Mathematical Modeling of a Carrier-Mediated Transport Process in a Liquid Membrane

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Abstract An analysis of the reaction diffusion in a carrier-mediated transport process through a membrane is presented. A simple approximate analytical expression of concentration profiles is derived in terms of all dimensionless parameters. Furthermore, in this work we employ the homotopy perturbation method to solve the nonlinear reaction–diffusion equations. Moreover, the analytical results have been compared to the numerical simulation using the Matlab program. The simulated results are comparable with the appropriate theories. The results obtained in this work are valid for the entire solution domain.

Keywords Carrier-mediated transport · Homotopy perturbation method · Liquid membrane · Nonlinear reaction diffusion equation

Introduction

In recent years, membrane-based processes have attracted considerable attention as a valuable technology for many industries. The liquid membrane process is a technology that combines solvent extraction and stripping in a single step. The transport mechanism in a liquid membrane is usually based on facilitated diffusion (Bartsch and Douglas 1996). Facilitated transport through liquid membranes has been investigated for more than 30 years as a potential separation technology (Baker and Blume 1990). Membrane separation is an important process in biological systems. Many synthetic membranes have been developed for industrial applications. Important conventional membrane technologies are microfiltration, ultrafiltration, reverse osmosis and gas separation (Lonsdale 1982). Carrier-mediated transport is described by subsequent partitioning, complexation and diffusion. Carrier-mediated transport has become an important area of study for engineers due to its applications in various biological and nonbiological systems (Schultz et al. 1974; Schultz 1977; Smith et al. 1977; Matson et al. 1977; Goddard 1977).

Four different types of liquid membranes can be distinguished: bulk, supported, emulsion and polymer inclusion membranes. Bulk liquid membranes (BLMs) consist of a source phase and a receiving phase separated by an immiscible membrane phase (Diederich and Dick 1984). Supported liquid membranes (SLMs) have the same configuration as BLMs. The carrier-mediated cotransport of alkali cations through an SLM is determined by diffusion of the carrier cation through the membrane (Izatt et al. 1989; Fyles et al. 1991). A further reduction in membrane thickness can be accomplished in emulsion liquid membranes (ELMs). These have a thinner membrane separating the source and receiving phases, although membrane thickness changes with the amount of material transported (Thien and Hatton 1988; Draxler and Mar 1986). A major drawback associated with SLMs is their poor stability. This factor has severely rendered liquid membranes mostly

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impractical for many large-scale applications (Sastre et al. 1998; de Gyves and de San Miguel 1999). Polymer inclusion membranes (PIMs) retain most of the advantages of SLMs while exhibiting excellent stability and versatility. In several cases, PIMs with higher fluxes than those of SLMs have been reported (Schow et al. 1996; Kim et al. 2000, 2001).

Barbero et al. (1995) reported limited cases of fast reaction and fast diffusion. Also, Barbero et al. (1995) obtained the solution of reaction–diffusion equations of facilitated diffusion using the boundary element method. However, to the best of our knowledge, there was no rigorous analytical expression corresponding to the concentration profiles for all values of parameters reported. The purpose of this communication is to arrive at an analytical expression for concentration species at a carrier-mediated transport process using the homotopy perturbation method (HPM).

Mathematical Formulation of the Problem and Analysis

The details of the model adopted have been fully described in Barbero et al. (1995). Figure 1 represents a general kinetic scheme of the carrier-mediated transport (facilitated diffusion) through a liquid membrane. Facilitated or carrier-mediated transport is a coupled transport process that combines a (chemical) coupling reaction with a diffusion process. The solute has first to react with the carrier to form a solute–carrier complex, which then diffuses through the membrane to finally release the solute at the permeate side. In carrier-mediated transport a solute, S, reacts homogeneously with a ligand, L, producing a complex, LS. A general scheme that represents the reaction occurring in carrier-mediated transport through a membrane is shown below:

$$L + S \xrightarrow[k_{-1}]{k_1} LS \tag{1}$$

Here, k_1 is the forward rate constant and k_{-1} is the reverse rate constant of the solute–carrier reaction. This reaction scheme is mathematically described by the following set of nonlinear reaction–diffusion equations (Barbero et al. 1995):

$$D_S \frac{d^2 c_S}{dx^2} = k_1 c_S c_L - k_{-1} c_{LS} \tag{2}$$

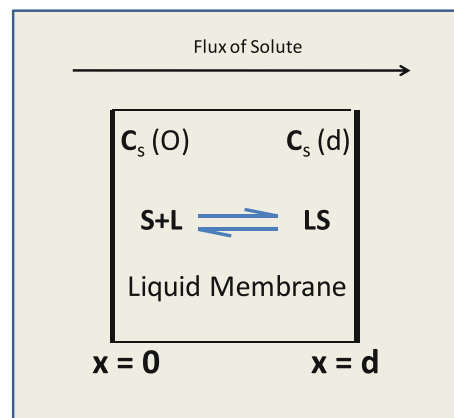$$D_L \frac{d^2 c_L}{dx^2} = k_1 c_S c_L - k_{-1} c_{LS} \tag{3}$$

$$D_{LS} \frac{d^2 c_{LS}}{dx^2} = -(k_1 c_S c_L - k_{-1} c_{LS}) \tag{4}$$

The boundary conditions are as follows:

$$c_S = c_S(0), \quad c_L = 0, \, c_{LS} = c_T \quad \text{at } x = 0 \tag{5}$$

$$c_S = 0, \quad c_L = c_T, \, c_{LS} = 0 \quad \text{at } x = d \tag{6}$$

Fig. 1 Schematic representation of carrier-mediated transport (facilitated diffusion) through a liquid membrane

where D_j and c_j denote the diffusion coefficient and concentration of species j ($j = S$, L and LS), respectively; c_T is the total carrier concentration; $c_S(0)$ is the interfacial concentration of solute; and d is the membrane thickness. Here, we can assume that $D_S = D_L = D_{LS} = D$. We have chosen that $c_S(0) = c_T = a$. Equations 2–4 are transformed to a dimensionless state by introducing the following parameters:

$$C_S^* = \frac{c_S}{a}, \, C_L^* = \frac{c_L}{a}, \, C_{LS}^* = \frac{c_{LS}}{a}, \, X = \frac{x}{d}, \, M = \frac{k_1 d^2 a}{D}, \, N = \frac{k_{-1} d^2}{D} \tag{7}$$

The nonlinear reaction–diffusion Eqs. 2–4 in dimensionless form are

$$\frac{d^2 C_S^*}{dX^2} = M C_S^* C_L^* - N C_{LS}^* \tag{8}$$

$$\frac{d^2 C_L^*}{dX^2} = M C_S^* C_L^* - N C_{LS}^* \tag{9}$$

$$\frac{d^2 C_{LS}^*}{dX^2} = -M C_S^* C_L^* + N C_{LS}^* \tag{10}$$

where C_S^*, C_L^* and C_{LS}^* represent the dimensionless concentration species and M and N are the dimensionless diffusion reaction parameters. The boundary conditions in dimensionless form are

$$C_S^* = 1, \quad C_L^* = 0, \quad C_{LS}^* = 1 \quad \text{when } X = 0 \tag{11}$$

$$C_S^* = 0, \quad C_L^* = 1, \quad C_{LS}^* = 0 \quad \text{when } X = 1 \tag{12}$$

Solution of Nonlinear Reaction–Diffusion Equations Using the Homotopy Perturbation Method

Many authors have applied the HPM to solve the nonlinear problem in physics and engineering sciences (Ghori et al.
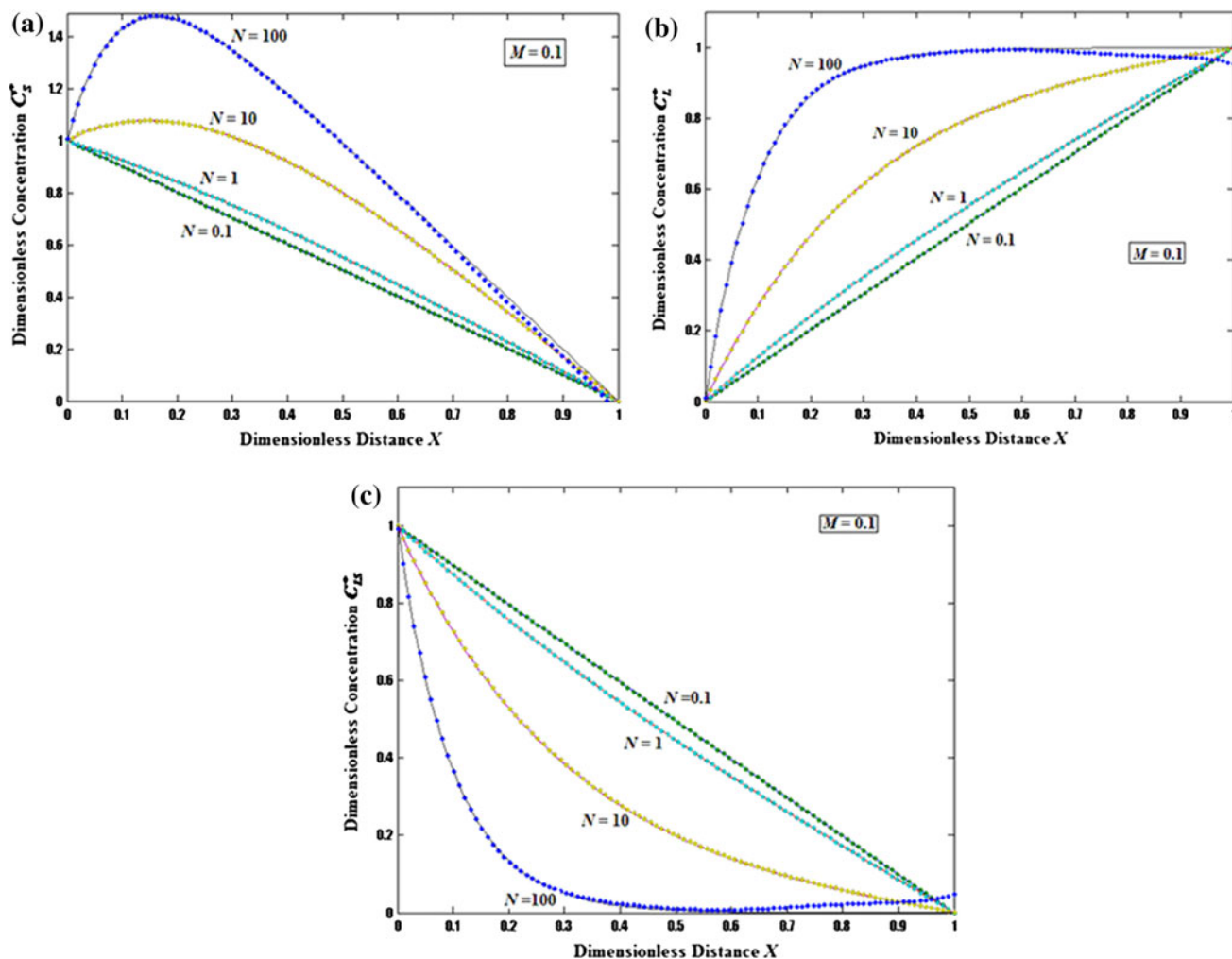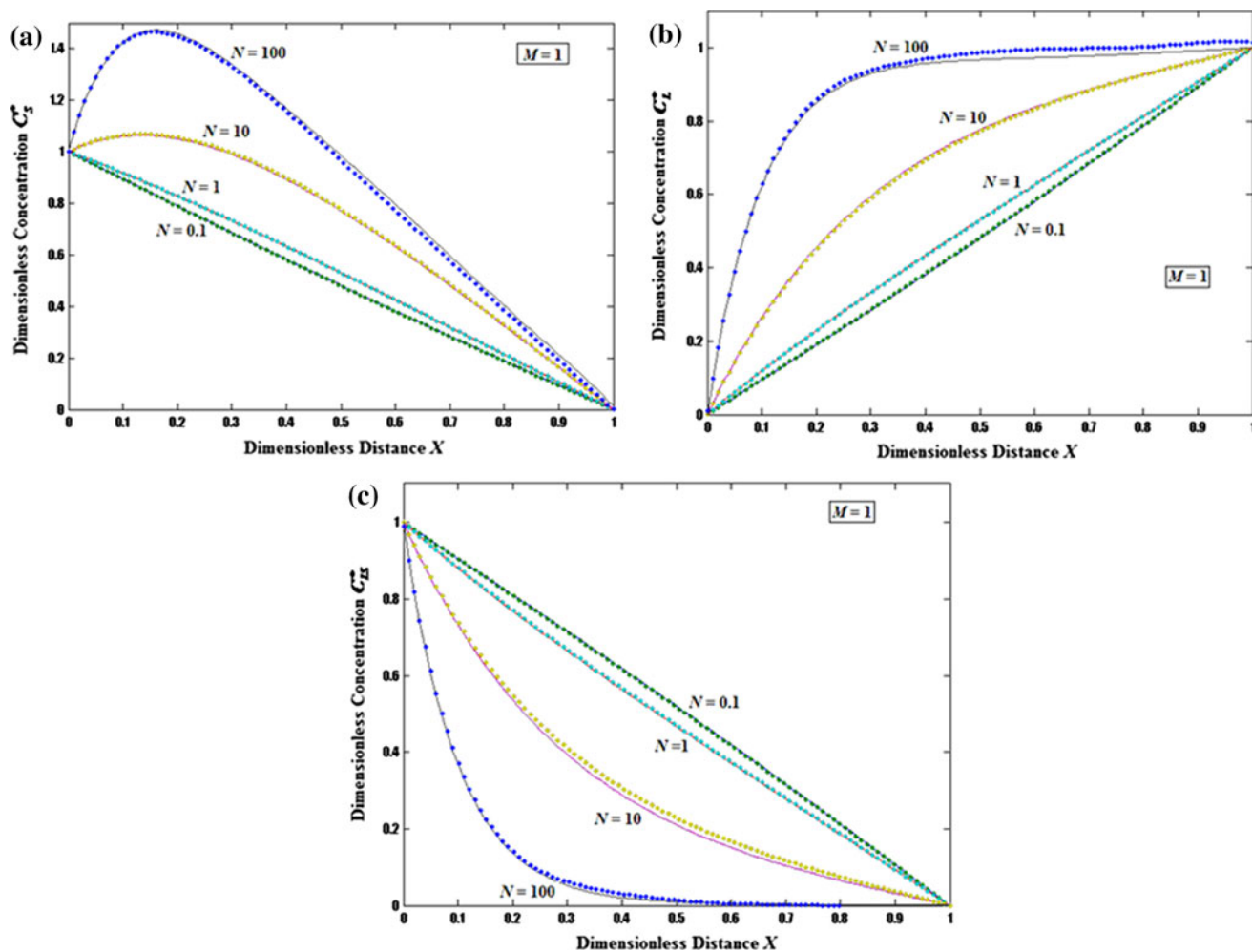
Fig. 2 Dimensionless concentration profiles C_j^* plotted from Eqs. 13–15 for all values of dimensionless parameter N when $M = 0.1$. *Solid lines* represent the analytical solution obtained in this work; *dotted lines* represent the numerical solution

2007; Ozis and Yildirim 2007; Li and Liu 2006; Mousa and Ragab 2008). Recently, this method has also been used to solve some of the nonlinear problem in physical sciences (Loghambal and Rajendran 2010; Meena and Rajendran 2010; Thiagarajan et al. 2011; Anitha et al. 2011). This method is a combination of homotopy in topology and classic perturbation techniques. He (1999, 2003a, 2003b) used the HPM to solve the Lighthill equation, the Duffing equation and the Blasius equation. The HPM is unique in its application, accuracy and efficiency. The HPM uses the imbedding parameter p as a small parameter, and only a few iterations are needed to search for an asymptotic solution. This method is especially suitable in solving this type of problem as it arises in carrier-mediated transport. Using this method (see Appendix 1), we can obtain the concentrations of species as follows:

$$C_S^*(X, M, N) = 2 - \left(2 + \frac{M}{12}\right)X - \frac{\sinh\sqrt{N}(1 - X)}{\sinh\sqrt{N}} + \frac{M}{6}X^3 - \frac{M}{12}X^4 \qquad (13)$$

$$C_L^*(X, M, N) = 1 - \frac{M}{12}X - \frac{\sinh\sqrt{N}(1 - X)}{\sinh\sqrt{N}} + \frac{M}{6}X^3 - \frac{M}{12}X^4 \qquad (14)$$

$$C_{LS}^*(X, M, N) = -\frac{2M}{N^2} + \frac{M}{N}X + \frac{2M\sinh\sqrt{N}X}{N^2\sinh\sqrt{N}} + \left(1 + \frac{2M}{N^2}\right)\frac{\sinh\sqrt{N}(1 - X)}{\sinh\sqrt{N}} - \frac{M}{N}X^2 \qquad (15)$$

Fig. 3 Dimensionless concentration profiles C_j^* plotted from Eqs. 13–15 for all values of dimensionless parameter N when $M = 1$. *Solid lines* represent the analytical solution obtained in this work; *dotted lines* represent the numerical solution

Equations 13–15 represent the new analytical expression of concentrations of species in carrier-mediated transport.

Numerical Simulation

The function pdex4 in the Matlab software (MathWorks, Natick, MA), which is a function of solving the initial-boundary value problems for parabolic–elliptic partial differential equations, is used to solve Eqs. 8–10 for the boundary conditions 11 and 12. Figures 2, 3, 4, and 5 illustrate the comparison of analytical results obtained in this work with the numerical results. Upon comparison, it is evident that both results give satisfactory agreement for all values of parameters. The Matlab program is also given in Appendix 2.

Discussion

The kinetic response of a liquid membrane depends on the concentration species. The concentration depends on the following two factors: M and N. The diffusion parameter M represents the ratio of the characteristic time of the enzymatic reaction to that of concentration diffusion. This parameter can be varied by changing the thickness of the membrane. This parameter describes the relative importance of diffusion and reaction in a liquid membrane. When M is small, the kinetics are dominant resistance; the uptake of concentration species is kinetically controlled. Under these conditions, the concentration species across the membrane is essentially uniform. When the diffusion parameter M is large, diffusion limitations are the principal determining factor.
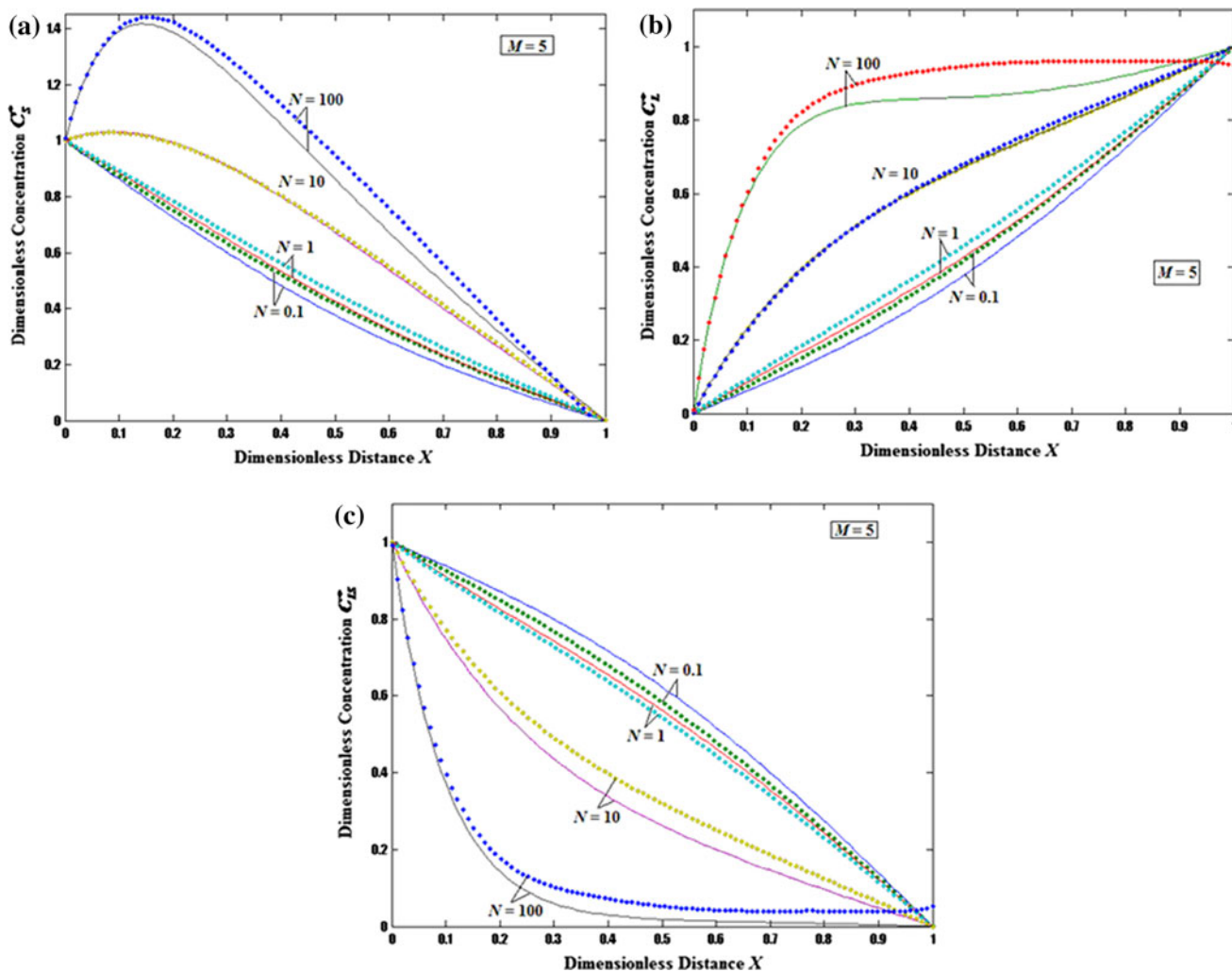
Fig. 4 Dimensionless concentration profiles C_j^* plotted from Eqs. 13–15 for all values of dimensionless parameter N when $M = 5$. *Solid lines* represent the analytical solution obtained in this work; *dotted lines* represent the numerical solution

Figures 2, 3, and 4 represent a series of dimensionless concentration species for various values of the dimensionless parameters N and M. From these figures, the concentration species of C_S^* and C_{LS}^* reach the maximum value 1 at $X = 0$ and the minimum value 0 at $X = 1$. The concentration C_L^* reaches the maximum value 1 at $X = 1$ and the minimum value 0 at $X = 0$. Moreover, all concentration species are linear when $N = 0.1$. It is evident that the dimensionless concentration C_S^* slowly increases when N increases. Furthermore, we noticed that there is a simultaneous increase in the values of concentration C_L^* as N increases and a simultaneous decrease in the values of concentration C_{LS}^* as N decreases. In addition, our analytical results were compared with the simulation results. The dimensionless concentration species C_j^* is shown in Fig. 5 for $M = 0.05$ and $N = 50$. From this figure, it is evident that the concentration C_S^* increases initially, attains its maximum value at $X = 0.1$ and then decreases. We
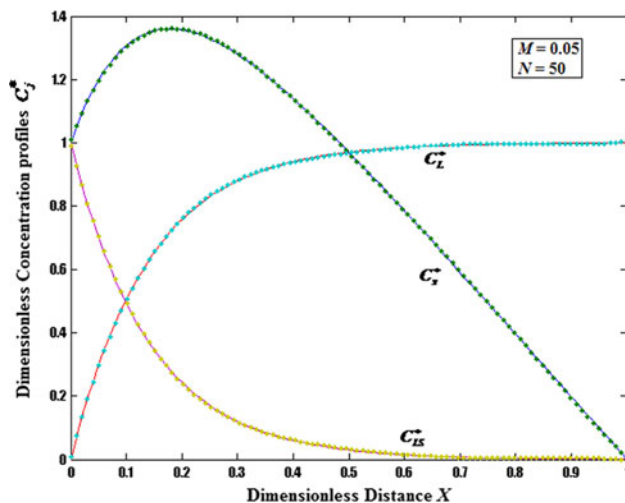
Fig. 5 A plot of dimensionless concentration profiles C_j^* through a membrane. *Curves* are plotted using Eqs. 13–15. *Solid lines* represent the analytical solution presented in this work; *dotted lines* represent the numerical solution

conclude that the concentration C_L^* decreases gradually and attains the steady state and that the value of concentration C_{LS}^* increases slowly and attains the steady state when $X \geq 0.7$.

Conclusion

In this work, the nonlinear reaction–diffusion equation for transport through the membrane has been solved analytically. We have presented analytical expressions corresponding to the concentration species in terms of M and N using the HPM. The analytical results will be useful for the determination of the thickness of the liquid membrane and the diffusion coefficients in this membrane. The theoretical results obtained can be used for optimization of the performance of the membrane. Also, the theoretical model described here can be used to obtain the parameters required to improve the design of the membrane.

Appendix 1: Approximate Analytical Solution of the Concentration Species Using the Homotopy Perturbation Method

In this appendix, we derive the solution of nonlinear reaction Eqs. 8–10 using He's HPM. To illustrate the basic concepts of this method, we consider the following non-linear differential equation (Ghori et al. 2007; Ozis and Yildirim 2007; Li and Liu 2006; Mousa and Ragab 2008):

$$L(u) + N(u) - f(r) = 0 \tag{16}$$

where L is a linear operator, N is a nonlinear operator and $f(r)$ is a given continuous function. We construct a homotopy $\Omega \times [0, 1] \rightarrow R$ which satisfies

$$(1-p)\frac{d^2 C_S^*}{dX^2} + p\left(\frac{d^2 C_S^*}{dX^2} - MC_S^* C_L^* + NC_{LS}^*\right) = 0 \tag{17}$$

$$(1-p)\frac{d^2 C_L^*}{dX^2} + p\left(\frac{d^2 C_L^*}{dX^2} - MC_S^* C_L^* + NC_{LS}^*\right) = 0 \tag{18}$$

$$(1-p)\left(\frac{d^2 C_{LS}^*}{dX^2} - NC_{LS}^*\right) + p\left(\frac{d^2 C_{LS}^*}{dX^2} + MC_S^* C_L^* - NC_{LS}^*\right) = 0 \tag{19}$$

Suppose the approximate solutions of Eqs. 17–19 have the form

$$\begin{cases} C_S^* = C_{S0}^* + pC_{S1}^* + p^2 C_{S2}^* + \dots \\ C_L^* = C_{L,0}^* + pC_{L,1}^* + p^2 C_{L2}^* + \dots \\ C_{LS}^* = C_{LS0}^* + pC_{LS1}^* + p^2 C_{LS2}^* + \dots \end{cases} \tag{20}$$

Substituting Eq. 20 into Eqs. 17–19 and equating the terms with the identical powers of p, we obtain

$$p^0 : \frac{d^2 C_{S,0}^*}{dX^2} = 0 \tag{21}$$

$$p^1 : \frac{d^2 C_{S,1}^*}{dX^2} - MC_{S,1}^* C_{L,0}^* + NC_{LS,0}^* = 0 \tag{22}$$

and

$$p^0 : \frac{d^2 C_{L,0}^*}{dX^2} = 0 \tag{23}$$

$$p^1 : \frac{d^2 C_{L,1}^*}{dX^2} - MC_{S,0}^* C_{L,0}^* + NC_{LS,0}^* = 0 \tag{24}$$

and

$$p^0 : \frac{d^2 C_{LS,0}^*}{dX^2} - NC_{LS,0}^* = 0 \tag{25}$$

$$p^1 : \frac{d^2 C_{LS,1}^*}{dX^2} + MC_{S,0}^* C_{L,0}^* - NC_{LS,1}^* = 0 \tag{26}$$

The initial conditions are as follows:

$$C_{S,0}^*(X = 0) = 1; \; C_{S,0}^*(X = 1) = 0 \tag{27}$$

$$C_{L,0}^*(X = 0) = 0; \; C_{L,0}^*(X = 1) = 1 \tag{28}$$

$$C_{LS,0}^*(X = 0) = 1; \; C_{LS,0}^*(X = 1) = 0 \tag{29}$$

and

$$C_{S,i}^*(X = 0) = 0; \; C_{S,i}^*(X = 1) = 0 \text{ for all } i = 1, 2, 3 \dots \tag{30}$$

$$C_{L,i}^*(X = 0) = 0; \; C_{L,i}^*(X = 1) = 0 \text{ for all } i = 1, 2, 3 \dots \tag{31}$$

$$C_{LS,i}^*(X = 0) = 0; \; C_{LS,i}^*(X = 1) = 0 \text{ for all } i = 1, 2, 3 \dots \tag{32}$$

Solving Eqs. 21, 23 and 25 and using the boundary condition Eqs. 27–29, we get

$$C_{S,0}^*(X) = 1 - X \tag{34}$$

$$C_{L,0}^*(X) = X \tag{35}$$

$$C_{LS,0}^*(X) = \frac{\sinh \sqrt{N}(1-X)}{\sinh \sqrt{N}} \tag{36}$$

Substituting the above values of $C_{S,0}^*$, $C_{L,0}^*$ and $C_{LS,0}^*$ and solving Eqs. 22, 24 and 26 using the boundary condition Eqs. 30–32, we obtain the following results:

$$C_{S,1}^*(X) = M\left(\frac{X^3}{6} - \frac{X^4}{12}\right) - \frac{\sinh\sqrt{N}(1-X)}{\sinh\sqrt{N}}$$
$$- \left(\frac{M}{2} + 1\right)X + 1 \tag{37}$$

$$C_{L,1}^*(X) = M\left(\frac{X^3}{6} - \frac{X^4}{4}\right) - \frac{\sinh\sqrt{N}(1-X)}{\sinh\sqrt{N}}$$
$$- \left(\frac{M}{2} + 1\right)X + 1 \tag{38}$$

$$C_{L,S,1}^*(X) = \frac{2M}{N^2\sinh\sqrt{N}}\left(\sinh\sqrt{N}(1-X) + \sinh\sqrt{N}X\right)$$
$$+ \frac{M}{N}\left(X - X^2 - \frac{2}{N}\right) \tag{39}$$

Adding Eqs. 34 and 37, we get Eq. 13 in the text. Similarly, we can get Eqs. 14 and 15.

Appendix 2: Matlab Program to Find the Numerical Solution of Equations 8–10

```
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)')
% ——————————————————————
function (c,f,s) = pdex4pde(x,t,u,DuDx)
M = 0.1;
N = 1;
c = (1; 1; 1);
f = (1; 1; 1).* DuDx;
F1 = –M*u(1)*u(2) + N*u(3);
F2 = –M*u(1)*u(2) + N*u(3);
F3 = M*u(1)*u(2)–N*u(3);
s = (F1; F2; F3);
% ——————————————————————
function u0 = pdex4ic(x);
u0 = (1; 0;0);
% ——————————————————————
function (pl,ql,pr,qr) = pdex4bc(xl,ul,xr,ur,t)
pl = (ul(1)–1; ul(2);ul(3)–1);
ql = (0;0; 0);
pr = (ur(1); ur(2)–1; ur(3));
qr = (0; 0; 0);
```

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