Analysis of gas transport in laminated semi-infinite solid: Novel method for complete membrane characterization during highly transient state

CrossMark

N. Al-Qasas, J. Thibault, B. Kruczek *

Department of Chemical & Biological Engineering, University of Ottawa, 161 Louis Pasteur Street, Ottawa, ON, Canada K1N 6N5

ABSTRACT

Gas transport in a two-layer membrane system, subjected to a step increase in feed pressure, is modeled under highly transient state in which the Layer 2 behaves as a semi-infinite solid. The system of governing partial deferential equations is solved using Laplace transforms, and the solution is used to obtain the expression for the pressure decay in the upstream volume. Accordingly, the pressure decay at short and long times is directly proportional to the square root of time, where the early and late slopes are dependent on the properties (i.e., diffusivity and solubility) of the materials of Layer 1 and Layer 2, respectively. Knowing the properties of the material of Layer 2, the material of Layer 1 can be fully characterized based on the early slope and the rate at which this early slope changes once the penetrant enters Layer 2. Since the thickness of Layer 1 in the two-layer system can be orders of magnitude smaller than that of a stand-alone membrane, the approach presented in this paper may allow characterizing barrier materials, which otherwise could not be characterized in a reasonable timeframe by traditional integral, permeation and sorption techniques. In addition, the new method may be used for characterization of the selective layer in thin film composite membranes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The knowledge of transport properties, i.e. permeability (P), diffusivity (D) and solubility (S) of small molecules in a membrane facilitates the systematic selection of membranes and prediction of their performances in actual applications. In addition, it enables the investigation of structure–property relationships in the process of developing of new membrane materials. It is commonly assumed that species transport in polymeric membrane follows the solution-diffusion mechanism in which:

$$P = DS \qquad (1)$$

In general, the methods for the determination of transport properties can be divided into three groups: (1) integral permeation, (2) differential permeation, and (3) sorption methods [1]. The time-lag method, which originates from the work of Daynes [2], is by far the most common integral permeation method and, at the same time, the most widely used for membrane characterization. In the time-lag method, the cumulative amount of a penetrant passes through a membrane as a result of a step change in feed pressure is determined as a function of time. The change in pressure downstream from the membrane in the downstream receiver is directly related to the gas flux emerging from the membrane. At steady state, the gas flux and thus the rate of pressure increase become constant. Extrapolating the linear portion of the pressure increase to the time axis allows the determination of the downstream time lag (θ_d), which in the simplest case is related to D through:

$$\theta_d = \frac{L^2}{6D} \qquad (2)$$

where, L is the membrane thickness. Alternatively, if the pressure decay in the upstream receiver was also monitored, extrapolating the linear portion of the pressure decay to the time axis would yield the upstream time lag (θ_u), which is given by:

$$\theta_u = -\frac{L^2}{3D} \qquad (3)$$

The permeability is directly proportional to the steady state slope of the pressure decay in the upstream receiver and the pressure increase in the downstream receiver. Then, knowing D and P, the solubility is determined from Eq. (1).

The time lags given by Eqs. (3) and (4) are often referred to as the adsorption time lags, because they result from an increase in feed pressure, and thus adsorption of penetrant by a membrane. Alternatively, time lags can be obtained using a membrane, which

* Corresponding author. Tel.: +1 613 562 5800x2047; fax: +1 613 562 5172.
E-mail address: bkruczek@uottawa.ca (B. Kruczek).

is initially in equilibrium with a gas, in case of which the experiment is initiated by a step decrease in feed pressure. The resulting downstream and upstream time lags are referred to as the desorption time lags [3–5]. The desorption time lag experiments are more challenging than the adsorption time lag experiments. However, the combination of the two is very useful when characterizing membranes with concentration-dependent diffusion coefficient [6].

Using adsorption integral permeation experiment, Rogers et al. [7] proposed a method for estimating the membrane properties at early times corresponding to Fourier numbers, $Fo < 0.15$ ($Fo = Dt/L^2$), at which the expression for the rate of pressure increase in the downstream volume dp/dt can be written as

$$\ln\left[\left(\frac{dp}{dt}\right)\sqrt{t}\right] = \ln\left[\frac{2ARTSp_o}{V_d}\sqrt{\frac{D}{\pi}}\right] - \frac{L^2}{4Dt} \tag{4}$$

where, A is the membrane area, V_d is the volume of the downstream reservoir, p_o is the pressure in the upstream receiver after its pressurization, T is the absolute temperature, and R is the universal gas constant. Plotting the left hand side of Eq. (4) versus $1/t$ should yield a straight line with a slope equal to $-L^2/4D$, from which D can be evaluated. After D has been determined, S can be calculated by solving Eq. (4).

Another variation of the integral permeation method based on the approximation of Rogers et al. was recently proposed by Al-Ismaily et al. [8], who re-derived Eq. (4) to a more convenient form:

$$\ln\left[\frac{p}{\sqrt{t}}\right] = \ln\left[\frac{4ARTSp_o}{V_d}\sqrt{\frac{D}{\pi}}\right] - \frac{L^2}{4Dt} \tag{5}$$

The determination of D from Eq. (5) does not require numerical differentiation of the experimental pressure increase, which is necessary when using Eq. (4), and which may introduce significant noise to the data. Moreover, instead of determining S from the intercept of Eq. (5), which requires extrapolation to $1/t = 0$, i.e. to infinitely long times at which Eq. (5) is not applicable, Al-Ismaily et al. focused on the determination of permeability P from the transient flux entering the membrane that was evaluated from the pressure decay in the upstream reservoir [8].

In differential permeation methods, the permeation rate through a membrane, following a step change in the driving force, is measured directly as a function of time [9]. The diffusivity can be determined from the half time ($t_{1/2}$):

$$D = \frac{L^2}{7.199t_{1/2}} \tag{6}$$

The half time is the time at which the relative permeation rate reaches the value of 0.5, i.e.

$$Q_{rel}(t) = \frac{Q(t) - Q_1}{Q_2 - Q_1} = 0.5 \tag{7}$$

where Q_1 and Q_2 are the initial and final steady state permeation rates through the membrane. If initially there was no pressure gradient across the membrane, $Q_1 = 0$ in Eq. (7).

The early times solution proposed by Rogers et al. [7] is also applicable to differential permeation methods. More specifically, the rate of pressure increase, dp/dt, in Eq. (4) is replaced by the time-dependent permeation rate through the membrane, $Q(t)$. Plotting $\ln[Q(t)\sqrt{t}]$ versus $1/t$ should yield a straight line with a slope equal to $-L^2/4D$, from which D can be evaluated. The permeability is determined from either the initial or the final steady state permeation rate.

Integration of $Q(t)$ over time provides the basis for a moment method [10]. More specifically, the quantity τ_p obtained from:

$$\tau_p = \int_0^\infty \left(1 - \frac{Q(t)}{Q_2}\right) dt \tag{8}$$

is equal to the time lag (θ_u) that would be measured in an integral permeation experiment at the same temperature and boundary conditions. Consequently, after estimating τ_p, D can be estimated from Eq. (2), while P can be evaluated from the new steady state permeation rate Q_2.

Sorption methods rely on the accurate monitoring of the mass of penetrant, $M(t)$, absorbed by the medium being characterized, following a step change in the concentration of the penetrant in the fluid that is in contact with the medium. In the simplest case, the fluid phase is a pure gaseous penetrant. The quantity $M(t)$ can be estimated by monitoring the increase in the mass of the medium using a microbalance, or by monitoring the total pressure of the gas phase. Unlike the integral and differential permeation methods, the penetrant in sorption methods does not leave the medium. Consequently, after long times, a new equilibrium (M_∞), rather than steady state transport, is established.

All techniques that are used for the differential permeation methods are also applicable for the sorption methods. Defining a half time ($t_{1/2}$) as the time required to absorb 50% of the penetrant that would be absorbed at the new equilibrium i.e., the time at which $M(t) = 0.5M_\infty$, the diffusivity in a slab membrane when the penetrant enters the membrane from both sides is given by [1]:

$$D = 0.04919\frac{L^2}{t_{1/2}} \tag{9}$$

Alternatively, at very short times, the plot of $M(t)/M_\infty$ versus $t^{1/2}$ is linear with the slope given by:

$$Slope = \frac{4}{L}\sqrt{\frac{D}{\pi}} \tag{10}$$

In terms of the sorption moment (τ_s), the diffusivity can be evaluated from:

$$D = \frac{L^2}{12\tau_s} \tag{11}$$

where:

$$\tau_s = \int_0^\infty \left(1 - \frac{M(t)}{M_\infty}\right) dt \tag{12}$$

The solubility in sorption methods is determined based on M_∞ at a given concentration of the penetrant in the fluid phase and the equilibrium pressure. Knowing D and S, the permeability is evaluated from Eq. (1).

Except for the methods based on the approximate solution of Rogers et al. [7] for early times, all the other methods require either attaining steady state transport or a new equilibrium, which in the case of barrier materials may take weeks or even months. On the other hand, the approximate solution of Rogers et al. [7], which is applicable only for permeation methods, is based on the penetrant exiting the membrane. At $Fo = 0.05$, the flux out of the membrane is just 3% of the steady state value, while at $Fo = 0.15$ (i.e. at the upper end at which the early time solution is applicable) it increases to 50% of the steady state value. In the case of barrier materials, for which the solution of Rogers et al. [7] would be most suitable, steady state fluxes are generally very small, making accurate measurements of transient fluxes out for the membrane practically impossible. On the other hand, at $Fo < 0.05$, at which a slab membrane behaves as a semi-infinite solid, transient fluxes into the membrane are much greater than the steady state value making them easier to be monitored from the rate of pressure decay in the upstream receiver (Δp_u).