

Modeling Diffusion Through Geomembranes

C. F. CHAN MAN FONG,¹ C. MORESOLI,² S. XIAO,³ Y. LI,¹ J. BOVENKAMP,⁴ D. DE KEE¹

¹ Department of Chemical Engineering, Tulane University, New Orleans, Louisiana 70118

² Department of Chemical Engineering, University of Sherbrooke, Sherbrooke, Quebec J1K 2R1, Canada

³ Oricolor Inc., C.P. 80 Montréal, Quebec H1B 5K1, Canada

⁴ Defence Research Establishment Suffield, Box 4000, Medicine Hat, Alberta T1A 8K6, Canada

Received 6 December 1996; accepted 18 December 1996

ABSTRACT: A phenomenological model that incorporates swelling is adopted and used to solve the one-dimensional sorption problem. The model predictions are in good agreement with experimental data, involving the transport of dichloromethane, trichloroethylene, and benzene through high-density polyethylene and poly(vinyl chloride) geomembranes. The theoretical curves predict weight-gain and flux-time profiles, including the case where the flux goes through a maximum. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1885–1889, 1998

Key words: diffusion; geomembranes; landfill liners

INTRODUCTION

Geomembranes are widely used as sealants against fluid percolation and buffers against pollutants. As such, they are extensively utilized as liners to separate chemicals from the surrounding environment in landfills, ponds, and underground storage tanks. A comprehensive study of the barrier properties of geomembranes is of utmost importance.

Several recent studies have evaluated the diffusivities of contaminants through polymeric geomembranes.^{1–3} It has been observed that in many cases the diffusion of the penetrants is accompanied by a swelling of the membrane, and in this case Fick's laws are no longer applicable.⁴ The transport of the penetrants through the membrane can be considered to be driven by the usual molecular diffusion and by a stress associated with the swelling of the membrane. In this article we present a phenomenological model of diffusion through polymers which incorporates both mechanisms.

MATHEMATICAL MODEL

Following Edwards and Cohen⁵ we assume that the chemical potential μ is a function of the concentration c and the stress σ . The equation governing the process of diffusion is

$$\frac{\partial c}{\partial t} = \text{div} \left[\frac{\partial \mu}{\partial c} \text{grad } c + \frac{\partial \mu}{\partial \sigma} \text{grad } \sigma \right] \quad (1)$$

As a first approximation we assume that $\left(\frac{\partial \mu}{\partial c}\right)$ and $\left(\frac{\partial \mu}{\partial \sigma}\right)$ are constants and are denoted by D and E , respectively.

Equation (1) simplifies to

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

We need to introduce a constitutive equation to describe the evolution of σ and its relation to c . We propose two equations which are the analogs of the Maxwell and the Jeffreys models in

Correspondence to: D. De Kee.

linear viscoelasticity.⁶ The Jeffreys model can be written as

$$\frac{\partial \sigma}{\partial t} + \beta \sigma = v_1 \frac{\partial c}{\partial t} + v_2 \frac{\partial^2 c}{\partial t^2} \quad (3)$$

where β is a constant and is the reciprocal of the relaxation time, and v_1 and v_2 are constants. By setting $v_2 = 0$, we have the Maxwell model.

If the polymer is in the glassy state, β is small and can be neglected; however, if it is in the rubbery state, β is not negligible. We assume that the membrane is in a rubbery state.

Note that if $E = 0$, eq. (2) reduces to Fick's law.

We next solve the one-dimensional sorption problem.

Formulation

We consider the one-dimensional diffusion through a membrane of thickness l . The diffusion is in the x -direction and the surface $x = 0$ is kept at the saturation concentration c_s . We introduce the following dimensionless quantities:

$$c^* = c/c_s, \quad x^* = x/l, \quad \sigma^* = \sigma/(v_1 c_s), \quad t^* = \beta t, \\ \gamma_1 = D/(l^2 \beta), \quad \gamma_2 = E v_1/(l^2 \beta), \quad \gamma_3 = v_2 \beta/v_1$$

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

$$c^*(x^*, 0) = 0, \quad \sigma^*(x^*, 0) = 0, \\ c^*(0, t^*) = 1, \quad c^*(1, t^*) = 0 \quad (6a)-(6d)$$

Solution

Eliminating σ^* from eqs. (4) and (5) yields

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

We assume the solution to be of the form

$$c^*(x^*, t^*) = u(x^*, t^*) + f(x^*) \quad (8)$$

Substituting eq. (8) into eq. (7), we obtain

$$\frac{\partial^2 u}{\partial t^{*2}} + \frac{\partial u}{\partial t^*} = \gamma_1 \frac{\partial^2 u}{\partial x^{*2}} + (\gamma_1 + \gamma_2) \\ \times \frac{\partial^3 u}{\partial x^{*2} \partial t^*} + \gamma_2 \gamma_3 \frac{\partial^4 u}{\partial x^{*2} \partial t^{*2}} + \frac{d^2 f}{dx^{*2}} \quad (9)$$

We choose f such that

$$\frac{d^2 f}{dx^{*2}} = 0, \quad (10a)$$

$$f(0) = 1, \quad f(1) = 0 \quad (10b), (10c)$$

The solution is

$$f = 1 - x^* \quad (11)$$

The conditions that u has to satisfy are now

$$u(0, t^*) = u(1, t^*) = 0, \\ u(x^*, 0) = x^* - 1 \quad (12a)-(12c)$$

The function u can be written as

$$u(x^*, t^*) = e^{-\lambda t^*} v(x^*) \quad (13)$$

where λ is a constant with positive real part.

Equations 12(a) and 12(b) imply

$$v(0) = v(1) = 0 \quad (14a), (14b)$$

Substituting eq. (13) into eq. (9) and using eqs. (10a), (14a), and (14b) we deduce that

$$v(x^*) = b \sin \mu x^*, \quad (15a)$$

$$\mu^2 = \lambda(\lambda - 1)/[\lambda(\gamma_1 + \gamma_2) - \gamma_1 - \lambda^2 \gamma_2 \gamma_3] \\ = s^2 \pi^2 \quad (15b), (15c)$$

where b is a constant, and s is a positive integer.

From eqs. (15b) and (15c) we can solve for λ :

$$\lambda = \left\{ \begin{aligned} & [1 + s^2 \pi^2 (\gamma_1 + \gamma_2)] \\ & \pm \sqrt{[1 + s^2 \pi^2 (\gamma_1 + \gamma_2)]^2 - 4s^2 \pi^2 \gamma_1 (1 + s^2 \pi^2 \gamma_2 \gamma_3)} \end{aligned} \right\} \\ \div 2(1 + s^2 \pi^2 \gamma_2 \gamma_3) \quad (16)$$

We now consider the Maxwell and the Jeffreys models separately.

Maxwell Model

In this case $\gamma_3 = 0$, the term inside the square root in eq. (16) is positive, we write λ as λ_s , and eq. (16) becomes

$$\lambda_s = \{[1 + s^2\pi^2(\gamma_1 + \gamma_2)] + \sqrt{[1 + s^2\pi^2(\gamma_1 + \gamma_2)]^2 - 4s^2\pi^2\gamma_1}\}/2 \quad (17)$$

Combining eqs. (8), (11), (12c), (13), (15a), and (17) yields

$$c^* = (1 - x^*) - \frac{2}{\pi} \sum_{s=1}^{\infty} \frac{\exp(-\lambda_s t^*) \sin s\pi x^*}{s} \quad (18)$$

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

$$Q(t^*) = \int_0^1 c^*(x^*, t^*) dt^* \quad (19)$$

On integrating we obtain

$$\frac{Q(t^*)}{Q(\infty)} = 1 - \frac{8}{\pi^2} \sum_{s=0}^{\infty} \frac{\exp(-\lambda_{2s+1} t^*)}{(2s+1)^2} \quad (20)$$

where $Q(\infty)$ is the value of $Q(t^*)$ as $t^* \rightarrow \infty$.

The flux F at time t^* leaving the surface $x^* = 1$ is given by

$$F = -D \left. \frac{\partial c}{\partial x} \right|_{x=1} = -l\beta c_s \gamma_1 \left. \frac{\partial c^*}{\partial x^*} \right|_{x^*=1} \quad (21a), (21b)$$

Combining eqs. (18) and (21b) yields

$$\frac{F}{l\beta c_s} = \gamma_1 \left[1 + 2 \sum_{s=1}^{\infty} (-1)^s \exp(-\lambda_s t^*) \right] \quad (22)$$

Jeffreys Model

In this case we assume that γ_3 is much greater than γ_1 and γ_2 , and that the terms inside the square root are negative. Equation (16) is now written as

$$\lambda = \alpha_s \pm i\omega_s, \quad (23a)$$

$$\alpha_s = [1 + s^2\pi^2(\gamma_1 + \gamma_2)] \div [2(1 + s^2\pi^2\gamma_2\gamma_3)] \quad (23b)$$

$$\omega_s^2 = \{4s^2\pi^2\gamma_1(1 + s^2\pi^2\gamma_2\gamma_3) - [1 + s^2\pi^2(\gamma_1 + \gamma_2)]^2\} \div [2(1 + s^2\pi^2\gamma_2\gamma_3)] \quad (23c)$$

Proceeding as in the case of the Maxwell model, we obtain

$$c^* = (1 - x^*) + \sum_{s=1}^{\infty} e^{-\alpha_s t^*} (a_s \cos \omega_s t^* + b_s \sin \omega_s t^*) \sin s\pi x^* \quad (24a)$$

$$a_s = -2/(\pi s),$$

$$b_s = a_s[\omega_s^2 + \alpha_s(\alpha_s - 1)]/\omega_s \quad (24b), (24c)$$

$$\frac{Q(t^*)}{Q(\infty)} = 1 - \frac{4}{\pi^2} \sum_{s=0}^{\infty} \frac{e^{-\alpha_{2s+1} t^*} (a_{2s+1} \cos \omega_{2s+1} t^* + b_{2s+1} \sin \omega_{2s+1} t^*)}{(2s+1)} \quad (25)$$

$$\frac{F}{l\beta c_s} = \gamma_1 \left[1 - \sum_{s=1}^{\infty} (-1)^s s \pi e^{-\alpha_s t^*} \times (a_s \cos \omega_s t + b_s \sin \omega_s t) \right] \quad (26)$$

RESULTS AND DISCUSSION

It is seen from eqs. (20), (22), (25), and (26) that, for the Maxwell model, the quantities $Q(t^*)/Q(\infty)$ and $F/(l\beta c_s)$ attain their equilibrium values monotonically and do not have a maximum, whereas for the Jeffreys model these quantities may have maxima.

We show that both possibilities exist.

Figures 1 to 3 show the experimental values of $Q(t)/Q(\infty)$ versus $t^{1/2}$ for the liquid sorption of dichloromethane (DCM), trichloroethylene (TCE), and for the vapor sorption of DCM in high-density polyethylene (HDPE) geomembranes.

The experimental procedures are described by Xiao and colleagues.³ In all three cases $Q(t)/Q(\infty)$ has no maximum and it is sufficient to consider the Maxwell model.

The experimental data are in good agreement with the model predictions [eq. (20)]. We note that in the case of liquid sorption of DCM, $\gamma_2 > \gamma_1$; whereas in the case involving vapor sorption, $\gamma_1 > \gamma_2$. We may conclude that liquid sorption is mostly stress-driven and that vapor sorption is controlled mostly by molecular diffusion.

Figures 4 and 5 illustrate flux-time evolutions in the case of pure benzene and a DCM aqueous

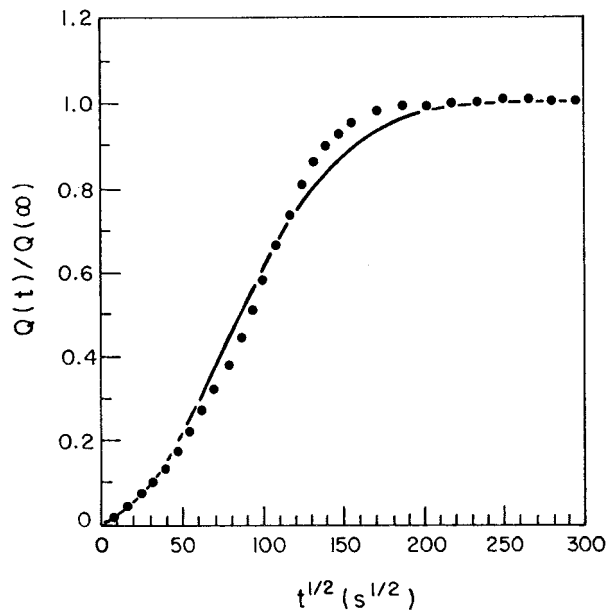


Figure 1 $Q(t)/Q(\infty)$ versus $t^{1/2}$ for liquid DCM in a HDPE (HP40) geomembrane at 303 K. (●) Experimental data; (—) model predictions (eq. 20). $\gamma_1 = 1.8 \times 10^{-11}$, $\gamma_2 = 1.0 \times 10^{-5}$, $\beta = 9.3 \times 10^{-5}$.

solution through poly(vinyl chloride) (PVC) geomembranes. In this case F goes through a maximum and we compare the experimental data with the Jeffreys model [eq. (26)]. It can be seen that

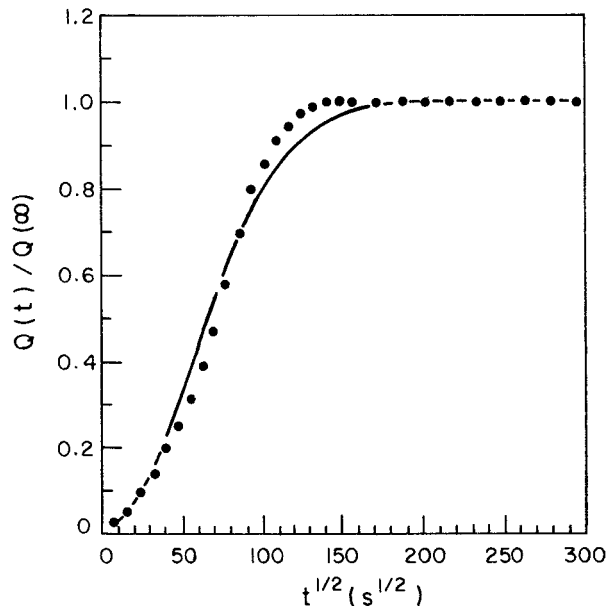


Figure 2 $Q(t)/Q(\infty)$ versus $t^{1/2}$ for liquid TCE in a HDPE (HP40) geomembrane at 303 K. (●) Experimental data, (—) model predictions (eq. 20). $\gamma_1 = 1.5 \times 10^{-12}$, $\gamma_2 = 3.0 \times 10^{-5}$, $\beta = 2.0 \times 10^{-7}$.

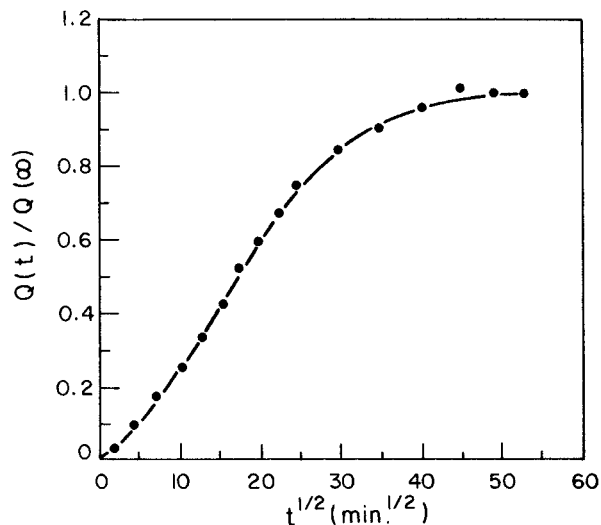


Figure 3 $Q(t)/Q(\infty)$ versus $t^{1/2}$ for DCM vapor at 100 mm Hg in contact with a HDPE (HD40) geomembrane at 303 K. (●) Experimental data, (—) model predictions (eq. 20). $\gamma_1 = 4.2 \times 10^{-2}$, $\gamma_2 = 6.2 \times 10^{-10}$, $\beta = 3.8 \times 10^{-5}$.

the agreement between experimental data and model predictions is reasonably good, although the predicted maxima are lower than the experimental values. The cause for the poor predictions at small times may be due to the fact that initially the membrane is in a glassy state ($\beta \approx 0$) and we have assumed it in a rubbery state. Furthermore, it has been observed that the concentration at the surface $x = 0$ reaches the saturation value only

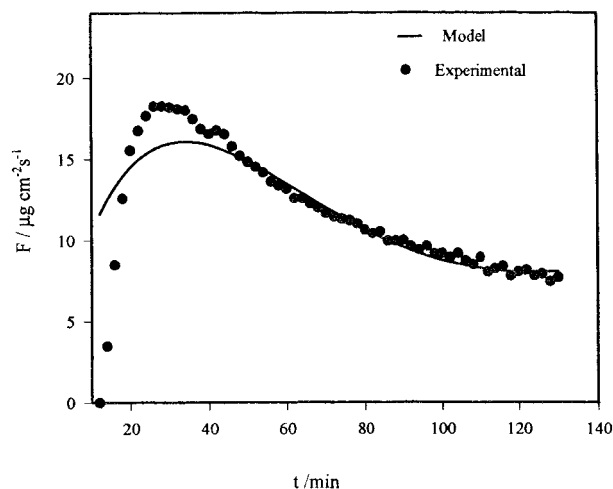


Figure 4 F versus t in a benzene PVC (GEO SF220) system at 298 K. (●) Experimental data, (—) model predictions (eq. 26). $\gamma_1 = 8.88 \times 10^{-5}$, $\gamma_2 = 8.19 \times 10^{-2}$, $\gamma_3 = 1.15 \times 10^3$, $\beta = 2.52$, $l = 0.52$ mm.

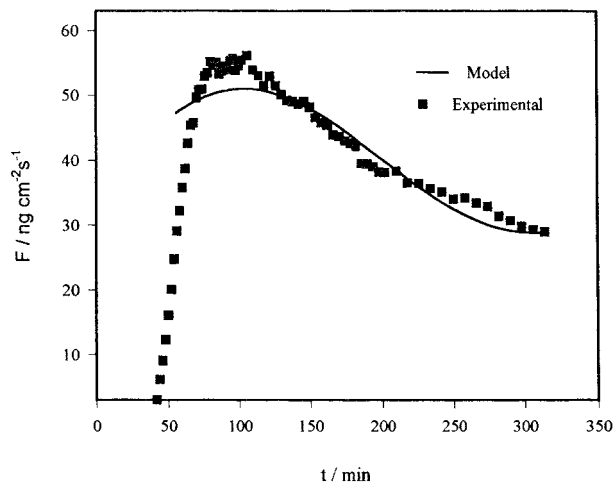


Figure 5 F versus t in a DCM PVC (GEOSF220) system at 298 K. The DCM is an aqueous (1,970 ppm) solution. (■) Experimental data, (—) model predictions (eq. 26). $\gamma_1 = 1.77 \times 10^{-4}$, $\gamma_2 = 0.111$, $\gamma_3 = 7.5 \times 10^3$, $\beta = 2.37$.

after a finite induction time.⁷ We note that in this case $\gamma_2 > \gamma_1$, implying that the diffusion is mainly stress-controlled. It is therefore appropriate to at-

tribute the existence of a maximum in F to σ and to consider the Jeffreys model.

We have shown that the model considered here is simple enough to allow for exact solutions to diffusion problems and can describe the behavior of organic penetrants through geomembranes.

REFERENCES

1. D. R. Ramsay, *Geosynthetics '93 Conference Proceedings*, Vancouver, BC, Canada, 1993, p. 645.
2. R. K. Rowe, L. Hrapovic, and N. Kosaric, *Geosynthetics International*, **2**, 507 (1995).
3. S. Xiao, C. Moresoli, J. Bovenkamp, and D. De Kee, *J. Appl. Polym. Sci.*, to appear.
4. J. Stastna and D. De Kee, *Transport Properties in Polymers*, Technomic Publishing Co., Lancaster, PA, 1995.
5. D. A. Edwards and D. S. Cohen, *AIChE J.*, **41**, 2345 (1995).
6. P. J. Carreau, D. De Kee, and R. P. Chhabra, *Polymer Rheology: Principles and Applications*, Hanser, New York, 1997.
7. F. A. Long and D. Richman, *J. Am. Chem. Soc.*, **82**, 513 (1960).