. Expansions (6) and (11) have both a very simple analytical form in terms of powers of the variable x with coefficients being very important and well-known special functions. But more important, both have an essential property for an expansion: they are asymptotic expansions in the respective regions $x \to x_0$ and $x \to \infty$. Moreover, both expansions (6) and (11) are accompanied by error bounds at any order of the approximation.

Acknowledgments

The financial support of The Government of Navarra (Res. 134/2002), The Government of Aragón (Cod. 161/02), Caja Rural de Navarra, MCYTDG1 and Feder (BFM2001-1793) is acknowledged.

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