



The effect of the downstream pressure accumulation on the time-lag accuracy for membranes with non-linear isotherms



Neveen Al-Qasas, Jules Thibault, Boguslaw Kruczek*

Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

ARTICLE INFO

Article history:

Received 20 November 2015
Received in revised form
14 March 2016
Accepted 22 March 2016
Available online 26 March 2016

Keywords:

Gas diffusion
Non-linear sorption
Time-lag
Downstream accumulation
Numerical simulation

ABSTRACT

The time-lag method based on downstream measurements is one of the most popular methods for gas membrane characterization. This method is commonly used to characterize all types of membranes, either glassy or rubbery, and regardless of the type of isotherm for a gas molecule/membrane system. The time-lag method has originally been derived for a linear isotherm system (Henry's relation) under the assumption of vacuum at the downstream side of the membrane. This zero-pressure assumption is obviously violated as a finite downstream volume is required to record a pressure change necessary to estimate the time lag. The objective of this investigation is therefore to critically assess the degree of validity of the downstream time-lag method under more realistic boundary conditions and for systems characterized with nonlinear isotherms such as dual-mode sorption. To achieve this objective, the mass diffusion equation was solved numerically by finite differences and numerical results were compared with known analytical solutions. This study provides a deeper understanding on the behavior of adsorption and the transport of molecules inside a membrane for the cases of linear isotherm and dual-mode sorption with complete immobilization and instantaneous equilibrium. Results clearly show that the sorption parameters have a major impact on the time required to achieve steady state as well as on the transient behavior before reaching steady state under ideal boundary conditions. Under the realistic boundary conditions, steady state can never be achieved and can only be approached due to gas accumulation in the downstream compartment. Conditions under which higher accuracy is obtained in the determination of the diffusion coefficient are discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the 1980s, polymeric gas separation membranes became an industrial reality and since then the range of their applications continuously increases [1]. Gas transport in polymeric membranes is governed by the solution-diffusion mechanism, in which the gas is first dissolved at the high pressure side of the membrane and then, driven by the concentration gradient, diffuses towards the low pressure side. Consequently, gas permeability in the membrane (P) is conveniently represented as a product of the solubility (S) and the diffusivity (D) of the gas in the membrane. Accurate determination of these transport coefficients is the key to the development of improved polymeric materials for gas separation membranes [2–4].

Typically, the three transport coefficients are determined in a single dynamic gas permeation experiment, often referred to as a time-lag experiment. A membrane, which is initially degassed, is

exposed to a step increase in feed pressure while time-dependent gas permeation across the membrane is determined from the rate of pressure increase in a fixed downstream volume on the other side of the membrane. The permeability is determined from the linear portion of the pressure versus time graph; extrapolation of that linear portion to the time axis gives a time lag (θ_d), which is related to the diffusivity by:

$$\theta_d = \frac{L^2}{6D} \quad (1)$$

where L is the membrane thickness. The solubility is simply the ratio of the permeability and diffusivity. The mathematical basis for the time-lag measurements was originally provided by Daynes in 1920 [5]. Eq. (1) is based on the assumption that the concentration of the gas in the membrane at the permeate side is zero at all time during the gas permeation experiment, which is obviously not the case, because for the downstream time-lag method to be used the permeating gas must be allowed to accumulate downstream from the membrane. Nevertheless, due to its simplicity, the time-lag analysis described above is widely used for the

* Corresponding author.

E-mail address: BKruczek@uottawa.ca (B. Kruczek).

characterization of gas transport coefficients in membranes.

The problem of the oversimplified boundary conditions used by the time-lag method has been addressed in the literature. Barrer [6] derived a more general form of the time-lag equation by allowing a nonzero concentration at the permeate side, and a nonzero initial concentration profile in the membrane. Paul and DiBenedetto [7] modified the time-lag method by using the actual boundary conditions that existed in their experimental setup. They derived a correction factor to accommodate for gas accumulation at the permeate side of the membrane in order to correct the experimentally-determined transport coefficients. Spacek and Kubin [8] further modified the time-lag analysis taking into consideration the pressure changes at both sides of the membrane. Barrie et al. [9] considered four different sets of initial and boundary conditions resembling practical experimental conditions. For each set of conditions, they obtained a general equation describing the rate of pressure increase and calculated the respective diffusivity via an iterative procedure by solving a set of nonlinear equations.

To minimize the error due to gas accumulation downstream from the membrane, the receiving volume should be as large as possible. Moreover, the sooner the linear extrapolation is taken, the smaller the effect of gas accumulation on the experimental time lag. On the other hand, a sufficient time must elapse from the beginning of the experiment to allow gas permeation to reach steady state. As a rule of thumb, it is recommended that the pressure data used for the linear extrapolation should be taken in the time frame between $3\theta_d$ and $4\theta_d$ [2,10,11]. Jenkins et al. [12] conducted a numerical investigation on the effect of the size of the receiving volume and the time frame used for extrapolation. They concluded that even when the downstream volume is very large and the boundary conditions are equivalent to those imposed by the simplified time-lag analysis, the linear extrapolation of the pressure response between $3\theta_d$ and $4\theta_d$ leads to an overestimation of the diffusivity by approximately 4%. An extended version of the numerical analysis of Jenkins et al. [12] was more recently presented by Taveira et al. [13]. In that study, the effect of performing a linear regression over a time frame in which the membrane concentration profile is not yet fully developed was discussed.

Eq. (1) also assumes that gas sorption in the membrane follows Henry's law, which is the case for rubbery polymers and non-interactive gases. In the case of glassy polymers, a dual-mode sorption model, in which both Henry's dissolution and Langmuir's hole filling are present, is applicable. Dual-mode sorption leads to a non-linear sorption isotherm and the diffusivity from the time-lag experiment represents an apparent rather than the real diffusivity of the gas in the membrane [14–17]. Different models for glassy polymers have been proposed depending on the mobility of molecules associated with Henry's and Langmuir molecules and the driving force [18–21]. The case, in which gas molecules in Henry's sites are the only ones contributing to diffusion, is referred to as a complete immobilization model [14,17]. Other workers [18,19,21–24] proposed that the molecules adsorbed in Langmuir's sites are not completely immobilized, and thus contributing to diffusion; this case is referred to as a partial immobilization model. The original complete immobilization model assumes instantaneous equilibrium between gas molecules adsorbed in Henry's and Langmuir's sites. However, some workers suggested relaxing this assumption and instead to consider a reversible reaction between the two populations of gas molecules [25–28]. Other models attempting to explain nonlinear sorption in glassy polymers were also proposed [29,30].

Dual-mode sorption in glassy polymers makes the derivation of the expression relating the diffusivity with the time lag more complex. For the simplest case of dual-mode sorption with complete immobilization of gas molecules in Langmuir sites, Paul [21]

derived an expression for the time lag using the concept asymptotic solution proposed by Frisch [31]. The asymptotic solution provides only the steady state pressure response, which is sufficient to obtain the expression for the time lag. On the other hand, the asymptotic solution does not allow estimating the time required to reach the steady state permeation. Moreover, to our best knowledge, the effect of gas accumulation on the error in time lag of membranes with non-linear sorption isotherms has not been addressed in the literature.

In this paper, numerical simulations of time-lag experiments for membranes in which dual-mode sorption with complete immobilization of gas molecules in Langmuir sites exists are presented. Assuming a zero gas concentration at the permeate-side of the membrane, the effect of sorption parameters and the feed pressure on the time required to reach steady state is investigated. The analysis is then extended by allowing the gas to accumulate at the permeate side of the membrane. For this more realistic case, the combined effect of sorption parameters, feed pressure and the volume downstream from the membrane on the magnitude of the minimum error and the time at which this minimum error occurs is analyzed and discussed.

2. Theoretical background

A membrane of thickness L , initially degassed, is subjected to a step change in pressure (from 0 to a constant value p_0). Due to instantaneous equilibrium, the concentration of the gas at the feed surface of the membrane ($x=0$) remains constant (C_0) during the entire experiment, while the gas diffuses towards the permeate surface of the membrane ($x=L$). If the gas concentration at the permeate surface of the membrane remains zero, and gas diffusivity in the membrane is constant, the time-lag experiment is described by Fick's 2nd law of diffusion given in Eq. (2), subject to the initial and boundary conditions (IBC) given by Eqs. (3)–(5):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2)$$

$$C(t < 0, x) = 0 \quad (3)$$

$$C(t, 0) = C_0 = p_0 S \quad (4)$$

$$C(t, L) = 0 \quad (5)$$

Eq. (4) implies linear sorption of gas in the membrane (e.g. Henry's law). Eq. (2) can be solved analytically by the method of separation of variables using the IBC specified by Eqs. (3)–(5). Expression for the time lag given by Eq. (1) is then derived from the pressure response at the permeate side of the membrane, which is obtained from the concentration gradient at the permeate interface of the membrane.

Unless the permeate side of the membrane is continuously evacuated, Eq. (5) is not valid. Consequently, in a more rigorous analysis Eq. (5) should be replaced by:

$$\frac{V_L}{RT} \frac{dp_L}{dt} = -DA \left. \frac{\partial C}{\partial x} \right|_{x=L} \quad (6)$$

where V_L is the volume downstream from the membrane, A is the membrane area, R is the universal gas constant and T the absolute temperature. The 2nd BC specified by Eq. (6) prevents obtaining analytical solution for Eq. (2). However, a semi-analytical solution

Download English Version:

<https://daneshyari.com/en/article/632412>

Download Persian Version:

<https://daneshyari.com/article/632412>

[Daneshyari.com](https://daneshyari.com)