Diffusion and Release of a Mobile Product in a Reactive Membrane System

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Introduction

When a polymer membrane containing an immobilized, reactive chemical is in contact with solution containing a reactive solute, the solute diffuses into the membrane and reacts with the immobilized chemical. As a result, the reactive solute and the immobilized chemical are consumed, and at the same time, mobile products may be produced within the membrane. The mobile products will diffuse out of the membrane under the driving force of the resulting concentration gradient. This process continues until all of the immobilized chemical is consumed. In this study, diffusion and release of a mobile product produced in a reactive membrane was investigated experimentally and theoretically.

Such a reactive membrane system has many possible applications. For example, it can be applied to a controlled release of drugs [1]. Acidic conditions in the body could be used to trigger a reaction within an implanted membrane to release a drug. Similarly, it can be used for a controlled release of agricultural chemicals [2]. Also, it may be relevant to reactive barrier membranes for retarding penetration of contaminants [3] if formation of undesired by-products is possible. Thus, the diffusion of the mobile products out of the reactive membrane is of great interest.

Theory

To describe the diffusion of the mobile product formed by the reaction within the membrane, we assume a diaphragm-cell setup. Two volumes are separated by the reactive membrane. One “upstream cell” volume (V_{up}) contains a high concentration of the reactive solute, and the other “downstream cell” volume (V_{down}) initially contains no solute. Our modeling is based on an equation derived by Yang et al. This equation allows us to predict how fast the immobilized chemical is consumed [4]:

$$\ell = \sqrt{\frac{2P_1 C_{1up} \nu t}{C_{20}}} \qquad (1)$$

where t is time, ℓ is the thickness of the depleted zone, C_{20} is the initial concentration of the immobilized chemical, P_1 is the permeability of the reactive solute, ν is the stoichiometric coefficient of reaction, and C_{1up} is the concentration of the reactive solute in the upstream cell. When ℓ becomes equal to the membrane thickness (L), breakthrough of the membrane occurs, and the concentration of the reactive solute in the downstream cell starts to increase. The time before the breakthrough occurs is called lag time. The equation above implies that increasing the immobilized chemical loading will lead to a larger lag time.

A diffusion equation with a reaction term describes the behavior of the mobile product before the membrane breakthrough, while a diffusion equation without a reaction term governs the system after the breakthrough with appropriate initial and boundary conditions:

$$\frac{\partial C_3}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial x^2} + \frac{P_1 C_{1up}\, \nu}{x} \delta(x - \ell) \tag{2}$$

$$\frac{\partial C_3}{\partial t} = D_3 \frac{\partial^2 C_3}{\partial x^2} \tag{3}$$

C_3 is the concentration of the mobile product in the membrane, D_3 is the diffusion coefficient of the mobile product, x is the distance into the membrane (x = 0 at the upstream end), and δ is the Dirac delta function. An analytical solution to this problem was derived based on a pseudo-steady state assumption: advancement of the reaction front is slow compared with diffusion of the product. The equations were also solved numerically without an assumption using the explicit Euler method.

Experimental

As explained in the Theory section, we used a diaphragm-cell to investigate the diffusion of the mobile product out of the reactive membrane in our experiments. The experimental setup is shown below:

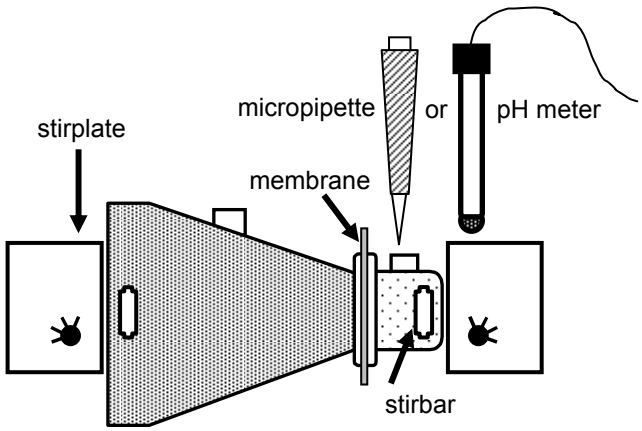

Figure 1 Illustration of the diaphragm-cell experimental setup.

Hydrochloric acid and a poly(vinyl alcohol) membrane containing zinc oxide particles were chosen as the reactive solute and the reactive membrane, respectively. The immobilized zinc oxide was dissolved by the penetrating hydrochloric acid. Zinc chloride was formed within the membrane and subsequently diffused out of the membrane into the two cells:

$$2HCl + ZnO \rightarrow ZnCl_2 + 2H_2O \tag{4}$$

The concentration of the acid and the mobile zinc in the cells were monitored using a pH meter and a colorimetric method, respectively. The experiments were also conducted with varied zinc

oxide loadings, acid concentrations, membrane thicknesses, and chamber volumes to determine the effects of these parameters.

Results and Discussion

Figure 2 shows a typical breakthrough curve for HCl. The concentration of acid is near zero until the breakthrough and then rises linearly. The lag time for this specific experiment was 83 min, while a typical lag time for a PVA membrane of this thickness without ZnO is 1 min. This result demonstrates the large effect of ZnO addition on extending the lag time.

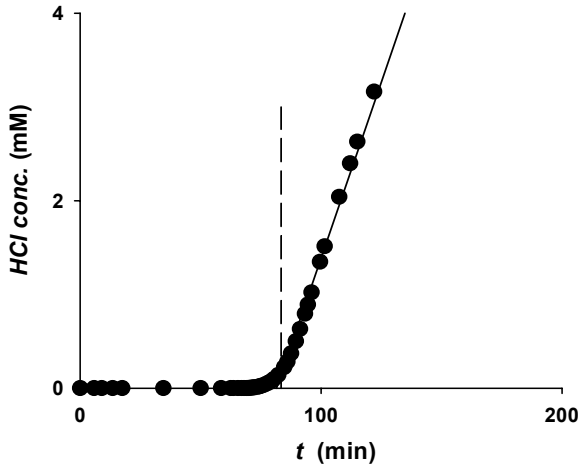

Figure 2 Breakthrough curve for a ZnO/PVA membrane challenged by HCl (C_{1up} = 0.01 M, C_{20} = 1.0 M, L = 154 μm, V_{down} = 12.8 mL, and V_{down} = 254 mL). The solid line is a regression of the linear part of the curve. The dotted line indicates the lag time.

Figure 3 shows concentration vs. time plots for the mobile product in the downstream and upstream cells. Figures 2 and 3 are from the same experiment. Note that the product concentration was much smaller in the upstream cell than in the downstream cell for most of the experiment because V_{up} was much larger than V_{down}. The product concentration in the upstream cell increased rapidly at the beginning, followed by a slow increase until the end. On the other hand, the product concentration in the downstream cell increased, reached a peak, and then decreased. The time when the maximum concentration was observed coincides with the lag time in Figure 2. This phenomenon is explained as follows. As long as ZnO remains in the membrane, there is a concentration peak of the product within the membrane, and the product concentration in the downstream cell keeps increasing. After the breakthrough, ZnO in the membrane is exhausted, and hence no more product is generated. The concentration peak within the membrane quickly vanishes, and the product diffusion is solely due to the remaining concentration gradient. Because the product concentration is higher in the downstream cell than in the upstream cell at the breakthrough, the product naturally starts to diffuse toward the upstream cell.

Figure 3 also shows that the analytical solutions to Equations (2) and (3) were successfully fit to the experimental data. This means that the analytical solution can describe the diffusion behavior of the product accurately. We used three fitting parameters, and their

values were determined as follows: P_1 = (6.61±1.58)×10^{-10} m^2/s, D_3 = (5.48±1.04) ×10^{-10} m^2/s, and a membrane-water partitioning coefficient of the mobile product = 0.676±0.342. Also, a comparison between the analytical solution and the numerical solution shows that the two solutions are almost identical. This suggests that the pseudo-steady state assumption made to derive the analytical solution was appropriate. The effects of the four parameters (C_{20}, C_{1up}, L, and V_{up}) on the maximum concentration of the product in the downstream cell were investigated both theoretically and experimentally. It was found that increasing the membrane thickness and the ZnO loading clearly increased the maximum concentration, while it was almost independent of the HCl concentration and the upstream cell volume.

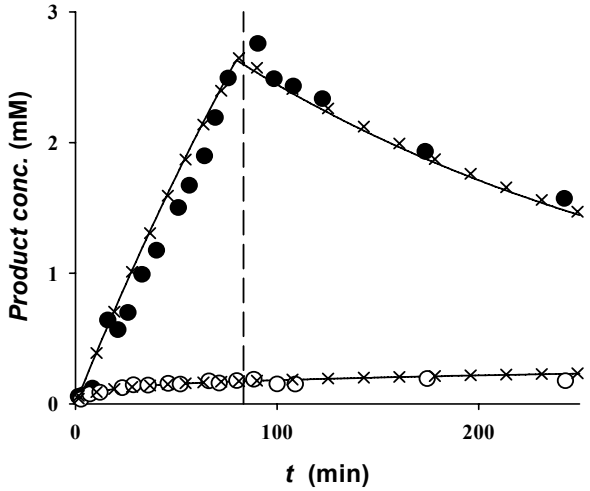

Figure 3 Concentrations of the mobile product in the downstream (●) and upstream cells (○). The solid lines are the model fit based on the analytical solution. The cross symbol (×) represents the numerical solution. The vertical dashed line indicates the lag time from Figure 2.

The results from this study will help predict how fast the immobilized chemical will be consumed, how fast the mobile product will diffuse out of the membrane, and the resulting concentration of the mobile produce on each side of the membrane for many practical applications. The presence of the maximum value in Figure 3 is especially interesting, and it may be exploited in useful ways.

References

1. Petratos, P. B., Chen, J., Felsen, D. and Poppas, D. P. (2002) "Local Pharmaceutical Release from a New Hydrogel Implant" J. Surg. Res. 103, pp. 55-60.
2. Zhao, J. and Wilkins, R. M. (2005) "Low Molecular Weight Polylactic Acid as a Matrix for the Delayed Release of Pesticides" *J. Agric. Food Chem.* 53, pp. 4076-4082.
3. Shimotori, T., Nuxoll, E. E., Cussler, E. L. and Arnold, W. A. (2004) Polymer Membrane Containing Fe^0 as a Contaminant Barrier" *Environ. Sci. Technol.* 38, pp. 2264-2270.
4. Yang, C., Nuxoll, E. E. and Cussler, E. L. (2001) "Reactive Barrier Films" *AIChE J.* 47, pp. 295-302.