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A simplified calculation procedure of concentration distribution in electrochemical systems

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A fast and practical method of computing electrolyte concentration profiles in terms of truncated Chebyschev polynomials is described and illustrated by numerical examples.

In many electrochemical systems such as the rotating disc electrode [1], two-dimensional laminar forced-flow between parallel-plate electrodes [2], magnetically augmented laminar natural convection in electrolysis [3], and the convective Warburg problem [4], the reacting ion-concentration distribution, which exists between the working electrode and the bulk of the electrolyte, may be expressed in terms of ϵ^{-x^3}-type integrands. In all cases the concentration distribution may also be expressed in terms of the incomplete gamma function $\gamma(1/3, u)$ where u is a lumped integration variable chosen appropriately for the given electrode/cell configuration. Incomplete gamma functions may, for instance, be computed by means of the related $I(u, p)$ functions compiled in Pearson's tables [5], but this procedure is not well suited for quick approximate estimations via simple computing devices (e.g., pocket calculators and pocket computers); numerical integration of the ϵ^{-x^3}-type functions via quadratures suffers from similar limitations.

A much less tedious computation may be carried out in terms of Chebyschev polynomials where the number of terms may be minimized for a predetermined order of accuracy; this important feature is linked to the fundamental property of Chebyschev polynomials: their magnitude is always less than unity [6, 7], regardless of the independent variable and the polynomial index. The strategy then is the following: (a) Express the $\gamma(1/3, u)$ function as a convergent power series, and (b) replace this series by a *shorter* Chebyschev equivalent which is used for numerical computation.

Considering step (a), the incomplete gamma function in its general form:

$$\gamma(\nu, z) \equiv \int_0^z t^{\nu-1} e^{-t} dt \qquad (1)$$

where t, z are real and $\nu > 1$ may be expressed as a convergent series [8–12]

$$\gamma(\nu, z) = \sum_{k=0}^{\infty} (-1)^k \frac{z^{\nu+k}}{k!(\nu+k)}. \qquad (2)$$

If the condition $\nu > 1$ is not satisfied, the translation property

$$\gamma(\nu, z) = \frac{1}{\nu}[\gamma(\nu+1, z) + z^{\nu} e^{-\nu}] \qquad (3)$$

may be employed. Thus, in the specific case of $\nu = 1/3$, the pertinent relationships are

$$\gamma(1/3, z) = 3[\gamma(4/3, z) + z^{1/3} e^{-z}] \qquad (4a)$$

$$\gamma(4/3, z) = \sum_{k=0}^{\infty} A_k z^{(k+4/3)} \qquad (4b)$$

where the magnitude of the coefficients

$$A_k \equiv (-1)^k \frac{1}{k!(k+4/3)} \qquad (4c)$$

decreases rapidly with k as shown in Table 1.

Considering step (b) for a specified value of $z = z_1$, Equation 4b may be rewritten as

$$\gamma(4/3, z_1) = \sum_{k=0}^{\infty} a_k z_1^k; \quad a_k \equiv A_k z_1^{4/3}. \qquad (5)$$

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Table 1. Numerical values of the first seven A_k *coefficients in Equation 4c*

k	A_k	$\sum_k A_k^*$
0	0·750 00	0·750 00
1	−0·428 57	0·321 43
2	0·150 00	0·471 42
3	−0·038 46	0·432 96
4	0·007 81	0·440 77
5	−0·001 31	0·439 45
6	0·000 18	0·439 64
7	-2×10^{-5}	0·439 62

* Corresponding to successive approximations of $\gamma(4/3, 1)$; after seven iterations, the hereby computed value compares with the value of 0·439 29 obtained from [5].

The coefficients α_k of the Chebyschev-equivalent

$$\gamma(4/3, z_1) = \sum_k \alpha_k T_k(z_1) \tag{6}$$

are related to a_k as shown in Table 2; more comprehensive tables (not needed for quick approximate computations) are given elsewhere (e.g. [12]).

Consider, as an illustrative example, the concentration field in a two-dimensional diffusion layer in laminar forced convection [2]:

$$\frac{c}{c_{\text{bulk}}} = \frac{1}{\Gamma(4/3)} \int_0^{\zeta} \epsilon^{-x^3} \, dx; \quad \Gamma(4/3) = 0{\cdot}892\,98. \tag{7}$$

Rewriting in terms of incomplete gamma functions,

Table 2. Computation of the α_k *coefficients of the Chebyschev polynomial* $\sum_{k=0}^{N} \alpha_k T_k(x)$ *equivalent to the power expansion* $\sum_{k=0}^{N} a_k x^k$ *[6]*

k	α_k $N=2$	α_k $N=3$
0	$a_0 + a_2/2$	$a_0 + a_2/2$
1	a_1	$a_1 + 3a_3/4$
2	$a_2/2$	$a_2/2$
3	–	$a_3/4$

$T_0 = 1; T_1(x) = x; T_2(x) = 2x^2 - 1;$
$T_3(x) = 4x^3 - 3x$

$$\frac{c}{c_{\text{bulk}}} = \frac{1}{\Gamma(4/3)} [\gamma(4/3, \zeta^3) + \zeta \epsilon^{-\zeta^3}]. \tag{8}$$

Let $z = \zeta^3$. Then, $\gamma(4/3, \zeta^3)$ may be directly calculated (using Equation 4b and Table 1) as

$$\gamma(4/3, z) \cong 0{\cdot}75 z^{4/3} - 0{\cdot}428\,57 z^{7/3} + 0{\cdot}15 z^{10/3} - 0{\cdot}038\,46 z^{13/3} + - \ldots \tag{9}$$

Taking now the specific value of $z = 0{\cdot}5$, Equation 9 may be rewritten as

$$\gamma(4/3, 0{\cdot}5) \cong a_0 + a_1 z + a_2 z^2 + a_3 z^3 \tag{10}$$

where $a_0 = 0{\cdot}2976; a_1 = -0{\cdot}1701; a_2 = 0{\cdot}059\,53; a_3 = -0{\cdot}1526$. The coefficients in Equation 6 are computed as shown in Table 2 and the expansion

$$\gamma(4/3, 0{\cdot}5) \cong 0{\cdot}3274 T_0 - 0{\cdot}1815 T_1 + 0{\cdot}029\,76 T_2 - 0{\cdot}003\,816 T_3 \tag{11}$$

is obtained. Since $|T_n| \leqslant 1{\cdot}0$ for all n, if the last two terms in Equation 11 are dropped, the maximum error magnitude is expected to be about 3×10^{-2} and the estimates $\gamma(4/3, 0{\cdot}5) = 0{\cdot}242\,35$; $c/c_{\text{bulk}} = 0{\cdot}810$ are obtained. If only the T_3-term is dropped in Equation 11, the expected maximum error magnitude is about $3{\cdot}8 \times 10^{-3}$ and the estimates of $\gamma(4/3, 0{\cdot}5) = 0{\cdot}2218$ and $c/c_{\text{bulk}} = 0{\cdot}787$ are obtained (representing about a 3% improvement). Thus, the simple linear relationship

$$\gamma(4/3, z) \cong \alpha_0 + \alpha_1 z \tag{12}$$

yields a good approximation to the definition integral; the drawback of the dependence of the $\{\alpha_k\}$ set on the numerical value of z is minor with respect to the simplicity of Equation 12.

Similarly, in the recently posed Warburg-impedance problem [4], the

$$F_o(\eta_i) = \frac{1}{\Gamma(4/3)} \int_{\eta_i}^{\infty} \epsilon^{-x^3} \, dx \tag{13}$$

function is converted to the form of

$$F_o(\eta_i) = 1 - \frac{\gamma(4/3, \eta_i^3) + \eta_i \epsilon^{-\eta_i^3}}{\Gamma(4/3)}$$

and for $\eta_i = \sqrt[3]{0{\cdot}5}$ the estimate:

$$1 - 0{\cdot}7874 = 0{\cdot}2126$$

is obtained.

Thus, Chebyschev polynomials may be seen to be very useful in the development of reasonably accurate low-order polynomial approximations for electrochemical computations via small-scale computing devices.

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