

Measurement of Oxygen Transport Parameters in Polymer Films Initially Saturated with Air

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Synopsis

The solubilities and diffusion coefficients of gases in polymer films can be determined from dynamic transport experiments. In the standard approach, a film initially free of the permeant of interest must be used. A new variation on the standard approach is presented for determining the transport parameters of oxygen from a transient experiment. The initial condition in the film is the normal oxygen saturation pressure (0.21 atm) and the applied oxygen pressure on the high side is 1 atm. Whereas this technique is generally applicable, it is particularly convenient for oxygen transport experiments because films stored in air do not have to be degassed before starting the experiment.

INTRODUCTION

The solubilities and diffusion coefficients of permeants in polymers are routinely measured by any of a number of variations on the diffusion cell technique originally proposed by Daynes.¹ In the usual experimental procedure, a polymer film, initially free of gas, is mounted in a diffusion cell. One face of the film is exposed to a chamber filled with a high pressure of gas; the other is exposed to an initially evacuated chamber in which the pressure is monitored with time. The flux of gas from the film into the low pressure chamber is zero at the beginning of the experiment. When the diffusion front from the high pressure side breaks through, the flux increases to a constant, maximum value as the "steady state" concentration profile is established across the film. At this point the downstream pressure increases linearly with time. The pressure continues to increase linearly until the pressure difference across the film begins to deviate appreciably from the initial value.^{2,3} The permeability of the film can be calculated from the steady state flux (the slope of the pressure vs. time curve). The diffusion coefficient can be calculated using the classic time lag technique,^{1,4} in which the steady state portion of the pressure vs. time curve is extrapolated back to zero pressure. Because the permeability is equal to the product of the solubility and the diffusion coefficient,⁵ the solubility is readily calculated.

Flow-through diffusion cells can offer advantages over the traditional apparatus described above.⁶⁻⁹ The experimentally accessible variable is the flux (rather than the integrated flux); a convenient way to determine the diffusion

coefficient is from the time required for the flux to increase from zero to one half of its steady state value.⁹

A practical problem arises (for either flow or nonflow experiments) when oxygen transport experiments are conducted. A film that has been stored in air must be degassed by sweeping an inert gas past both surfaces to remove oxygen diffusing out of the film. The time required for degassing, especially for good barrier films of even moderate thickness, can be quite long. For example, if we use the expression for time lag $\delta^2/6D$ as a characteristic response time, a 5-mil polycarbonate film responds in several minutes at room temperature. The response time of a 5-mil polyethylene terephthalate film, on the other hand, is many hours. It would be very convenient to perform dynamic oxygen transport experiments starting with films saturated at the ambient oxygen pressure so that the degassing step could be eliminated for good barriers.

Fatt¹⁰ recognized that the permeant free initial condition is not always convenient in time lag measurements. He devised a modified time lag experiment for nonflow systems. In this approach, a film is initially at equilibrium with the gas in both chambers. At time zero the low pressure side is evacuated. The flux out the film is rapid at first as the low pressure side of the film degasses and slowly decays to the steady state value. The steady state portion of the pressure vs. time plot can be extrapolated back to zero pressure to determine a modified time lag (negative in value) which can be related to the diffusion coefficient. While this technique works for air-saturated films, it requires that air at 1 atm can be used to provide the driving force. In many cases, however, especially with good barrier films, more than 0.21-atm driving force is desired.

In this paper we describe a new technique suited for measurements in flow cells for determining the diffusion coefficient of oxygen in polymers from the dynamic response of films initially saturated with ambient oxygen. A requirement for this technique to work is that at time zero the oxygen partial pressure on the high side is substantially higher than the initial 0.21 atm in the film. One atmosphere of oxygen pressure is adequate; the primary limitation is the sensitivity of the detector.

As in the traditional techniques, the flux of oxygen from the film into the low pressure side is monitored with time. At the beginning of the experiment, a large flux is observed because the initial charge of oxygen degasses. The flux decays as the degassing proceeds until the diffusion front from the high pressure side breaks through. At this point the flux begins to increase again until the steady state flux is achieved.

An analytical expression for the time of the flux minimum has been derived and can be used to determine the diffusion coefficient. The time of the minimum depends upon the ratio of the initial to high side concentrations in the film. If the experiment is done at room temperature, this ratio of concentrations is equal to the ratio of the partial pressure for equilibration to that on the high side of the film during the experiment and can therefore be readily determined. Also, we will show that the steady state permeability of a film can be predicted from the magnitude of the flux at the flux minimum.

We present first the results of conventional oxygen transport experiments on degassed polycarbonate and polyetherimide films to determine the permeabilities and diffusion coefficients. Next we show the transient response of the

same films that are initially saturated with air. Finally, we develop an analytical expression for the time of the flux minimum and compare the results of this new technique to those of the traditional one.

EXPERIMENTAL

Oxygen flux measurements were made with a MOCON Ox-Tran 100, which is a commercially available instrument. The Ox-Tran is based on a flow system in which oxygen passes by one side of the film mounted in a diffusion cell and an inert carrier gas flows by the other side of the film. The carrier gas sweeps oxygen that has diffused through the film to a detector. The Ox-Tran 100 has a sensitive electrochemical detector that makes it possible to measure extremely low concentrations of oxygen in the inert carrier gas. Further details of the MOCON Ox-Tran operation are given elsewhere.¹¹

The MOCON Ox-Tran 100 comes equipped with sample holder (diffusion cell) that provides a 100 cm² circular diffusion area. A new brass diffusion cell was machined for these experiments for two reasons. First, because the permeability of oxygen in the materials considered here is extremely high, a new cell was designed to provide only 5 cm² of diffusion area to cut down the signal to the detector. Second, the total gas volume in the cell was greatly reduced to minimize the carrier gas holdup. Therefore, the plug-flow time lag in the tubing between the brass block and the detector was small and could be neglected in the calculations.

The brass block was jacketed with copper tubing to permit passage of water from a temperature bath to provide an isothermal environment. Temperature was measured with a Stow Laboratories electronic thermometer model 911 PL.

On the top side of the film, a pure oxygen gas stream at 1 atm pressure was passed to provide the "high" pressure driving force for permeation. On the "low" pressure side of the film, an argon carrier gas stream swept oxygen that had diffused through the film to the detector. The film was sealed at the edges with Apiezon grease. The polymer film was secured in the brass block, and connections were made through the standard package testing ports provided on the MOCON Ox-Tran.

Degassed Film Experiments

For conventional measurement, a 19.5-mil polycarbonate (obtained from GE Sheet Products, Pittsfield, MA) film was degassed by passing inert past both surfaces. Degassing was deemed complete when no signal could be detected by the MOCON. At this time, the oxygen flow past the high side was begun. The flux is plotted vs. dimensionless time as apparent film permeability normalized with the steady state permeability in Figure 1. The steady state permeability is 260 cm³(STP) mil/100 in.² day atm. From the time for the flux (permeability) to reach 1/2 of its steady state value, the diffusion coefficient is determined to be 3.89×10^{-8} cm²/s. The analytical solution¹² assuming the permeability and the diffusion coefficient from this experiment has also been plotted on this figure. The transport parameters of oxygen in polycarbonate have been reported in the literature¹³; the values of the solubility and

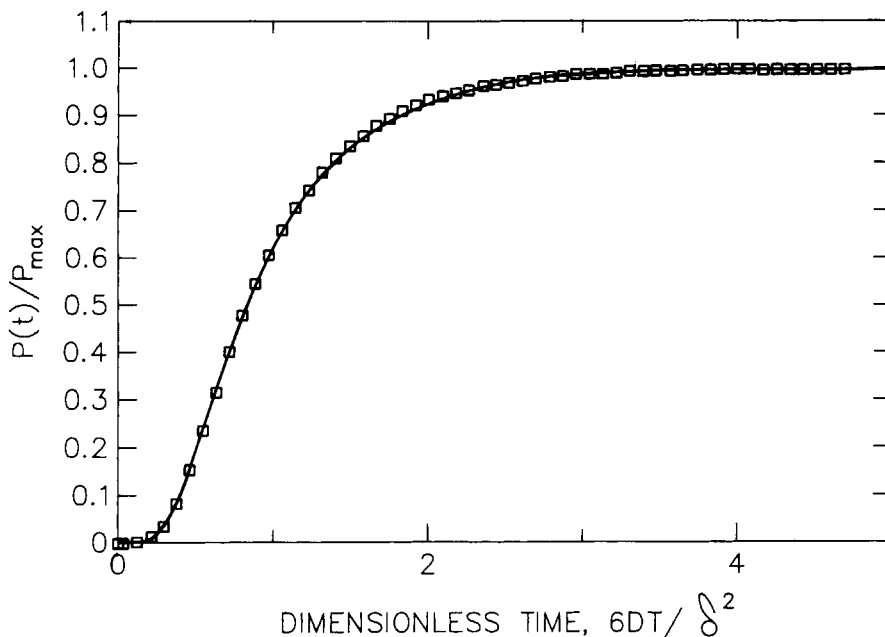


Fig. 1. Flux vs. time curve for degassed 19.5 mil polycarbonate film.

diffusion coefficient measured here are consistent with those reported previously.

The analogous plot for a 9.5-mil polyetherimide film (GE Sheet Products ULTEMTM) is shown in Figure 2. The steady state permeability is 65 cm³(STP) mil/100 in.² day atm, and the diffusion coefficient is 5.96×10^{-9} cm²/s.

Equilibrated Film Experiment

These experiments were repeated using the same films, only this time the films were saturated with air at the temperature of the experiment (32°C). Each experiment was started by placing the equilibrated film into the diffusion cell and immediately starting the oxygen flow to the high pressure side and sweep gas to the low pressure side. The sensor was not placed "on line" for a few minutes to allow the oxygen in the low pressure side to be removed by the sweep gas. The results are presented as normalized apparent permeability vs. time in Figure 3 for the polycarbonate film. The theoretical solution has been plotted on the same figure using the diffusion coefficient and steady state permeability measured in time lag experiment. From the time of the flux minimum and the magnitude of the flux at the flux minimum, we calculate a diffusion coefficient of 3.23×10^{-8} cm²/s and a permeability of 291 cm³(STP) mil/100 in.² day atm, both within about 10% of the values determined from the conventional experiment. The final steady state permeability actually measured is 260 cm³(STP) mil/100 in.² day atm, essentially the same as in the degassed experiment.

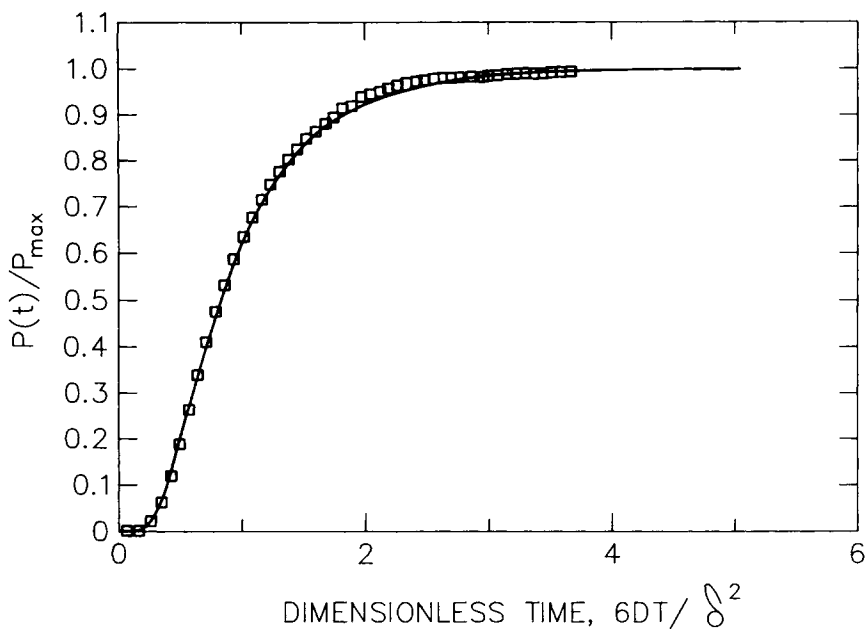


Fig. 2. Flux vs. time curve for degassed 9.5 mil polyetherimide film.

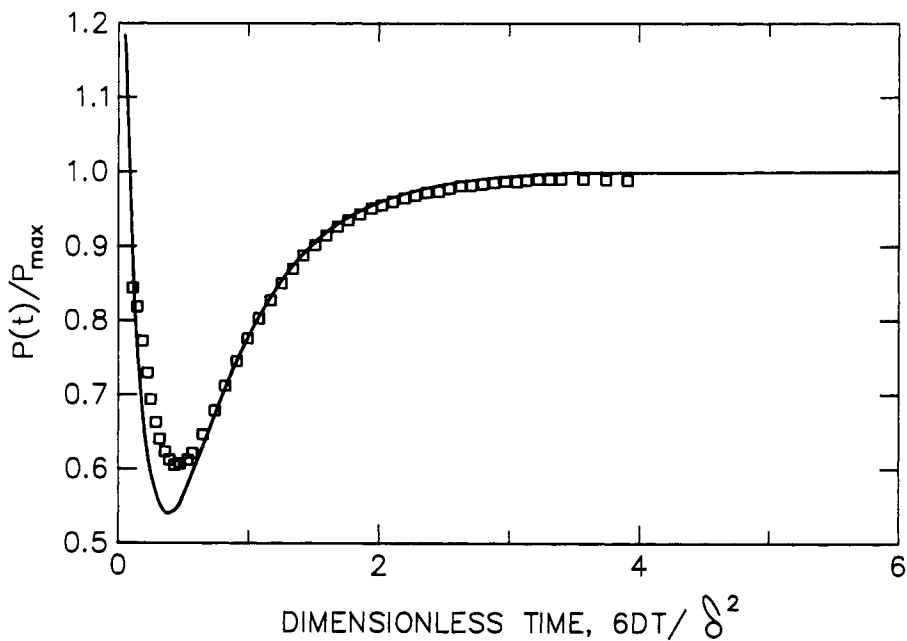


Fig. 3. Flux vs. time curve for air saturated 19.5 mil polycarbonate film.

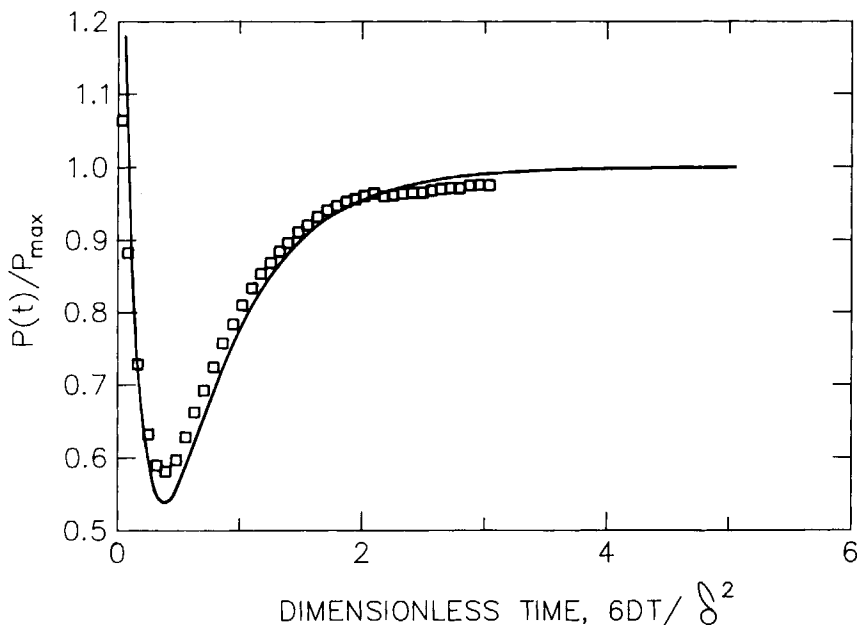


Fig. 4. Flux vs. time curve for air saturated 9.5 mil polyetherimide film.

The results of the polyetherimide experiment are shown in Figure 4. Interpretation in terms of the model yields a diffusion coefficient of 5.0×10^{-9} cm^2/s and a steady state permeability of $62 \text{ cm}^3(\text{STP}) \text{ mil}/100 \text{ in.}^2 \text{ day atm}$. The model was fit using the diffusion coefficient of the conventional experiment but the final steady state permeability of this experiment. Of course, the steady state permeabilities should be the same; the difference of about 5% gives a feel for the reproducibility of these measurements.

THEORY

Carslaw and Jaeger¹² present the solution for the concentration profile in a polymer film as a function of position and time where the bounding surfaces are maintained at fixed, unequal concentrations and the initial profile is arbitrary. The flux out of the film at the low pressure side is proportional to the derivative with respect to position of the concentration evaluated at the low pressure side boundary.

When the initial profile is everywhere zero (the film is degassed), the expression for the flux is particularly simple.¹ Ziegel et al.⁹ evaluated this expression for the time for the flux to rise to one half of its steady state value:

$$\tau_{1/2} = \delta^2 / 7.2 t_{1/2} \quad (1)$$

This flux half-time can be readily determined from a plot of flux vs. time and is used to calculate the diffusion coefficient.

When the film initially contains a uniform but nonzero pressure of the permeant of interest (e.g., saturated with air), the expression for the total flux,

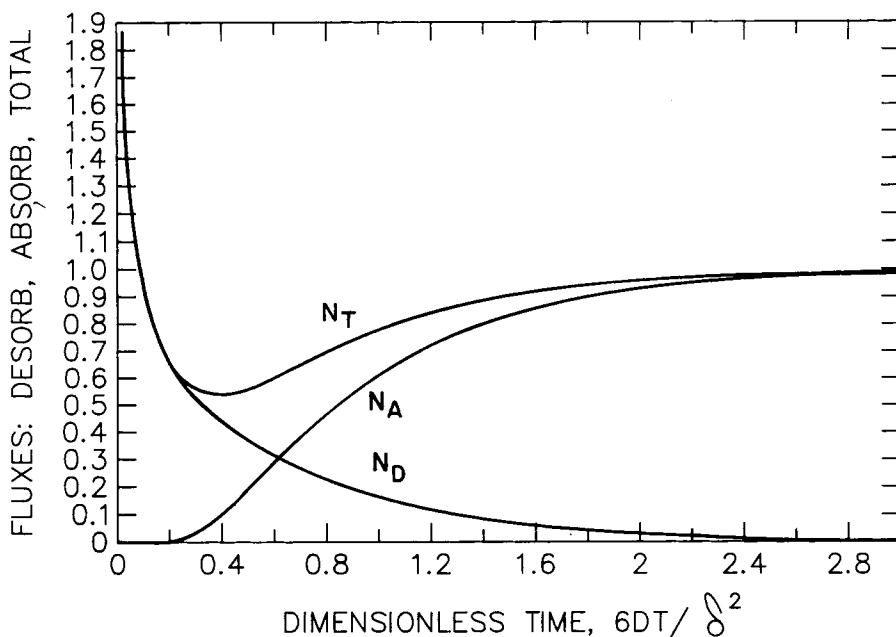


Fig. 5. Components of total flux from air saturated film.

N_T , is a bit more complex:

$$N_T = - \left. \frac{\partial \theta}{\partial \xi} \right|_{\xi=1} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 \pi^2 \tau} + 2\theta_0 \sum_{n=1}^{\infty} [1 - (-1)^n] e^{-n^2 \pi^2 \tau} \quad (2)$$

Notice that the flux expression can be divided into two contributions: the first term is the flux resulting from degassing, and the second term is the flux resulting from permeation through the film. For a given set of conditions, the two contributions to the total flux are shown in Figure 5. The minimum in the flux occurs as the degassing term falls off and the permeation term builds.

The time of the flux minimum is found by taking the time derivative of the flux, setting it equal to zero, and solving for time. For a film equilibrated in air and then exposed to 1 atm of oxygen, the minimum in flux occurs at $\tau_{\min} = 0.0633\delta^2/D$.

Also, a direct relationship exists between the magnitude of the flux at the time of the flux minimum and the magnitude of the flux at steady state. For films equilibrated in air and run in 1 atm of oxygen, the steady state flux is 1.82 times that at the minimum. The details of this development are presented in the Appendix.

DISCUSSION

This technique represents a new way to evaluate transport properties by dynamic permeation measurements. It is particularly advantageous for oxygen

measurements in good barrier materials because the time-consuming degassing step is obviated. An additional advantage of this technique is that, in principle, the steady state permeability can be calculated as soon as the minimum in the flux curve is reached; the answer is known about eight times faster than waiting for steady state.

We caution readers who may use an OXTRAN or other device to measure steady state oxygen permeabilities of air-saturated films that great care must be taken to ensure that steady state has been reached before making a measurement. In practice, instruments equipped with flow through cells are frequently used only to measure steady state permeabilities. Also, if a large number of sample cells are used in conjunction with a single sensor, it is inconvenient to make transient measurements. When this is the case, the initial profile of oxygen in the film is not of direct concern because the steady state permeability ultimately reached is independent of the initial profile. However, after a film has been mounted in a diffusion cell, it is necessary to wait until a steady state profile has been established across the film before a steady state permeability can be measured. If a good estimate of the diffusion coefficient of the permeant in the film is available, then the time to steady state can be calculated; if a good estimate of D is not available, however, the approach to steady state must be inferred from successive measurements. It is in the making of this judgment about steady state that an appreciation of the nature of the dynamic response, which does depend upon the initial profile, is important.

A close approach to steady state is usually assumed if several successive readings of flux remain unchanged. For initially degassed films, this method works well. (The measurements must be made over a time scale long enough to be sensitive to an increasing permeability if steady state has not been reached.) For initially air-saturated films, however, this method can lead to a misinterpretation of the results. If the successive measurements are made near the time of the flux minimum, when the flux vs. time curve is locally very flat, steady state would be wrongly assumed. Under these circumstances, the "steady state" permeability would be underreported by at least a factor of 2. It is necessary to understand how the system will respond dynamically to ensure that a valid measurement is made, even though the dynamic response does not affect the steady state permeability.

APPENDIX: DERIVATION OF OXYGEN FLUX-TIME EQUATION

The dimensionless diffusion equation describing this problem is written

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \xi^2} \quad (3)$$

with the boundary conditions

$$\theta(\xi = 1, \tau) = 0$$

$$\theta(\xi = 0, \tau) = 1$$

and initial condition

$$\theta_0(\zeta, 0) = \frac{S(T_0)}{S(T)} \frac{p_0(\zeta, \tau < 0)}{p(\zeta = 1, \tau)} \tag{4}$$

The dimensionless groups are given by

$$\zeta = \frac{x}{\delta}$$

$$\theta_i = \frac{c_i}{c(\zeta = 0, \tau)}$$

$$\tau = \frac{Dt}{\delta^2}$$

where c_i [cm³(STP)/cm³] is oxygen concentration, S [cm³(STP)/cm³ atm] is the solubility coefficient for oxygen, T (K) is the temperature, and p_i (atm) is oxygen pressure.

For Mocon experiments, $p_0(\zeta, \tau = 0) = 0.21$ atm and $p(\zeta = 1, \tau) = 1$ atm. When the film is equilibrated at the experiment temperature T , the ratio of the solubility coefficients in eq. (4) cancel. However, if the film is stored at a temperature different from that during the experiment, a correction term involving the heat of gas sorption, Δh_s , must be used. In practice, over only a few degrees temperature this correction will be moderately small.

Carslaw and Jaeger¹² give a general solution for the concentration profile as a function of time and position. For the oxygen flux experiment, we write Carslaw and Jaeger's solution as a sum of two concentration terms: the first due to the desorption of oxygen initially in the film, the second from the absorption and diffusion of oxygen from the high pressure side of the film. These are referred to as θ_D and θ_A , respectively, and are:

$$\theta_A = 1 - \zeta - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin(n\pi\zeta) e^{-n^2\pi^2\tau} \tag{5}$$

$$\theta_D = -\frac{2\theta_0}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n - 1}{n} \sin(n\pi\zeta) e^{-n^2\pi^2\tau} \tag{6}$$

The experimental measurement is oxygen flux at $\zeta = 1$ which is evaluated from the gradient of concentration:

$$N_A = -\left. \frac{\partial \theta_A}{\partial \zeta} \right|_{\zeta=1} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2\pi^2\tau} \tag{7}$$

$$N_D = -\left. \frac{\partial \theta_D}{\partial \zeta} \right|_{\zeta=1} = 2\theta_0 \sum_{n=1}^{\infty} [1 - (-1)^n] e^{-n^2\pi^2\tau} \tag{8}$$

The total flux N_T which is measured is given by the sum

$$N_T = N_A + N_D \tag{9}$$

We define a characteristic time τ_{min} , where the flux curve goes through a minimum. Evaluation of τ_{min} is carried out by taking the time derivative of N_T and setting it equal to zero:

$$\sum_{n=1}^{\infty} (-1)^n + \theta_0 [1 - (-1)^n] n^2 e^{-n^2\pi^2\tau} = 0 \tag{10}$$

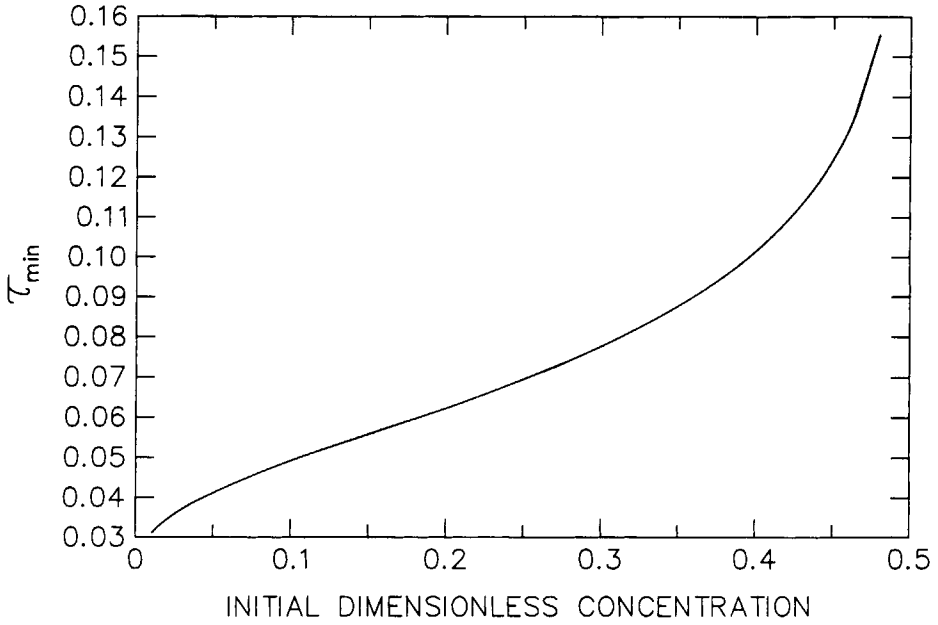


Fig. 6. Time of flux minimum vs. initial concentration of oxygen in the film.

We see that τ_{\min} varies with the initial condition of oxygen in the film. In Figure 6 the value τ_{\min} is plotted as a function of the initial oxygen concentration in the film. Valid solutions for a minimum in the flux curve exist only in the range $0 < \theta_0 < 0.5$. Outside of this range, there is no minimum in the flux curve, as is shown in Figure 7, where the flux is plotted for three initial conditions of oxygen in the film: $\theta_0 = 0$, 0.21, and 0.5.

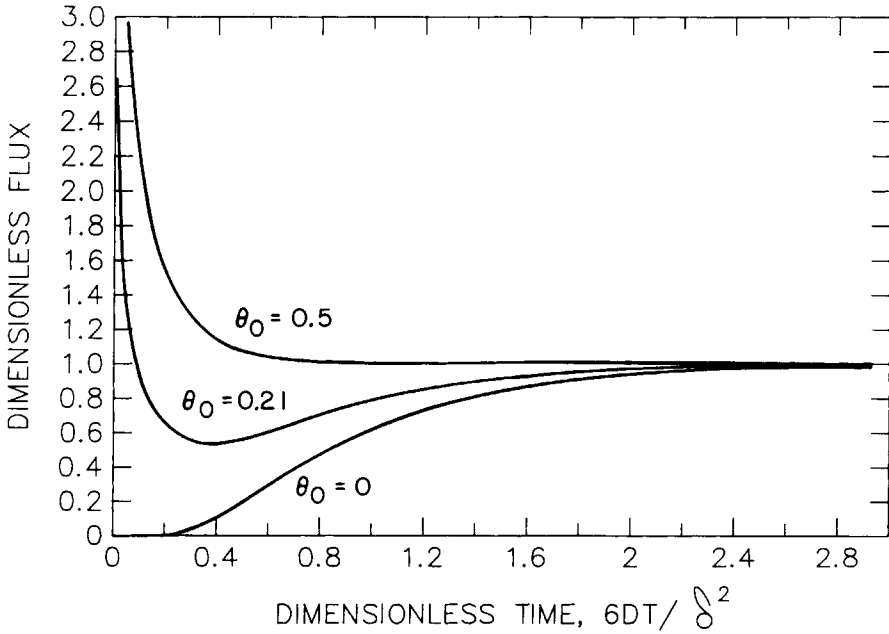


Fig. 7. Flux vs. time for three values of initial oxygen concentration. Minimum only occurs for intermediate values.

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