Journal of Membrane Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Mixed matrix membranes applications: Development of a resistance-based model

Arian Ebneyamini, Hoda Azimi, F. Handan Tezel, Jules Thibault*

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

ARTICLE INFO

Keywords:
Mixed matrix membranes
Effective permeability
Pervaporation and gas separation
Resistance-based model
Finite difference method

ABSTRACT

In this study, a model for the prediction of the mass transport through ideal mixed matrix membranes (MMMs) for pervaporation and gas separation processes has been introduced. A Resistance-Based (RB) model was used in conjunction with a three-directional Finite Difference (FD) numerical solution to derive a semi-empirical model for calculating the effective permeability of ideal mixed matrix membranes. Predictions of the effective permeability obtained with the proposed model were compared with the estimated permeability for ideal MMMs using numerous analytical solutions such as Maxwell, Lewis-Nielsen, Bruggeman and Hennepe models. The extended RB model was theoretically able to predict accurately the effective permeability of ideal MMMs over a large range of filler volume fraction. Higher deviations were observed between the predictions of the extended RB model and the estimations of the majority of the other models in the case of MMMs containing higher permeable fillers and larger amount of filler material.

1. Introduction

The theoretical description of the mass transport through mixed matrix membranes (MMM's) is paramount to optimize the membrane separation processes via these high performance materials. According to the solution-diffusion theory, three steps can be used to describe the mass transport of species within the membrane film: (1) sorption of species on the feed side of the membrane, (2) diffusion of components through the membrane, and (3) desorption from the permeate side of the membrane [1–4]. Therefore, the permeate flux of a component for pervaporation and gas separation processes is proportional to the partial pressure gradient (or concentration gradient) as the driving force, the membrane thickness and the permeability of the component. Moreover, the permeability is the product of the solubility and the diffusion coefficient of penetrants through the membrane. Eq. (1) gives the expression of the permeate flux of component m in membrane separation processes. Solubility of a species in a membrane could be defined based on: (1) the equilibrium partial pressure where S, with units of mol m^{-3} bar^{-1}, relates the concentration of a species in the sorbed phase to its equilibrium partial pressure on the feed side, or (2) the mass concentration of a species where S^*, with units of g m^{-3}/g m^{-3}, is the ratio of the concentration in the membrane to the one in the feed solution. Therefore, the permeability of component m in the membrane could be expressed using different units (mol m^{-1} h^{-1} bar^{-1} and m^2 h^{-1}) for which the permeability would obviously have different values. However, the type of driving force (partial pressure or concentration gradient) is the determining factor to select the proper units to express permeability without any impact on the estimation of partial permeate fluxes (See Eq. (1) where the permeate flux is expressed in g m^{-2} h^{-1}).

$$J_m = \frac{(D_m S_m) M_m \,\Delta p_m}{\delta} = \frac{P_m M_m \,\Delta p_m}{\delta} = \frac{(D_m S_m^*)\,\Delta C_m}{\delta} = \frac{P_m^* \Delta C_m}{\delta} \tag{1}$$

Various models such as Maxwell [5], Bruggeman [6], Lewis-Nielsen [7,8] and Pal [9] have been introduced to estimate the effective permeability of ideal mixed matrix membranes for gas separation processes. These models are based on the permeability of the continuous phase (P_c), permeability of the dispersed phase (P_d) and the volume fraction (ϕ) of the solid fillers within the polymer matrix [10]. Table 1 presents a summary of the analytical models introduced for the estimation of component permeability in ideal MMMs. Among these models, the Maxwell model is the most commonly used for the prediction of the effective permeability of ideal MMMs for gas separation applications (Eq. (2)). The Maxwell model was originally presented to describe the dielectric properties of composite materials containing spherical particles. However, the Maxwell model is only applicable for

Abbreviations: BOT, Böttcher Model; BRG, Bruggeman Model; FD, Finite Difference; HIG, Higuchi Model; HPF, High Permeable Fillers; HNP, Hennepe Model; LN, Lewis-Nielsen Model; LPF, Low Permeable Fillers; MMM, Mixed Matrix Membrane; MXW, Maxwell Model; PAL, Pal Model; RB, Resistance Base; VBA, Visual Basic for Applications

* Corresponding author.
E-mail address: Jules.Thibault@uottawa.ca (J. Thibault).

http://dx.doi.org/10.1016/j.memsci.2017.08.065
Received 25 June 2017; Received in revised form 14 August 2017; Accepted 26 August 2017

Nomenclature

A	Area (m^2)
b	Parameter of Correction Factor Equation (dimensionless)
C	Concentration ($g\,m^{-3}$)
C_M	Parameter of Correction Factor Equation (dimensionless)
d	Diffusion Pathway (m)
D	Diffusion Coefficient ($m^2\,h^{-1}$)
H	Variable Defined in Eq. (6)
J	Permeate Flux ($g\,m^{-2}\,h^{-1}$)
K_H	Empirical Constant in Higuchi Model (dimensionless)
L_1	Size of the RB Element (m)
L_2	Size of the Filler (m)
M	Molecular Weight ($g\,mol^{-1}$)
m	Component
N	Number of Nodes
P	Permeability ($mole\,m^{-1}\,h^{-1}\,bar^{-1}$)
p	Partial Pressure (bar)
P^*	Permeability ($m^2\,h^{-1}$)
R_i	Resistance ($h\,bar\,mole^{-1}$)
S	Solubility Coefficient ($mole\,m^{-3}\,bar^{-1}$)
S^*	Solubility Coefficient ($g\,m^{-3}/g\,m^{-3}$)
t	Time (h)
x	x Coordinate
y	y Coordinate
z	z Coordinate
δ	Thickness (m)
ϕ	Volumetric Filler Content (dimensionless)
τ	Correction Factor (dimensionless)

Superscripts

L	Left
R	Right

Subscripts

c	Continuous Phase
d	Dispersed Phase
Eff	Effective
f	Feed
FD	Finite-Difference Method
HPF	High Permeable Filler
i	x Coordinate for Node Position in FD Model
j	y Coordinate for Node Position in FD Model
k	z Coordinate for Node Position in FD Model
LPF	Low Permeable Filler
m	Component
MMM	Mixed Matrix Membrane
r	Relative
RB	Resistance-Based Model

low amounts of filler loading within the polymer matrix (less than 0.2 volume fraction of the filler) based on the assumption that diffusion in and around a particle is not affected by the diffusion streamlines around the neighbouring particles [10].

$$P_{Eff} = P_c \frac{P_d + 2P_c - 2\phi(P_c - P_d)}{P_d + 2P_c + \phi(P_c - P_d)} \tag{2}$$

In addition, a resistance-based model has been proposed by Hennepe et al. to predict the effective permeability of permeating species in a mixed matrix membrane for pervaporation separation (Eq. (3)) [11,12]. The model was able to predict the separation performance for the pervaporation of some alcohols from water using zeolite-PDMS mixed matrix membranes.

Table 1
Predictive models for the relative effective permeability (P_r) of species in ideal MMMs.

Model	Equation
Maxwell (MXW) [5]	$P_r = \frac{P_{Eff}}{P_c} = \frac{P_d + 2P_c - 2\phi(P_c - P_d)}{P_d + 2P_c + \phi(P_c - P_d)}$
Bruggeman (BRG) [6]	$(P_r)^{1/3}\left(\frac{P_d - P_c}{P_d - P_r P_c}\right) = (1-\phi)^{-1}$
Böttcher (BOT) [13]	$\left(1 - \frac{1}{P_r}\right)\left(\frac{P_d}{P_c} + 2P_r\right) = 3\phi\left(\frac{P_d}{P_c} - 1\right)$
Higuchi (HIG) [14]	$P_r = 1 + \frac{3\,\phi\,\beta}{1 - \phi\,\beta - K_H(1-\phi)\beta^2}$ $\beta = \frac{P_d - P_c}{P_d + 2P_c} \quad (K_H = 00.78)$
Lewis-Nielsen (LN) [7,8]	$P_r = \frac{1 + 2\phi\left(\frac{P_d - P_c}{P_d + 2P_c}\right)}{1 - \psi\phi\left(\frac{P_d - P_c}{P_d + 2P_c}\right)}$ $\psi = 1 + \left(\frac{1-\phi_{Max}}{\phi_{Max}^2}\right)\phi$
Hennepe (HNP) [11]	$P_r = \frac{1}{1 - \phi^{1/3} + \frac{1.5\phi^{1/3}P_c}{P_c(1-\phi) + 1.5P_d\phi}}$
Pal (PAL) [9]	$(P_r)^{1/3}\left(\frac{P_d - P_c}{P_d - P_r P_c}\right) = \left(1 - \frac{\phi}{\phi_{Max}}\right)^{-\phi_{Max}}$

$$P_{Eff} = \frac{1}{\frac{1-\phi^{1/3}}{P_c} + \frac{1.5\phi^{1/3}}{P_c(1-\phi) + 1.5P_d\phi}} \tag{3}$$

The factor 1.5 in Eq. (3) was added to account for the tortuosity factor due to the presence of the particles. As a result, the permeability prediction of the Hennepe's model for an identical permeability of the components in both phases ($P_c = P_d$) deviates from the asymptotic permeability, and the prediction of the effective permeability still remains a function of the filler volume fraction [12]. In addition, a small error for the determination of the diffusional area in the derivation of this equation was also made. Indeed, the denominator of the second term in the denominator of Eq. (3) should be $P_c(1-\phi^{2/3}) + P_d\phi^{2/3}$ while excluding at the same time the tortuosity factor of 1.5 [12].

In this work, it was desired to resort to a simple predictive model to estimate the effective permeability (P_{Eff}) of species in ideal MMMs. Therefore, a Resistance-Based (RB) model has been introduced to estimate the effective permeability of migrating components in a homogenously dispersed mixed matrix membrane with the assumption of ideal polymer-filler interface morphology. In addition, an accurate solution was obtained by finite difference numerical solution (referred as FD model in this paper) for an identical membrane to predict the effective permeability of the ideal mixed matrix membranes for different ratios of the permeability in the dispersed and continuous phases as well as for different volumetric filler contents within the polymer matrix. Results of the finite difference solution was compared to the RB model predictions in order to define a correction factor for the RB model to account for the three-directional (3D) diffusional pathway of migrating species through MMMs. The simple one-directional RB model multiplied by the correction factor is referred as "Extended RB model" in this investigation. The predictions obtained with the Extended RB model were compared with different analytical solutions (see Table 1) for estimating the effective permeability of species in ideal MMMs.

2. RB model development for the mass transport through MMMs

In this section, a new semi-empirical model was developed to calculate the effective permeability of species in MMMs with an ideal