Reactive Barrier Films

Chuanfang Yang, Eric E. Nuxoll, and E. L. Cussler
Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

Immobile reactive groups within films used as packaging materials can retard transport of solutes like oxygen and water vapor. A theory developed for these films shows that these groups do not affect the steady-state transport across the film, but that they do increase the time before permeability begins. The theory is verified by experiments with acid barriers made of polyvinylalcohol containing colloidal zinc oxide. These results imply that the time that barrier polymers are effective can be increased about two orders of magnitude. When reactive groups are combined with impermeable flakes, this time can be increased about three orders of magnitude. For example, a polymer barrier currently effective for one hour can be made effective for over one year.

Introduction

Barrier films are the key to packaging for products like food and electronics. For foods like coffee, beer, and meat, these films aim to exclude oxygen. For electronics, these films resist penetration of water, which can cause cracking of dielectric coatings like silica. For other high value added products including pharmaceuticals, the films may attempt to stop both oxygen and water.

In many cases, these barriers are made of metal films, which are normally highly impermeable to oxygen, water, and other solutes. However, for many products including meat and fish, consumers prefer packaging which is transparent and yet still flexible. This implies making these materials from flexible polymers, which are either above their glass transition temperature or are plasticized to become rubbery. Unfortunately, such polymers are often more permeable to oxygen and water than is desirable.

Faced with this challenge, we can make a better barrier film by reducing its permeability, by increasing its tortuosity, and by changing its reactivity. Each of these ideas merits discussion.

(1) Reducing Barrier Permeability. This strategy, which has received the most attention in the past, implies synthesizing new polymers with smaller permeabilities. Because the permeability is the product of the diffusion coefficient and the partition coefficient, we can get a smaller permeability either by reducing diffusion or partition. In glassy polymers, permanent gases like oxygen have similar partition coefficients and different diffusion coefficients, so the best hope is to seek new polymers with small diffusion coefficients. However, glassy polymers are not suitable for flexible packaging. In rubbery polymers, many solutes have similar diffusion coefficients but different partition coefficients so the best hope is to seek new polymers with small values of partition coefficients.

We believe that this area has already been broadly and deeply investigated by skilled polymer scientists. We have not made it a focus of this article.

(2) Increasing Barrier Tortuosity. A second route to better barriers is to incorporate impermeable flakes of materials like mica or clay into an existing polymer film. Smaller flakes like clay are preferred for food applications, because the film then remains transparent. Such flakes reduce permeability of any polymer by increasing tortuosity and reducing the area available for diffusion. Our past studies and others (Michaels et al., 1975; Wakeman and Mason, 1979; Cussler et al., 1988; Falla et al., 1996) show that these reductions depend only on the volume fraction and the shape of the flakes; they do not depend on the size of the flake or the properties of the polymer. In this sense, the results echo those of Clerk Maxwell (1881) for spheres and of Rayleigh (1892) for cylinders.

Using clay flakes can routinely reduce the permeability by a factor of ten and occasionally by a factor of one hundred. We will return to this potential reduction in our discussion of barriers later in the article. However, we have not made this strategy a focus of our experiments.

(3) Changing Barrier Reactivity. A third strategy for making better barrier films involves incorporating reactive groups into the membrane. These reactive groups then retard penetration of solutes like oxygen and water as they diffuse across the membrane. Reactive groups for oxygen suggested in the

---

Correspondence concerning this article should be addressed to E. L. Cussler.

patent literature center on double bonds in additives like castor oil or in the polymer backbone itself (Speer et al., 1996; Katsumoto and Ching, 1998; Schmidt et al., 1999; Gauthier and Speer, 1999). Reactive groups for water could include colloidal desiccants like silica gel and calcium oxide.

This strategy of reactive barrier films is the focus of this article. Interestingly, we should not expect these reactive groups to affect the steady-state permeability of these films, so that it does not supply a route to better membrane separations. The reactive groups do dramatically affect the time that a solute takes to first leak through the barrier.

In the next section, we develop a theory for reactive barrier films. We then report experiments which test this theory for acid barriers, chosen not because of their practical value, but because they clearly illustrate the ideas involved. Finally, we discuss how these ideas can supply a basis for developing better barriers for solutes like oxygen and water.

Theory

To see how solute penetrates a reactive barrier, we imagine a thin barrier separating two well-stirred solutions. The diffusing solute "1" is initially present in one solution, but not in the barrier or in the second solution. An immobile reagent solute "2" is present in the barrier, but not in the two adjacent solutions. At time zero, solute "1" begins to diffuse from the first solution across the barrier and into the second solution.

We want to find the concentration of the diffusing solute in this second solution as a function of time. To do so, we write mass balances within the barrier

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial z^2} - kc_1c_2 + k'c_3 \tag{1}$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial z^2} - kc_1c_2 + k'c_3 \tag{2}$$

$$\frac{\partial c_3}{\partial t} = D_3 \frac{\partial^2 c_3}{\partial z^2} + kc_1c_2 - k'c_3 \tag{3}$$

where c_3 is the concentration of reaction product, the D_i's are the appropriate diffusion coefficients; and k and k' are the forward and reverse reaction rate constants. These mass balances are subject to the conditions

$$t = 0 \quad \text{all } z \quad c_1 = 0 \quad c_2 = c_{20} \quad c_3 = 0 \tag{4}$$

$$t > 0 \quad z = 0 \quad c_1 = HC_{10} \tag{5}$$

$$z = \ell \quad c_1 = 0 \tag{6}$$

where H is a partition coefficient. Other conditions depend on details of the chemical reactions.

Many solutions to Eqs. 1–6 are known. The most familiar is the case for no chemical reaction, for which (Daynes, 1920; Crank, 1975)

$$\frac{c_1}{HC_{10}} = 1 - \frac{z}{\ell} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\sin(n\pi z/\ell)}{n} e^{-Dn^2\pi^2 t/\ell^2} \tag{7}$$

The concentration in the second solution is found from another mass balance

$$V\frac{dC_1}{dt} = A\left(-D\frac{\partial c_1}{\partial z}\bigg|_{z=\ell}\right) \tag{8}$$

subject to

$$t = 0 \qquad C_1 = 0 \tag{9}$$

In these results, A is the barrier area and V is the volume of the second solution. The result at larger times is

$$\frac{C_1}{C_{10}} = \left[\frac{DH}{\ell}\left(\frac{A}{V}\right)\right]\left(t - \frac{\ell^2}{6D}\right) \tag{10}$$

When C_1 is plotted vs. t, the slope gives a measure of the permeability (DH). The intercept, often called the "lag time," allows estimates of the diffusion coefficient D (Paul, 1971; Paul and Koros, 1976).

The solutions of Eqs. 1–6 for reacting systems are more complex and less familiar (Aris, 1975; Gough and Leypoldt, 1980; Siegel, 1991). In this section, we will consider only three cases, all assuming fast reaction. In more quantitative terms, this means that the various Damkohler numbers, like ($k'\ell^2/D_3$), are much greater than one. In the first two cases, we will consider fast, reversible reactions with excess species "2." In the third case, we turn to a fast, irreversible reaction with a finite amount of reagent "2." We will discuss cases of slower chemical reactions later in this article.

When the reaction rates are fast and reversible, we expect that within the membrane

$$c_3 = \left(\frac{k}{k'}\right)c_1c_2 \tag{11}$$

When species "2" is present in excess, this may be written as

$$c_3 = Kc_1 \tag{12}$$

where the apparent equilibrium constant K equals (kc_2/k'). This equilibrium does not mean that the reaction terms in Eqs. 1–3 sum to zero, but that they are indeterminant, the product of large rate constants and small concentration differences.

We now turn to the first special case, which has been widely studied as a form of "facilitated diffusion" (Cussler, 1997). In this case, we assume that all diffusion coefficients are equal, that is, $D_1D_2 = D_3$. In this limit, we add Eqs. 1 and 3 and insert Eq. 12 to find

$$(1+K)\frac{\partial c}{\partial t} = D(1+K)\frac{\partial^2 c_1}{\partial z^2} \tag{13}$$

Because the boundary conditions on Eq. 13 are also those in Eqs. 4–6, the solution of Eq. 13 is that given in Eq. 7. However, Eq. 8 is now

$$V\frac{dC_1}{dt} = AD\left(-\left.\frac{\partial c_1}{\partial z}\right|_{z=\ell} - \left.\frac{\partial c_3}{\partial z}\right|_{z=\ell} \right)$$

$$= AD(1+K)\left.\left(-\frac{\partial c_1}{\partial z} \right)\right|_{z=\ell} \quad (14)$$

again subject to Eq. 9. After some work, we find

$$\frac{C_1}{C_{10}} = \left[\frac{DH}{\ell}(1+K)\frac{A}{V}\right]\left(t - \frac{\ell^2}{6D}\right) \quad (15)$$

In this first, facilitated diffusion case, the flux is *increased* by a factor of $(1+K)$ because species "1" can cross the membrane either in a free state or complexed to form species "3". However, the lag time is unchanged from Eq. 10, the case without reaction. This prediction of unaltered lag time is not always supported experimentally, perhaps because of unequal diffusion coefficients (Ward, 1970). Nonetheless, the reaction causes the barrier to be breached more quickly, which is the antithesis of what we want.

The second special case of interest assumes the same fast reaction leading to Eq. 12, but also assumes that both reagent and product are immobile. In other words, D_2 and D_3 are zero. In this case, Eq. 1 and Eq. 3 are again added and combined with Eq. 12 to find Eq. 13. This result again has the solution given in Eq. 7, but with D replaced by $D/(1+K)$. Now, however, the material crossing the membrane is *not* given by the mass balance in Eq. 14, but by that in Eq. 8. Thus the result corresponding to Eq. 10 and Eq. 15 is

$$\frac{C_1}{C_{10}} = \left[\frac{DH}{\ell}\frac{A}{V}\right]\left(t - \frac{\ell^2}{6D}(1+K)\right) \quad (16)$$

When the reaction involves immobile reagents and products, the flux at longer times is not changed from the case without reaction. Phrased in other terms, the rate of solute leaking through the barrier is unaffected once the reaction is in equilibrium at all positions. However, the lag time in Eq. 16 is increased by a factor of $(1+K)$ over the lag time without reaction given in Eq. 10. This larger lag means a better barrier.

The third special case discussed in this section also assumes a fast reaction with an immobile reagent. Now, however, we also assume that the amount of reagent is finite and that the reaction is irreversible. In this case, we can find an approximate analytical solution if we assume that all the reaction occurs at a front, located at a time dependent position $\ell'(t)$. When this reaction front moves slowly, the mass balance on the solute diffusing between $z=0$ and $z=\ell'$ is

$$0 = D\frac{d^2 c_1}{dz^2} \quad (17)$$

subject to

$$z = 0 \qquad c_1 = HC_{10} \quad (18)$$

$$z = \ell' \qquad c_1 = 0 \quad (19)$$

Thus

$$j_1 = -D\left.\frac{dc_1}{dz}\right|_{z=\ell'} = \frac{DH}{\ell'}C_{10} \quad (20)$$

Because the reaction front moves slowly, we make an unsteady-state mass balance on the immobile reagent

$$\frac{d}{dt}(A\,\ell' c_{20}) = \nu A j_1 \quad (21)$$

where ν is a stoichiometric coefficient, the number of moles of species "2" consumed by a mol of species "1." This is subject to

$$t = 0 \qquad \ell' = 0 \quad (22)$$

Combining Eqs. 20–22, we find

$$\ell' = \left[\frac{2\nu DHC_{10}t}{c_{20}}\right]^{1/2} \quad (23)$$

When ℓ' equals ℓ, we have exhausted all the reagent within the barrier film. After this lag time, the flux is just the steady-state result. As a result

$$\frac{C_1}{C_{10}} = \left[\frac{DH}{\ell}\frac{A}{V}\right]\left[t - \frac{\ell^2}{2\nu DH}\left(\frac{c_{20}}{C_{10}}\right)\right] \quad (24)$$

This result is not exact, for it says that there is no lag time if c_{20} is zero, while in fact the lag is given by Eq. 10. This discrepancy is a consequence of the pseudo-steady-state approximation in Eq. 17. We will see below that the lag predicted in Eq. 24 for any significant irreversible reaction is much larger than that in Eq. 10, for no reaction.

The results in this section suggest ways to estimate altered permeability in reactive barrier films. These results are summarized in Table 1. Note that the steady-state permeability is enhanced by reactions with mobile reagents and unaltered by

Table 1. Predicted Properties of Reactive and Nonreactive Barriers*

Type of Barrier	Permeance	Lag Time	Key Eq.
Nonreactive	$\frac{DH}{\ell}$	$\frac{\ell^2}{6D}$	(10)
Reversible Reaction Yielding a Mobile Product**†	$\frac{DH}{\ell}(1+K)$	$\frac{\ell^2}{6D}$	(15)
Reversible Reaction Yielding an Immobile Product**	$\frac{DH}{\ell}$	$\frac{\ell^2}{6D}(1+K)$	(16)
Irreversible Reaction Yielding an Immobile Product	$\frac{DH}{\ell}$	$\frac{\ell^2}{2\nu DH}\frac{c_{20}}{C_{10}}$	(24)

*The values given are for a solute diffusing across a barrier into a volume, when both barrier and volume are initially solute free.

**This assumes excess reagent, as suggested by Eqs. 11–12.

†This is a case of "facilitated diffusion."

reactions with immobile reagents. Note also that the lag times are unaltered with mobile reagents but increased by reactions with immobile reagents. Because the increases in lag times are potentially large, they suggest the experiments described in the next section.

Experimental Studies

Hydrochloric acid (Mallinckrodt), sulfuric acid (Fisher), acetic acid (Aldrich), nitric acid (EM Science), and zinc oxide (Aldrich, ≤ 1 μm) were all reagent grade and were used as received. All water was doubly distilled. Barrier films were made of polyvinylalcohol (DuPont Elvanol grade 71-30, molecular weight 138,000–146,500) as follows. A 5–10 wt. % solution was prepared by heating with stirring at 90°C for one to four hours. If desired, zinc oxide was added. The solution was carefully degassed under vacuum for half an hour. The films were then cast on glass or Teflon, using a doctor blade. They were dried overnight, and baked one hour at 150°C. The resulting films are slightly yellow and strong. The films were swelled in water for at least one day, which roughly doubles their mass; as used, they are about half water.

These films were mounted in a Teflon diaphragm cell shown in Figure 1. Each compartment of the diaphragm cell was 15.0 cm^3, and the film area between the compartments was 5.3 cm^2. Each compartment was stirred at approximately 80 rpm; cutting the stirring in half did not affect the transport rate. To start an experiment, aqueous acid, typically at a concentration C_{10} of 0.15 M, was placed in one compartment. The acid concentration in the second compartment C_1, with an initial pH around 8, was measured vs. time with an Orion 420A pH electrode attached to a Mac SE/30 data acquisition system. The pH in this second receiving compartment never exceeded 4, so that this second acid concentration C_1 is always much less than that in the first compartment C_{10}. As a result, the data can be analyzed with the equation

$$\frac{C_1}{C_{10}} = \left[\frac{DH}{\ell}\left(\frac{A}{V}\right)\right](t - t_o) \qquad (25)$$

which has the same form as Eqs. 10 and 24. As a result, the normal exponential relation used for the diaphragm cell is not necessary.

Results

The theory developed above predicts that films with reactive groups have dramatically different behavior than films without these groups. When the reactive groups are mobile, the theory predicts the familiar increased permeability typical of facilitated diffusion, which is the key to liquid membrane separations (Cussler, 1997). When the reactive groups are immobile, the theory predicts a steady-state permeability which is little changed from the nonreactive case. The theory also predicts a greatly increased time to reach steady state, that is, a large lag time. This increased lag time is the focus of the experimental results reported here.

We wanted to measure lag times which were experimentally convenient, typically around a few minutes to an hour. In fact, the patented barrier films for oxygen and other solutes suggest chemistries which have lag times of months or more (Schmidt et al., 1999). We decided not to measure oxygen barriers, but to invent a model system which could be more easily studied.

We choose to study water-swollen films of polyvinylalcohol loaded with colloidal zinc oxide. When the zinc oxide is absent, acid will diffuse across this film quickly. When zinc oxide is present, acid permeability will lag for half an hour or so. These are not attractive properties for a commercial bar-

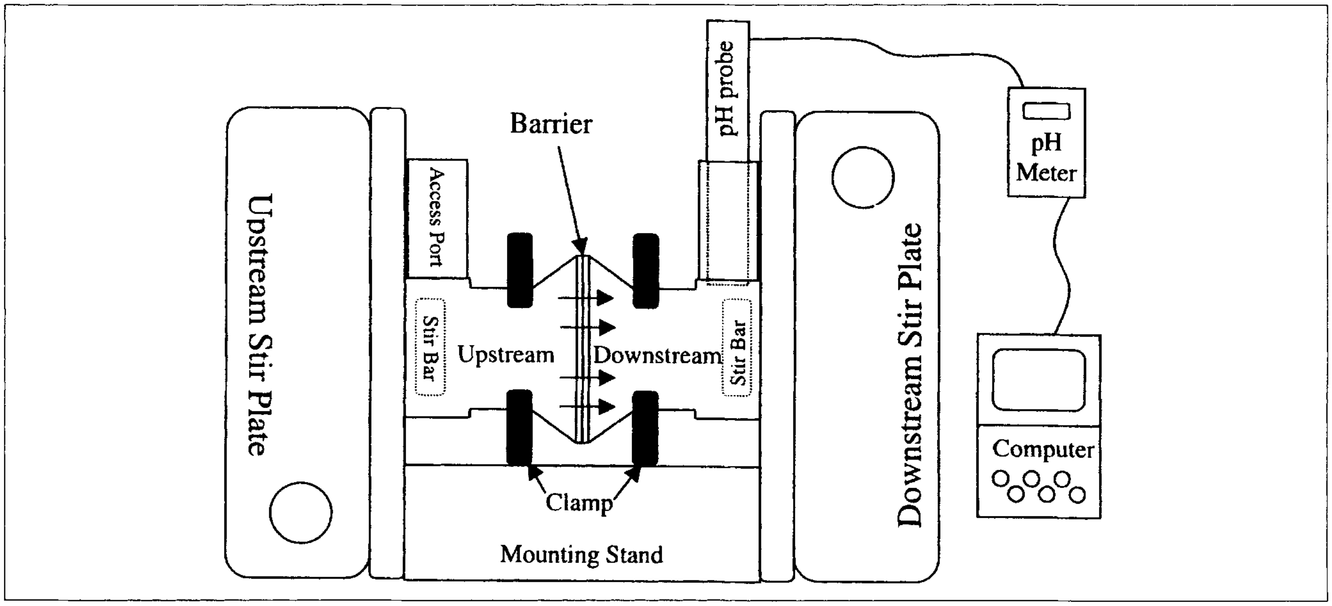

Figure 1. Experimental apparatus.

Two well-stirred volumes are separated by a barrier film containing reagent. Acid diffusing from left to right across the barrier is measured vs. time with the electrode shown.

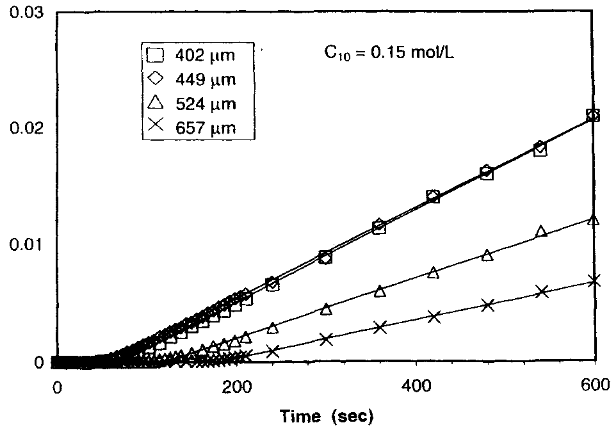

Figure 2. Typical data.

Acid diffusion in the apparatus shown in Figure 1 shows a lag time followed by a linear increase. The feed solution is 0.15 M HCl.

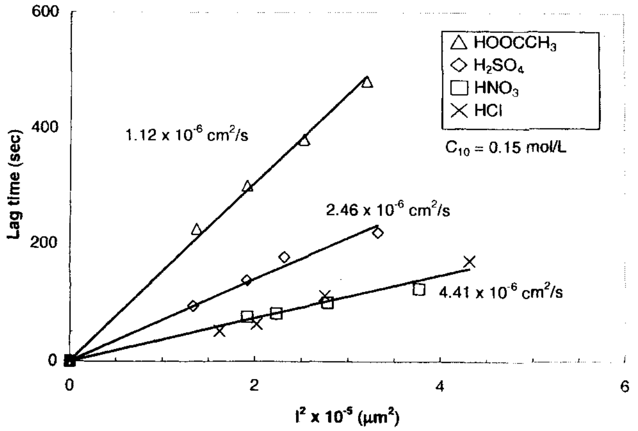

Figure 4. Lag times vs. barrier thickness.

As expected, the lag time varies with the square of thickness for all the films studied. The diffusion coefficients inferred from these lags are shown on the different lines.

rier film, but they are easy times to measure experimentally, and so provide an effective way to check our theory. If the theory is successful, we can speculate on the design of new barrier systems.

We will find it easiest to discuss the results of this model system in two parts. First, we will discuss the results without zinc oxide, which illustrate the nonreactive case developed above. Then we move onto the reactive case, with its much longer lags.

Nonreactive Films. Typical experimental results for a nonreactive film are shown in Figure 2. As suggested by Eq. 25, the acid concentration C_1 keeps its initial value of zero for a while, and then rises linearly with time. We can use Eq. 10 and data like these to find the partition coefficient H and the diffusion coefficient D. The partition coefficient H has a value of 0.92; it is close to one because the film is swollen with water. The diffusion coefficient is found to be 4.4×10^{-6} cm^2/s, somewhat less than the value in water. Again, this seems reasonable, for the polymer chains should slow the diffusion.

Both the partition coefficient and the diffusion coefficient depend on the acid which is diffusing, as shown in Figure 3. The values of HCl and HNO$_3$ are similar, perhaps because the diffusion coefficients of these acids in water are the same. Sulfuric acid is slower, like its diffusion in water. Acetic acid is the slowest, for reasons that are not clear to us. Perhaps the partition includes altered ionization; perhaps the polymer chains restrict transport of the larger acetate.

As expected from Eq. 10, the lag times for all these acids vary with the square of the film thickness, as shown in Figure 4. Note that these lags are short: for HCl, a film 602 μm thick gives a lag of around two minutes. This is dramatically shorter than the results for reactive barriers, discussed next. For now, however, Figures 2–4 provide reassurance that the nonreactive films are behaving just as anticipated by Daynes' original 1920 article.

Reactive Films. The results for reactive barrier films are very different, as shown in Figure 5. Now, a 602 μm film with 10% zinc oxide has a lag not of two minutes but of almost an hour. The data in Figure 5 also show different slopes and

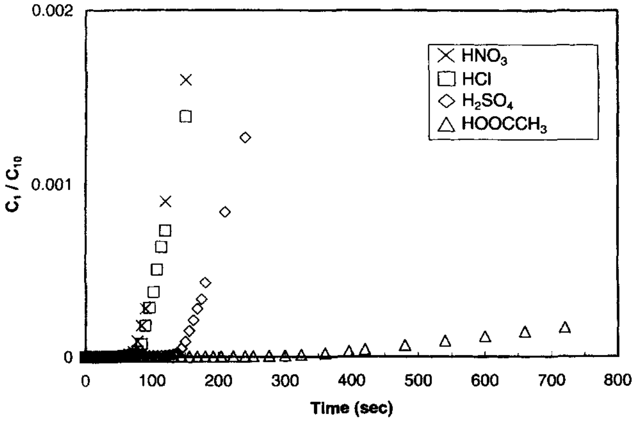

Figure 3. Lag times for different acids.

The data, for 0.15 M acid diffusing across a 438 μm barrier, show the effect of anion partitioning.

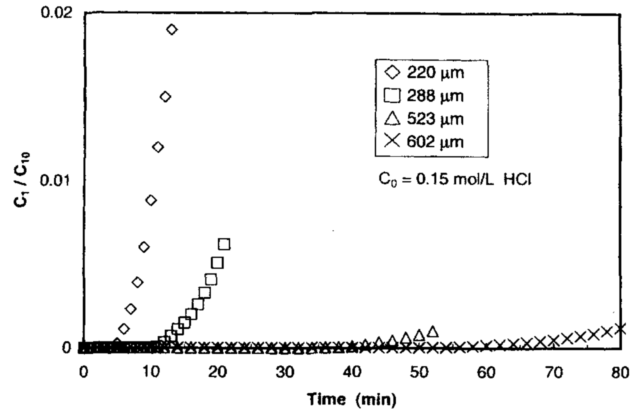

Figure 5. Lag times in a reactive barrier.

This barrier, containing 10 wt. % ZnO, is challenged with 0.15 M HCl.

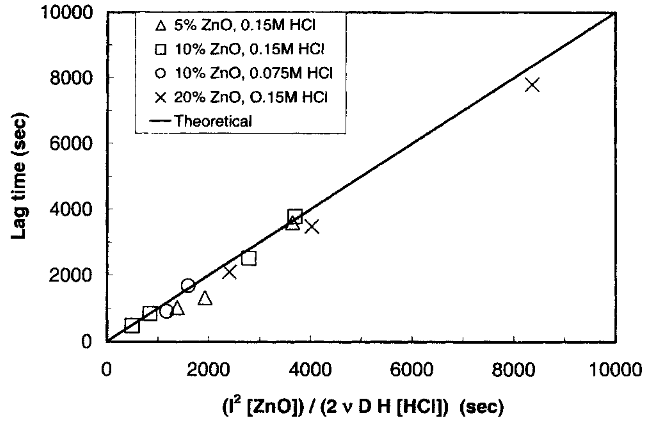

Figure 6. Experimental vs. predicted lag times.

The experimental values, found from data like those in Figure 5, agree closely with those predicted from Eq. 24, shown as the solid line.

hence different permeances, but this is largely the result of different thicknesses. The dramatic change is in the lag time.

We can use results like those in Figures 2 and 5 to check the theory developed above. For this case of acid reacting with zinc oxide, the lag time is predicted by Eq. 24. In this equation, the film thickness ℓ, the concentration of the immobile reagent c_{20}, and the acid concentration C_{10} are measured for the particular experiment. The stoichiometric coefficient ν is two: two moles of HCl react with each mol of ZnO. The diffusion coefficient D and the partition coefficient H can be found using Eq. 10 from the intercept and slope of data like those in Figure 2. Thus, we can predict the lag times from Eq. 24.

These predicted lag times are plotted vs. the experimental values in Figure 6. The solid line shown on the figure is not the best fit of the data, but the relation expected from Eq. 24. Theory and experiment agree remarkably well. We are especially pleased that the data are consistent with the factor of two on the abscissa. The original derivation for a nonreactive film predicts a factor of six (cf. Eq. 10). This is inconsistent with our data.

At the same time, the measured lag times in Figure 6 are slightly less than those predicted. More specifically, a best fit of the data does not give a slope of 1.00, but of 0.95. In some cases, this may be due to reactions in the barrier which are not instantaneous, an important point which we will discuss in more detail later. In this acid barrier case, we suspect that this small discrepancy is more likely due to nonuniform dispersion of the zinc oxide. If the film had some regions with less ZnO, these depleted regions would leak acid first, and give a reduced slope on a plot like Figure 6.

Finally, we should stress that the effects discussed in this article have been observed by others. Ironically, they have sometimes been viewed as an annoyance interfering with the mechanism of steady-state transport. For example, Wen and Kocherginsky (2000) studied diffusion of acids across polyacrylonitrile membranes, and found unexpectedly long lag times. They attributed these lag times to reversible protonation of the nitrile group. This is consistent with the arguments presented in this article, although the Wen and Kocherginsky case studied lies between the cases of a reversible reaction with an immobile product and an irreversible reaction with an immobile product summarized in Table 1. The effects in this article may also have contributed to difficulties in reproducing reported selectivities in other reactive membranes.

Discussion

The results above support the theory derived earlier, and so provide a strong rationale for building better barrier films. However, the results are for barriers to acid, and not commercially interesting barriers to oxygen or water. As result, we now should address two important questions:

(1) If the theory is right, how good a barrier can we make for oxygen or water?

(2) What about the theory is most likely to be wrong when it is applied to these systems?

We will partially answer these questions in this section.

Estimated lag times

We begin by considering how good a barrier we can expect to make for acid, oxygen, and water. To answer this question, we first assume that all such barriers will contain impermeable flakes which increase the tortuosity and hence reduce the diffusion. This change in diffusion is approximately given by Cussler (1997)

$$\frac{D}{D_o}=\frac{1}{1+\alpha^2\phi^2}$$

where ϕ is the volume fraction of flakes and α is their aspect ratio. Thus, if our films are 10% flakes with an aspect ratio of thirty, then diffusion in a flake-filled film will be one-tenth in that of a film without flakes.

We now turn to specific properties of barriers for acid, oxygen and water, as summarized in Table 2. For acid, we consider a 602 μm film of the polyvinylalcohol used in the experiment above. For a nonreactive, flake-free film, the permeance (DH/ℓ) is 5.9×10^{-5} cm^2/s and the lag time ($\ell^2/6D$) is 2 min. For a water-swollen flaked-filled reactive film containing 0.20 g ZnO cm^3, the permeance is 5.9×10^{-6} cm^2/s, ten times less because of the flakes. The lag time changes more dramatically (cf. Eq. 24)

$$\frac{\ell^2}{2\nu DH}\frac{c_{20}}{C_{10}}$$

$$=\frac{(0.0602\ \text{cm})^2}{2\left(\frac{1}{2}\right)\left[\frac{1}{10}4.2\times10^{-6}\frac{\text{cm}^2}{\text{s}}\right](0.92)}\ \frac{\dfrac{0.20\ \text{mol}}{\text{cm}^3\ 81.4\ \text{g}}}{\dfrac{0.15\times10^{-3}\ \text{mol}}{\text{cm}^3}}=43\ \text{h}$$

The increase in lag, over three orders of magnitude, is about one-third the effect of the flakes and two-thirds the result of the zinc oxide. Reactive barriers can work better.

For barriers to oxygen and water, we give estimates in Table 2 for three polymers: low density polyethylene, an inexpensive benchmark; polyacrylonitrile, an excellent oxygen barrier; and polyvinylidene chloride or Saran, a common food

Table 2. Estimated Permeances and Lag Times for Nonreactive and Flake Filled Reactive Barrier Films*

		Non-Reactive		Reactive, with Flakes		
Solute	Polymer	Permeance, cm/s**	Lag Time	Reagent	Permeance, cm/s	Lag Time
Hydrochloric Acid	Polyvinyl alcohol	$5.9\times10^{-5\dagger}$	2 min	0.2 g/cm^3 ZnO	7×10^{-6}	10 h
Oxygen‡	Low density polyethylene	1.0×10^{-5}	2 s	0.1 g/cm^3 linolenic acid	1.0×10^{-6}	40 h
	Polyacrylonitrile	6.8×10^{-10}	—		6.8×10^{-11}	70 years
	Polyvinylidene chloride	1.7×10^{-8}	—		1.7×10^{-9}	3 years
Water§	Low density polyethylene	3.0×10^{4}	2 s	0.1 g/cm^3 CaO	3.0×10^{-5}	15 h
	Polyacrylonitrile	2.2×10^{-3}	—		2.2×10^{-4}	2 h
	Polyvinylidene chloride	3.2×10^{-5}	30 s		3.2×10^{-5}	14 h

*In the acid case, the film is assumed to be 602 μm thick. In all other cases, it is assumed to be 25 μm thick. In all cases, the volume of clay flakes of 30 aspect ratio is 10%.

**Estimated from Polymer Handbook, except as noted.

†Without flakes; interpolated from experiments in this work.

‡At 0.21 atm.

§Saturated vapor at 25°C.

packaging material. Because these polymers are normally used as thin films, we assume only a 25 μm thickness. From the permeabilities (DH) given in the literature, we can easily calculate the permeances (DH/ℓ) shown in the table. Because diffusion coefficients are less commonly given, we cannot calculate the lag times, but believe these are normally less than a minute.

The reactive films are very different. Again, we assume the films contain 10% flakes. For oxygen, we take the oxygen in air and the reactive species as linolenic acid, a component of one of the drying oils which one barrier patent suggests blending into olefins (Speer et al., 1996). For water, we assume saturated water vapor at 25°C and the reactive species as calcium oxide, a common dessicant.

The results shown in Table 2 again assume that the permeance in the reactive film just drops ten times because of the flakes. Again, the effect on the lag times is more dramatic. For example, for oxygen diffusing across polyvinylidene chloride, the lag is now about three years. The lags for water are shorter, because the smaller water molecule has a higher permeance in these polymers.

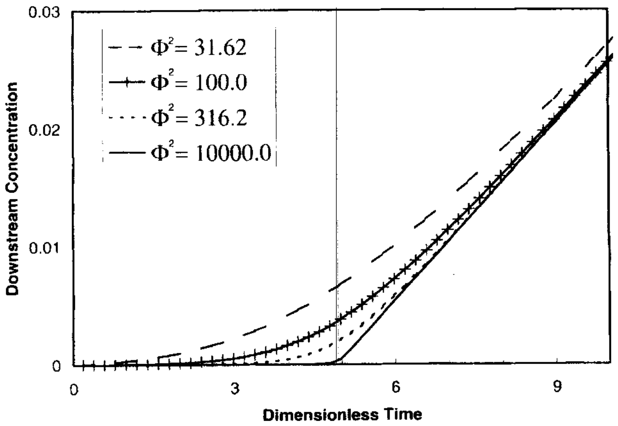

Figure 7. Downstream concentration as a function of time and reaction rate.

The results shown give the dimensionless concentration C_1/C_{10} as a function of the dimensionless time (Dt/ℓ^2) and the Thiele modulus $(kc_{20}\,\ell^2/D)^{1/2}$.

What part of the theory will fail?

Because of the large lag times estimated in Table 2, we are now interested in when the theory will fail. To be sure, the theory works well for barriers to acid. Will it work for other solutes like oxygen?

We believe that the answer to this question depends most significantly on the rate of the reaction between the mobile solute and the immobile reactant. To explore this argument more completely, we consider only the case of irreversible reaction. When this reaction is very fast, as it is for diffusing hydrochloric acid reacting with colloidal zinc oxide, then the analysis culminating in Eq. 24 will be accurate, as shown by the results in Figure 6. When this reaction is very slow, it won't affect transport, and the concentration will change as suggested by Eq. 10.

However, what if the reaction is neither very fast nor very slow? To answer this question, we must rewrite Eqs. 1–2 as

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial z^2} - kc_1c_2 \tag{26}$$

$$\frac{\partial c_2}{\partial t} = -kc_1c_2 \tag{27}$$

where the diffusion coefficient D_2 has been set equal to zero because the reactive species "2" is immobile. These equations are still subject to the constraints in Eqs. 4–6. Now, however, because the reaction rates are not infinitely fast, we cannot make the pseudo-steady-state approximation in Eqs. 17–21. Now, we really must solve the problem.

We have solved this problem by finite difference methods to get the concentration as a function of position, time, and a new variable within the membrane. The new variable is the Thiele modulus Φ, defined as

$$\Phi^2 = \frac{k\,\ell^2 c_{20}}{D_1} \tag{28}$$

From this concentration profile, we can find the flux which has crossed the membrane (at $z = \ell$). We then can calculate the downstream concentration as a function of time from Eq. 8.

The results, shown in Figure 7, are both expected and surprising. As expected, a slower reaction rate means that the downstream concentration rises earlier. Surprisingly, the lag time is independent of reaction kinetics. In hindsight, we can rationalize this by recognizing that at large times, the details of the reaction will be less important. The only significant issue will be the total amount of reagent, which will determine the lag time. We plan to explore this important point in considerably more detail in future experiments. For the present, we note only that the theory presented here should be accurate when the Thiele modulus is one-hundred or greater. In any case, reactions with immobile sites can dramatically improve the properties of thin polymer films.

Acknowledgments

This work was supported by the Department of Defense (DOD DAA H04-95-1-0094) and by the National Science Foundation (CTS 96-27361). Chuanfang Yang was partially supported by the Li Foundation. E. E. Nuxoll holds an NSF graduate fellowship.

Notation

A = barrier area
α = aspect ratio of flakes
c_i = concentration of species i inside the barrier
C_i = concentration of species i outside the barrier
D_i = diffusion coefficient of species i
H = partition coefficient
k, k' = forward and reverse reaction rate constants
K, K' = equilibrium constants
ℓ = barrier thickness
ℓ' = thickness of reacted layer
ϕ = volume fraction of flakes
t = time
t_o = lag time
V = volume of adjacent solution
ν = stoichiometric coefficient
z = position

Literature Cited

Aris, R., *Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Clarendon Press, Oxford (1975).

Crank, J., *The Mathematics of Diffusion*, Clarendon Press, Oxford (1975).

Cussler, E. L., S. E. Hughes, W. J. Ward, and R. Aris, *J. Memb. Sci.*, **38**, 161 (1988).

Cussler, E. L., "Facilitated and Active Transport," D. R. Paul and Y. P. Yampolskii, eds., CRC Press, Boca Raton, FL, 273 (1994).

Cussler, E. L., *Diffusion*, Cambridge University Press, Cambridge (1997).

Daynes, H., *Proc. Roy. Soc.*, **A97**, 286 (1920).

Falla, W. R., M. Mulski, and E. L. Cussler, "Estimating Diffusion through Flake-Filled Membranes," *J. Memb. Sci.*, **119**, 129 (1996).

Gauthier, W. D., and D. V. Speer, "Methods and Compositions for Improved Oxygen Scavenging," U.S. Patent No. 5,981,676 (Nov. 9, 1999).

Gough, D. A., and J. K. Leypoldt, "A Novel Rotated Disk Electrode and Time Lag Method for Characterizing Mass Transport in Liquid-Membrane Systems," *AIChE J.*, **26**, 1013 (1980).

Katsumoto, K., and T. Y. Chang, "Multicomponent Oxygen Scavenging Composition," U.S. Patent No. 5,776,361 (July 7, 1998).

Maxwell, J. Clerk, *Treatise on Electricity and Magnetism*, Clarendon, Oxford (1881).

Michaels, A. S., S. K. Chandrasekaran, and J. E. Shaw, "Drug Permeation through Human Skin," *AIChE J.*, **21**, 985 (1975).

Paul, D. R., "Membrane Separation of Gases Using Steady Cyclic Operation," *IEC Proc. Des. Dev.*, **10**, 375 (1971).

Paul, D. R., and W. J. Koros, "Effect of Partially Immobilizing Sorption on Permeability and the Diffusion Lag Time," *J. Poly. Sci. Poly. Phys. IV*, 675 (1976).

Schmidt, S. L., W. N. Collette, E. A. Coleman, and S. M. Krishnakumar, "Transparent Package with Aliphatic Oxygen Scavenger," U.S. Patent No. 5,592,066 (Sept. 14, 1999).

Siegel, R. A., "Algebatic, Differential and Integral Relations for Membranes in Series," *J. Phys. Chem.*, **95**, 2556 (1991).

Speer, D. V., C. R. Morgan, W. P. Roberts, and A. W. VanPutte, "Multilayer Structure for a Package for Scavenging Oxygen," U.S. Patent No. 5,529,833 (June 25, 1996).

Strutt, W., Lord Rayleigh, "On the Influence of Obstacles Arranged in Rectangular Order upon the Properties of a Medium," *Philos. Mag.*, **34**, 481 (1892).

Wakeman, W. A., and E. A. Mason, "Diffusion in Multiperforate Laminae," *Ind. Engr. Chem.*, **18**, 301 (1979).

Ward, W. J., III, "Analytical and Experimental Studies of Facilitated Transport," *AIChE J.*, **16**, 405 (1970).

Wen, L., and N. M. Kocherginsky, "Coupled H^+/Anion Transport Through Polyanaline Membranes," *J. Memb. Sci.*, **1**, 31 (2000).

Manuscript received Apr. 27, 2000, and revision received Aug. 9, 2000.