NUMERICAL SOLUTION OF TWO-POINT BOUNDARY VALUE PROBLEM BY COMBINED TAYLOR SERIES METHOD WITH A TECHNIQUE FOR RAPIDLY SELECTING SUITABLE STEP SIZES

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A novel numerical method, based on the combined Taylor series method with a technique for rapidly selecting suitable step sizes, is given for solving two-point boundary value problems. The differential equation for an immobilized enzyme reaction is considered as a model system. Comparisons between numerical and exact solutions for the first-order reaction show that the proposed method promises superhigh-order accuracy that is almost the same as machine accuracy over wide ranges of relevant parameters. The final value of the increment or decrement used to obtain a new estimate in the Newton-Raphson iterative scheme is found to be approximately the same as the relative error of the calculated value, which means that this final value is useful to predict the accuracy of a numerical solution of the differential equation that does not provide an analytical solution. Moreover, it is shown that the selected stepsizes are suitable values that cause little loss-of-significance errors.

Introduction

The two-point boundary problem is a very important differential equation system that appears in various fields in chemical engineering. This is reflected by the variety of numerical techniques that have been proposed to solve this problem^{4, 7, 9}.

On the other hand, any computer has a limitation to storing numerical values, which makes it difficult to maintain the value finally obtained as a result of repeated arithmetic at the same level as the machine accuracy. There are some sources of error causing a decrease in the accuracy of the calculated value¹; the round-off error, truncation error, *loss-of-significance* errors, and so on. The round-off error, which occurs when a numerical value is rounded to store in memory, is essentially inevitable as long as floating-point arithmetic is used. However, this kind of error does not affect the accuracy of the calculated value to a significant degree because rounding comes in randomly up or down and the errors cancel out during repetition of the arithmetic operation. Proof on the validity of this description will be given later.

The Taylor series method was originally a technique to solve initial-value problems and provides a highly stable and efficient procedure for computation^{2, 3, 5} although it is not so popular at present because derivation of the formu-

las for higher derivatives is not easy. If the formulas have been obtained analytically, however, the Taylor series method has the potential of giving a numerical solution of higher accuracy than other methods. First of all, the truncation error can easily be removed by summing each term of monotonically decreasing Taylor series until the ratio of the higher- and first-derivative terms is below machine accuracy. In addition, the *loss-of-significance* errors, which are considered to markedly influence the accuracy of the calculated values, could be removed to some extent by selecting suitable stepsizes. The simplest way to determine a satisfactory stepsize is to check whether the absolute value of each term is decreased monotonically. However, even if this condition is satisfied, there is no guarantee that the selected stepsize can completely remove the *loss-of-significance* errors and, consequently, introduction of a highly reliable technique is required to select the suitable stepsize. Nagasue *et al.* previously found a simple way to satisfy this requirement⁶, in which one selects an initial value for the stepsize so that the ratio of two of the first several terms of the Taylor series becomes equal or close to unity and checks whether the absolute value of each term decreases monotonically; if this criterion is not satisfied, the stepsize is halved and the same procedure is iterated.

In this work, therefore, we apply the combined Taylor series method with this technique to the two-point boundary value problem and examine the accuracies of the

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Table 1 Equations of average enzymatic activity for the possible combination of type of enzymatic and geometry of the support

Type	G	Equations
I	1	$\frac{1}{6\sigma} (D + E)$
	2	$\frac{\sigma+1}{3\sigma^2} \left(D + \frac{\sigma-1}{\sigma+1} E \right)$
	3	$\frac{1}{2\sigma^3} \{ (\sigma+1)^2 D + 3 \ln(\sigma^2 - \sigma + 1) + \sigma(\sigma-2) E \}$
II	1	$\frac{1}{6\sigma} (D + E)$
	2	$\frac{1}{3\sigma^2} (-D + E)$
	3	$\frac{1}{\sigma^3} \ln(1 + \sigma^3)$

where $D = \ln\{(\sigma+1)^2/(\sigma^2-\sigma+1)\}$ and $E = 2\sqrt{3}[\tan^{-1}\{(2\sigma-1)/\sqrt{3}\} + \pi/6]$

numerical solutions. As a result, we indicate that this simple technique is useful to determine suitable stepsizes rapidly and the obtained numerical solutions have a superhigh-order accuracy that is almost equal to machine accuracy.

1. Theory

1.1 Differential equation system

In this work, we consider the two-point boundary value problem concerning an immobilized enzyme system. The reason for this selection is that the differential equation is nonlinear and has some physically important parameters, such as the Thiele modulus, Biot number, and dimensionless substrate concentration in a bulk liquid, with which we can easily change the degree of nonlinearity. Mass balance for the substrate inside of the support yields⁸⁾

$$\frac{1}{x^{G-1}} \frac{d}{dx} \left(x^{G-1} \frac{dy}{dx} \right) = \frac{\alpha}{\varepsilon} \frac{E_s(x)y}{1 + \beta y} = r(y) \quad (1)$$

with the boundary conditions:

$$\left. \frac{dy}{dx} \right|_{x=0} = 0 \quad (2)$$

$$\left(y + \frac{1}{Bi} \frac{dy}{dx} \right) \Big|_{x=1} = 1 \quad (3)$$

For simplicity, the squared Thiele modulus, ϕ^2 , is designated by α . The enzymic activity distribution function, $E_s(x)$, involved in Eq. (1) is given by

$$E_s(x) = \frac{1}{1 + c(d-x)^3} \quad (4)$$

and the average enzymic activity, ε , is written as

$$\varepsilon = G \int_0^1 E_s(x) x^{G-1} dx \quad (5)$$

When the enzyme is uniformly distributed throughout the porous structure of the support, we have $E_s(x) = 1$ (or $c = 0$) and $\varepsilon = 1$. For nonuniform distribution, on the

other hand, the following two cases are considered. The first case has a profile of enzymic activity decreasing towards the center of the support from its external surface, and we set $c = \sigma^3$ and $d = 1$, while we take $c = -\sigma^3$ and $d = 0$ for the second case with an entirely reverse profile. The larger the value of σ , which is a positive real number, the more steeply the activity distribution profile changes. After insertion of Eq. (4), Eq. (5) was integrated for the possible combination of the type of enzymic distribution and the geometry of the support. The results are summarized in **Table 1**.

1.2 Algorithm for solution of two-point boundary value problem based on Newton-Raphson method

We assume a value of y at the center of the support, $x = 0$, to be

$$y|_{x=0} = \gamma \quad (6)$$

and solve the two-point boundary value problem given by Eqs. (1)-(3) as an initial-value problem by the Taylor series method described in the next section, so that we obtain the values of $y|_{x=1}$ and $(dy/dx)|_{x=1}$. These values are then used to calculate

$$f(\gamma) = \left(y + \frac{1}{Bi} \frac{dy}{dx} \right) \Big|_{x=1} - 1 \quad (7)$$

If γ is an exact value, we have $f(\gamma) = 0$, but this would not be true because γ is an arbitrarily assumed value. Here, we introduce the Newton-Raphson method to determine the exact value of γ that satisfies $f(\gamma) = 0$ and to obtain simultaneously the solution to Eq. (1) that satisfies the boundary conditions given by Eqs. (2) and (3). To determine a new estimate of γ , the Newton-Raphson iterative scheme requires the derivative of $f(\gamma)$ with respect to γ , i.e., $f^*(\gamma)$. Therefore, Eqs. (1), (2), and (6) are differentiated with respect to γ to give the following equations:

$$\frac{1}{x^{G-1}} \frac{d}{dx} \left(x^{G-1} \frac{dy^*}{dx} \right) = \frac{\alpha}{\varepsilon} \frac{E_s(x) y^*}{\varepsilon(1 + \beta y)^2} \quad (8)$$

$$\left. \frac{dy^*}{dx} \right|_{x=0} = 0 \quad (9)$$

$$y^*|_{x=0} = 1 \quad (10)$$

where y^* signifies $dy/d\gamma$. The initial conditions given by Eqs. (9) and (10) are used to solve Eq. (8) by the Taylor series method described later. Consequently, we obtain $y^*|_{x=1}$ and $(dy^*/dx)|_{x=1}$. These values are then substituted into the following equation derived by differentiating Eq. (7) with respect to γ :

$$f^*(\gamma) = \left(y^* + \frac{1}{Bi} \frac{dy^*}{dx} \right) \Big|_{x=1} \quad (11)$$

Thus, we calculate $\Delta\gamma$ by

$$\Delta\gamma = f(\gamma) / f^*(\gamma) \quad (12)$$

and get a new estimate of γ by $\gamma^{(1)} = \gamma^{(0)} - \Delta\gamma$ if the criterion

$$|\Delta\gamma/\gamma| < \varepsilon_n \quad (13)$$

is not satisfied. This series of calculations is terminated by iterating one more time after the criterion has been satisfied.

As an example, consider a case where the calculation is carried out with standard double-precision real numbers, whose accuracy is 15-16 decimal digits of accuracy and the numerical value is usually displayed in 16 digits. In this case, we set the error tolerance equal to $\varepsilon_n = 10^{-9}$ and terminate the calculation by iterating one more time after the criterion given by Eq. (13) has been satisfied. The resulting numerical solution should probably possess superhigh-order accuracy if no loss-of-significance errors occur. This is because the Newton-Raphson method converges quadratically. As indicated later, the accuracy of the numerical solution thus obtained can successfully be estimated from the final value of $|\Delta\gamma/\gamma|$.

1.3 Taylor series formulas for solution of differential equation

Let us consider the domain $[0, 1]$ for the independent variable x as follows

$$\begin{aligned} 0 &= x_0 < x_0 + \Delta_0 = x_1 < x_1 + \Delta_1 \\ &= x_2 < \cdots < x_M + \Delta_M = x_{M+1} = 1 \end{aligned} \quad (14)$$

At a given interval $x_m \leq x \leq x_{m+1}$ we set

$$x = x_m + \xi \quad (0 \leq \xi \leq \Delta_m) \quad (15)$$

and expand y into the Taylor series:

$$y(x) = y(x_m + \xi) = \sum_{i=0}^{\infty} a_{m,i} \xi^i \quad (16)$$

Applying Eq. (16) and its first and second derivatives to Eq. (1) and setting the coefficients of the same power of ξ equal to zero, we get equations for $a_{m,i}$. In order to reduce the occurrence of overflow or underflow, however, each term in the series of Eq. (16) may be calculated collectively without separating $a_{m,i}$ from ξ^i . In addition, if we select Δ_m for ξ , Eq. (16) becomes

$$y(x_{m+1}) = y(x_m + \Delta_m) = \sum_{i=0}^{\infty} a_{m,i} \Delta_m^i = \sum_{i=0}^{\infty} A_{m,i} \quad (17)$$

Then, equations for $A_{m,i}$ involved in Eq. (17) are given as follows. For the first interval ($x_m = x_0 = 0 \leq x \leq x_1$), we gather all terms having the same power of ξ and set them equal to zero. If we now define

$$W_{0,i} = \beta S_{0,i} + i(G+i-2)(1+\beta\gamma)A_{0,i} \quad (18)$$

and

$$S_{0,i} = \sum_{j=2}^{i-2} j(G+j-2)A_{0,j}A_{0,i-j} \quad (19)$$

we get

$$A_{0,0} = \gamma \quad (20)$$

$$A_{0,1} = 0 \quad (21)$$

and

$$A_{0,i} = \frac{W_{0,i} - \beta S_{0,i}}{(1+\beta\gamma)(G+i-2)i} \quad (i=2, 3, 4, \dots) \quad (22)$$

where $S_{0,i}$ ($i=2, 3, 4, \dots$) is calculated by Eq. (19) with $S_{0,2} = S_{0,3} = 0$, and $W_{0,i}$ is calculated by the recursion formula

$$\begin{aligned} W_{0,i} &= \frac{\Delta_0}{1+c\Delta^3} [c\{3d(dW_{0,i-1} - W_{0,i-2}\Delta_0) \\ &\quad + W_{0,i-3}\Delta_0^2\} + \frac{\alpha}{\varepsilon} A_{0,i-2}\Delta_0] \\ &\quad (i=2, 3, 4, \dots; W_{0,-1} = W_{0,0} = W_{0,1} = 0) \end{aligned} \quad (23)$$

Therefore, calculating $A_{0,i}$ successively by use of Eqs. (19) to (23) and applying the calculated values to the following equations, we get the values of y and y' at the second point x_1 .

$$y_1 = y(x_1) = y(x_0 + \Delta_0) = \sum_{i=0}^{\infty} A_{0,i} \quad (24)$$

$$y'_1 = \frac{dy(x_1)}{dx} = y'(x_0 + \Delta_0) = \frac{1}{\Delta_0} \sum_{i=1}^{\infty} i A_{0,i} \quad (25)$$

For a given interval $x_m \leq x \leq x_{m+1}$ ($1 \leq m \leq M$), we also define

$$\begin{aligned} W_{m,i} &= \beta S_{m,i} + (1+\beta y_m)(i-1) \\ &\quad [ix_m A_{m,i} + (G+i-3)A_{m,i-1}\Delta_m] \end{aligned} \quad (26)$$

and

$$S_{m,i} = \sum_{j=2}^{i-2} (j-1) [jx_m A_{m,j} + (G+j-3)A_{m,j-1}\Delta_m] A_{m,i-j} \quad (27)$$

Then, we get

$$A_{m,0} = y_m \quad (28)$$

$$A_{m,1} = y'_m \Delta_m \quad (29)$$

and

$$\begin{aligned} A_{m,i} &= -\frac{1}{i \cdot x_m} \left[(G+i-3)A_{m,i-1}\Delta_m - \frac{W_{m,i} - \beta S_{m,i}}{(1+\beta y_m)(i-1)} \right] \\ &\quad (i=2, 3, 4, \dots) \end{aligned} \quad (30)$$

where $S_{m,i}$ ($i=2, 3, 4, \dots$) is calculated by Eq. (27) with $S_{m,2} = 0$, and $W_{m,i}$ is calculated by the recursion formula

$$\begin{aligned} W_{m,i} &= \frac{\Delta_m}{1+c(d-x_m)^3} [c\{3(d-x_m)((d-x_m)W_{m,i-1} \\ &\quad - W_{m,i-2}\Delta_m) + W_{m,i-3}\Delta_m^2\} \\ &\quad + \frac{\alpha}{\varepsilon} \Delta_m (x_m A_{m,i-2} + A_{m,i-3}\Delta_m)] \\ &\quad (i=2, 3, 4, \dots; W_{m,-1} = W_{m,0} = W_{m,1} = 0; A_{m,-1} = 0) \end{aligned} \quad (31)$$

which was derived from the equation obtained by gathering all terms with the same power of ξ and setting them equal to zero. Thus, calculating $A_{m,i}$ successively by use of Eqs. (27) to (31) and applying the calculated values to

the following equations, we obtain the values of y and y' at the point x_{m+1} .

$$y_{m+1} = y(x_{m+1}) = y(x_m + \Delta_m) = \sum_{i=0}^{\infty} A_{m,i} \quad (32)$$

$$y'_{m+1} = y'(x_{m+1}) = y'(x_m + \Delta_m) = \frac{1}{\Delta_m} \sum_{i=1}^{\infty} i A_{m,i} \quad (33)$$

Likewise, we expand y^* into the Taylor series:

$$y^*_{m+1} = y^*(x_{m+1}) = y^*(x_m + \Delta_m) = \sum_{i=0}^{\infty} A^*_{m,i} \quad (34)$$

Also, differentiation of Eq.(34) with respect to x gives

$$y^{*'}_{m+1} = \frac{dy^*(x_{m+1})}{dx} = y^{*'}(x_m + \Delta_m) = \frac{1}{\Delta_m} \sum_{i=1}^{\infty} i A^*_{m,i} \quad (35)$$

To obtain equations of $A^*_{m,i}$ involved in Eqs. (34) and (35), we differentiate Eqs. (19)-(23) and (27)-(31) with respect to γ . For the first interval, thus, we have

$$A^*_{0,0} = 1 \quad (36)$$

$$A^*_{0,1} = 0 \quad (37)$$

$$A^*_{0,i} = \frac{1}{(1 + \beta\gamma)(G + i - 2)i} \left[W^*_{0,i} - \beta S^*_{0,i} - \frac{\beta}{1 + \beta\gamma} (W_{0,i} - \beta S_{0,i}) \right] \quad (i = 2, 3, 4, \dots) \quad (38)$$

where

$$W^*_{0,i} = \frac{\Delta_0}{1 + c d^3} \left[c \{ 3d (dW^*_{0,i-1} - W^*_{0,i-2} \Delta_0) + W^*_{0,i-3} \Delta_0^2 \} + \frac{\alpha}{\varepsilon} A^*_{0,i-2} \Delta_0 \right] \quad (i = 2, 3, 4, \dots; W^*_{0,-1} = W^*_{0,0} = W^*_{0,1} = 0) \quad (39)$$

$$S^*_{0,i} = \sum_{j=2}^{i-2} j(G + j - 2) (A^*_{0,j} A_{0,i-j} + A_{0,j} A^*_{0,i-j}) \quad (i = 2, 3, 4, \dots; S^*_{0,2} = S^*_{0,3} = 0) \quad (40)$$

Similarly, for a given interval $x_m \leq x \leq x_{m+1}$ ($1 \leq m \leq M$) we have

$$A^*_{m,0} = y^*_{m,0} \quad (41)$$

$$A^*_{m,1} = y^{*'}_{m,1} \Delta_m \quad (42)$$

$$A^*_{m,i} = \frac{1}{i \cdot x_m} \left[(G + i - 3) A^*_{m,i-1} \Delta_m - \frac{1}{(1 + \beta y_m)(i - 1)} \left\{ W^*_{m,i} - \beta S^*_{m,i} - \frac{\beta y^*_{m,i}}{1 + \beta y_m} (W_{m,i} - \beta S_{m,i}) \right\} \right] \quad (i = 2, 3, 4, \dots) \quad (43)$$

$$W^*_{m,i} = \frac{\Delta_m}{1 + c(d - x_m)^3} \left[c \{ 3(d - x_m)((d - x_m)W^*_{m,i-1} - W^*_{m,i-2} \Delta_m) + W^*_{m,i-3} \Delta_m^2 \} + \frac{\alpha}{\varepsilon} \Delta_m (x_m A^*_{m,i-2} + A^*_{m,i-3} \Delta_m) \right] \quad (i = 2, 3, 4, \dots; W^*_{m,-1} = W^*_{m,0} = W^*_{m,1} = 0; A^*_{m,-1} = 0) \quad (44)$$

$$S^*_{m,i} = \sum_{j=2}^{i-1} (j - 1) \left[\{ j x_m A^*_{m,j} + (G + j - 3) A^*_{m,j-1} \Delta_m \} A_{m,j-1} + \{ j x_m A_{m,j} + (G + j - 3) A_{m,j-1} \Delta_m \} A^*_{m,i-j} \right] \quad (i = 2, 3, 4, \dots; S^*_{m,2} = 0) \quad (45)$$

1.4 Initial value of the substrate concentration at $x=0$

The speed and reliability of convergence by the Newton-Raphson method depends on the suitability of an initial value selected for the substrate concentration at the center of the support, γ . We select this value as follows.

(1) $\alpha / \varepsilon > 250,000$

The system is diffusion-controlled and the substrate concentration is sufficiently small at $x = 0$. Therefore, γ is set to zero.

(2) $\alpha / \varepsilon < 10^{-20}$

The system is reaction-controlled and the substrate concentration distribution is approximately uniform throughout the porous structure of the support. Therefore, the value of γ is set to unity.

(3) $10^{-20} \leq \alpha / \varepsilon \leq 250,000$

In this range of α / ε , we determine the initial value of γ based on the Newton-Raphson iterative scheme. Solving Eq. (1) by use of the initial conditions at $x = 0$, i.e., $\gamma = y(0) = 0$ and $y'(0) = 0$, we have $y(x) = 0$ and $y'(x) = 0$. Applying these results to Eq. (7) gives

$$f(0) = y(1) + (1/Bi) y'(1) - 1 = -1 \quad (46)$$

Under the condition of $y(x) = 0$, on the other hand, Eq. (8) becomes

$$\frac{1}{x^{G-1}} \frac{d}{dx} \left(x^{G-1} \frac{dy^*}{dx} \right) = \frac{\alpha}{\varepsilon} E_s(x) y^* \quad (47)$$

with the conditions of $y^*(0) = 1$ and $y^{*'}(0) = 0$. When the enzymic activity distribution is uniform, thus, $E_s(x) = 1$, Eq. (47) can be analytically solved for each geometry of the support. Setting $x = 0$ in the respective analytical equations that express the substrate concentration profile in a support, we obtain

$$\gamma = \frac{1}{\cosh \sqrt{\alpha} + (1/Bi) \sqrt{\alpha} \sinh \sqrt{\alpha}} \quad \text{for } G = 1 \quad (48)$$

$$\gamma = \frac{1}{I_0(\sqrt{\alpha}) + (1/Bi) \sqrt{\alpha} I_1(\sqrt{\alpha})} \quad \text{for } G = 2 \quad (49)$$

and

$$\gamma = \frac{\sqrt{\alpha}}{(1 - 1/Bi) \sinh \sqrt{\alpha} + (1/Bi) \sqrt{\alpha} \cosh \sqrt{\alpha}} \quad \text{for } G = 3 \quad (50)$$

On the other hand, when the enzymatic activity distribution is nonuniform, i.e., $E_s(x) \neq 1$, on the other hand, we must solve Eq. (47) numerically to obtain the values of $y^*(1)$ and $y^{*'}(1)$. Then, we calculate $f^*(0)$ by

$$f^*(0) = y^*(1) + (1/Bi) y^{*'}(1) \quad (51)$$

and substitute this value into the equation:

$$\gamma = 0 - \frac{f(0)}{f'(0)} = \frac{1}{y^*(1) + (1/Bi)y^{*'}(1)} \quad (52)$$

The value of γ thus obtained is used as its initial value.

1.5 Methods for selecting suitable stepsizes and judging achievement of convergence

If a higher-derivative term whose absolute value is larger than those of the first several terms appears in the course of doing the sum of successive terms of the Taylor series, then the Taylor polynomial approximation would fail. This is due to the use of an inappropriate stepsize. To overcome this problem, we select an initial value of the stepsize as follows.

For the first interval, we set

$$|A_{0,2}| = \delta |A_{0,0}| = \delta \gamma \quad (53)$$

and apply Eqs. (20) and (22) to this equation. Then, taking into consideration the inequality

$$0 \leq \Delta_0 \leq 1 \quad (54)$$

we get

$$\Delta_0 = \min \left(1, \left| \frac{2\delta G(1+cd^3)(1+\beta\gamma)}{\alpha/\varepsilon} \right|^{1/2} \right) \quad (55)$$

where δ is an arbitrary constant equal or close to unity. Thus, we calculate $A_{0,i}$ successively using the stepsize given by Eq. (55) and check simultaneously if each term satisfies the relation

$$|A_{0,0}| > |A_{0,i}| \quad (i = 1, 2, 3, \dots) \quad (56)$$

If this relation does not hold, then we change the present stepsize as

$$\Delta_0 = \Delta_0 / 2 \quad (57)$$

and iterate the same calculation from the beginning. The check using Eq. (56) must be made for every term because the values of the infinite series do not necessarily decrease monotonically. For example, if $c = 0$, then the values of $A_{0,1}, A_{0,3}, A_{0,5}, A_{0,7}, \dots$ become zero. When the values of the series become small slowly, we also apply Eq. (57) if the criterion

$$|A_{0,i}| < \varepsilon_a |A_{0,0}| \quad (\text{for example, } \varepsilon_a = 10^{-18}) \quad (58)$$

is not satisfied until i becomes equal to $i_{\max}$ ($= 20-50$). As a result of repetition of such a procedure, we will eventually find a suitable stepsize that satisfies Eq. (56) for every i , and obtain simultaneously values of y_1, y'_1, y^*_1 , and $y^{*'}_1$ that are almost free from loss-of-significance errors.

In the case of $x_m \leq x \leq x_{m+1}$ ($1 \leq m \leq M$) we describe a general procedure to predict an initial value for Δ_m for example, in the preparation for alternating series. When $y'(x_m) \equiv 0$ or $|y_m| \geq |y'_m|$, we have $A_{m,1} \equiv 0$. Therefore, setting

$$|A_{m,2}| = \delta |A_{m,0}| \quad (59)$$

we get

$$\Delta_m = \left| \frac{2\delta x_m}{(G-1)(y'_m/y_m) - (\varepsilon/\alpha)x_m \{1+c(d-x_m)^3\}(1+\beta y_m)} \right|^{1/2} \quad (60)$$

On the other hand, when $y(x_m) \equiv 0$ or $|y_m| < |y'_m|$ is satisfied, $A_{m,0} \equiv 0$. Therefore, setting

$$|A_{m,2}| = \delta |A_{m,1}| \quad (61)$$

gives

$$\Delta_m = \left| \frac{2\delta x_m}{G-1-(\varepsilon/\alpha)x_m(y'_m/y'_m) \{1+c(d-x_m)^3\}(1+\beta y_m)} \right|^{1/2} \quad (62)$$

At a sufficiently large value of i , moreover, Eq. (30) becomes

$$\left| \frac{A_{m,i}}{A_{m,i-1}} \right| \cong \left| \frac{G+i-3}{i} \right| \frac{\Delta_m}{x_m} \cong \frac{\Delta_m}{x_m} \quad (63)$$

Since $|A_{m,i}|$ is considered to decrease slowly under such a condition, we take the value given by

$$\Delta_m = \tilde{\delta} x_m \quad (64)$$

where $\tilde{\delta}$ is an arbitrary constant equal or close to 1/2. Thus, we compare the value given by Eq. (60) or (62) with the value given by Eq. (64) and adopt a smaller value as the initial value of the stepsize. Furthermore, if we take into consideration the relation:

$$0 < \Delta_m \leq 1 - x_m \quad (65)$$

the above technique to select a suitable stepsize can be summarized as follows.

If $|y_m| \geq |y'_m|$, we take

$$\Delta_m = \min \left(1 - x_m, \tilde{\delta} x_m, \left| \frac{2\delta x_m}{(G-1)(y'_m/y_m) - (\varepsilon/\alpha)x_m \{1+c(d-x_m)^3\}(1+\beta y_m)} \right|^{1/2} \right) \quad (66)$$

while, if $|y_m| < |y'_m|$ we use

$$\Delta_m = \min \left(1 - x_m, \tilde{\delta} x_m, \left| \frac{2\delta x_m}{G-1-(\varepsilon/\alpha)x_m(y'_m/y'_m) \{1+c(d-x_m)^3\}(1+\beta y_m)} \right|^{1/2} \right) \quad (67)$$

Using the initial value of the stepsize thus selected, we calculate the values of $A_{m,i}$ for successive i , and check if the inequality

$$|A_{m,i}| < |A_{m,0}| \quad (i = 1, 2, 3, \dots) \quad (68)$$

is satisfied. If this relation does not hold, the present stepsize is changed as

Fig. 1 Plots of the relative errors of dimensionless substrate concentrations at the center of the support calculated by the proposed method to their exact solutions for first-order reaction against the Thiele modulus

$$\Delta_m = \Delta_m / 2 \quad (69)$$

and the calculation is iterated from the beginning. In this case, the check by use of Eq. (68) must be made for the appropriate number of successive i . Furthermore, taking into consideration the case where the Taylor series decreases slowly, we also employ Eq. (69) if the criterion

$$|A_{m,i}| < \varepsilon_a \cdot \max(|A_{m,0}|, |A_{m,1}|) \quad (70)$$

is not satisfied until $i = i_{\max}$. As a result of repeating this procedure, we could eventually find a suitable stepsize that satisfies Eq. (68) for every i , and will obtain simultaneously the values of y_{m+1} , y'_{m+1} , y^*_{m+1} , and y'^*_{m+1} that are almost free from the loss-of-significance errors.

1.6 Effectiveness factor

The general purpose of a theoretical analysis of the immobilized enzyme system is not only to discuss characteristics of the substrate concentration distribution inside of the support but also to elucidate the extent of diffusional effects on the over-all reaction rate. This is achieved by calculation of the effectiveness factor written as

$$Ef = \frac{G(1+\beta)}{\alpha} \frac{dy}{dx} \Big|_{x=1} \quad (71)$$

In the following, therefore, we also examine the accuracy of the effectiveness factor calculated on the basis of the combined Taylor series method with the suitable stepsize finding technique proposed here.

2. Results and Discussion

In the first-order reaction that is catalyzed by the enzyme immobilized on a spherical support ($G = 3$) in the absence of film-diffusional resistance ($Bi = \infty$), the dimensionless substrate concentration at the center of the support is analytically expressed as

$$\gamma = y(0) = \frac{\sinh(\phi x)}{x \sinh(\phi)} \Big|_{x=0} = \frac{\phi}{\sinh(\phi)} \quad (72)$$

Fig. 2 Plots of the relative errors of effectiveness factors calculated by the proposed method to their exact solutions for first-order reaction against the Thiele modulus

Fig. 3 Relationship between the integer N_e expressed by rounding off the value of $-\log_{10}(\varepsilon_r)$ below its decimal point and the number of decimal digits N_d that are identical between numerical and exact solutions

The relative errors of the numerical solutions by the proposed method to the exact values by Eq. (72), defined as

$$\text{Relative error of } \gamma = \left| \frac{\gamma_{\text{Analytical}} - \gamma_{\text{Numerical}}}{\gamma_{\text{Analytical}}} \right| \quad (73)$$

were calculated for various values of ϕ and the results are shown by solid circles in **Figure 1**. Since the machine accuracy is about 10^{-15} with standard double-precision real numbers¹⁾, a relative error less than this value indicates that calculation has been executed in the vicinity of the limitation of computer performance. Evidently, the calculated values when ϕ is less than or equal to 30 are satisfied with this condition. As ϕ becomes greater than 30, the relative error tends to increase because the substrate concentration in the support has an extremely steep gradient so it becomes very difficult to calculate with high accuracy.

Fig. 4 Plots of the value of $|\Delta\gamma/\gamma|$ used to find a new estimate the Newton-Raphson iterative scheme and the execution time against the stepsize selected

However, the degree of this increase in the relative error is slight and its value is no more than 10^{-13} even at $\phi = 500$ which is a sufficiently large value for practical applications.

Under the same condition, the effectiveness factor can be analytically written as

$$Ef = 3 \frac{\phi \cosh(\phi) - \sinh(\phi)}{\phi^2 \sinh(\phi)} \quad (74)$$

The relative errors of the effectiveness factors calculated by the proposed method to the exact values by Eq. (74), defined as

$$\text{Relative error of } Ef = \left| \frac{Ef|_{\text{Analytical}} - Ef|_{\text{Numerical}}}{Ef|_{\text{Analytical}}} \right| \quad (75)$$

are plotted against the Thiele modulus in **Figure 2**. As evident from Eq. (71), calculation of the effectiveness factor requires a numerical value at the external surface of the support. As can easily be predicted from the fact that the numerical calculation of the differential equation by the Taylor series method proceeds from the center towards the external surface of the support, the lower level of the relative error of the effectiveness factor is higher than that of γ as given in Fig. 1. This reflects the fact that in the region of $\phi \leq 20$, where the concentration distribution does not change steeply, the relative errors of the effectiveness factor are slightly larger than those of γ . Since most of the relative errors lie below 10^{-15} as shown in Fig. 2, however, it is obvious that the effectiveness factor has also been calcu-

lated in the neighborhood of the limit of the machine accuracy. In the region of $\phi \geq 50$, on the other hand, it becomes very difficult to maintain accuracy at such a level since an extremely large concentration gradient is formed throughout the porous structure of the support. Consequently, the relative errors of the effectiveness factor are increased with the increase of ϕ by taking almost the same values as the relative errors of γ , suggesting that in this range of ϕ , the accuracies of the values calculated for the dimensionless substrate concentration are almost the same over the entire range within the support.

Figures 1 and 2 also include the plots of ϵ_f , i.e., the value of $|\Delta\gamma/\gamma|$ when convergence is completed in the Newton-Raphson iterative scheme. These values, shown by triangles, agree well with the relative errors of γ for all values of ϕ (Fig. 1). On the other hand, the relative errors of the effectiveness factor are not in good agreement in the region of smaller ϕ (Fig. 2). This is due to the fact that the effectiveness factor is a calculated value using the substrate concentration gradient at the external surface of the support. However, taking into consideration that the machine accuracy lies between 10^{-15} and 10^{-16} in double precision, it would be possible to say that the relative errors of the effectiveness factor are also similar to the values of ϵ_f over the entire range of ϕ . These results suggest that we can approximately predict the accuracy of the numerical solution by the proposed method from the value of ϵ_f . This is very convenient to evaluate the accuracy of the numerical solution to the nonlinear differential equations that can not be solved analytically.

Fig. 5 Plots of the logarithm of dimensionless substrate concentration at the center of support, the effectiveness factor, and the execution time against the Thiele modulus

Besides the relative error, the use of the value N_d , which represents the number of the decimal digits that are identical between the numerical and exact solutions, is considered another way to indicate the accuracy of the numerical solution. Therefore, we calculated a value of $-\log_{10}(\epsilon_f)$ using the data shown in Fig. 1 and expressed it in terms of an integer, N_f , by rounding off the value below its decimal point. **Figure 3** presents the plots of these calculated values against N_d , where the numerical figures given together with each data point signify the number of superimposed data points. All the data are located on a straight line with a gradient of unity or at the right-hand side of the line, showing clearly that N_d can easily be predicted from N_f .

Figure 4 shows the relationship between the values of ϵ_f and δ when ϕ is equal to 10, 100, 300, and 500, respectively, in the Michaelis-Menten type reaction with $\beta = 10$. At each value of ϕ , ϵ_f tends to increase as the value of δ becomes smaller than unity, in other words, as the step number increases. This means that even if the number of interval point is increased, the accuracy of the calculated value is not necessarily improved, but rather lowered. On the other hand, we may consider the use of a value greater

Table 2. Calculated values of dimensionless substrate concentration at center of support, effectiveness factor, final value of $|\Delta\gamma/\gamma|$, and step number (Michaelis-Menten reaction; $G = 3$, $Bi = \infty$, and $\beta = 1$)

ϕ	γ	E_f	ϵ_f	M_f
0.1	9.991669097366715(-1)	9.998333333432545(-1)	0.00(-00)	1
1	9.191098383083468(-1)	9.833433070748370(-1)	0.00(-00)	1
10	1.310281601970095(-3)	4.051448339385890(-1)	2.99(-16)	10
100	1.010551842017687(-41)	4.635878362259703(-2)	7.97(-15)	56
200	7.500679890284338(-85)	2.334064964891022(-2)	2.21(-14)	107
300	4.182183506696701(-128)	1.559625367042621(-2)	2.41(-14)	159
400	2.073597280205449(-171)	1.171062094863860(-2)	5.45(-14)	212
500	9.640177992967793(-215)	9.374942978346257(-3)	6.92(-14)	264

than unity for δ , but this is not meaningful because the Taylor series probably diverges under such a condition. Moreover, ϵ_f tends to increase over the whole range of δ as ϕ increases. This is because the conditions of the calculation become very severe due to a steep variation of the substrate concentration profile in the support with increasing ϕ . In addition, Fig. 4 also exhibits the time required to obtain a solution, *i.e.*, the execution time, when we performed the calculation using an NEC personal computer PC-9801 with a CPU 80386. For each value of ϕ , the execution time tends to increase as the value of δ becomes less than unity. Also, it tends to increase with increasing ϕ . From both the execution time and the accuracy of the calculated values, we can conclude that a reasonable value for δ is around unity.

Equations (1) to (3) with $G = 3$, $\beta = 1$, and $Bi = \infty$ were numerically solved and the dimensionless substrate concentration at the center of the support, the effectiveness factor, and the execution time are plotted against the Thiele modulus in **Figure 5** where all the data are shown by circles. The resistance exerted to a substrate diffusing through the porous structure of the support increases with increase of ϕ , so that the system approaches a diffusion-controlled condition, leading to a significant decrease in the substrate concentration at the center of the support. This in turn causes an exponential decrease in the effectiveness factor with increasing ϕ , which is further followed by a remarkable increase of the execution time at values of ϕ greater than 100. However, note that the calculation was terminated within at most 90 seconds even at $\phi = 500$; the use of a state-of-the-art computer would dramatically reduce the execution time.

Table 2 lists the values of γ , E_f , ϵ_f , and the step number M_f when calculation was iterated one more time after the error tolerance of 10^{-9} was satisfied. All the values of ϵ_f are less than 10^{-13} . Surprisingly, the value of ϵ_f , which can be approximately regarded as the relative error, is only 6.92×10^{-14} at $\phi = 500$ in spite of the fact that the ratio of the substrate concentrations at the external surface and center of the support is more than 10^{210} . Furthermore, the Thiele modulus was increased until γ approached 10^{-308} , which is the lower limit of general compilers on personal computers. As a result, we found that the accuracy of the calculated value was maintained at the same level. Over

Table 3 Calculated values of dimensionless substrate concentration at center of the support, effectiveness factor, final value of $|\Delta\gamma/\gamma|$, and step number (Michaelis-Menten reaction; $G = 3$, $\phi = 10$, and $\beta = 1$)

Bi	γ	E_f	ε_f	M_f
∞	1.310281601970095(-3)	4.051448339385890(-1)	2.99(-16)	10
1000	1.298447938020797(-3)	4.030287981922712(-1)	8.55(-16)	10
100	1.199199388620584(-3)	3.847103757322081(-1)	2.01(-15)	10
10	6.432734868186112(-4)	2.571390182298649(-1)	1.38(-15)	8
1	9.783271216664676(-5)	5.379057409035704(-2)	1.07(-15)	7
0.1	1.006317790887314(-5)	5.933790488176975(-3)	1.00(-16)	7
0.01	1.008636119202212(-6)	5.993337899679837(-4)	5.57(-16)	6
10^{-3}	1.008862263275459(-7)	5.999333378993740(-5)	1.66(-15)	6
10^{-5}	1.008887074955595(-9)	5.999993333337927(-7)	4.32(-16)	6
10^{-7}	1.008887323008069(-11)	5.999999933333330(-9)	6.07(-16)	6

such a wide range of parameters, no one has reported this high level of accuracy for numerical solutions. It is seen that as the value of ϕ is increased, in other words, as accurate calculation becomes difficult due to the increase in the concentration gradient, the step number is automatically increased. The values of γ , E_f , ε_f , and M_f were further calculated by changing Bi as a parameter at $\phi = 10$ and $\beta = 1$, and the results are summarized in **Table 3**. There is no film-diffusional resistance when the value of Bi is infinite. As Bi is decreased, the resistance is increased and the system approaches a diffusion-controlled condition. Despite widely changed Bi , the value of ε_f remains at a very small level, showing that the calculation has been executed in the limitation of the machine accuracy. On the basis of the calculated values shown in Tables 2 and 3, we can conclude that the combined Taylor series method with the technique to select a suitable stepsize gives numerical solutions that agree with the exact values by usually 14-16 digits and at least 12 digits.

Of the step numbers listed in Tables 2 and 3, the maximum value is 264 for $\phi = 500$. Considering that this is a solution to an initial-value problem, it is very surprising that the relative error of the solution was maintained at an order of 10^{-14} for such a large step number in spite of the fact that the ratio of the dimensionless substrate concentrations at the start and end of the calculation was extremely different. This is proof that the stepsizes selected in this calculation were suitable values that caused little loss-of-significance errors.

At $\phi=500$, which gave the maximum step number, we further investigated how many times the stepsize predicted from Eq. (55), (66), or (67) is halved until the criterion of convergence given by Eq. (56) or (68) is satisfied. As a result, we found that the criterion is always satisfied at only one trial in this differential equation system, showing clearly that prediction of the stepsize has been efficiently carried out. Finding out a suitable stepsize in a short time leads directly to a shortening of the execution time. From the fact that we never needed to halve the selected stepsize, it is clear that the execution time has appreciably been saved, which is one of the advantages of the stepsize-finding technique used in this work.

Conclusions

In this work, we proposed a novel numerical method, based on the combined Taylor series method with a technique for rapidly selecting suitable stepsizes, for solving two-point boundary value problems and examined the accuracies of the numerical solutions of the differential equation concerning an immobilized enzyme reaction. Consequently, we obtained the following conclusions.

1) The proposed method gives numerical solutions whose accuracies are almost the same as machine accuracy of the computer over wide ranges of the Thiele modulus and Biot number.

2) The final value of the increment or decrement used to obtain a new estimate of the substrate concentration at the center of the support in the Newton-Raphson iterative scheme was approximately the same as the relative error of the calculated value, showing that this value is useful to estimate the accuracy of the numerical solution to the differential equation that does not have an analytical solution.

3) The value obtained by rounding off the value of $-\log_{10}(\varepsilon_f)$ below its decimal point is useful to predict the number of decimal digits that are identical between the numerical and exact values.

4) The use of the selected stepsize, given as the ratio of two of the first several terms of the Taylor series, gives numerical solutions that are almost free from loss-of-significance errors, indicating that the stepsize-finding scheme used here is very useful.

Nomenclature

$A_{i,j}$	=	each term involved in Taylor series	[-]
Bi	=	Biot number	[-]
c	=	parameter involved in Eq. (4)	[-]
d	=	parameter involved in Eq. (4)	[-]
E_f	=	effectiveness factor	[-]
E_s	=	enzymic activity distribution function	[-]
G	=	geometric factor that takes 1, 2, or 3 for a slab, cylinder, or sphere, respectively	[-]
M	=	step number	[-]
M_f	=	step number when convergence is completed	[-]
N_d	=	number of decimal digits that are identical between numerical and exact solutions	[-]
N_l	=	integer expressed by rounding off a value of $-\log_{10}(\varepsilon_f)$ below its decimal point	[-]
$S_{i,j}$	=	variables defined by Eqs. (19) and (27)	[-]
$W_{i,j}$	=	variables defined by Eqs. (23) and (31)	[-]
x	=	dimensionless coordinate	[-]
y	=	dimensionless substrate concentration	[-]
y^*	=	derivative of dimensionless substrate concentration with respect to γ	[-]
α	=	squared Thiele modulus, i.e., ϕ^2	[-]
β	=	ratio of substrate concentration in a bulk liquid and Michaelis constant	[-]
γ	=	dimensionless substrate concentration at center of a support	[-]
Δ	=	stepsize	[-]
δ	=	parameter connecting with two of first several terms in Taylor series	[-]
$\tilde{\delta}$	=	parameter connecting with two of first several terms in Taylor series	[-]
ε	=	average enzymatic activity	[-]

ε_a	= error tolerance when truncating in course of doing sum of monotonically decreasing terms of Taylor series	[-]
ε_f	= final value of $ \Delta\gamma/\gamma $ in Newton-Raphson iterative scheme	[-]
ε_n	= error tolerance in Newton-Raphson iterative scheme	[-]
ξ	= increment involved in Eq. (16)	[-]
ϕ	= Thiele modulus	[-]
'	= derivative with respect to x	[-]
*	= derivative with respect to γ	[-]

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