Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 29 July 1999

To cite this Article Ramraj, Ritesh , Farrell, Stephanie and Loney, Norman W.(1999) 'Mathematical Modeling of a Flat-Membrane-Controlled Release Device', Separation Science and Technology, 34: 11, 2251 — 2258
To link to this Article: DOI: 10.1081/SS-100100770
URL: http://dx.doi.org/10.1081/SS-100100770

SEPARATION SCIENCE AND TECHNOLOGY, **34**(11), pp. 2251–2258, 1999

Mathematical Modeling of a Flat-Membrane-Controlled Release Device

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ABSTRACT

The closed form solution to a mathematical model of a flat membrane device successfully predicts the release profile of benzoic acid. Physically, the device consists of a given concentration of benzoic acid in octanol (reservoir) bounded by a microporous flat film (Cellgard 2400) with water-filled pores. The prediction shows excellent agreement with the experimentally derived release profile (maximum difference $< 10\%$). Predicted results are obtained from the use of the steady state plus the first term of the transient solution (infinite series) and with the use of the first nonzero eigenvalue.

INTRODUCTION

A novel controlled release device based on aqueous–organic partitioning was mathematically modeled. The device consists of a reservoir containing the agent to be released and is bounded by a flat microporous membrane (Cellgard 2400). The agent is expected to partition between the phases at the aqueous–organic interface of the reservoir and the pore mouth and then diffuse through the membrane pore liquid into a surrounding solution.

There are many equations describing controlled release by solute diffusion in the literature. Those equations are usually results of lumped parameter modeling such as mentioned in Cussler (1) or Farrell and Sirkar (2). A major difficulty with such a modeling result is the need to provide case-by-case exper-

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imental measurements of the lumped parameter such as the mass transfer coefficient or permeability.

In this work we present a distributed parameter model which relies more on fundamental physics than on experimental results. However, experimental results (base case) are required to verify the theory. Below we focus on the solute concentration profile through the membrane device. The experimental models which include the benzoic acid/octanol system are described elsewhere by Farrell (3).

THEORY

This model describes the release of relatively small molecules such as benzoic acid. Initially the solute to be released is present in solution or suspension in a reservoir. The reservoir is bounded by a microporous membrane without nonporous coating. The pores of the membrane are filled with a liquid which is immiscible with the reservoir phase.

In addition, we assumed the following:

- Diffusion of the agent (benzoic acid) is Fickian.
- Interfacial boundary layers are not influential here.
- Diffusivities of the agent is independent of concentration.
- The aqueous–organic partition coefficient for the agent is independent of concentration.
- Reservoir and bath solutions are ideal.
- Uniform temperature exists throughout the system.
- The aqueous and organic phases are immiscible.

Then suppose the agent initially exists in a solution in the reservoir at a concentration below its saturation value in the solvent. Following Jost (4) and Bird (5), the governing equation for the agent concentration in the reservoir is

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} \tag{1}$$

and

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} \tag{2}$$

is the governing equation for the agent in the membrane. The subscripts refer to the respective region as shown in Fig. 1. D_2 is an effective diffusivity and is defined as

$$D_2 = D\varepsilon/\tau \tag{3}$$

where D is the agent diffusivity in the pore liquid, ε is the membrane porosity, and τ is the membrane tortuosity. Both the agent diffusivity in the pore liq-

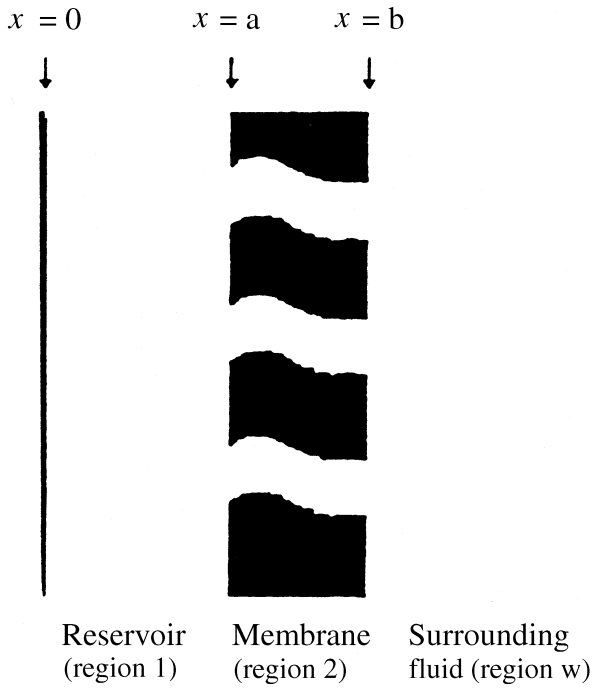

FIG. 1 The reservoir and membrane regions of the controlled release device.

uid (D) and in the reservoir liquid (D_1) are calculated using the Wilke–Chang correlation (6). The quantity τ was defined and measured for various systems by Prasad and Sirkar (7); here we used the value given there for a hydrophobic membrane. The porosity value (0.38) is a manufacturer-supplied quantity.

Equations (1) and (2) are subject to the following boundary conditions:

$$C_1(a, t) = m_{1,2}C_2(a, t) \tag{4}$$

$$\frac{\partial C_1(0, t)}{\partial x} = 0 \tag{5}$$

$$D_1 \frac{\partial C_1(a, t)}{\partial x} = D_2 \frac{\partial C_2(a, t)}{\partial x} \tag{6}$$

$$V_w \frac{\partial C_2(b, t)}{\partial t} = -D_2\alpha_2 m_{2,w} \frac{\partial C_2(b, t)}{\partial x} \tag{7}$$

Further, since all of the agent is initially present in the reservoir phase, then

$$C_1(x, 0) = C_1^0 \tag{8}$$

$$C_2(x, 0) = 0 \tag{9}$$

Equation (4) is a statement of the equilibrium partitioning at the reservoir/pore liquid interface with $m_{1,2}$ being the partition coefficient. Equation

(5) indicates that the solute concentration is expected to be finite at the bottom of the reservoir. Equation (6) displays the continuity of the agent flux across the reservoir/pore interface, while Eq. (7) accounts for the material leaving the membrane and entering the surrounding water bath. The quantity α_2 is the membrane area at the outer wall (cm^2).

In deriving the solution to the model, we recast the model in a dimensionless form by introducing the following quantities:

$$u_1(\xi, \theta) = \frac{C_1(x, t)}{C_1^0} \tag{10}$$

$$u_2(\xi, \theta) = \frac{C_2(x, t)}{C_1^0} \tag{11}$$

where

$$\xi = x/b, \qquad \theta = D_1 t/b^2 \tag{12}$$

The dimensionless model now consists of the following eight equations:

$$\frac{\partial u_1}{\partial \theta} = \frac{\partial^2 u_1}{\partial \xi^2} \tag{13}$$

$$\frac{D_1}{D_2}\frac{\partial u_2}{\partial \theta} = \frac{\partial^2 u_2}{\partial \xi^2} \tag{14}$$

$$u_1(a/b, \theta) = m_{1,2} u_2(a/b, \theta) \tag{15}$$

$$\frac{\partial u_1(0, \theta)}{\partial \xi} = 0 \tag{16}$$

$$\frac{D_1}{D_2}\frac{\partial u_1(a/b, \theta)}{\partial \xi} = \frac{\partial u_2(a/b, \theta)}{\partial \xi} \tag{17}$$

$$\beta \frac{\partial u_2(1, \theta)}{\partial \theta} = -\frac{\partial u_2(1, \theta)}{\partial \xi} \tag{18}$$

$$u_1(\xi, 0) = 1 \tag{19}$$

$$u_2(\xi, 0) = 0 \tag{20}$$

where

$$\beta = \frac{V_w D_1}{b m_{2,w} D_2 \alpha_2} \tag{21}$$

This type of coupled system of equations is very amenable to the technique of Laplace transform. As such we let

$$\bar{u}_1(\xi, s) = \int_0^\infty u_1(\xi, \theta)\, e^{-s\theta}\, d\theta \quad \text{and} \quad \bar{u}_2(\xi, s) = \int_0^\infty u_2(\xi, \theta) e^{-s\theta}\, d\theta \tag{22}$$

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such that Eqs. (13), (14), (19), and (20) transform to the second-order linear differential equations:

$$s\bar{u}_1 - 1 = \frac{d^2\bar{u}_1}{d\xi^2} \tag{23}$$

and

$$\frac{D_1}{D_2}\, s\bar{u}_2 = \frac{d^2\bar{u}_2}{d\xi^2} \tag{24}$$

subject to the transformed boundary conditions:

$$\bar{u}_1(a/b, s) = m_{1,2}\bar{u}_2(a/b, \mathrm{s}) \tag{25}$$

$$\frac{d\bar{u}_1(0, s)}{d\xi} = 0 \tag{26}$$

$$\frac{D_1}{D_2}\,\frac{d\bar{u}_1(a/b, \mathrm{s})}{d\xi} = \frac{d\bar{u}_2(a/b, \mathrm{s})}{d\xi} \tag{27}$$

$$\beta s\bar{u}_2(1, s) = -\frac{d\bar{u}_2(1, s)}{d\xi} \tag{28}$$

The solutions to the dimensionless model, Eqs. (23)–(28), are

$$\bar{u}_1 = \frac{1}{s} + \frac{\sqrt{\dfrac{D_2}{D_1}}\,[\lambda\beta D_2/D_1 \cos\lambda(1 - a/b) + \sin\lambda(1 - a/b)]\cos\lambda\sqrt{D_2/D_1}\xi}{sq(\lambda)} \tag{29}$$

and

$$\bar{u}_2 = \frac{[\beta\lambda D_2/D_1 \sin\lambda(1 - \xi) - \cos\lambda(1 - \xi)]}{sq(\lambda)} \sin(\lambda\, a/b\,\sqrt{D_2/D_1}) \tag{30}$$

where

$$\begin{aligned} q(\lambda) = m_{1,2}[\lambda\beta D_2/D_1 \sin\lambda(1 - a/b) - \cos\lambda\,(1 - a/b)]\sin\left(\lambda\,\frac{a}{b}\sqrt{D_2/D_1}\right) \\ - \sqrt{D_2/D_1}\,[\lambda\beta D_2/D_1 \cos\lambda(1 - a/b) \\ + \sin\lambda(1 - a/b)]\cos\left(\lambda\,\frac{a}{b}\sqrt{D_2/D_1}\right) \end{aligned} \tag{31}$$

The substitution

$$i\lambda = \sqrt{\frac{D_1 s}{D_2}} \tag{32}$$

where i is the imaginary unit, was used in Eqs. (29)–(31).

Equations (29) and (30) are inverted by means of the residue theorem (8) to give

$$u_1(\xi, \theta) = \frac{m_{1,2}a/b}{1 + \beta\frac{D_2}{D_1} + \frac{a}{b}(m_{1,2} - 1)} + \sum_{n=1}^{\infty} \frac{\sqrt{D_2/D_1}[\lambda_n \beta D_2/D_1 \cos\lambda_n(1 - a/b) + \sin\lambda_n(1 - a/b)]\cos\left(\lambda_n \frac{D_2}{D_1}\xi\right)\exp\left[-\left(\lambda_n^2 \frac{D_2}{D_1}\theta\right)\right]}{\left(\frac{\lambda}{2}\frac{dg}{d\lambda}\right)\Big|_{\lambda=\lambda_n}} \quad (33)$$

and

$$u_2(\xi, \theta) = \frac{a/b}{1 + \beta\frac{D_2}{D_1} + \frac{a}{b}(m_{1,2} - 1)} + \sum_{n=1}^{\infty} \frac{[\lambda_n \beta D_2/D_1 \sin\lambda_n(1 - \xi) - \cos\lambda_n(1 - \xi)] \times \sin\left(\lambda_n \frac{a}{b}\sqrt{D_2/D_1}\right)\exp\left[-\left(\lambda_n^2 \frac{D_2}{D_1}\theta\right)\right]}{\left(\frac{\lambda}{2}\frac{dq}{d\lambda}\right)\Big|_{\lambda=\lambda n}} \quad (34)$$

where the eigenvalues, λ_n, are defined by

$$\tan\lambda_n(1 - a/b) = \frac{m_{1,2}\tan\left(\lambda_n \frac{a}{b}\sqrt{D_2/D_1}\right) + D_2/D_1\sqrt{D_2/D_1}\beta\lambda_n}{\lambda_n m_{1,2} D_2/D_1\,\beta\tan\left(\lambda_n \frac{a}{b}\sqrt{D_2/D_1}\right) - \sqrt{D_2/D_1}} \quad (35)$$

Then using Eq. (11), the concentration profile of the agent at $x = b$ can be predicted.

RESULTS AND DISCUSSION

Using the required physical quantities Eq. (35) was solved to find the first eigenvalue (λ_1). With this eigenvalue and the appropriate physical quantities, the steady state and first term of the infinite series of Eq. (34) are used in Eq. (11) to calculate the concentration profile leaving the membrane as a function of time.

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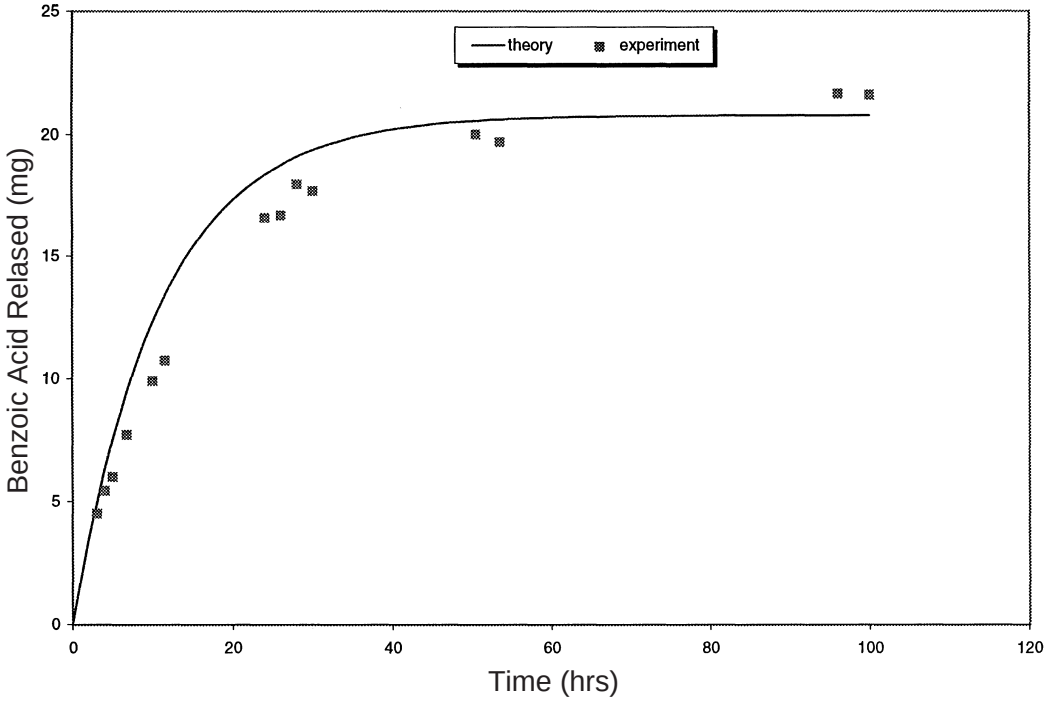

FIG. 2 Release profile of benzoic acid.

Figure 2 shows a comparison between actual experimental benzoic acid concentration leaving the membrane device and that predicted by our model. All pertinent physical parameters including diffusivity (D), tortuosity (τ), porosity (ε), and partition coefficient (m) are the same as those used and discussed in the thesis by Farrell (3). While the model prediction of the benzoic acid released appears to be higher over the periods ranging from 5–50 hours, the largest discrepancy is less than 10%. That is, at 30 hours the model predicts 19.4 mg of benzoic acid will be released while the experimental data suggests that 17.7 mg is released. However, there may be some inconsistency in the measurement as 18 mg is released after 28 hours. Furthermore, only the first term of the transient part of Eq. (34) is used in the prediction, and perhaps an additional term may bring the model results into closer agreement. It should be kept in mind, however, that the amount of effort required to improve the accuracy of the predicted results may not be justifiable for preliminary designs.

CONCLUSIONS

The closed form solution to the mathematical model of a flat membrane device predicts the release profile of benzoic acid from the device. This analytical solution should prove very helpful in predicting preliminary results for the

design of control release devices. A reduction in the costs of experimentation is also expected due to the reduced number of such trials.

NOMENCLATURE

a	distance solute must traverse to reach the membrane (cm)
b	membrane distance solute must traverse to reach the bath (cm)
C_i	solute concentration (mg/mL) in the appropriate region
C_1^0	initial solute concentration in reservoir (mg/mL)
D_i	solute diffusivity (cm^2/s) in the appropriate region
$m_{1,2}$	distribution coefficient for the solute between Regions 1 and 2
$m_{2,w}$	partition coefficient for pore liquid/water bath (= 1 if pore liquid is water)
t	time (second)
V_w	water bath volume (mL)
α_2	membrane area at the outer wall (cm^2)
λ_n	The nth eigenvalue of the system

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Received by editor May 1, 1998
Revision received October 1998

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