Transport of Small Molecules Through Mechanically Elongated Polymeric Membranes

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ABSTRACT: This contribution presents an analysis of the problem of diffusion through membranes, incorporating a realistic downstream boundary condition. The analysis can be applied to operations involving geomembranes. Graphs are presented to show the effect of the various dimensionless parameters. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1200–1203, 2005

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INTRODUCTION

Due to the low cost of production and their strength, geomembranes are widely used as barriers, buffers, liners, and sealants against pollutants. Several research papers address the problem of diffusion though geomembranes.[1–3] The problem of diffusion though geomembranes has been discussed for the case where the concentration of the pollutant on the downstream side of the membrane is assumed to be 0.[1,3,4] This type of boundary condition is ideally suited for experimental verification. In real life, however, the pollutant permeation through the membrane may be seeping into another medium. Here, we present a theoretical study of the case where the boundary condition on the downstream side of the membrane is a flux, proportional to the concentration.[3,5]

Mathematical formulation

We follow the mathematical model developed by Cohen.[6,7] The chemical potential μ is assumed to be a function of the concentration c and the stress σ. The governing equation for the process of diffusion is

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[\frac{\partial \mu}{\partial c} \nabla c + \frac{\partial \mu}{\partial \sigma} \nabla \sigma \right] \tag{1}$$

We assume that μ is a function of c and σ [i.e., $\mu = \mu(c, \sigma)$]. As a first approximation, we assume that $\partial\mu/\partial c$

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and $\partial\mu/\partial\sigma$ are the constants D and E, respectively. Equation (1) then reduces to

$$\frac{\partial c}{\partial t} = D\nabla^2 c + E\nabla^2\sigma \tag{2}$$

In addition, we need a constitutive equation relating σ to c. We choose an equation of the Jeffrey's type,[8] given by

$$\frac{\partial\sigma}{\partial t} + \beta\sigma = \nu_1 \frac{\partial c}{\partial t} + \nu_2 \frac{\partial^2 c}{\partial t^2} \tag{3}$$

where β is a constant, which can be considered to be the reciprocal of a relaxation time; ν_1 and ν_2 are constants. A Maxwell-type model is obtained by setting $\nu_2 = 0$. If the polymer is in the glassy state, β is small and negligible; however, in the rubbery state, β cannot be neglected. We will assume that the membrane is in a rubbery state for our present investigation. We also note that if $E = 0$, eq. (2) reduces to Fick's law. Let us consider the one-dimensional diffusion through a membrane of thickness l. The diffusion is assumed to be in the x direction and the surface at $x = 0$ is kept at the saturation concentration c_s. Initially c and σ are assumed to be 0 and at $x = l$, the flux $\partial c/\partial t = \alpha c$.

We now introduce the following nondimensional quantities:

$$c^* = \frac{c}{c_s}, \quad x^* = \frac{x}{l}, \quad \sigma^* = \frac{\sigma}{\nu_1 c_s}, \quad t^* = \beta t,$$

$$\gamma_1 = \frac{D}{l^2\beta}, \quad \lambda_2 = \frac{E\nu_1}{l^2\beta}, \quad \gamma_3 = \frac{\nu_2\beta}{\nu_1}, \quad \alpha^* = \alpha l$$

We will suppress the superscript * in the sequel. Equations (2) and (3) in dimensionless form are

$$\frac{\partial c}{\partial t} = \gamma_1 \frac{\partial^2 c}{\partial x^2} + \gamma_2 \frac{\partial^2 \sigma}{\partial x^2} \quad (4)$$

$$\frac{\partial \sigma}{\partial t} + \sigma = \frac{\partial c}{\partial t} + \gamma_3 \frac{\partial^2 c}{\partial t^2} \quad (5)$$

The initial and boundary conditions are

$$c(x,0) = 0, \quad \sigma(x,0) = 0, \quad c(0,t) = 1,$$

$$\frac{\partial c}{\partial x}(1,t) = \alpha c(1,t) \quad (6a\text{–}d)$$

Solution

Eliminating σ from eqs. (4) and (5), we get

$$\frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = \gamma_1 \frac{\partial^2 c}{\partial x^2} + (\gamma_1 + \gamma_2) \frac{\partial^3 c}{\partial x^2 \partial t} + \gamma_2 \gamma_3 \frac{\partial^4 c}{\partial x^2 \partial t^2} \quad (7)$$

Assuming $c = X(x)T(t)$ (separation of variables method), we obtain

$$\frac{T'' + T'}{\gamma_1 T + (\gamma_1 + \gamma_2)T' + \gamma_2\gamma_3 T''} = \frac{X''}{X'} = -\eta^2 \quad (8)$$

where η is a parameter. For $\eta = 0$, the appropriate solution satisfying the boundary conditions is

$$X_0 = 1 + \frac{\alpha}{1 - \alpha} x, \quad T_0 = 1, \quad 0 \le \alpha \le 1 \quad (9)$$

We assume that $X_\eta(0) = 0$ and $X_\eta' = \alpha X_\eta(1)$ for other (nontrivial) values of the parameter η. Thus, $\eta = \eta_s$, $s = 1, 2, 3\ldots$ and $X_s \propto \sin \eta_s x$ and $T_s = A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}$, where η_s are the roots of the transcendental equation

$$\alpha \tan \eta = \eta \quad (10)$$

Thus,

$$X_s T_s = \lfloor A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t} \rfloor \sin \eta_s x \quad (11)$$

where

$$\lambda_{1,2}(s) = \frac{[1 + (\gamma_1 + \gamma_2)\eta_s^2] \pm \sqrt{[1 + (\gamma_1 + \gamma_2)\eta_s^2]^2 - 4\eta_s^2\gamma_1(1 + \gamma_2\gamma_3\eta_s^2)}}{2(1 + \gamma_2\gamma_3\eta_s^2)}$$

$$(12)$$

We note that the characteristic functions of $\sin \eta_s x$ are orthogonal. The complete solution for c is then given by

$$c(x,t) = 1 + \frac{\alpha}{1 - \alpha} s$$

$$+ \sum_{s=1}^{\infty} [A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}]\sin \eta_s x \quad (13)$$

Using the orthogonality of $\sin \eta_s$ and the initial condition, we have

$$A_s + B_s = \frac{2}{\eta_s[1 - \alpha(1 + \alpha^2\eta_s^2)]} \quad (14)$$

We need one more relation between A_s and B_s to determine the solution completely. This relation is obtained by solving for σ, using eqs. (5) and (13), and then by insuring compatibility of the solutions for c and σ with respect to eq. (4). Substituting the expression (13) for c in eq. (5), we have

$$\frac{\partial \sigma}{\partial t} + \sigma = -\sum_{s=1}^{\infty} [A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}]\sin \eta_s x$$

$$+ \gamma_3 \sum_{s=1}^{\infty} [A_s \lambda_1^2(s)e^{-\lambda_1(s)t} + B_s \lambda_2^2(s)e^{-\lambda_2(s)t}]\sin \eta_s x \quad (15)$$

The solution for eq. (15) is

$$\sigma = \sum_{s=1}^{\infty} \left[\frac{A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}}{1 - \lambda_1(s)} (e^{-\lambda_2(s)t} - e^{-t}) \right.$$

$$\left. + \frac{B_s \lambda_2(s)(\gamma_3\lambda_2(s) - 1)}{1 - \lambda_2(s)} (e^{-\lambda_2(s)t} - e^{-t}) \right] \sin \eta_s x \quad (16)$$

Substituting solutions (13) and (16) into eq. (4), we obtain one new equation

$$\frac{A_s \lambda_1(s)(\gamma_3\lambda_1(s) - 1)}{1 - \lambda_1(s)} + \frac{B_s \lambda_2(s)(\gamma_3\lambda_2(s) - 1)}{1 - \lambda_2(s)} = 0 \quad (17)$$

Solving for A_s and B_s from eqs. (14) and (17), we have

$$A_s = \frac{-2(1 + \gamma_2\gamma_3\eta_s^2)^2[1 - \lambda_1(s)][\gamma_3\lambda_2(s) - 1]\lambda_2(s)}{\eta_s(\gamma_3 - 1)\sqrt{[1 + (\gamma_1 + \gamma_2)\eta_s^2]^2 - 4\eta_s^2} \, \gamma^1(1 + \gamma_2\gamma_3\eta_s^2)}$$

$$B_s = \frac{-2(1 + \gamma_2\gamma_3\eta_s^2)^2[1 - \lambda_2(s)][\gamma_3\lambda_1(s) - 1]\lambda_1(s)}{\eta_s(\gamma_3 - 1)\sqrt{[1 + (\gamma_1 + \gamma_2)\eta_s^2]^2 - 4\eta_s^2} \, \gamma^1(1 + \gamma_2\gamma_3\eta_s^2)} \quad (18)$$
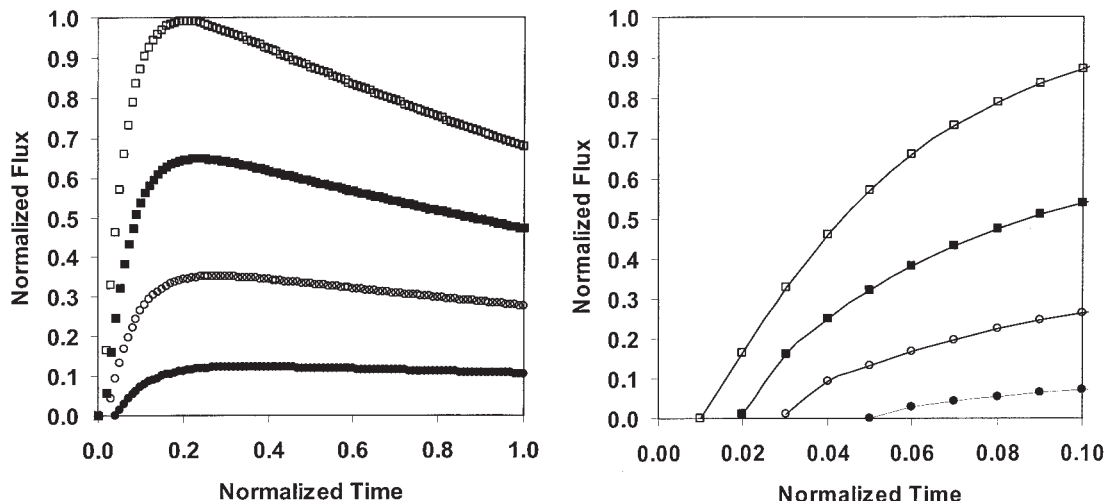
Figure 1 (a) Effect of γ_1 on normalized flux versus normalized time. $\gamma_2 = 1.0$, $\gamma_3 = 1.0$, $\gamma_1 = \square$ 0.9, ■ 0.7, ○ 0.5, ● 0.3. (b) Effect of γ_1 on normalized flux at shorter normalized times. $\gamma_2 = 1.0$, $\gamma_3 = 1.0$, $\gamma_1 = \square$ 0.9, ■ 0.7, ○ 0.5, ● 0.3.

The mass of penetrant $Q(t)$ in the membrane at any time is

$$Q(t) = \int_0^1 c(x,t)dx \qquad (19)$$

which yields

$$\frac{Q(t)}{Q(\infty)} = 1 + \frac{2(1-\alpha)}{2-\alpha} \sum_{s=1}^{\infty} \frac{1}{\eta_s}$$
$$\times [A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}](1 - \cos \eta_s x) \quad (20)$$

where $Q(\infty)$ is the value of $Q(t)$ as $t \to \infty$. The flux F at time t leaving the surface $x = 1$ is given by

$$F = -D\frac{\partial c}{\partial x}\Big|_{x=1} = -\frac{D\alpha}{1-\alpha}$$

$$+ D \sum_{s=1}^{\infty} \eta_s[A_s e^{-\lambda_1(s)t} + B_s e^{-\lambda_2(s)t}](\cos\eta_s x) \quad (21)$$

DISCUSSION

Figures 1-3 show flux versus time profiles predicted by eq. (21) for values of $\alpha = 0.01$. These figures show a profile where the flux has a maximum and will reach steady state at a later time. Experimental work for the permeation of acetone though elongated nitrile rubber and the permeation of dichloromethane through PVC exhibited similar behavior even though the boundary conditions of the experimental data differ from the mathematical model presented in this article.[1,9–11] While the experimental data are associated with a

negligible concentration of the permeant on the downstream side of the membrane, this mathematical model considers a constant flux.

Figure 1(a,b) shows the effect of parameter γ_1 on the predictions of eq. (21). The value of γ_1 is increased from 0.3 to 0.9 while keeping γ_2 and γ_3 equal to unity. Figure 1(a) indicates that the flux increases and the time to reach the maximum flux decreases with increasing γ_1. This behavior is in agreement with experimental data as γ_1 is proportional to D, the molecular diffusion coefficient.[12,13] Figure 1(b) is a zoom out of Figure 1(a) for shorter normalized times. As shown in Figure 1(b), the breakthrough time decreases as the values of γ_1 increase. The breakthrough time has been experimentally correlated to the thickness of the membrane for various polymer-solvent systems, so the

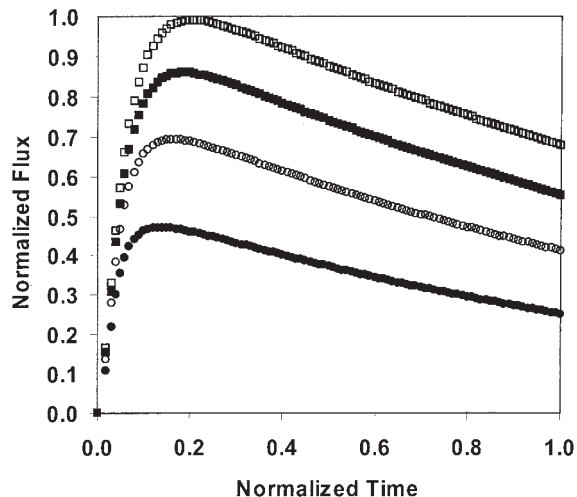**Figure 2** Effect of γ_2 on normalized flux versus normalized time. $\gamma_1 = 1.0$, $\gamma_3 = 1.0$, $\gamma_2 = \square$ 0.9, ■ 0.7, ○ 0.5, ● 0.3.
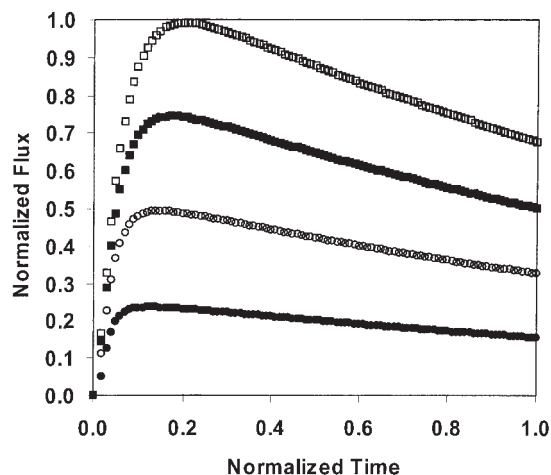
Figure 3 Effect of γ_3 on normalized flux versus normalized time. $\gamma_1 = 1.0$, $\gamma_2 = 1.0$, $\gamma_3 = \square$ 0.9, $\blacksquare$ 0.7, $\bigcirc$ 0.5, $\bullet$ 0.3.

trend predicted by eq. (21) also agrees with experimental data as transport through thinner membranes exhibits shorter breakthrough times.[11,14]

Figure 2 shows the effect of parameter γ_2 on the predictions of the mathematical model presented in this work. The value of γ_2 is increased from 0.3 to 0.9, while keeping γ_1 and γ_3 equal to unity. Figure 2 indicates that the flux as well as the time to reach a maximum flux increase with increasing values of γ_2. The increase in flux is in agreement with experimental data, as a larger γ_2 implies a larger effect of E, the elastic diffusion coefficient, on the transport of chemicals through polymeric membranes. This prediction may be useful in explaining previously reported cases of stress-enhanced transport.[10,11,14] An increase in γ_2 also increases the time to reach a maximum flux. This prediction is also in agreement with experimental data as an increase in mechanical deformation of the polymeric membrane implies an alignment of the polymer chains and hence an increase in localized crystallinity. This morphological change, increasing the value of E, causes the transport of the solvent to be slower so the time to reach a maximum flux decreases.[14–16]

Figure 3 shows the effect of parameter γ_3. The flux-time behavior predicted for different γ_3 is very similar to the one exhibited by γ_2. An increase in flux as well as larger times to reach a flux maximum result with an increasing γ_3, while keeping γ_1 and γ_2 equal to unity. This behavior is explained as γ_3 is a function of ν_1 and ν_2, which is a measure of the viscoelastic behavior of the polymer membrane.

We expect that experiments obeying the set of boundary conditions used in this work will exhibit similar flux versus time profiles.

In summary, the mathematical procedure developed in this article, and the resulting flux versus time, eq. (21), could be used to model and predict the effect of mechanical deformation on the transport of solvents through polymeric membranes.

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