

Highly accurate solution of the axial dispersion model expressed in S-system canonical form by Taylor series method

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Abstract

A numerical method for solving an axial dispersion model (two-point boundary value problem) with extremely high-order accuracy is presented. In this method, one first recasts fundamental differential equations into S-system (synergistic and saturable system) canonical form and then solves the resulting set of simultaneous first-order differential equations by the shooting method combined with a variable-order, variable-step Taylor series method. As a result, it is found that over wide ranges of systemic parameters (Peclet number, dimensionless kinetic constant, and reaction order), this method promises numerical solutions with the superhigh-order accuracy that is comparable to the machine accuracy of the computer used. The advantage of the numerical method is also discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Axial dispersion model; Two-point boundary value problem; Superhigh-order accuracy; Taylor series method; Shooting method; S-system

1. Introduction

An axial dispersion model [1] is a two-point boundary value problem that has been widely used to design tubular flow reactors because this simple model can successfully express combined effects of the reactant flow and chemical reaction on the performance of an actual tubular flow reactor [2]. This two-point boundary value problem was numerically solved by various methods, such as the finite-difference method [3–6], quasi-linearization method [7], orthogonal collocation method [8–10], and Galerkin method [11]. In the finite-difference method, however, the solution of this differential equation system is very unstable and requires strict selection of the stepsize according to the magnitudes of the systemic parameters; Peclet number and dimensionless kinetic constant [12]. Nevertheless, the accuracy of the numerical solution is not so high. In contrast, the orthogonal collocation method [13] provides highly accurate numerical solutions over wide ranges of systemic parameters. The authors [14] previously examined the accuracy of the numerical solution to the axial dispersion model by the orthogonal collocation method, in which the expressions derived from Lagrange's interpolation formulas were used to accurately calculate the collocation constants; in general, designated by $A_{i,j}$ and $B_{i,j}$ [15]. As a result, it was found that the

numerical solutions have the accuracies of more than 10 significant-digits in double precision in a practical range of the reactor operation. For larger values of Peclet number and dimensionless kinetic constant, on the other hand, the numerical calculation was unstable and the accuracy of the solution was never improved even when the number of the collocation points was increased up to 500. This is considered due to an unavoidable loss in significant digits generated when solving algebraic equations (approximate equations to the relevant differential equation expressed in terms of the collocation coefficients) by matrix operation.

In the engineering calculation, it may be sufficient if the numerical solution has three-significant digits of accuracy in a practical range of the reactor operation. According to our calculated results [14,15], the orthogonal collocation method satisfies this requirement. On the other hand, it would be useful to develop a numerical calculation method which always gives numerical solutions of the superhigh-order accuracy that is comparable to the machine accuracy of the computer used. In principle, such an extreme requirement could be met only by the Taylor series method. In a previous paper, the authors [16–18] applied the shooting method combined with a variable-order, variable-step Taylor series method to the two-point boundary value problem for an immobilized enzyme reaction and found that the numerical solution gives the superhigh-order accuracy over very wide ranges of systemic parameters; for example, the relative error of the numerical solution was in the order of 10^{-14} even when

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Nomenclature

A_i	variable defined by Eq. (6)
B_i	variable defined by Eq. (7)
D_{ij}	variable defined by Eq. (4)
G_i	variable defined by Eq. (8)
g_{ij}	exponential parameter
$\Delta\gamma$	difference between old and new values for γ
H_i	variable defined by Eq. (9)
h_{ij}	exponential parameter
Δ_i	increment in independent variable t to the next solution point
k	dimensionless kinetic constant
N	number of dependent variables
n	reaction order
Pe	Peclet number
p	order of finite expansion
t	independent variable
X_i	dependent variable
Y_i	logarithm of X_i
y	dimensionless reactant concentration
y_a	dimensionless reactant concentration in Eq. (31)
y_b	dimensionless reactant concentration in Eq. (31)
y^*	first derivative of y with respect to γ
Z	dimensionless distance from reactor outlet (= $1 - z$)
z	dimensionless distance from reactor inlet
<i>Greek symbols</i>	
α_i	multiplicative parameter
β_i	multiplicative parameter
γ	dimensionless reactant concentration at $Z = 0$
ε_a	error tolerance used in Eq. (34)
ε_n	error tolerance used in Eq. (19)

the dimensionless substrate concentration in the support was changed from 1 to 10^{-303} at a Thiele modulus of 700.

Although one can expect an extremely high accuracy for the numerical solution given by the Taylor series method, it is always a cumbersome task to derive and generalize formulas for higher derivatives. Moreover, one is forced to modify the computer program greatly at each problem. To overcome these disadvantages, the authors [19] previously proposed an efficient numerical method for solving two-point boundary value problems with the superhigh-order accuracy by the use of a Taylor series solution in logarithmic space to simultaneous first-order differential equations expressed in S-system (synergistic and saturable system) canonical form [20]. In this method, one first recasts the relevant differential equation into S-system canonical form and then solves the resulting simultaneous first-order differential equations by the combined shooting method with a variable-order, variable-step Taylor series method. Major advantages of this method are that one can always have absolute reliance

on the numerical solution because of its superhigh-order accuracy and solve various types of two-point boundary value problems by changing S-system parameters included in the generalized computer program.

In the present work, the author applies this numerical method to the axial dispersion model with a kinetic equation in power-law form and investigates the accuracies of the numerical solutions obtained for various combinations of systemic parameters (Peclet number, dimensionless kinetic constant, and reaction order). The author also discusses the usefulness of this method.

2. Theory

2.1. Taylor series solution for initial-value problems expressed in S-system canonical form

A general form of the equations to describe an S-system is given by [21]

$$X_i^{(1)} = \alpha_i \prod_{j=1}^N X_j^{g_{ij}} - \beta_i \prod_{j=1}^N X_j^{h_{ij}} \quad (i = 1, 2, \dots, N) \quad (1)$$

where $X_i^{(1)}$ signifies the first derivative of X_i with respect to the independent variable t . A finite Taylor series for solution of Eq. (1) in logarithmic space can be written as [20]

$$Y_i(t + \Delta_i) = Y_i(t) + \sum_{m=1}^p \frac{Y_i^{(m)}(t)}{m!} \Delta_i^m = Y_i(t) + \sum_{m=1}^p D_{i,m} \quad (i = 1, 2, \dots, N) \quad (2)$$

where Y_i is the logarithm of X_i , Δ_i the increment in t to the next solution point, i.e., stepsize, p the order of the finite expansion, and $Y_i^{(m)}(t)$ the m th derivative of $Y_i(t)$ evaluated at t . When $m = 1$,

$$\begin{aligned} D_{i,1} &= Y_i^{(1)} \cdot \Delta_i = \left(\frac{X_i^{(1)}}{X_i} \right) \cdot \Delta_i \\ &= \Delta_i \cdot \alpha_i \prod_{j=1}^N X_j^{g'_{ij}} - \Delta_i \cdot \beta_i \prod_{j=1}^N X_j^{h'_{ij}} \\ &= \Delta_i \cdot \alpha_i \exp \left(\sum_{j=1}^N g'_{ij} Y_j \right) - \Delta_i \cdot \beta_i \exp \left(\sum_{j=1}^N h'_{ij} Y_j \right) \\ &= \check{A}_i^{(1)} - \check{B}_i^{(1)} \quad (i = 1, 2, \dots, N) \end{aligned} \quad (3)$$

where $g'_{ij} = g_{ij} - \delta_{ij}$ and $h'_{ij} = h_{ij} - \delta_{ij}$, with $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. When $m \geq 2$,

$$D_{i,m} = \frac{Y_i^{(m)}}{m!} \Delta_i^m = \frac{\check{Y}_i^{(m)}}{m} = \frac{\check{A}_i^{(m)} - \check{B}_i^{(m)}}{m} \quad (4)$$

in which

$$\check{Y}_i^{(m)} = \check{A}_i^{(m)} - \check{B}_i^{(m)} = \frac{Y_i^{(m)} \cdot \Delta_i^m}{(m-1)!} \quad (5)$$

$$\check{A}_i^{(m)} = \frac{\sum_{q=1}^{m-1} \check{A}_i^{(m-q)} \check{G}_i^{(q)}}{m-1} \quad (6)$$

$$\check{B}_i^{(m)} = \frac{\sum_{q=1}^{m-1} \check{B}_i^{(m-q)} \check{H}_i^{(q)}}{m-1} \quad (7)$$

$$\check{G}_i^{(q)} = \sum_{j=1}^N g'_{ij} \check{Y}_j^{(q)} \quad (8)$$

$$\check{H}_i^{(q)} = \sum_{j=1}^N h'_{ij} \check{Y}_j^{(q)} \quad (9)$$

where the symbol $\check{}$ indicates that the corresponding variable is calculated by including the value of Δ_i , thereby reducing generation of overflow or underflow errors.

Based on the above fundamental equations and algorithm, it is possible to write a generalized computer program that guarantees extremely high accuracy for the numerical solution to the S-system equations. This means that whenever a given nonlinear differential equation can be recast into the S-system canonical form given by Eq. (1), one can expect highly accurate solutions to the differential equation by use of the generalized program as a library.

2.2. Recasting

As was indicated by Savageau and Voit [22], a given differential equation can easily be recast into the S-system canonical form regardless of the degree of its nonlinearity. The two-point boundary value problem that will be investigated here includes first- and second-order derivatives and these also must be recast. In general, an autonomous system which consists of n th-order ordinary differential equations can be transformed to n sets of first-order differential equations. In the case of the two-point boundary value problem, this transformation produces at least two sets of simultaneous first-order differential equations and the number of equations is further increased according to the degree of nonlinearity of the resulting first-order differential equations.

2.3. Differential equation for an axial dispersion model

The axial dispersion model for a tubular flow reactor [1] is given by

$$\frac{1}{Pe} \frac{d^2 y}{dz^2} - \frac{dy}{dz} = ky^n \quad (10)$$

subjected to the following boundary conditions:

$$1 = \left(y - \frac{1}{Pe} \frac{dy}{dz} \right) \Big|_{z=0} \quad (11)$$

$$\frac{dy}{dz} \Big|_{z=1} = 0 \quad (12)$$

where y is the dimensionless reactant concentration, z the dimensionless coordinate whose origin is located at the reactor inlet, Pe the Peclet number, k the dimensionless kinetic constant, and n the reaction order. Transformation of Eqs. (10)–(12) by use of the relation of $Z = 1 - z$ gives the following equations:

$$\frac{1}{Pe} \frac{d^2 y}{dZ^2} + \frac{dy}{dZ} = ky^n \quad (10')$$

$$1 = \left(y + \frac{1}{Pe} \frac{dy}{dZ} \right) \Big|_{Z=1} \quad (11')$$

$$\frac{dy}{dZ} \Big|_{z=0} = 0 \quad (12')$$

2.4. Algorithm for solution of two-point boundary value problems by shooting method [23]

An arbitrary value for y at $Z = 0$ is assumed to be

$$y|_{Z=0} = \gamma \quad (13)$$

and Eq. (10)' is integrated numerically from $Z = 0$ to 1 to obtain the values of $y|_{Z=1}$ and $(dy/dZ)|_{Z=1}$. These values are used to calculate $f(\gamma)$, defined as

$$f(\gamma) = \left(y + \frac{1}{Pe} \frac{dy}{dZ} \right) \Big|_{Z=1} - 1 \quad (14)$$

If γ is a true value, $f(\gamma)$ should be equal to zero. However, it will probably take a value other than zero because γ is an arbitrarily assumed value. Thus, the Newton–Raphson method is used to obtain a new estimate for γ . This procedure is repeated until the relation of $f(\gamma) = 0$ is satisfied and consequently, a solution to the two-point boundary value problem is determined.

The Newton–Raphson method requires a value of the derivative of $f(\gamma)$ with respect to γ , i.e. $f^*(\gamma)$, which is evaluated as follows. Differentiation of Eqs. (10)' and (13) with respect to γ give

$$\frac{1}{Pe} \frac{d^2 y^*}{dZ^2} + \frac{dy^*}{dZ} = kny^{n-1} y^* \quad (15)$$

$$y^*|_{Z=0} = 1 \quad (16)$$

where the symbol $*$ indicates the derivative of a given dependent variable with respect to γ . Integration of Eq. (15) from $Z = 0$ to 1 gives the values of $y^*|_{Z=1}$ and $(dy^*/dZ)|_{Z=1}$. These values are then used to calculate $f^*(\gamma)$ by

$$f^*(\gamma) = \left(y^* + \frac{1}{Pe} \frac{dy^*}{dZ} \right) \Big|_{Z=1} \quad (17)$$

which was derived by differentiating Eq. (14) with respect to γ . Thus, one calculates $\Delta\gamma$ by

$$\Delta\gamma = \frac{f(\gamma)}{f^*(\gamma)} \quad (18)$$

and checks if the criterion

$$\left| \frac{\Delta\gamma}{\gamma} \right| < \varepsilon_n \quad (19)$$

is satisfied. If this is not satisfied, a new estimate for γ is calculated by

$$\gamma|_{\text{New}} = \gamma|_{\text{Old}} - \Delta\gamma \quad (20)$$

and the same procedure is iterated from the beginning.

2.5. Recasting of two-point boundary value problem into S-system equations

To recast the differential equation given by Eq. (10)' into S-system equations, each variable is set as follows:

$$\begin{aligned} y &\rightarrow X_1, & \frac{dy}{dZ} &\rightarrow X_2, \\ y^* &\rightarrow X_3, & \frac{dy^*}{dZ} &\rightarrow X_4, & Z &\rightarrow t \end{aligned}$$

As a result of recasting, the following four simultaneous first-order differential equations are given:

$$X_1^{(1)} = X_2 \quad (21)$$

$$X_2^{(1)} = k Pe X_1^n - Pe X_2 \quad (22)$$

$$X_3^{(1)} = X_4 \quad (23)$$

$$X_4^{(1)} = nk Pe X_1^{n-1} X_3 - Pe X_4 \quad (24)$$

subjected to the following initial conditions:

$$X_1|_{t=0} = \gamma \quad (25)$$

$$X_2|_{t=0} = 0 \quad (26)$$

$$X_3|_{t=0} = 1 \quad (27)$$

$$X_4|_{t=0} = 0 \quad (28)$$

Table 1 lists S-system parameters, α_i , β_i , g_{ij} , and h_{ij} , involved in Eqs. (21)–(24).

Thus, Eqs. (21)–(24) are simultaneously integrated from $Z = 0$ to 1 by the Taylor series method to obtain the values

of $X_i|_{t=1}$ ($i = 1, 2, 3$, and 4). These values are then used to calculate $f(\gamma)$ and $f^*(\gamma)$ by

$$f(\gamma) = \left(X_1 + \frac{1}{Pe} X_2 \right) \Big|_{t=1} - 1 \quad (29)$$

$$f^*(\gamma) = \left(X_3 + \frac{1}{Pe} X_4 \right) \Big|_{t=1} \quad (30)$$

Eqs. (29) and (30) were obtained by recasting Eqs. (14) and (17), respectively. The values of $f(\gamma)$ and $f^*(\gamma)$ are used to calculate $\Delta\gamma$, which is further used to check if Eq. (19) is satisfied. Unless the criterion is satisfied, a new estimate is calculated by Eq. (20) and the same procedure is repeated from the beginning.

2.6. Estimation method of γ

An initial value for γ is necessary to simultaneously integrate Eqs. (21)–(24). As described later, when the initial value for γ is not suitable, halving the present stepsize is repeated. Consequently, the progress of the integration is stopped at a certain position of $Z < 1$. In the present work, therefore, γ was repeatedly estimated in the following procedure.

The values of y_a and y_b are set at zero and unity, respectively, to calculate the initial value for γ by

$$\gamma = \frac{1}{2}(y_a + y_b) \quad (31)$$

and the integration by the Taylor series method is started. If the progress of the integration is stopped at $Z < 1$, the new estimate of γ is calculated by substituting the present value of γ to y_b in Eq. (31) and the same procedure is repeated. When the integration has been successfully executed up to $Z = 1$, the root-finding is changed to the Newton–Raphson method.

2.7. Virtual zero value for dependent variables and its modification method

The present numerical method integrates Eqs. (21)–(24) in logarithmic space, which causes a problem when the dependent variable takes a zero value. In fact, the initial values for X_2 and X_4 are equal to zero, as shown in Eqs. (26) and (28), respectively. To cope with this problem, the author used a much smaller value than γ for the zero value. That

Table 1

S-system parameters obtained by recasting axial dispersion model with a kinetic equation in power-law form

i	α_i	$g_{i,j}$				β_i	$h_{i,j}$			
		$j = 1$	$j = 2$	$j = 3$	$j = 4$		$j = 1$	$j = 2$	$j = 3$	$j = 4$
1	1	0	1	0	0	0	0	0	0	0
2	$k Pe$	n	0	0	0	Pe	0	1	0	0
3	1	0	0	0	1	0	0	0	0	0
4	$nk Pe$	$n - 1$	0	1	0	Pe	0	0	0	1

is, a value of 100^{-100} was used as a virtual zero value and this value was successively modified by multiplying the estimated γ by 10^{-20} , the magnitude of which value was determined by taking into consideration that a numerical value has 15–16 significant digits in double precision.

2.8. Methods for selecting suitable stepsizes and judging completion of convergence

If a term whose absolute value is larger than those of the first few terms appears in the process of summing the Taylor series, the catastrophic cancellation of significant digits probably occurs. Similarly, if the absolute values of the successive terms are very small compared with those of the first few terms, the swamp of information probably occurs. To solve these problems, the author used a stepsize calculated from the equation that was derived by setting the ratio of first- and second-derivatives of the Taylor series at unity, i.e.,

$$\left| \frac{D_{i,1}}{D_{i,2}} \right| = 1 \quad (32)$$

This easily leads to

$$\Delta_i = 2 \left| \frac{Y_i^{(1)}}{Y_i^{(2)}} \right| \quad (33)$$

Thus, Δ_i for each dependent variable is calculated by Eq. (33) and the smallest value among them is used as an initial value of the stepsize at this step. Then, $D_{i,j}$ ($i = 0, 1, 2, 3, \dots$) are consecutively calculated and summed up until the criterion:

$$\left| \frac{D_{i,j}}{D_{i,0}} \right| < \varepsilon_a \quad (\varepsilon_a = 10^{-18}) \quad (34)$$

is satisfied. In the process of summing the Taylor series, moreover, unless the inequality:

$$|D_{i,j}| > |D_{i,j+1}| \quad (35)$$

is satisfied, the present stepsize is halved as

$$\Delta_i = \frac{1}{2} \Delta_i \quad (36)$$

and the same procedure is iterated from the beginning. As a special case of the Taylor series, furthermore, it is considered that Eq. (35) is satisfied but the Taylor series converges very slowly and Eq. (34) is not satisfied even for a sufficiently large value of i . In such a case, it is not efficient to subsequently carry out the summation of the Taylor series. Therefore, unless Eq. (34) is satisfied by $i = i_{\max} (= 25)$, the present stepsize is halved and then the same procedure is iterated. According to the procedure described here, a suitable stepsize will be finally found that satisfies Eq. (35) for every value of i and Eq. (34) for successive values of i ($\leq i_{\max}$) and the values of y_1, y_1', y_1^* , and y_1^{*} , which do not include the loss-of-significance error remarkably, will be obtained.

In the present work, the calculation was performed in double precision with SYMANTEC C++ (Version 8.1) running on a PowerBook 3400C. With standard double-precision real numbers, PC languages such as C, PASCAL, FORTRAN, and BASIC usually guarantee 15–16 significant digits of accuracy [24]. Therefore, a value of 10^{-10} is set for ε_n and the calculation is repeated one more time after the criterion given by Eq. (19) is satisfied. This is because the Newton–Raphson method converges quadratically. If the loss-of-significance error is little generated, the numerical solution thus obtained is expected to have the superhigh-order accuracy.

3. Results and discussion

3.1. Step number (the number of total integration steps)

Changes in the step number with the progress of the integration of Eqs. (21)–(24) from a virtual zero value to unity are shown in Fig. 1, where the calculation was carried out for $Pe = 10$ and 1000 at $n = 1$ and $k = 10$. In both cases, the step number increases linearly with the logarithmic value of Z at the same rate. In other words, almost the same step number is required for the integration per one tick of the Z -coordinate regardless of different parameter conditions. This means that the execution time becomes longer if a smaller value is used for the virtual zero. In the present work, therefore, the author repeatedly modified the virtual zero when γ was estimated by the Newton–Raphson method, according to the procedure described in Section 2.7. Consequently, the integration time for one trial was remarkably reduced after the first trial.

3.2. Process of convergence

The value of X_1 is the dimensionless reactant concentration and its maximum value is equal to unity. If γ is not suitable, the stepsize is halved many times toward zero and consequently, the integration stops at a certain position of

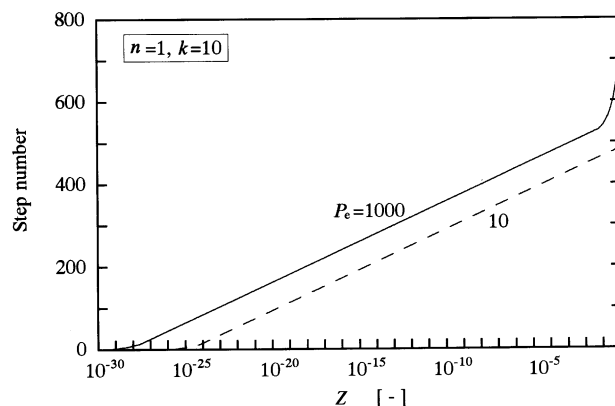


Fig. 1. Changes in step number with progress of integration.

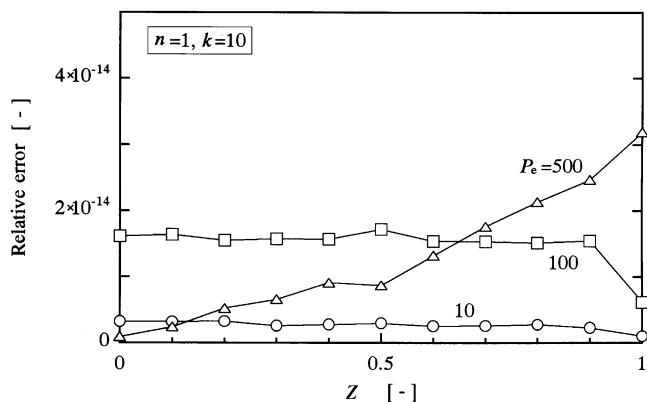


Fig. 2. Relative errors of dimensionless reactant concentrations calculated at a given position in a tubular flow reactor.

$Z < 1$. This is due to the fact that X_1 becomes larger than unity before the integration reaches $Z = 1$. That is, the calculation is diverged if a suitable value is given for γ . In the present work, therefore, estimation of γ was carried out in the two ways as described in Section 2.6. First, the initial value of γ was set at 0.5 by Eq. (31) and the integration was started. If X_1 exceeded unity at $Z < 1$, then γ was set at 0.25 as a result of replacing y_b by γ in Eq. (31) and the integration was executed again. This modification of γ was repeated until y was ranged between 0 and 1 at $Z = 1$ and the estimation was then succeeded to the Newton–Raphson method. As the calculation condition became severe, consecutive modification of γ by Eq. (31) was necessary, especially for $n \neq 1$ and larger values of Pe and k . For smaller γ , the integration tended to diverge at the position of Z closer to unity.

3.3. Effect of Peclet number

The relative errors of the dimensionless reactant concentrations calculated at a given position in the reactor are shown in Fig. 2, where Pe was changed from 10 to 500 at $n = 1$ and $k = 10$. The relative error is in the order of 10^{-15} at $Pe = 10$ and is increased with the increase of Pe . For example, at $Pe = 500$, this value is increased gradually from 2.42×10^{-15} to 3.19×10^{-14} . This is surprising because in this case, the dimensionless reactant concentration is changed from 0.368 to 5.50×10^{-5} . This result indicates high performance of the present numerical method.

The dimensionless reactant concentrations calculated at a given position in the reactor are shown in Fig. 3, where Pe was changed as a parameter over its wide range from 1 to 1000 at $n = 1$ and $k = 10$. The analytical solutions for the first-order reaction are also shown by solid lines in this figure. The relative errors for these numerical solutions were all below 3.19×10^{-14} , suggesting that the calculation was carried out with the accuracy that is comparable to the machine accuracy. Under the condition of $Pe = 1000$, shown by a broken line, calculation by the analytical solution was impossible because the exponential function term included

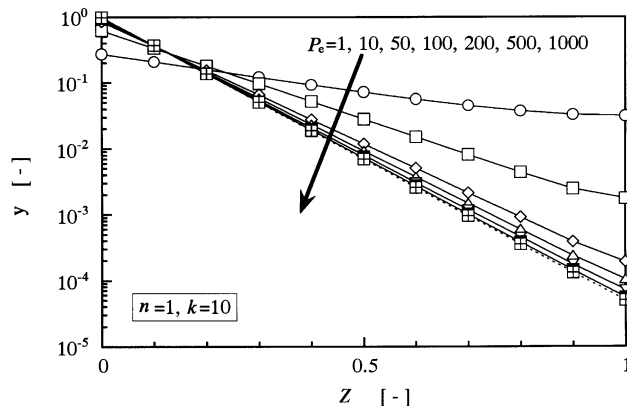


Fig. 3. Comparison between numerical and analytical solutions for dimensionless reactant concentrations calculated at a given position in a tubular flow reactor.

in this equation caused an overflow error. Conversely, the numerical solution was obtainable. This result clearly shows an advantage of numerically solving the differential equation by the present method.

Fig. 4(a)–(c) shows changes in the execution time, step number, and final value of $|\Delta\gamma/\gamma|$, respectively, over a wide range of Pe from 0.1 to 1000. For the first-order reaction, all the calculations except for $Pe = 1000$ were completed in 52 s. When $n = 2$, the execution time is clearly increased with the increase of Pe and is longer than the case of $n = 1$ regardless of smaller step numbers because repeated estimation of γ by Eq. (31) was necessary in this case. The execution times at $n = 2$ and 5 are almost the same over the whole range of Pe . For all the reaction orders, the step number increases with the increase of Pe . This is because the larger the value of Pe , the smaller the dimensionless reactant concentration at $Z = 0$. In the present reaction system, there is no analytical solution except for $n = 1$. Therefore, the final value of $|\Delta\gamma/\gamma|$ was used to estimate the accuracy of the numerical solution instead of the relative error, as carried out in previous papers [16,19]. As seen in Fig. 4(c), most of these values are in the order of 10^{-15} , showing that the numerical solutions were obtained with the superhigh-order accuracy.

3.4. Effect of dimensionless kinetic constant

The dimensionless reactant concentrations calculated at a given position in the reactor are shown in Fig. 5, where k was changed as a parameter over its wide range from 1 to 1000 at $n = 1$ and $Pe = 10$. The analytical solutions for the first-order reaction are also shown by solid lines in this figure. The numerical solutions are completely identical to their respective analytical solutions. The relative errors of these numerical solutions were all below 5.00×10^{-14} , suggesting that the calculation was carried out at a level of the machine accuracy. This high level of accuracy is surprising because under the condition of $k = 1000$, the dimensionless reactant concentration is decreased from 0.0951 to 8.83×10^{-43} .

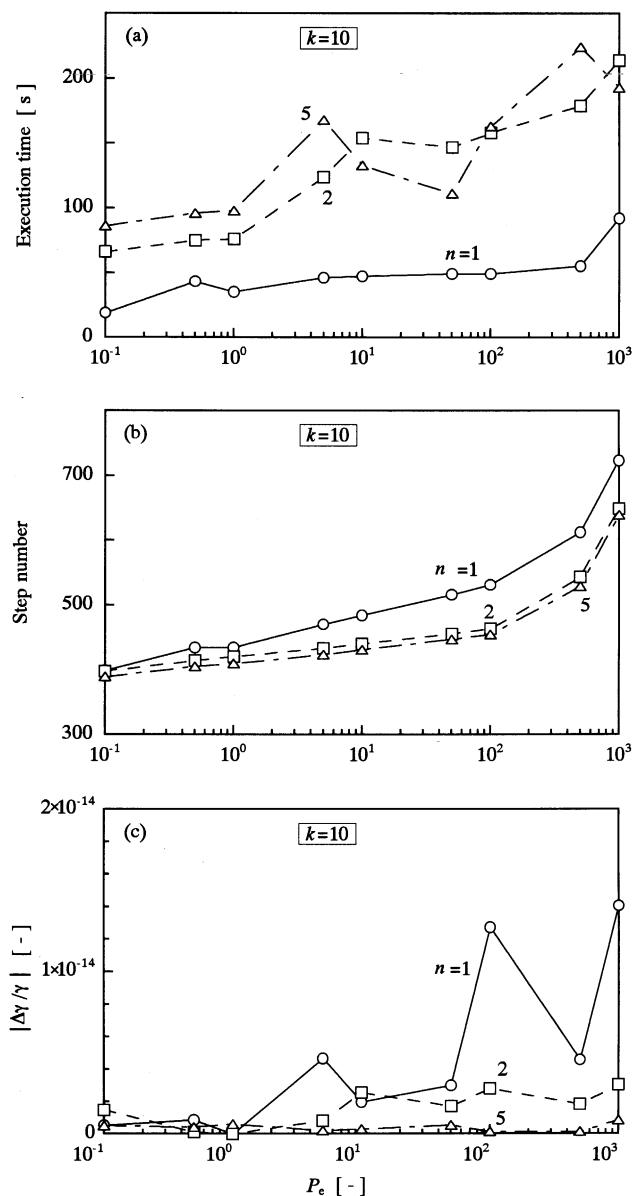


Fig. 4. Effects of Peclet number on the present numerical calculation method.

Fig. 6(a)–(c) shows changes in the execution time, step number, and final value of $|\Delta\gamma/\gamma|$, respectively, over a wide range of k from 0.1 to 1000. For every n , the execution time is increased with the increase of k . When $n=2$, the execution time is increased significantly with the increase of k because estimation of γ by Eq. (31) was always necessary at $n=2$ and 5. When $n=1$, the step number is exponentially increased from 500 at $k=0.1$ to 1302 at $k=1000$. This is because the larger the value of k , the smaller the dimensionless reactant concentration at $Z=0$. The final values of $|\Delta\gamma/\gamma|$ are below 3.20×10^{-14} . It should be emphasized that the present method gives a numerical solution with the superhigh-order accuracy even when the step number exceeds 1000.

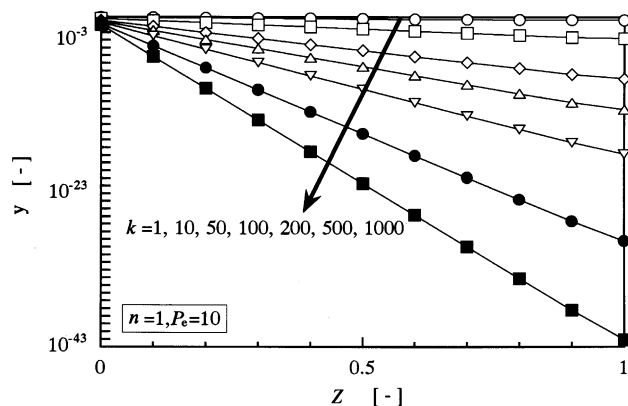


Fig. 5. Comparison between numerical and analytical solutions for dimensionless reactant concentrations calculated at a given position in a tubular flow reactor.

3.5. Effect of reaction order

The dimensionless reactant concentrations calculated at a given position in the reactor are shown in Fig. 7, where n was changed as a parameter from 0.8 to 5 at $k=10$ and $Pe=10$. The numerical solution for $n=1$ is completely identical to the analytical solution, as shown by a broken line in this figure. The execution time was 205 s at $n=0.8$ because of its large step number. For $n \geq 2$, the calculation was completed within 160 s. The step number showed a maximum of 605 at $n=0.8$ and rapidly decreased with the increase of n . Similarly, the final value of $|\Delta\gamma/\gamma|$ showed a maximum of 1.0×10^{-14} at $n=1$ and then decreased rapidly with the increase of n , suggesting that the calculated values have superhigh-order accuracies.

3.6. About oscillation of the calculated values

A schematic relationship between $f(\gamma)$ and γ is given in Fig. 8. The shapes of the curves suggest that if $n=1$, the Newton–Raphson method can use a wide range of γ ($0 < \gamma < 1$) as the initial value, but if $n \neq 1$, it cannot find a solution by itself and must rely on other methods. In the present work, therefore, the root-finding scheme described in Section 2.6 was introduced to obtain an initial value of γ that does not stop the progress of the integration at $Z < 1$, prior to applying the Newton–Raphson method. On the other hand, the number of iteration was varied according to the initial values of y_a and y_b . As evident from Figs. 4(c) and 6(c), this variation gave a remarkable influence on the execution time. At each relationship between $f(\gamma)$ and γ , given for a combination of Pe , k , and n , it seems that there are respective optimum values for y_a and y_b , which makes the number of iterations small. Therefore, if one solves the algebraic equation after determination of the optimum initial values, the calculated values could be continuously ranged. However, this work is so tedious and

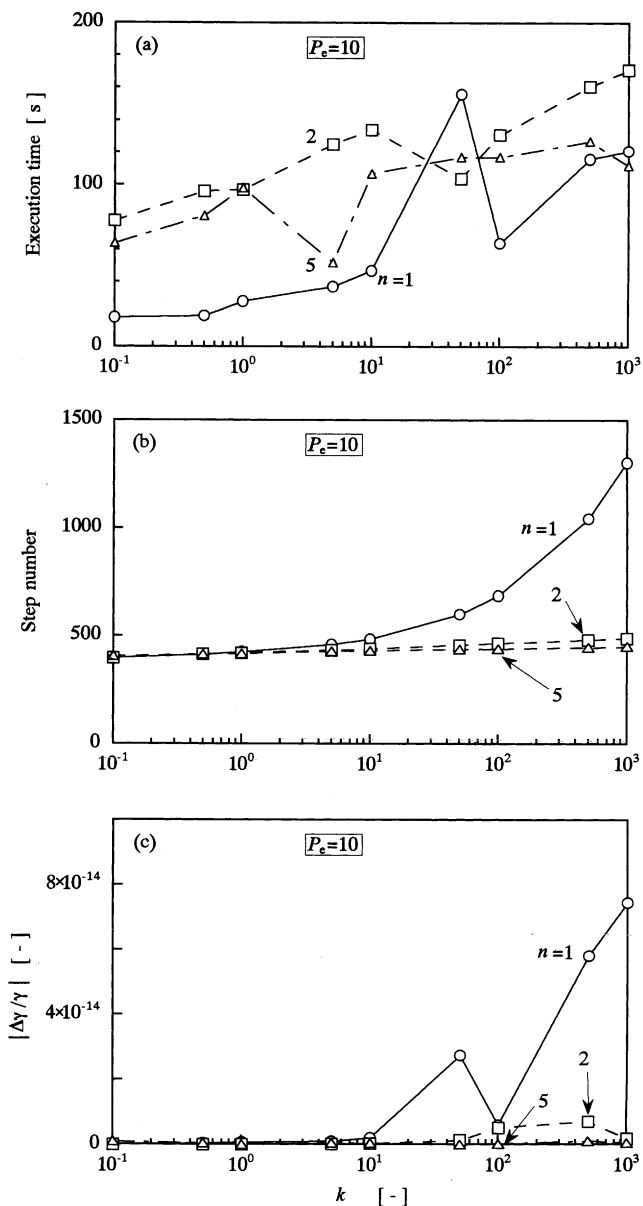


Fig. 6. Effects of dimensionless kinetic constant on the present numerical calculation method.

impractical, so that all the calculations were made by fixing the initial values of y_a and y_b at 0 and 0.8, respectively.

On the other hand, the oscillation of $|\Delta\gamma/\gamma|$, seen in Figs. 4(a) and 6(a), is considered due to the fact that the calculated values were obtained by repeating the calculation one more time after the calculated values were satisfied with the criterion given by Eq. (19) and then plotted directly; therefore, the relative errors of the calculated values are not minimum. In addition, it is considered that the extent of the loss-of-significance errors produced in the process of a large number of arithmetic calculations was different at each relationship between $f(\gamma)$ and γ for a combination of Pe , k , and n . However, since the relative errors of the

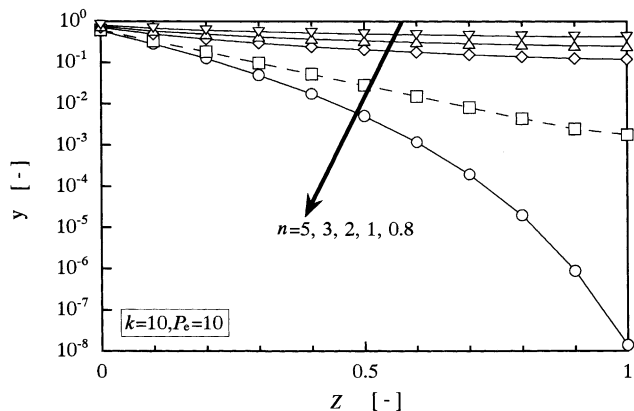


Fig. 7. Comparison between numerical and analytical solutions for dimensionless reactant concentrations calculated at a given position in a tubular flow reactor.

calculated values are estimated to be in the order of or less than 10^{-14} , it would be meaningless to discuss the continuity of the calculated values in the regime close to the computer accuracy. Thus, no further investigation was made.

3.7. Advantages and applications of the present numerical method

As is evident from the calculated results given here, the present numerical method for two-point boundary value problems can give numerical solutions of superhigh-order accuracy over wide ranges of systemic parameters (Pe , k , and n). Moreover, the present method makes it possible to rapidly solve different types of two-point boundary value problems. For example, one can easily apply the present method to the immobilized-enzyme reaction model and obtain numerical solutions with the superhigh-order accuracy [16,19]. In this case, the user needs only to recast the fundamental differential equations into the S-system canonical form, inputting the S-system parameters included in the recast first-order differential equation and the data for $f(\gamma)$, $f^*(\gamma)$, and initial conditions.

Several applications of the present numerical method are considerable. First, this method is useful for engineering

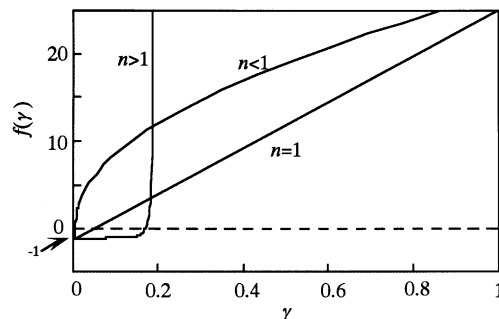


Fig. 8. A schematic relationship between $f(\gamma)$ and γ .

calculations. In the engineering field, it may be sufficient if calculated values are accurate to three significant digits. However, the conventional methods do not always guarantee this level of accuracy over wide ranges of systemic parameters. Furthermore, even when the numerical method gives a solution that is accurate to three significant digits, this level of accuracy is insufficient if the system is constituted by several different types of differential equations. For example, in the design of a packed-bed immobilized enzyme reactor, one must solve the two-point boundary value problem repeatedly at selected points in the reactor [25–27]. This certainly increases calculation errors.

Second, the present method can be used as a standard to evaluate the performance of other numerical methods, as was used to examine the accuracy of the orthogonal collocation method in the previous paper [15].

Third, the present method can be used to make a standard diagram or table which is never forgiven to include any calculation error [28].

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