

NON LINEAR BOUNDARY VALUE PROBLEM
IN IRREVERSIBLE SECOND-ORDER HOMOGENEOUS REACTION

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ABSTRACT

Theoretical analysis corresponding to irreversible homogeneous reaction on finite-layer diffusion impedance is reported in this manuscript. It is also relevant for solid electrolytes and membranes. The non-linear coupled system of diffusion equations were analytically solved by using Homotopy perturbation method. Herin, we report the approximate analytical expressions pertaining to the concentration of solute R, product P and the reactant S for small values of diffusion and kinetic parameters. The numerical solution of this problem is also reported using Matlab/Scilab program. Also we found excellent agreement between the analytical results and numerical results upon comparison.

Keywords: Non-linear reaction-diffusion equations; Impedance; Membrane; Homotopy perturbation method; Analytical solution.

1. INTRODUCTION

In electrode processes the electrochemical impedance spectroscopy plays a vital role. It is a powerful experimental tool for identifying various mechanisms in an electrode process (Chapman, 2010). The diffusional resistance in semi-infinite regime also contributes to the measured impedance. Interfacial phenomena, ionic migration and diffusional effects can modify the impedance. The diffusional impedance may be obtained on the basis of an appropriate transport model for the phase adjacent to the electrode surface (Orazem, 2008; Lasia, 1999; Lasia, 2002; Montella, 1999; Montella, 2000).

The analytical expression for the diffusional impedance can be obtained from Fick's law, which describes mass transport due to a concentration gradient.

The concentration-dependent diffusivities, ionic migration or homogeneous reaction affects the mass-transfer resistance in the phase adjacent to an electrode. An exact analytical expression of concentration cannot be obtained due to non-linear terms in the transport equations. Many authors (Drossbach, 1964; Franceschetti, 1991; Diard, 1999; Franceschetti, 1979) analyzed the diffusion of a reactant to an electrode surface across a stagnant diffusion layer of thickness. Recently Chapman and Antano (Chapman, 2010) analyzed the simple diffusion of this reactant across a stagnant diffusion layer and find the approximate concentration profiles and impedance behavior using computational method (orthogonal collocation and matrix transformation). However, to the best of our knowledge, there is no simple and closed analytical expressions available till date to account for the concentrations for an irreversible homogeneous reaction on finite-layer diffusion impedance for steady-state conditions. The purpose of this paper is to obtain the closed-form solution of diffusional impedance using Homotopy perturbation method for steady state condition.

2. MATHEMATICAL FORMULATION OF THE PROBLEM

The reaction scheme for the case of a catalytic electrochemical-chemical (EC') mechanism with diffusion and irreversible second-order reaction in a stagnant diffusion layer can be represented as follows (Chapman, 2010):



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The electrode reaction of solute R, either oxidation or reduction, produces the soluble product P. In the solution, P reacts irreversibly with electrochemically inactive reactant S, present in the bulk solution, by an irreversible second-order reaction with the reaction-rate constant k_2 to produce product(s) Y and to regenerate R. For convenience we refer to reactant S as the “substrate”, by analogy with enzyme catalysis. The overall process is electrochemically driven conversion of S to Y, catalyzed by R, with some accumulation of P if the homogeneous reaction is not fast enough to consume all of that produced at the electrode. A specific example is oxidation of sulfite (S) to sulfate (Y) catalyzed by ferrous ion (R), which forms reactive ferric ion (P) at an anode. Neglecting ionic migration, the boundary value problem which has to be solved in this case can be written in the dimension form as follows (Macdonald, 1987):

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial z^2} + k_2 C_P C_S \quad (3)$$

$$\frac{\partial C_P}{\partial t} = D_P \frac{\partial^2 C_P}{\partial z^2} - k_2 C_P C_S \quad (4)$$

$$\frac{\partial C_S}{\partial t} = D_S \frac{\partial^2 C_S}{\partial z^2} - k_2 C_P C_S \quad (5)$$

where D_i is the molecular diffusion coefficient of species i . Distance z across the diffusion layer is measured normal to the electrode surface. Now the non-linear differential equations (3) - (5) in dimensionless form are as follows:

$$\frac{\partial R}{\partial t} = \frac{\partial^2 R}{\partial x^2} + kPS \quad (6)$$

$$\frac{\partial P}{\partial t} = \frac{\partial^2 P}{\partial x^2} - kPS \quad (7)$$

$$\frac{\partial S}{\partial t} = \frac{\partial^2 S}{\partial x^2} - kPS \quad (8)$$

where the dimensionless concentrations are given by, $R \equiv [C_R / C_{Sb}]$, $P \equiv C_P / C_{Sb}$ and $S \equiv [C_S / C_{Sb}]$. The dimensionless distance and time are $x = z/\delta$ and $\tau = [tD/\delta]$. For simplicity we have assumed that all three diffusion coefficients are equal with value D , a simplification that is not necessary. With these choices the dimensionless rate constant k is defined as $k \equiv [k_2 C_{Sb} / \delta^2 D]$, and the dimensionless frequency ω is defined as $\omega = [\omega \delta^2 / D]$. Two other parameters of the problem are the concentration ratios $\alpha \equiv [C_{Rb} / C_{Sb}]$ and $\gamma \equiv [C_{R0,SS} / C_{Sb}]$. Now, the six boundary conditions become:

$$R = \gamma + \varepsilon \sin(\omega \tau), \quad \frac{\partial P}{\partial x} = -\frac{\partial R}{\partial x}, \quad \frac{\partial S}{\partial x} = 0 \quad \text{when } x = 0 \quad (9)$$

$$S = 1, R = \alpha \quad \text{and } P = 0 \quad \text{when } x = 1 \quad (10)$$

At steady- state condition, the Eqs. (6)-(8) become:

$$\frac{\partial^2 R}{\partial x^2} + kPS = 0 \quad (11)$$

$$\frac{\partial^2 P}{\partial x^2} - kPS = 0 \quad (12)$$

$$\frac{\partial^2 S}{\partial x^2} - kPS = 0 \quad (13)$$

The dimensionless steady-state boundary conditions are as follows:

$$R = \gamma, \quad P = \alpha - \gamma, \quad \frac{\partial S}{\partial x} = 0 \quad \text{when } x = 0 \quad (14)$$

$$R = \alpha, \quad P = 0 \quad \text{and} \quad S = 1 \quad \text{when } x = 1 \quad (15)$$

3. SOLUTION OF BOUNDARY VALUE PROBLEM USING THE HOMOTOPY PERTURBATION METHOD (HPM)

Recently, many authors have applied the HPM to various problems and demonstrated the efficiency of the HPM for handling non-linear structures and solving various physics and engineering problems (Ghori, 2007 ; Ozis, 2007; Li, 2006; Mousa, 2008). This process is a combination of homotopy in topology and classic perturbation techniques. Ji-Huan He used the HPM to solve the Lighthill equation (He, 1999), the Duffing equation (He, 2003) and the Blasius equation (He, 2003). The idea has been used to solve non-linear boundary value problems (He, 2006), integral equations (Golbabai, 2008; Ghasemi, 2007; Biazar, 2009), Klein-Gordon and Sine-Gordon equations (Odibat, 2007), Emden-Flower type equations (Chowdhury, 2007) and various other problems. This wide variety of applications shows the power of the HPM to solve functional equations.

The HPM is unique in its applicability, accuracy and efficiency. More recently, Meena and Rajendran (Meena, 2010) solved the system of coupled non-linear reaction diffusions equations in an electroactive polymer film deposited on an inlaid microdisc electrode using Homotopy perturbation method. Using this method (see Appendix B), we can obtain the following solution to Eqs. (11), (12) and (13):

$$R(x) = \gamma + (\alpha - \gamma)x + \kappa \left[\frac{2(\alpha - \gamma)x}{3} - \frac{(\alpha - \gamma)x^2}{2} + \frac{(\gamma - \alpha)x^3}{6} \right] \quad (16)$$

$$P(x) = \alpha - \gamma + (\gamma - \alpha)x - \kappa \left[\frac{(\alpha - \gamma)x}{3} - \frac{(\alpha - \gamma)x^2}{2} - \frac{(\gamma - \alpha)x^3}{6} \right] \quad (17)$$

$$S(x) = 1 + \kappa \left[\frac{(\gamma - \alpha)x}{3} + \frac{(\alpha - \gamma)x^2}{2} + \frac{(\gamma - \alpha)x^3}{6} \right] \quad (18)$$

Eqs. (16), (17) and (18) represents the analytical expression of the concentration of solute R , product P and reactant S respectively for small values of reaction and kinetic parameters. Also the above analytical expression of concentration of solute R , product P and reactant S satisfies the boundary conditions (Eqs. (14) - (15)).

4. NUMERICAL SIMULATION

The non-linear differential equations Eq. (11) to Eq. (13) are also solved using numerical methods. The function `pdex4` in matlab software which is a function of solving two-point boundary value problems (BVPs) is used to solve those equations. Its numerical solution is compared with the solution obtained by using Homotopy perturbation method and it gives a satisfactory result. The Matlab/Scilab program is also given in Appendix C.

5. DISCUSSION

Eqs. (16)-(18) are the new simple analytical expressions of the concentrations of the solute R , the product P and the reactant S respectively. The concentration profiles and impedance behavior depends upon diffusion and kinetic reaction-rate constant k, α and γ . In Fig. 1 the profiles of the solute, product as well as the reactant concentrations are presented. From these figures it is inferred that the value of normalized concentration of reactant $S \approx 1$ for all small values of rate constant. Also at $x = 0$, $R + P = \alpha$ and $x = 1$, $R + P + S = \alpha + 1$. The normalized concentration of the solute R is represented in Fig. 2(a)-2(c). From these figures it is evident that the value of the solute

concentration R increases for all small possible values of the parameters α , γ and κ . Fig. 3(a)-3(c) stand for the normalized concentration profile of the product P . It is clear that the value of the product concentration P decreases when the parameters κ and γ increases. It seems decreasing when the parameter α increases. Fig. 4(a)-4(c) represents the normalized concentration profiles of the reactant S . From these figures it is obvious that for the increases in the values of the parameters κ and α the concentration decreases. When γ increases we observe that the concentration of S increases.

6. CONCLUSIONS

This paper reports a mathematical treatment for analyzing simple diffusion of the reactant across a stagnant diffusion layer. In this paper, we have evaluated a theoretical model for a homogeneous reaction in the diffusion layer coupled with the electrode process. The approximate expressions for the concentrations of the solute, product and reactant in steady-state condition were obtained using Homotopy perturbation method. This method is an extremely simple method and it is also a promising method to solve other non-linear equations. Furthermore, the analytical results were compared with the numerical results and found to be in good agreement. The method described here may be applied to analysis of membrane-transport experiments as well as other cases of ionic transport in semiconductors and solid electrolytes.

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APPENDIX A

Basic Concepts of the HPM

The HPM method has overcome the limitations of traditional perturbation methods. It can take full advantage of the traditional perturbation techniques, so a considerable deal of research has been conducted to apply the homotopy technique to solve various strong non-linear equations. To explain this method, let us consider the following function:

$$D_o(u) - f(r) = 0, \quad r \in \Omega \quad (\text{A.1})$$

with the boundary conditions of

$$B_o(u, \frac{\partial u}{\partial n}) = 0, \quad r \in \Gamma \quad (\text{A.2})$$

where D_o is a general differential operator, B_o is a boundary operator, $f(r)$ is a known analytical function and Γ is the boundary of the domain Ω . In general, the operator D_o can be divided into a linear part L and a nonlinear part N . Eq. (A.1) can therefore be written as

$$L(u) + N(u) - f(r) = 0 \quad (\text{A.3})$$

By the homotopy technique, we construct a homotopy $v(r, p) : \Omega \times [0,1] \rightarrow \Re$ that satisfies

$$H(v, p) = (1 - p)[L(v) - L(u_0)] + p[D_o(v) - f(r)] = 0. \quad (\text{A.4})$$

$$H(v, p) = L(v) - L(u_0) + pL(u_0) + p[N(v) - f(r)] = 0. \quad (\text{A.5})$$

where $p \in [0, 1]$ is an embedding parameter, and u_0 is an initial approximation of Eq. (A.1) that satisfies the boundary conditions. From Eq. (A.4) and Eq. (A.5), we have

$$H(v,0) = L(v) - L(u_0) = 0 \quad (\text{A.6})$$

$$H(v,1) = D_o(v) - f(r) = 0. \quad (\text{A.7})$$

When $p=0$, Eq. (A.4) and Eq. (A.5) become linear equations. When $p=1$, they become non-linear equations. The process of changing p from zero to unity is that of $L(v) - L(u_0) = 0$ to $D_o(v) - f(r) = 0$. We first use the embedding parameter p as a "small parameter" and assume that the solutions of Eq. (A.4) and Eq. (A.5) can be written as a power series in p as follows:

$$v = v_0 + pv_1 + p^2v_2 + \dots \quad (\text{A.8})$$

Setting $p = 1$ results in the approximate solution of Eq. (A.1):

$$v = \lim_{p \rightarrow 1} v = v_0 + v_1 + v_2 + \dots \quad (\text{A.9})$$

This is the basic idea of the HPM.

APPENDIX B

Approximate analytical solutions of the mediator substrate

Using the HPM, we construct a homotopy for Eq. (11) and Eq. (12) as follows:

$$(1 - p) \left(\frac{\partial^2 R}{\partial \chi^2} \right) + p \left(\frac{\partial^2 R}{\partial \chi^2} + \kappa PS \right) = 0 \quad (\text{B.1})$$

$$(1-p)\left(\frac{\partial^2 P}{\partial \chi^2}\right) + p\left(\frac{\partial^2 P}{\partial \chi^2} - \kappa PS\right) = 0 \quad (\text{B.2})$$

and

$$(1-p)\left(\frac{\partial^2 S}{\partial \chi^2}\right) + p\left(\frac{\partial^2 S}{\partial \chi^2} - \kappa PS\right) = 0 \quad (\text{B.3})$$

The approximate solution of (B.1) is

$$R = R_0 + pR_1 + p^2R_2 + \dots \quad (\text{B.4})$$

the approximate solution of (B.2) is

$$P = P_0 + pP_1 + p^2P_2 + \dots \quad (\text{B.6})$$

and the approximate solution of (B.3) is

$$S = S_0 + pS_1 + p^2S_2 + \dots \quad (\text{B.7})$$

Substituting Eq. (B.4) into Eq. (B.1) and arranging the coefficients of p powers, we have

$$p^0 : \frac{\partial^2 R_0}{\partial \chi^2} = 0 \quad (\text{B.8})$$

$$p^1 : \frac{\partial^2 R_1}{\partial \chi^2} + kPS = 0 \quad (\text{B.9})$$

Substituting Eq. (B.6) into Eq. (B.2) and arranging the coefficients of p powers, we have

$$p^0 : \frac{\partial^2 P_0}{\partial \chi^2} = 0 \quad (\text{B.10})$$

$$p^1 : \frac{\partial^2 P_1}{\partial \chi^2} - kPS = 0 \quad (\text{B.11})$$

Substituting Eq. (B.7) into Eq. (B.3) and arranging the coefficients of p powers, we have

$$p^0 : \frac{\partial^2 S_0}{\partial \chi^2} = 0 \quad (\text{B.12})$$

$$p^1 : \frac{\partial^2 S_1}{\partial \chi^2} - kPS = 0 \quad (\text{B.13})$$

The initial approximations are as follows:

$$R_0(0) = \gamma, R = \alpha \text{ at } \chi = 1 \quad (\text{B.14})$$

$$P_0(0) = \alpha - \gamma, P = 0 \text{ at } \chi = 1 \quad (\text{B.15})$$

$$S_0(0) = 1, \frac{\partial S}{\partial \chi} = 0 \quad (\text{B.16})$$

Solving the Eq. (B.8) and (B.12) using the boundary condition (B.14)-(B.16) we can obtain R_0 , P_0 and S_0 as follows:

$$R_0 = (\alpha - \gamma)x + \gamma \quad (\text{B.17})$$

$$P_0 = (\gamma - \alpha)x + \alpha - \gamma \quad (\text{B.18})$$

$$S_0 = 1 \quad (\text{B.19})$$

Substituting Eq. (B.18) and Eq. (B.19) into Eq. (B.9) and then solving we obtain the solution to Eq. (B.9):

$$R_1 = -\kappa \left[\frac{(\alpha - \gamma)x}{3} - \frac{(\alpha - \gamma)x^2}{2} - \frac{(\gamma - \alpha)x^3}{6} \right] \quad (\text{B.20})$$

Substituting Eq. (B.18) and Eq. (B.19) into Eq. (B.11) and then solving we obtain the solution to Eq. (B.11):

$$P_1 = \kappa \left[\frac{(\gamma - \alpha)x^3}{6} + \frac{(\alpha - \gamma)x^2}{2} - \frac{(\alpha - \gamma)x}{3} \right] \quad (\text{B.21})$$

Substituting Eq. (B.18) and Eq. (B.19) into Eq. (B.12) and then solving we obtain the solution to Eq. (B.12):

$$S_1 = \kappa \left[\frac{(\gamma - \alpha)x}{3} + \frac{(\alpha - \gamma)x^2}{2} + \frac{(\gamma - \alpha)x^3}{6} \right] \quad (\text{B.22})$$

Adding Eq. (B.17) and Eq. (B.20), we get Eq. (16) (the concentration of the solute, R) in the text. Similarly, by adding Eq. (B.18) and Eq. (B.21) we get Eq. (17) (the concentration of the product, P) in the text. Also adding Eq. (B.19) and Eq. (B.22), we get Eq. (18) (the concentration of the reactant, S) in the text.

APPENDIX C:

Numerical solutions of equations (11) – (13) using Scilab/Matlab program.
function pdex4

```

m = 0;
x = linspace(0,1);
t = linspace(0,1000);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1 = sol(:,:,1);
u2 = sol(:,:,2);
u3 = sol(:,:,3);
figure
plot(x,u1(end,:))
title('u1(x,t)')
figure
plot(x,u2(end,:))
title('u2(x,t)')
figure
plot(x,u3(end,:))
title('u3(x,t)')
% -----
function [c,f,s] = pdex4pde(x,t,u,DuDx)
K=0.5; %These parameter values are used in Fig.2
c = [1;1;1];
f = [1;1;1].* DuDx;
F1= K *u(2)*u(3);
F2=- K *u(2)*u(3);
F3=- K *u(2)*u(3);

```

```

s = [F1;F2;F3];
% -----
function u0 = pdex4ic(x)
u0 = [0; 0; 1];
% -----
function [pl,q1,pr,qr] = pdex4bc(xl,ul,xr,ur,t)
pl = [ul(1)-0.5;ul(2)-0.3;0];
q1 = [0;0;1];
pr = [ur(1)-0.8;ur(2);ur(3)-1];
qr = [0; 0; 0];
    
```

FIGURE CAPTIONS

Figure: 1(a)-(c): Steady-state dimensionless concentrations of R , P and S versus the normalized distance χ calculated for various values of the parameters. The curves are plotted using Eqs. (16) to (18).

Figure: 2(a)-(c): Profile of the normalized steady state concentration of R versus the normalized distance χ for various values of the parameters α , γ and κ . The concentrations were computed using Eq. (16).

Figure: 3(a)-(c): Profile of the normalized steady state concentration of P versus the normalized distance χ for various values of the parameters α , γ and κ . The concentrations were computed using Eq. (17).

Figure: 4(a)-(c): Profile of the normalized steady state concentration of S versus the normalized distance χ for various values of the parameters α , γ and κ . The concentrations were computed using Eq. (18).

Fig.1

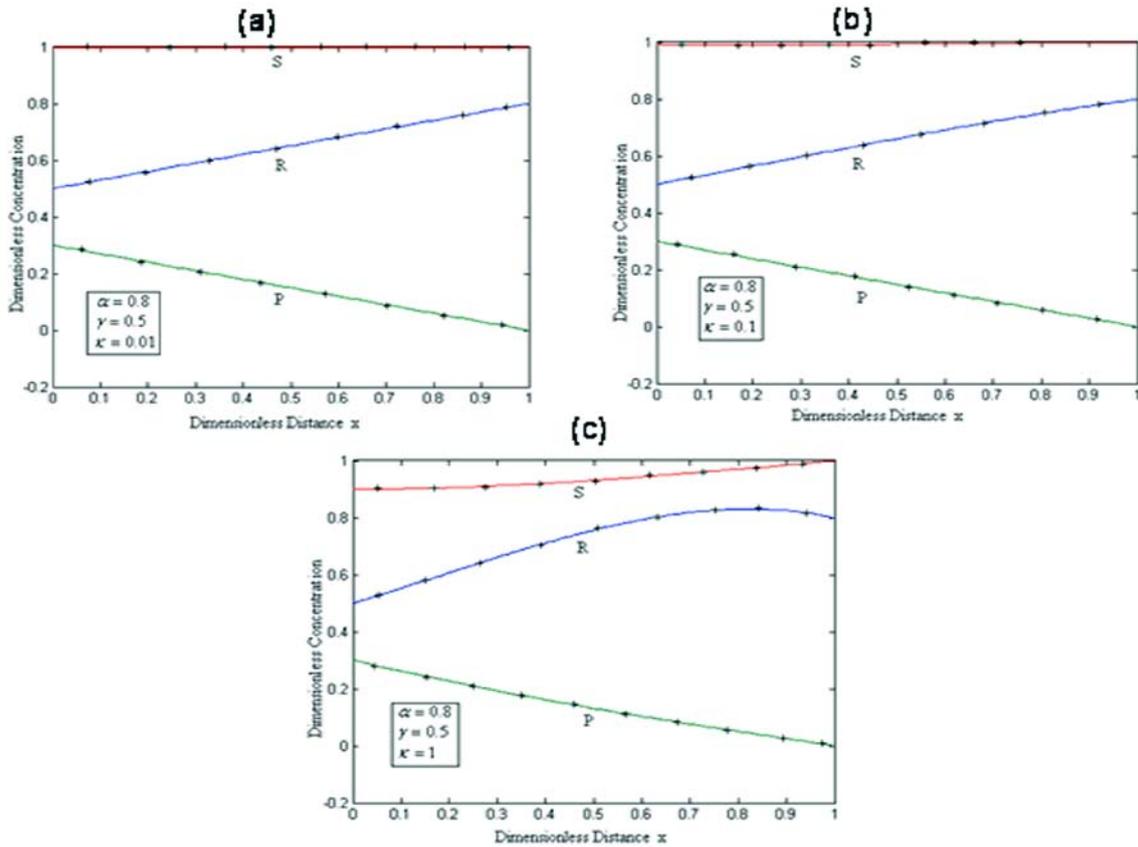


Figure: 1(a)-(c): Steady-state dimensionless concentrations of R , P and S versus the normalized distance χ calculated for various values of the parameters. The curves are plotted using Eqs. (16) to (18).

Fig. 2

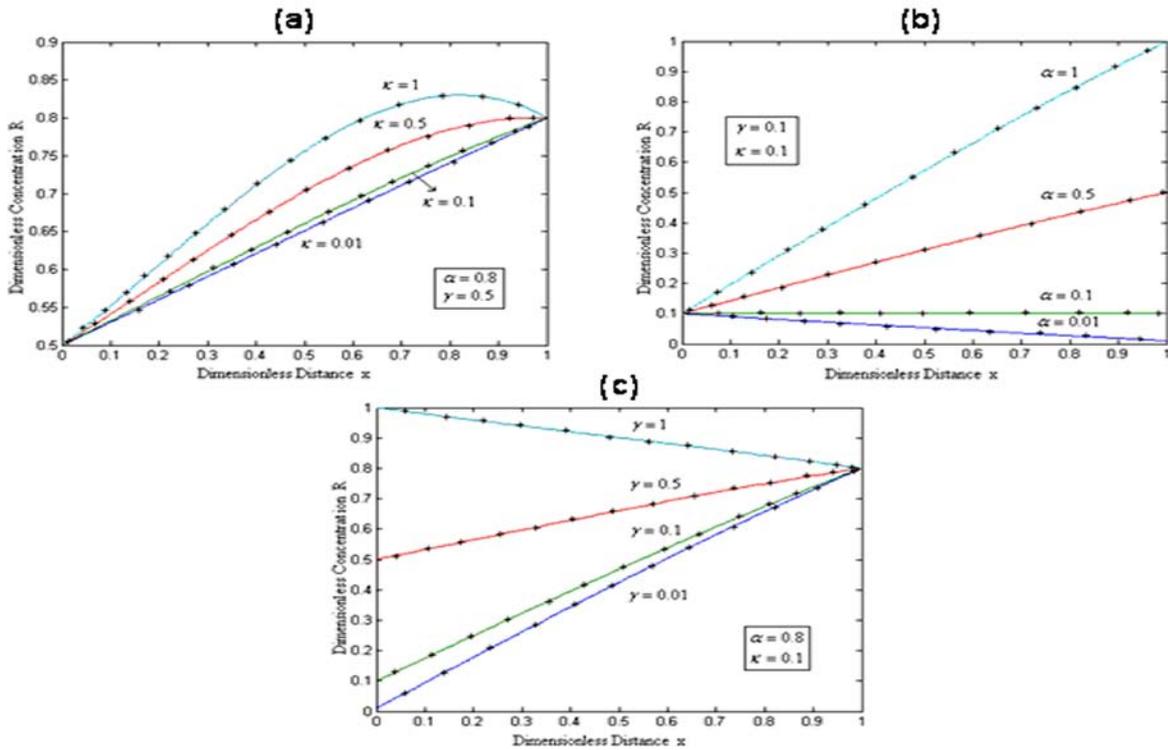


Figure: 2(a)-(c): Profile of the normalized steady state concentration of R versus the normalized distance χ for various values of the parameters α , γ and κ . The concentrations were computed using Eq. (16).

Fig. 3

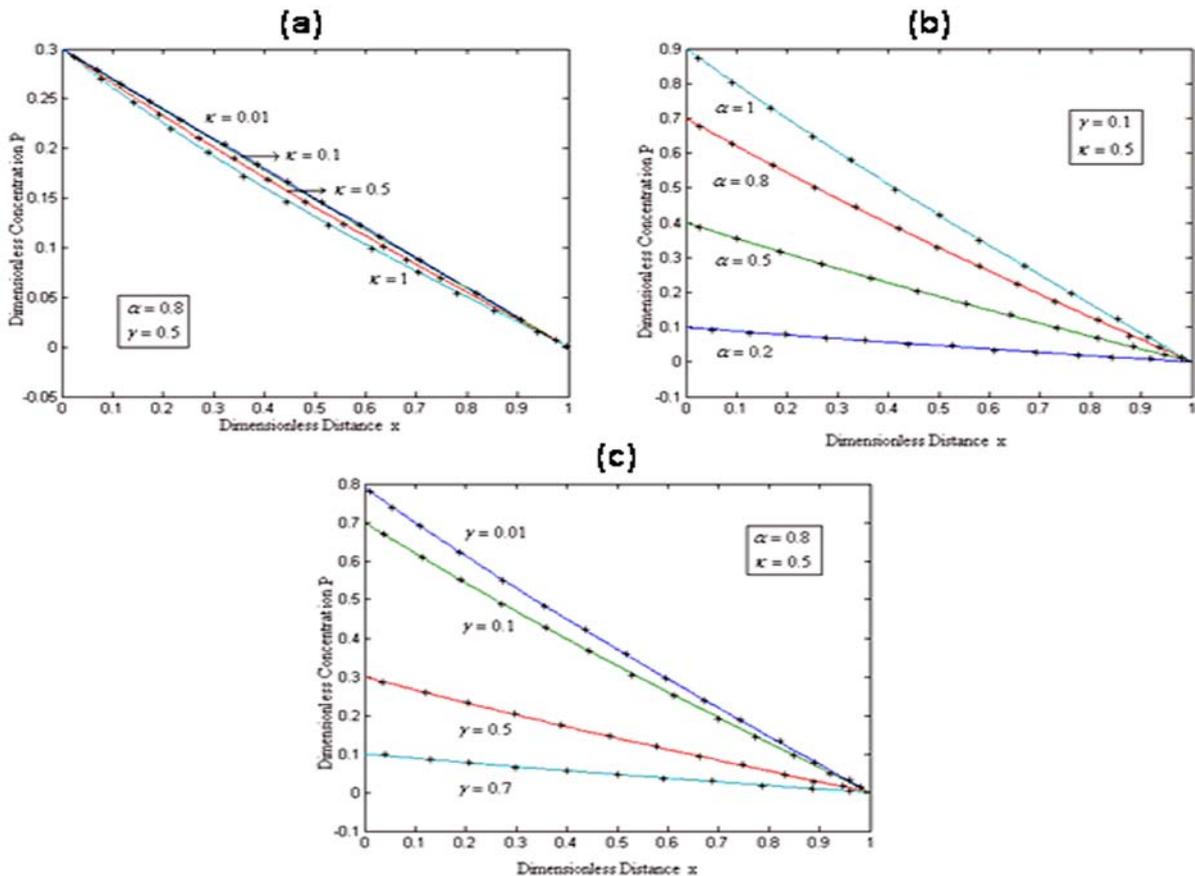


Figure: 3(a)-(c): Profile of the normalized steady state concentration of P versus the normalized distance χ for various values of the parameters α , γ and κ . The concentrations were computed using Eq. (17).

Fig. 4

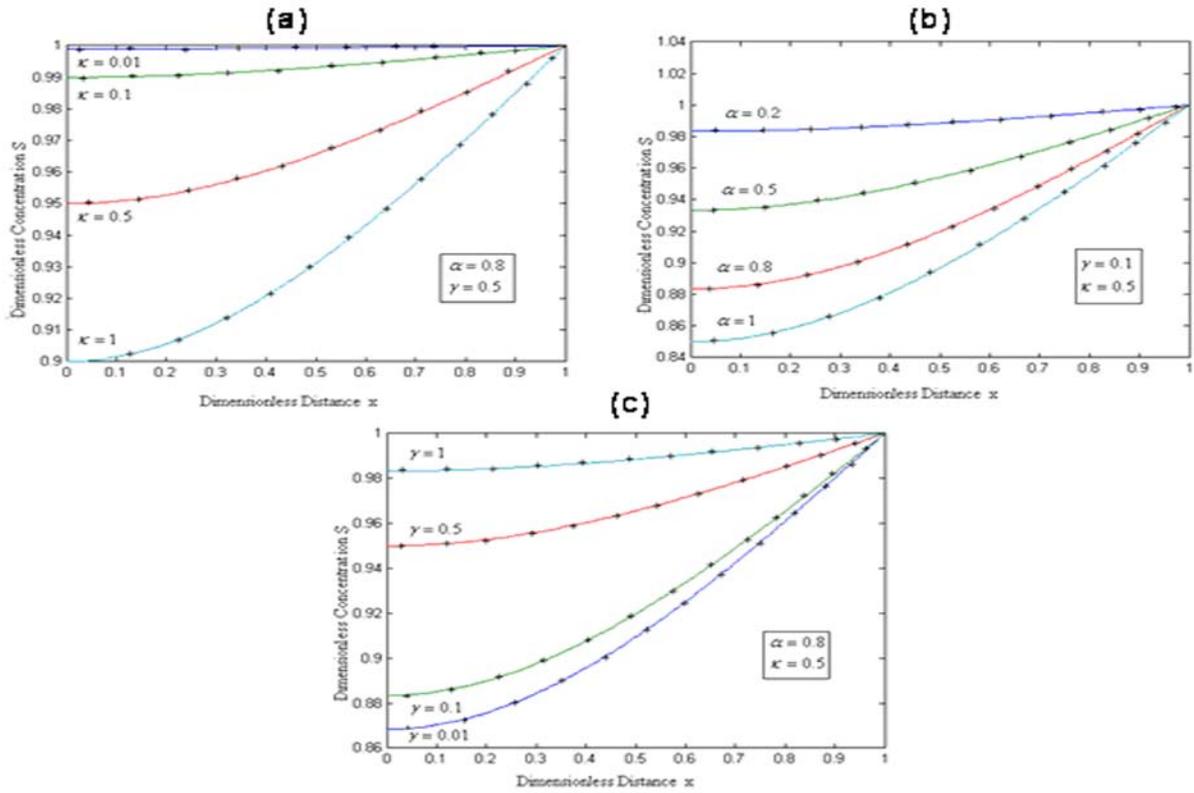


Figure: 4(a)-(c): Profile of the normalized steady state concentration of S versus the normalized distance χ for various values of the parameters α , γ and κ . The concentrations were computed using Eq. (18).

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