Simulation of Multicomponent Gas Transport through Mixed-Matrix Membranes

Gloria M. Monsalve-Bravo, Simon Smart, Suresh K. Bhatia*

School of Chemical Engineering, The University of Queensland, Brisbane QLD 4072, Australia

AUTHOR INFORMATION

Corresponding Author

*e-mail: s.bhatia@uq.edu.au
ABSTRACT

We extend the Maxwell-Stefan (M-S) formulation of irreversible thermodynamics to multicomponent transport in mixed-matrix membranes (MMMs), using a simulation-based rigorous modeling approach (SMA) through finite-element method (FEM) solution of the three-dimensional (3-d) transport problem in full-scale MMMs. In the new approach, we generalize the dual-mode/partial immobilization (DM/PI) theory for the local permeability in glassy polymers to describe multicomponent permeation in pure glassy polymer membranes and MMMs, by reformulating the M-S constitutive equations in the Onsager formalism considering concentration-dependent transport diffusivities and non-uniform concentration gradients across the MMM. In this way, the new M-S formulation explicitly considers effects of intrinsic MMM features such as finite filler particle size and isotherm nonlinearity in the MMM constituent phases, as well as mixture-related effects, such as competitive adsorption and friction amongst permeants, on the calculation of the mixture fluxes (permeabilities). This is achieved without introduction of empirical fitting parameters in the MMM permeability calculation and only requiring single-gas experimental or simulation-based adsorption and permeation data on the individual MMM materials to predict the mixture perm-selectivity in the MMM as a whole. Further, we validate the new approach by using available experimental permeation data for the separation of an equimolar binary mixture of propylene (C\textsubscript{3}H\textsubscript{6}) and propane (C\textsubscript{3}H\textsubscript{8}) in ZIF-8/PIM-6FDA-OH MMMs, with the rigorous simulation results showing very good agreement with both experimental single and mixed-gas permeabilities and perm-selectivities.

KEYWORDS

Mixed-matrix membrane, mixture transport; multicomponent adsorption and diffusion; membrane simulations, Maxwell-Stefan equations
1. INTRODUCTION

Membrane technologies have emerged as a suitable solution for applications with profound environmental and industrial significance such as carbon dioxide capture [1–3], natural gas purification [4–6] and light hydrocarbon separation [7–9]. Amongst membrane alternatives, mixed-matrix membranes (MMMs), comprising a selective inorganic dispersed phase embedded in a continuous polymer matrix, have been shown to overcome limitations of conventional polymer and inorganic membranes [1,10,11]. Such composite membranes combine the high intrinsic selectivity of advanced molecular sieving materials (e.g. zeolites, carbons, metal-organic frameworks) with the robust processing capabilities and mechanical properties of glassy polymers [12,13]. Thus, these features allow MMMs to provide better selectivity than their polymer counterparts [10,14,15], and therefore exceed the intrinsic trade-off between permeability and selectivity in polymers [16,17].

Over the last decades, much effort has been devoted to the optimization of MMMs in practice [7,11,18–21], with a number of experimental works even reporting near ideal polymer-particle interface and high MMM selectivity based on pure permeant fluxes [4,18,22,23]. While some experimental studies have also focused on gas mixtures; including CO₂/CH₄ [5,19], H₂/CO₂ [24], O₂/N₂ [25], C₂H₄/C₂H₆ [26] and C₃H₆/C₇H₈ [7,27]; achieving high selectivity at common industrial operating pressures (2–10 bar) is often limited by the confluence of effects of different mechanisms, which include polymer plasticization [5,14], competitive adsorption [5,14] and friction between molecules of different permeants [14].

Amongst these factors, polymer plasticization is caused by the membrane exposure to highly soluble permeants that by strongly interacting with the polymer increase its chain mobility and free volume [14,28,29], weakening the membrane size-sieving ability and largely leading to decreased selectivities in practice [5,14,30,31]. Over the past decade, there has been much experimental activity devoted to the fabrication of plasticization-resistant MMMs [6,32–36], in which different cross-linking techniques have
been shown to suppress plasticization, improve the membrane durability and selectivity [5,22,37,38].

Furthermore, selectivity enhance in cross-linked membranes was recently verified through molecular dynamics (MD) simulations of various chitosan/graphene oxide membranes [39], in which cross-linked nanostructures were simulated using a multiscale approach.

Alternatively, the other two factors affecting mixture transport in MMMs (i.e. competitive adsorption and permeant friction) have received much less attention [2,14]. While both phenomena have been hypothesized to have a strong effect on the MMM selectivity [5,7,14,19,27,40], only a few experimental studies report the sensitivity of mean diffusivity and solubility coefficients to the mixture composition in plasticization-resistant MMMs [26,41]. Furthermore, there is no agreement of the effect of these mechanisms on the membrane selectivity, with some studies reporting similar or even better selectivities for the mixture when compared to pure-gas feeds [25], while others report an opposite tendency [7,19,27,40]. Thus, effects of adsorbate-adsorbate interactions on the selectivity have remained little understood, and largely overlooked in permeation models for MMMs [2,14].

Models for mixture permeation in MMMs are based on early theories for the transport in composite media, grounded on the effective medium theory (EMT) [2,14,42,43]. In these early models, the MMM permeability is always based on the permeability and volume fraction of the membrane constituent phases (i.e. filler phase and polymer matrix) while considering the driving force (e.g. pressure gradient) constant across the MMM [2,14,44]. Under these considerations, existing permeation models are unable to accommodate effects of features such as the interplay between isotherm nonlinearity and finite filler particle size in the calculation of the single-gas permeabilities; recently shown to be not captured by the Darken thermodynamic factor or free volume concepts alone [45]. The task is made even more complex by the need to capture effects of permeant interactions on the selectivity, with EMT models only considering competitive adsorption through the extended Langmuir or dual-mode models [46–48]; however, these always assume concentration-independent transport diffusivities when predicting the mixture permeabilities (fluxes) [49–51]. Besides this limitation, permeant fluxes are largely considered
independent of the concentration gradient of the other species in the mixture [51–53], even though this
latter assumption has been shown inadequate in the transport of gas mixtures in rubbery polymer [54–
57] and zeolite-based membranes [58–60] through molecular dynamics (MD) simulations as well as the
Maxwell-Stefan (M-S) approach to the mass transfer [61].

To overcome limitations of early permeation models, we extend here the M-S formulation of
irreversible thermodynamics [61] for predicting multicomponent transport in MMMs. We note that while
the formulation has been previously used to describe the binary mixtures transport through flake-like
MMMs [42,62], the approach has been only applied in the low pressure Henry’s law limit, and thus
disregards effects of both competitive adsorption and permeant friction in the calculation of the mixture
fluxes. In this work, we explicitly consider these effects using a simulation-based rigorous modeling
approach (SMA) [44,63,64], with the SMA based on numerical solution of coupled partial differential
equations (PDEs) on a given three-dimensional (3-d) computational system via the finite-element method
(FEM) [64–66]. Consequently, the SMA explicitly accommodates effects of intrinsic MMM features
such as filler particle size [66], isotherm nonlinearity [45] and non-uniformity of the concentration field
[67], without introducing empirical fitting parameters in the permeability (flux) calculation.

Besides the above, a key advantage of our M-S formulation is that it only requires single-gas
experimental or simulation-based (e.g. MD) adsorption equilibrium and permeation data on the
individual MMM materials to predict the mixture permeabilities in the MMM as a whole. To do so, we
characterize the mixture steady-state fluxes by reformulating the M-S constitutive equations [68] through
the Onsager formalism [69], following the Hu-Bhatia approach [70] for multicomponent transport in
pore networks. Thus, by adapting their formulation for the transport in a single pore, we extend the dual-
mode/partial immobilization (DM/PI) theory [49,50] for single-gas transport in glassy polymers to
describe mixed-gas permeation in pure glassy polymer membranes and MMMs, as it considers the
contribution to the permeant fluxes of two parallel diffusion modes (i.e. Henry and Langmuir) arising
from the gas transport through the semi-permanent gaps between polymer chains. In this way, our local
transport diffusivities are not only dependent on the M-S diffusivities in these two transport modes, but also on the non-uniform partial pressure gradients of all species in the mixture. Furthermore, we show that our simulation technique leads to accurate mixed-gas permeability predictions at pressures relevant to actual industrial operation (1 – 8 bar), with the new approach validated by using available permeation data for the separation of C$_3$H$_6$/C$_3$H$_8$ in PIM-6FDA-OH membranes and ZIF-8/PIM-6FDA-OH MMMs [27,71].

2. MODELING MIXTURE PERMEATION IN MIXED-MATRIX MEMBRANES

Existing models for mixtures permeation are grounded on effective medium theory (EMT), while describing the mixed-gas permeabilities in the MMM constituent phases through the solution-diffusion mechanism [10,11,14]. Based on this transport mechanism, the permeability of species $i$ in phase $k$ is defined as [43,72–76]:

$$
P_{ki} = \left< D^k_i \right> \left< S^k_i \right>$$

(1)

where the concentration-averaged diffusivity, $\left< D^k_i \right>$, and solubility coefficients, $\left< S^k_i \right>$, of species $i$ in the phase $k$ are often expressed as [51,72,73,77,78]:

$$
\left< D^k_i \right> = \frac{1}{(c_{ki} - c_{ki})} \int_{c_{ki}}^{c_{ki}} D^k_i(c_{ki})dc_{ki}
$$

(2)

$$
\left< S^k_i \right> = \frac{(c_{ki} - c_{ki})}{(p_{i2} - p_{i1})}
$$

(3)

with $c_{ki}$ being the adsorbed concentration of species $i$ in $k^{th}$-phase and $p_i$ the partial pressure of species $i$ while subscripts 1 and 2 denote the retentate and permeate sides of the membrane, respectively. Then, upon considering $D^k_i$ to be concentration-independent, $p_{i2} \approx 0$ and $c_{ki} \approx 0$ [43,47,49,78], Eq. (2) simplifies to $\left< D^k_i \right> = D^k_i$, Eq. (3) to $\left< S^k_i \right> = c_{ki} / p_{i1}$ and the permeability in Eq. (1) may be rewritten as [79]:

$$
P_{ki} = D^k_i \left< S^k_i \right>
$$

(4)
\[ P_{i}(p_{ni}) = D_{i}^{c_{i}} \frac{c_{i}}{P_{ni}} \] (4)

where Eq. (4) is usually used in conjunction with an EMT model, such as that of Maxwell [80] or Bruggeman [81], to describe the mixture permeabilities in the MMM [43,47]. We consider the Chiew-Glandt model [82], as it has been shown to describe well single-gas permeabilities in MMMs having relative small mean filler particle size at moderate/high filler loadings \( \phi \leq 0.645 \) [44,45,66,83]. In this model, the permeability of species \( i \) in the MMM \( (P_{i}) \) is given by [82]:

\[ P_{i}(p_{ni}) = P_{\alpha}(p_{ni}) \left[ 1 + 2\beta_{i} \langle \phi \rangle + (\kappa_{i} - 3\beta_{i}^{2})(\langle \phi \rangle)^{2} \right] \] (5)

with \( \beta_{i} = (\alpha_{i} - 1)/(\alpha_{i} + 2) \), \( \alpha_{i} = P_{\beta}(p_{ni})/P_{\alpha}(p_{ni}) \) and \( \kappa_{i} = a_{i}(\beta_{i}) + b_{i}(\beta_{i}) \langle \phi \rangle^{2} \) [66,83]. Here, \( \langle \phi \rangle \) is the mean filler phase volume fraction and, \( P_{\beta} \) and \( P_{\alpha} \) are the permeabilities of species \( i \) in the filler and polymer phases following Eq. (4). In general, the adsorption isotherm in the filler is assumed well-described by the extended Langmuir model [7,20,21,84–86], which leads to [43,47]:

\[ P_{\beta}(p_{ni}) = D_{\beta}^{c_{\beta}k_{\beta}} i = 1,2,\cdots,n \] (6)

by following Eq. (4), with \( n \) being the number of species in the mixture. Here, \( D_{\beta} \) is the concentration-independent Fickian diffusivity in the filler phase, and \( c_{\beta} \) and \( k_{\beta} \) are the saturation concentration and affinity constant of species \( i \) in the filler phase, respectively. Similarly, adsorption equilibrium in glassy polymer matrices is assumed well-described by the extended dual-mode isotherm [40,49,52,78,84,87], which leads to [37,46]:

\[ P_{i}(p_{ni}) = D_{i}^{h} k_{hi} + D_{i}^{l} \frac{c_{i}k_{li}}{1 + \sum_{i=1}^{n} k_{li}p_{ni}} i = 1,2,\cdots,n \] (7)

upon considering two parallel transport environments in Eq. (4) [49,50], with \( n \) having the same connotation as in Eq. (6). Here, \( D_{i}^{h} \) and \( D_{i}^{l} \) are the concentration-independent Fickian diffusivities in
the Henry and Langmuir environments, respectively, and $k_{hi}$, $c_{si}$ and $k_{ci}$ are the Henry’s law constant, saturation concentration and affinity constant of species $i$ in the polymer phase, respectively. Further, Eq. (7) is known as the dual-mode/partial immobilization (DM/PI) model [87,88], as the permeant is assumed fully mobile in the Henry’s law environment and partially mobile in the Langmuir environment [47,48,53,87]. Then, once the permeability of each component in the MMM is calculated via Eqs. (5)-(7), the separation factor of species $i$ relative to species $j$ ($\alpha$) may be calculated as [40,72,78,89].

$$\alpha = \frac{P_i}{P_j} \left(\frac{\Delta p_i / p_i}{\Delta p_j / p_j}\right)$$

with Eq. (8) simplifying to:

$$\alpha_p = \frac{P_i}{P_j}$$

upon considering the downstream partial pressures negligible ($p_{i2} \approx p_{j2} \approx 0$) [40,51,72], with $\alpha_p$ being the ideal selectivity or perm-selectivity. In what follows, we refer to Eqs. (5)-(7) and (9) as the EMT model and to Eqs. (7) and (9) as the DM/PI model.

While both DM/PI and EMT models are commonly used as reference in practical applications [43,47,90], they are often found to fail when compared to experimental mixture permeation data [46,48,51,87]. This is because these models are limited to systems operating at low pressure [2,91], in which it is appropriate to assume negligible friction between permeating species and concentration-independent Fickian diffusivities [48]. Further, while Kamaruddin and Koros [51] later attempted to include friction-related effects in the permeability calculation by including the bulk-flux contribution in the DM/PI model, known as the frame of reference/bulk flow model [46,48,53], the model has been shown to fail when describing gas mixtures with strong adsorbate-adsorbate interactions [48,53]. This is because the bulk flow model also assumes concentration-independent Fickian diffusivities in the permeability calculation. We note here that while assuming uniform concentration gradients across the MMM together with constant Fickian diffusivities represents the main limitations of both DM/PI and
EMT models, all early EMT models are also limited to systems with relative small particle size [44,45,66,67].

3. SIMULATION OF THE GAS PERMEATION IN MIXED-MATRIX MEMBRANES

The M-S approach [61] for mass transfer has been widely applied to calculate mixture fluxes (i.e. permeability) of polymer [53–55,57] and inorganic porous membranes [59,60,92–94]. However, the approach is less commonly used for characterizing mixture transport in MMMs [2,14]. To date, only Sheffel and Tsapatsis have shown applicability of the M-S formulation, considering flake-like MMMs [42,62], using the finite-element method (FEM) to solve the membrane scale model imbedding the M-S constitutive equations, while also assuming validity of the low pressure Henry’s law limit. This assumption leads to uniform local permeability profiles across the MMM, and effects of both non-uniformity of the driving force arising from nonlinear adsorption equilibrium in the MMM, as well as adsorbate-adsorbate interaction effects arising from permeant friction and competitive adsorption in the MMM, therefore remain to be addressed.

In the following section, we relax these early assumptions upon reformulation of the M-S constitutive equations [61] through the Onsager formalism [69] to simultaneously solve the coupled three-dimensional (3-d) partial differential equations (PDEs) describing the transport in full-scale MMMs, using the COMSOL Multiphysics® software package together with MATLAB®. Here, we consider a full-scale (3-d) MMM as a semi-infinite flat composite system comprising randomly distributed spherical fillers embedded to a continuous matrix, in which the composite thickness is finite in the permeation direction (\(x\)-direction) and infinite in the remaining directions (\(y\)-direction and \(z\)-direction).

3.1. Formulation of the transport problem in the mixed-matrix membrane

Following our work [45], we constructed 3-d MMMs with randomly distributed spherical fillers using a Force-Biased algorithm (FBA) [95]. For every packing fraction, we generated five independent non-overlapping uniform size sphere configurations and averaged all simulation results amongst these
configurations. Consequently, simulation results in Section 4 correspond to averaged values, in which
error bars that accompany every data point correspond to the standard deviation amongst simulated
configurations at fixed mean filler volume fraction.

Figure 1 depicts exemplary simulation boxes for three relative particle sizes (\( \rho = 0.002, 0.080, 0.160 \)) having a mean filler volume fraction equal to \( \langle \phi \rangle = 0.1 \). Here, we define the mean filler volume fraction
as \( \langle \phi \rangle = \phi_o (1 - 2\rho) = 4\pi N r_o^3/(3d w \ell) \) [66], with \( \phi_o \) being the filler loading in a membrane with negligible
particle size, i.e. for sufficiently large system size such that \( \rho \rightarrow 0 \). Further, \( N \) is the number of
particles in the simulation box, \( r_o \) the particle radius, \( \ell \) the MMM thickness in the \( x \)-direction
(permeation direction), \( w \) the width in the \( y \)-direction and \( d \) the depth in the \( z \)-direction. Table A-1 of
Appendix A lists dimensions of simulation boxes (\( d, w \) and \( \ell \)) and filler particle sizes (\( r_o \)).

Our simulations consider the steady-state transport of a binary gas mixture through 3-d MMMs,
following:

\[
(\nabla \cdot J_i) = 0, \quad i = 1, 2
\]

with boundary conditions:

\[
x = 0, \quad C_{bi}(0, y, z) = C_{b1}
\]

\[
x = \ell, \quad C_{bi}(\ell, y, z) = C_{b2}
\]

where \( J_i \) is the steady-state flux of species \( i \) at location \((x, y, z)\) in the MMM. Further, we consider the
pseudo-bulk concentration in the MMM as the field variable, with \( C_b = p_i/R_g T_g \) where \( R_g \) and \( T_g \) are
the universal ideal gas constant and temperature, respectively. Thus, $C_\text{bi1}$ in Eq. (11) and $C_\text{bi2}$ in Eq. (12) correspond to the retentate and permeate pseudo-bulk concentrations of species $i$ in the MMM, respectively. Following our work [66], equality of fluxes and pseudo-bulk concentrations are set as boundary conditions at the filler-matrix interface, while periodic boundary conditions are applied at the membrane ends in the $y$ and $z$ directions (c.f. Figure 1).

Upon expressing the flux of species $i$ ($J_i$) in Eq. (10) through the Onsager formalism [69], while assuming local equilibrium between the membrane surface and bulk gas, with the chemical potential gradient of species $i$ following $d\mu_i = R_g T_g d(\ln C_i)$, the fluxes in the filler ($J_f$) and continuous ($J_c$) phases may be rewritten as:

$$J_f = -R_g T_g \left[ \sum_{j=1}^{n_i} \frac{\Omega^f_j}{C_{bj}} \nabla C_{bj} \right], \quad i = 1, 2$$  

(13)

$$J_c = -R_g T_g \left[ \sum_{j=1}^{n_i} \frac{\left(\Omega^h_j + \Omega^l_j\right)}{C_{bj}} \nabla C_{bj} \right], \quad i = 1, 2$$  

(14)

where $\Omega^f_j$ are the position-dependent Onsager phenomenological coefficients in the filler phase while $\Omega^h_j$ and $\Omega^l_j$ correspond to those in the Henry and Langmuir environments of the glassy polymer matrix, respectively, as defined in Section 3.2. Further, Eq. (14) is inspired by Barrer’s parallel treatment [49] for the Fickian diffusivity of pure gases in glassy polymers [46,48,50,87,96]. Consequently, the total flux through the polymer matrix ($J_c$) in Eq. (14) corresponds to the summation of the fluxes based on two parallel transport modes [49] with $J_c = J_{hi} + J_{\mu}$ [50,96], where $J_{hi}$ and $J_{\mu}$ are the fluxes of species $i$ in the Henry and Langmuir environment, respectively. Here, our parallel treatment for the permeant flux calculation in the polymer phase corresponds to a distinctive feature of our M-S formulation in comparison to earlier adaptations of the approach for multicomponent transport in glassy polymers [42,53,62,97], always assuming the gas diffusion to be negligible in either the Henry or Langmuir environment.
3.2. Characterization of Onsager phenomenological coefficients

Following Hu and Bhatia’s [70] treatment for the transport at the single pore level, we adapt the M-S constitutive equations [61] to define the Onsager phenomenological coefficients [69]. Thus, we consider the permeant flux in the $k^{th}$-phase and/or environment to be defined by [61]:

$$
\frac{c_{ki}}{R_g T_g} \nabla \mu_i = \sum_{j=1}^{n} \frac{c_{ij}J_{kj} - c_{ij}J_{kj}}{c_{ij}D_{ij}^k} + \frac{J_{ki}}{D_i^k}, \quad i = 1, 2, \ldots, n
$$

(15)

where $k = f$ denotes the filler phase while $k = h$ or $k = l$ denote the Henry and Langmuir environments in the polymer phase, respectively. Thus, by combining Eq. (15) with Onsager’s flux definition following Eq. (10)-(14), the phenomenological coefficients are given by [70]:

$$
\Omega_{ij}^k = \frac{1}{R_g T_g} \left[ \frac{c_{ij}c_{ij}R_y D_{ij}^k D_{ij}^k}{R_y - c_{ij}c_{ij}D_{ij}^k D_{ij}^k} \right], \quad i, j = 1, 2; \quad i \neq j
$$

(16)

$$
\Omega_{ij}^k = \frac{1}{R_g T_g} \left[ \frac{c_{ij}c_{ij}c_{ij}c_{ij}D_{ij}^k D_{ij}^k D_{ij}^k}{R_y - c_{ij}c_{ij}D_{ij}^k D_{ij}^k} \right], \quad i, j = 1, 2; \quad i \neq j
$$

(17)

with $R_y = c_{ij}D_{ij}^k + c_{ij}D_{ij}^k$, $c_{ij} = \sum_i c_{ij}$, $\Omega_{ij}^k = \Omega_{ji}^k$, and $D_{ij}^k = D_{ij}^k$. Here, $c_{ij}$ is the adsorbed concentration of species $i$ in the $k^{th}$-phase and/or environment, defined in Section 3.3. Further, $D_i^k$ is the M-S diffusivity of species $i$ in the $k^{th}$-phase and/or environment while $D_{ij}^k$ is M-S cross-diffusivity of species $i$ and $j$ in the $k^{th}$-phase and/or environment, defined in Section 3.4.

3.3. Multicomponent adsorption equilibrium

To solve Eq. (10)-(14), an appropriate definition of the adsorption equilibrium is required. Several theories have been proposed [98–100] to describe mixture adsorption equilibrium in solid adsorbents, including the multicomponent Langmuirian theory (MLT) [101] and ideal adsorbed solution theory (IAST) [102], that are commonly used to describe adsorption equilibria in pure polymer [42,46,53,97] and inorganic [58,99,103,104] membranes. We consider both theories in our simulations while assuming...
the single-gas adsorption in the filler and polymer phases well-described by the Langmuir and dual-mode models [45].

3.3.1. **Multicomponent Langmuirian theory**

Following the multicomponent Langmuirian theory (MLT) [101], the adsorbed concentration in the filler phase, \( c_{fi}^i(C_{hi}) \), is given by [46,47,84]:

\[
c_{fi}^i(C_{hi}) = \frac{c^i_{fi}k_{fi}C_{hi}(x, y, z)}{1 + \sum_{j=1}^{n-2} k_{fi}C_{bj}(x, y, z)}, \quad i = 1, 2
\]

(18)

with \( c^i_{fi} \) and \( k_{fi} \) having the same connotation as in Eq. (6). Similarly, we consider the extended dual-mode model to describe the adsorbed concentration in the polymer, \( c_{ci}^i(C_{hi}) \), as [84,105]:

\[
c_{ci}^i(C_{hi}) = c_{hi}^i(C_{hi}) + c_{li}^i(C_{hi})
\]

(19)

\[
c_{hi}^i(C_{hi}) = k_{hi}C_{hi}(x, y, z), \quad i = 1, 2
\]

(20)

\[
c_{li}^i(C_{hi}) = \frac{c^i_{li}k_{li}C_{hi}(x, y, z)}{1 + \sum_{j=1}^{n-2} k_{li}C_{bj}(x, y, z)}, \quad i = 1, 2
\]

(21)

where \( c_{hi}^i \) and \( c_{li}^i \) are the adsorbed concentration of species \( i \) in Henry and Langmuir environment, respectively. Here, \( k_{hi} \), \( c^i_{fi} \) and \( k_{li} \) have the same connotation as in Eq. (7).

3.3.2. **Ideal adsorbed solution theory**

Based on the ideal adsorbed solution theory (IAST) [102], we consider that the mixture adsorption in both filler and continuous phases is well-described by [98,102,106]:

\[
\int_0^{C_{hi}} \frac{c_{ci}}{C_{hi}} dC_{by} = \int_0^{C_{by}} \frac{c_{li}}{C_{by}} dC_{by}
\]

(22)

\[
C_{hi} = C_{by}^{n}x_{hi}, \quad i = 1, 2
\]

(23)

\[
\sum_{i=1}^{n-2} x_{hi} = 1
\]

(24)
\[
\frac{1}{c_T^k} = \sum_{i=1}^{n_{c_i}} x_{ki} c_{ki}^n
\]  
(25)

\[c_{ki} = c_{ki}^n x_{ki}, \quad i = 1, 2\]  
(26)

where \(c_T^k\) is the total adsorbed concentration in the \(k^{th}\)-phase and/or environment while \(c_{ki}\) and \(x_{ki}\) are the adsorbed concentration and mole fraction of species \(i\) in the \(k^{th}\)-phase and/or environment, respectively. Here, superscript \(o\) represents the pure component at the standard state, with \(c_{ki}^o = I(C_{hi}^o)\) in Eq. (25) assumed well-fitted by pure component adsorption data [99]. Thus, we consider the Langmuir model to describe well the standard state in the filler phase, following [7,107]:

\[c_{ki}^o = \frac{c_{ki}^s k_{ki} C_{hi}^o}{1 + k_{ki} C_{hi}^o}, \quad i = 1, 2\]  
(27)

where \(c_{ki}^s\) and \(k_{ki}\) have the same connotation as in Eq. (6). Further, we consider the dual-mode model to describe well the standard state in the polymer, with [50,71,96]:

\[c_{ki}^o = c_{ki}^o + c_{ki}^s\]  
(28)

\[c_{hi}^o = k_{hi} C_{hi}^o, \quad i = 1, 2\]  
(29)

\[c_{ki}^o = \frac{c_{ki}^s k_{ki} C_{hi}^o}{1 + k_{ki} C_{hi}^o}, \quad i = 1, 2\]  
(30)

where \(k_{hi}\), \(c_{ki}^s\), and \(k_{ki}\) have the same connotation as in Eq. (7).

3.4. Definition of the Maxwell-Stefan diffusivities

We here define the M-S diffusivities for calculation of the Onsager phenomenological coefficients in each phase or transport environment in the MMM, as described below.

3.4.1. Single Maxwell-Stefan diffusivities (\(D_i^s\))

We estimate \(D_i^s\) via Eq. (1) using single-gas experimental permeation data in pure polymer and inorganic membranes. In the filler phase, we consider that the Fickian diffusivity (\(D_i^f\)) in Eq. (2) is given
by the Darken relation following \( D_i^k \approx D_i^k(0)\Gamma_{ki} \) with \( \Gamma_{ki} = d \ln C_{hi} / d \ln c_{ki} \) \([108,109]\) while assuming Langmuirian adsorption in Eq. (1), which leads to \([45,110,111]\):

\[
P_{fi} = \left\langle D_i^f \right\rangle \left\langle S_i^f \right\rangle = \frac{1}{R_g T_g} \left[ \frac{D_i^f c_i^s}{(C_{hi2} - C_{hi1})} \ln \left( \frac{1 + k_{fi} C_{hi2}}{1 + k_{fi} C_{hi1}} \right) \right]
\]

(31)

where \( P_{fi} \) is permeability in a pure inorganic membrane, with \( c_i^s \) and \( k_{fi} \) having the same connotation as in Eq. (6) and, \( D_i^f \) is the M-S diffusivity of species \( i \) in the filler phase.

In the polymer phase, we consider dual-mode adsorption in both Eqs. (1) and Eq. (2) also through the Darken model \((D_i^k \approx D_i^k(0)\Gamma_{ki})\), which leads to \([45]\):

\[
P_{ci} = \left\langle D_i^c \right\rangle \left\langle S_i^c \right\rangle = \frac{1}{R_g T_g} \left[ D_i^c k_{hi} + \frac{D_i^c c_i^s}{(C_{hi2} - C_{hi1})} \ln \left( \frac{1 + k_{ci} C_{hi2}}{1 + k_{ci} C_{hi1}} \right) \right]
\]

(32)

where \( P_{ci} \) is permeability in a polymer membrane, with \( k_{hi}, c_i^s \) and \( k_{ci} \) having the same connotation as in Eq. (7). Here, \( D_i^h \) and \( D_i^l \) are the M-S diffusivities of species \( i \) in the Henry and Langmuir environment, respectively. We note that even though Eqs. (6) and (31) for inorganic membranes, and Eqs. (7) and (32) for glassy polymer membranes, are based on the same definition of the permeability in Eq. (1), our single-gas permeabilities in Eqs. (31) and (32) consider the Fickian diffusivity dependence on concentration through the Darken model while Eqs. (6) and (7) assume concentration-independent Fickian diffusivities.

### 3.4.2. Exchange Maxwell-Stefan diffusivities \((D_{ij}^k)\)

We consider friction effects negligible in the filler, with M-S cross-diffusivities given by:

\[
D_{ij}^f \rightarrow \infty
\]

(33)

based on experimental permeation data \([110,112,113]\) and Molecular Dynamics (MD) simulations \([92,114]\) of mixtures of light hydrocarbons (e.g. \( C_2H_4/C_2H_6 \) and \( C_3H_6/C_3H_8 \)) in ZIF-8, indicating that these permeants have very weak diffusional correlation effects in such material. However, we recognize
that diffusion interactions may be significant in other fillers [61,109], and suggest the use of the Vignes interpolation formula [115] and adaptations [61,109] to characterize $D_i^f$ in other inorganic materials.

Further, such interpolation formula has been shown to reasonably represent correlation effects of binary mixtures in polymer membranes [56,97]. Thus, we define the M-S exchange diffusivities in the polymer phase as:

$$D_{ij}^x = (D_i^h)^{x_i} (D_j^l)^{x_j}$$  \hspace{1cm} (34)

where superscript $k = h$ or $k = l$ denote the Henry and Langmuir environments, respectively. Further, $x_{ik} = c_{ik}/c_T^k$ corresponds to the adsorbed molar fraction of species $i$ in the $k^{th}$-environment. Here, the use of Eq. (34) to describe interaction effects in both Henry and Langmuir transport environments arises from the consideration that both diffusion modes have a significant contribution to the total flux through the polymer [49]. This is because the mean Fickian diffusivity in the Henry environment has been shown to be about one to two orders of magnitude larger than that in the Langmuir environment for single-gases [46,47,87], with even the Henry environment governing the transport at high pressures. We note that this limiting case differs from the low pressure Henry’s law limit, in which interaction effects in the transport may be assumed negligible due to the low gas concentration in the system [42,62,79].

In summary, Eqs. (10)-(14), (16)-(21), (33) and (34) characterize the mixture transport through full-scale MMMs using the MLT to describe the adsorption equilibrium while Eqs. (10)-(14), (16), (17), (22)-(30), (33) and (34) characterize the mixture transport through full-scale MMMs using the IAST to describe the adsorption equilibrium. Here, we use a stationary fully coupled parallel sparse direct solver (MUMPS) to obtain all numerical solutions, as implemented in COMSOL Multiphysics® software package. Further, we implemented the FEM using adjustable tetrahedral meshes constraining maximum and minimum mesh element size to linearly decrease with increase of the mean filler volume fraction in the simulation box, as described elsewhere [66].
3.5. Mixture permeability and perm-selectivity

After simultaneously solving Eqs. (10)-(14), (16)-(21), (33) and (34) in the case of MLT and Eqs. (10)-(14), (16), (17), (22)-(30), (33) and (34) in the case of IAST, we calculate the mixture perm-selectivity via Eq. (9) considering the permeability of species $i$ in the MMM to follow [19,87]:

$$P_i = \frac{J_{i,x}}{R_g T_g (-\Delta C_{bi})}, \quad \Delta C_{bi} = C_{bi2} - C_{bi1}$$  \hspace{1cm} (35)

where $J_{i,x}$ is the steady-state flux through the membrane, given by:

$$J_{i,x} = \frac{\int \int_{yz} J_i(x,y,z) dydz}{\int \int_{yz} dydz}$$  \hspace{1cm} (36)

which is independent of $x$ for the semi-infinite flat MMM. Further, we calculate local position-dependent transport properties in the membrane as [45]:

$$g_i(x) = \frac{\int \int_{yz} g_i(x,y,z) dydz}{\int \int_{yz} dydz}$$  \hspace{1cm} (37)

where $g_i(x,y,z)$ is the local value of a given property of species $i$ at location $(x,y,z)$ and $g_i(x)$ corresponds to the mean value of $g_i(x,y,z)$ at location $x$ in the membrane.

In the next section, we compare permeability predictions of the DM/PI and EMT models (c.f. Section 2) and our simulation results to experimental permeation data for the separation of $C_3H_6/C_3H_8$ mixtures in pure PIM-6FDA-OH membranes [27,71] and ZIF-8/PIM-6FDA-OH MMMs [27]. The parameter values used in our simulations and the DM/PI and EMT models are listed in Table A-1 of Appendix A, with all based on experimental adsorption and permeation of pure $C_3H_6$ and $C_3H_8$ in individual PIM-6FDA-OH [71] and ZIF-8 [107] materials.

4. RESULTS AND DISCUSSION

We adopt the following conventions in the subsequent sections. We refer to propylene ($C_3H_6$) as species $A$ and propane ($C_3H_8$) as species $B$. Subscripts or superscripts $f$ and $c$ denote the filler phase.
and polymer matrix, respectively. Further, single-gas experimental and simulation profiles are depicted using closed symbols while those for the mixture use open symbols, with error bars depicted along with the symbols. All theoretical profiles based on either DM/PI or EMT models are depicted using lines. In all figures, percentage deviation amongst predictions (i.e. simulation or DM/PI and EMT models) and experimental data accompany every predicted profile, with this deviation following color conventions of the figure legend. Here, percentage deviations are calculated as the percentage normalized root-mean-squared error (NRMSE), using the mean value of the experimental data to normalize all root-mean-squared errors.

4.1. Comparison of MLT and IAST predicted mixture adsorption isotherms

Because we consider the mixture adsorption equilibrium either following the MLT (c.f. Section 3.3.1) or IAST (c.f. Section 3.3.2) in our simulations, we first compare predictions of these theories of the $C_3H_6$ adsorbed concentration (species $A$) in the filler phase, $c_{fA}$, in Figure 2(a) and polymer matrix, $c_{cA}$, in Figure 2(b). Here, insets in Figure 2 depict the $C_3H_8$ adsorbed concentration (species $B$) in each phase ($c_{fB}$, $c_{cB}$). In all cases, we consider five $A/B$ percentage molar fractions (i.e. 0/100, 25/75, 50/50, 75/25, 100/0), with the abscissa in Figure 2 corresponding to the total pressure ($p_t = p_A + p_B$) in the system. Further, symbols correspond to the single-gas experimental adsorption data in both filler [107] and polymer [71] phases, and continuous lines in Figure 2 correspond to the single-gas predicted adsorption isotherms, while dashed and dotted lines correspond to those based on MLT and IAST, respectively.

In Figure 2, we fitted the single-gas experimental adsorbed concentrations of both $C_3H_6$ and $C_3H_8$ to the Langmuir model in the filler and dual-mode model in the polymer, with our isotherm parameter fits reported in Table A-1 (c.f. Appendix A). Here, the single-gas adsorption models are in excellent agreement with the experimental isotherms, having percentage deviations of at most 4.5% for $C_3H_8$ in
ZIF-8 (c.f. Inset in Figure 2(a)) and also closely matching values reported by Zhang et al. for this material [7]. Further, both MLT and IAST provide comparable predictions of the mixed-gas \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) adsorbed concentrations for every \( A/B \) percentage molar fraction. In Figure 2(a), the adsorbed concentrations based on IAST are slightly greater for \( \text{C}_3\text{H}_6 \) and slightly lower for \( \text{C}_3\text{H}_8 \) than those based on MLT at \( p_t \geq 2 \text{ bar} \), with an opposite tendency shown in the polymer in Figure 2(b). This correspondence amongst theoretical predictions is associated with the similarity of the saturation capacity values of both \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) in both filler and polymer materials (c.f. Table A-1), as the MLT has been shown to lead to identical predictions as the IAST when saturation capacities of all species in mixture are the same [98,116].

![Figure 2](image.png)

**Figure 2.** Comparison of mixture adsorption isotherms based on MLT and IAST for five \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) percentage molar fractions (0/100, 25/75, 50/50, 75/25, 100/0) in (a) ZIF-8, and (b) PIM-6FDA-OH. Pure gas experimental data is also shown, based on literature results [7,71].

### 4.2. Single-gas permeation

A key achievement of this work is that the proposed simulation technique only requires single-gas experimental or simulation-based permeation data of the individual MMM materials (c.f. Table A-1) to predict both single-gas and mixed-gas transport in the MMM as a whole. Here, we compare the single-gas permeability predictions of simulation and theoretical (i.e. DM/PI and EMT) models to the
experimental permeabilities of pure C$_3$H$_6$ and C$_3$H$_8$ in PIM-6FDA-OH membranes [71] and ZIF-8/PIM-6FDA-OH MMMs [27]. Thus, we study single-gas permeation in these membrane systems under two typical conditions: (i) increasing the filler loading (i.e. mean filler volume fraction) at fixed transmembrane total pressure, and (ii) increasing the transmembrane total pressure difference at fixed filler loading, both discussed as follows.

First, we compare predicted (simulation and EMT model) and experimental pure C$_3$H$_6$ permeability, $P_d$, profiles with increase of mean filler volume fraction, $\langle \phi \rangle$, in Figure 3. The inset in Figure 3 depicts the pure C$_3$H$_8$ permeability, $P_b$, profiles with increase in $\langle \phi \rangle$. In both cases, we consider three filler relative particle sizes ($\rho = r_o/\ell$) in our simulations, with $\rho = 0.002$, 0.080 and 0.160. Here, the dotted line at $\langle \phi \rangle = \phi_o(1-2\rho) = 0.439$ in Figure 3 corresponds to the random closed-packed limit for a semi-infinite MMM with $\rho = 0.160$ (c.f. Figure 1), where $\phi_o = 0.645$ corresponds to the nominal random close-packed limit (c.f. Section 3) [45,66]. In Figure 3, we use the relative particle size ($\rho = r_o/\ell$) to compare predicted and experimental $P_d$ and $P_b$ profiles because this is the natural scaling variable, and permeability in MMMs has been shown to be sensitive to this ratio and not to the individual $r_o$ and $\ell$ values [66]. Consequently, any combination of $r_o$ and $\ell$ keeping $\rho$ constant leads to the same MMM permeability.

In Figure 3, the EMT model closely matches the simulation results when relative particle size is negligible (i.e. $\rho = 0.002$) for both C$_3$H$_6$ and C$_3$H$_8$, with this tendency expected and detailed discussed elsewhere [44,45,66]. Nevertheless, this model over-predicts the experimental permeabilities of both C$_3$H$_6$ and C$_3$H$_8$ in the MMM, with the experimental data lying far below the model predictions at high loadings ($\langle \phi \rangle \geq 0.4$) while having percentage deviations of 45.3% and 32.6%, respectively. This large difference between predictions of the EMT model and the experimental permeabilities suggests that the
mean relative filler particle size \( \rho = \frac{r}{\ell} \) is large in the fabricated MMMs. This tendency is corroborated by comparing the experimental permeabilities with the simulation profiles for the considered particle sizes (i.e. \( \rho = 0.002, 0.080 \) and 0.160) in Figure 3, with only simulated MMMs having \( \rho = 0.160 \) closely matching the experimental permeabilities of both \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) in the ZIF-8/PIM-6FDA-OH MMMs at high loadings (\( \langle \phi \rangle \geq 0.4 \)). Here, percentage deviations between simulations and experiments are about 40%, 15% and 5% for \( \rho = 0.002, 0.080 \) and 0.160, respectively.

**Figure 3.** Comparison of single-gas permeability prediction of simulation and EMT models with increase of the mean filler volume fraction with the experimental \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) permeabilities in ZIF-8/PIM-6FDA-OH MMMs [27].

Even though the ZIF-8 mean particle size was reported about \( r_o \approx 0.16 \mu m \) (bimodal distribution with 95.5% of ZIF-8 particles having \( r_o \approx 0.155 \mu m \) and 3.5% having \( r_o \approx 0.391 \mu m \)) in the casting solutions [27], final dried MMMs, with thicknesses of 40 \( \mu m \leq \ell \leq 60 \mu m \), were qualitatively shown to have larger particle sizes through transmission electron microscopy (TEM) images of a fraction of the MMM cross-section; in agreement with simulation results in Figure 3. Further, excellent compatibility between ZIF-8 and PIM-6FDA-OH was reported upon analysis of the TEM images [27], in which no interfacial gaps were detected. However, we note that while strong filler-polymer interaction may lead to polymer
rigidification around the filler particle [47,117,118], with the rigidified layer often assumed to have thicknesses between 20–200 nm and permeability about 20–35% lower than that in the bulk polymer. In practice [47,117–121], it has been recently shown that through MD simulations of MMMs that this layer is only about 1–2 nm thick comprising 2–3 layers of rigidified polymer [122]. Consequently, the effect of polymer rigidification on the MMM permeability is only significant when the interfacial thickness is comparable to the filler particle size, with this tendency also signaled in recent simulation work of the transport of various gases (He, H₂, CO₂, N₂) in perfluoropolymer/SAPO-34 MMMs [123].

Thus, because no interfacial gaps were detected in the TEM images and the particle size was seen to be of the order of microns, we conclude that no interfacial defect-related effects had significance on the gas permeability in the ZIF-8/PIM-6FDA-OH MMMs.

We note that filler packing structures beyond dotted limit at \( \langle \phi \rangle = \phi_o (1-2\rho) = 0.439 \) in Figure 3 are not fully random, and thus some particles rearrange to form crystalline regular regions within the simulation box [95,124]. However, because variation of the filler packing structure has been shown to have a weak effect on the MMM permeability [45,66,125,126], we consider \( \rho = 0.160 \) in our simulations of the mixture transport through MMMs. Further, while Pinnau and coworkers [27] also fabricated MMMs with \( \langle \phi \rangle \approx 0.6 \) and \( \langle \phi \rangle \approx 0.72 \), permeation data of these membranes are not considered here. This is because our simulations consider non-overlapping sphere packing structures (c.f. Figure 1), and to generate structures with \( \rho = 0.160 \) and \( \langle \phi \rangle \geq 0.50 \) (\( \phi_o \geq 0.74 \)), particles are required to overlap in the simulation box [127].

Second, we study the effect of increasing the transmembrane total pressure difference, \( \Delta p_T = |p_2 - p_1| \), on the effective permeability in Figure 4. Here, Figure 4(a) depicts a comparison of the single-gas predicted and experimental \( C_3H_6 \) permeability, \( P_d \), profiles in a polymer membrane while Figure 4(b) depicts a comparison of those in a MMM having a relative particle size of \( \rho = 0.160 \) and mean filler
volume fraction of $\langle \phi \rangle \approx 0.4$, with simulation results only shown for $\rho = 0.160$ because predictions based on this relative particle size well-matched the experimental permeabilities in Figure 3. The insets in Figure 4 accordingly compare the single-gas predicted and experimental perm-selectivity, $\alpha_p$, profiles with increase of $|\Delta p_t|$ in each membrane. Further, dashed trends in Figure 4(a) correspond to predictions based on the DM/PI model while continuous ones in Figure 4(b) correspond to those based on EMT model.

Figure 4. Effect of transmembrane total pressure on the pure C$_3$H$_6$ and C$_3$H$_8$ permeabilities in (a) PIM-6FDA-OH membranes [71], and (b) ZIF-8/PIM-6FDA-OH MMMs [27], with simulations considering $\langle \phi \rangle \approx 0.4$ and $\rho = 0.160$.

In Figure 4(a), DM/PI model results closely match the experimental permeability profile of C$_3$H$_6$ and C$_3$H$_6$/C$_3$H$_8$ perm-selectivity in the PIM-6FDA-OH membrane, having percentage deviations of 1.4% and 3.2%, respectively. This tendency is expected, as the DM/PI model in Eqs. (7) and (9) is fitted to the experimental single-gas permeabilities [71] to estimate the concentration-independent transport diffusivities in the Henry’s law and Langmuir environments (c.f. Table A-1). Similarly, simulations well-match the experimental single-gas C$_3$H$_6$ permeability and C$_3$H$_6$/C$_3$H$_8$ perm-selectivity profiles [71], with this tendency expected because Eq. (32) is also fitted to the pure C$_3$H$_6$ and C$_3$H$_8$ permeabilities [71] to estimate the M-S diffusivities in the Henry’s law and Langmuir environments (c.f. Table A-1).
Further, to calculate the $\alpha_p$ in the inset of Figure 4(a), we estimated the Fickian and M-S diffusivities considering a decrease of 10% in the $C_3H_8$ permeability between 2–8 bar in Eqs. (7) and (32), respectively. This is based on the reported experimental mixed-gas $C_3H_8$ permeabilities in PIM-6FDA-OH [71], shown to decrease about 10% between 2–8 bar and leading to $D^f_B/D^h_B \approx 0.029$ and $D^f_B/D^h_B \approx 0.33$ (c.f. Table A-1), consistent with experimentally-based single-gas $C_3H_8$ mean Fickian diffusivity ratios ($D^f_B/D^h_B$) in polyimides [37,46].

In Figure 4(b), the EMT model over-predicts both experimental $C_3H_6$ permeability and $C_3H_6/C_3H_8$ perm-selectivity in the MMM, with percentage deviations of 33.6% and 6.8%, respectively. This tendency is expected and associated with the EMT assumption of negligible filler particle size in the MMM on the permeability calculation [44,45,66]. Further, because the EMT model over-prediction of the permeability is about 10% greater for $C_3H_6$ than $C_3H_8$ (c.f. Figure 3), $\alpha_p$ is found to increase for $|\Delta p| \geq 2$ bar in the inset of Figure 4(b) based on this model. Alternatively, simulation predictions suggest a decrease of $\alpha_p$ with increase of $|\Delta p|$, closely matching the single-gas experimental $C_3H_6$ permeability and $C_3H_6/C_3H_8$ perm-selectivity in the MMM, with percentage deviations of 7.5% and 1.7%, respectively. Further, even though the single-gas experimental perm-selectivities are only available at $|\Delta p| = 2$ bar in Figure 4(b), we show that an increase of $|\Delta p|$ leads to a decrease of the MMM perm-selectivity for this system in the next section.

4.3. Mixed-gas permeation with equimolar feed composition

We study the separation of an equimolar $C_3H_6/C_3H_8$ mixture in PIM-6FDA-OH membranes [27,71] and ZIF-8/PIM-6FDA-OH MMMs [27]. Thus, Figure 5 depicts a comparison of the predicted and experimental mixed-gas $C_3H_6$ permeability, $P_4$, profiles with increase of the transmembrane total pressure difference, $|\Delta p|$, with insets in Figure 5 depicting the perm-selectivity, $\alpha_p$, profiles with
increase of $|\Delta p|$. Here, Figure 5(a) corresponds to a pure polymer membrane and Figure 5(b) to a MMM having $\rho = 0.160$ and $\langle \phi \rangle \approx 0.4$. In each case, the simulations consider the MLT (c.f. Section 3.3.1) and IAST (c.f. Section 3.3.2) to describe the multicomponent adsorption equilibrium, with circle symbols in Figure 5 corresponding to the MLT and cross symbols to the IAST. Further, experimental data in Figure 5(a) corresponds to the average of the permeabilities and selectivities of two different PIM-6FDA-OH membranes fabricated by Pinnau and coworkers in their sequence of works [27,71].

**Figure 5.** Effect of transmembrane total pressure on the mixed $^{3}C_{3}H_{6}$ and $^{38}C_{3}H_{8}$ permeabilities in (a) PIM-6FDA-OH membranes [27,71], and (b) ZIF-8/PIM-6FDA-OH MMMs [27], with simulations considering $\langle \phi \rangle \approx 0.4$ and $\rho = 0.160$.

In Figure 5(a), the DM/PI model over-predicts the experimental $^{3}C_{3}H_{6}$ permeability and $^{38}C_{3}H_{8}/C_{3}H_{8}$ perm-selectivity profiles, having large deviations of 57.6% and 119.5%, respectively. These deviations are associated with the DM/PI model assumption of concentration-independent Fickian diffusivities in both the Henry’s law and Langmuir environments (c.f. Section 2). Further, upon comparison of Figure 4(a) and Figure 5(a), it is evident that the DM/PI model predicts an increase of the permeability of $^{3}C_{3}H_{6}$ in the mixture when compared to the single-gas permeability profiles. However, this tendency is inconsistent with both experimental and simulation profiles, in which the permeability of $^{3}C_{3}H_{6}$ in the mixture is about 35% lower than pure $^{3}C_{3}H_{6}$. In Figure 5(b), the EMT model also over-predicts
experimental $C_3H_6$ permeability and $C_3H_6/C_3H_8$ perm-selectivity, having percentage deviations of 53.2% and 98.4%, respectively. Similar to Figure 5(a), this is tendency associated with EMT model assumptions of constant Fickian diffusivities and constant permeabilities in all phases of the MMM.

In Figure 5, our simulations well-match the experimental $C_3H_6$ permeability and $C_3H_6/C_3H_8$ perm-selectivity profiles. Here, both MLT and IAST lead to comparable predictions of the effective permeability, with percentage deviations of about $10-20\%$. We associate the increase of the percentage deviation of our mixture simulation results ($10-20\%$) in Figure 5 when compared to the single-gas deviations ($1-10\%$) in Figure 4 with experimental differences amongst permeation studies [27,71]; as the mixed-gas permeabilities and perm-selectivities in PIM-6FDA-OH were reported about $10-20\%$ larger in the former of these [71] than in the latter [27].

### 4.4. Effect of mixture composition on the membrane performance

Figure 6 depicts a comparison of the $C_3H_6/C_3H_8$ mixture permeabilities and perm-selectivity predictions based on our simulations and theoretical (i.e. DM/PI and EMT) models to the experimental permeabilities with increase of the $C_3H_8$ feed molar fraction, $y_{B1}$, at $\Delta p = 2$ bar. Thus, Figure 6(a) depicts $C_3H_8$ permeability, $P_A$, profiles with increase of $y_{B1}$ in the polymer membrane, in which inset accordingly depicts $C_3H_8$ permeability, $P_B$, profiles. Similarly, Figure 6(b) depicts $C_3H_6$ and $C_3H_8$ permeability profiles in a MMM with $\rho = 0.160$ and $\langle \phi \rangle = 0.4$. Further, Figure 6(c) and (d) depict the perm-selectivity, $\alpha_p$, profiles with increase of $y_{B1}$ in the polymer membrane and MMM, respectively. In all cases, simulation predictions are based on the MLT, as the MLT is less computationally intensive than IAST and both theories provide comparable predictions of the mixture $c_{ki}$ (c.f. Figure 2), $P_i$ and $\alpha_p$ at $|\Delta p| = 2$ bar (c.f. Figure 5).
Figure 6. Effect of C<sub>3</sub>H<sub>8</sub> feed composition on the mixture permeabilities and perm-selectivity for |Δp| = 2 bar: C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> permeabilities in (a) PIM-6FDA-OH membrane [27,71] and (b) ZIF-8/PIM-6FDA-OH MMM [27], and perm-selectivity in (c) PIM-6FDA-OH membrane [27,71] and (d) ZIF-8/PIM-6FDA-OH MMM [27]. The MMM has ⟨φ⟩ = 0.3 and ρ = 0.160, and simulations use MLT.

In Figure 6(a) and (b), both DM/PI and EMT models predict an increase in the C<sub>3</sub>H<sub>6</sub> permeability with increase of the C<sub>3</sub>H<sub>8</sub> molar concentration in the feed for both membrane systems, and having percentage deviations of 19.5% and 48.6%, respectively. This tendency is inconsistent with both experimental and simulation results suggesting a decrease of C<sub>3</sub>H<sub>6</sub> permeability with increase of the C<sub>3</sub>H<sub>8</sub> molar concentration in the feed. Here, our simulations closely match the experimental permeabilities, with percentage deviations of only 3.7% and 5.6% in the polymer and mixed-matrix, respectively. In insets
of Figure 6(a) and (b), the theoretical models predict near constant $C_3H_8$ permeability with increase of $y_{B1}$ in both membranes while experimental and simulation-based permeability profiles suggest a decrease of the $C_3H_8$ permeability with increase of the $C_3H_8$ molar concentration in the mixture. Furthermore, both experimental and simulation-based profiles suggest that mixed-gas conditions speed up $C_3H_8$ transport through the pure polymer membrane and mixed-matrix while at the same time slow down $C_3H_6$ transport, with these interaction effects not captured neither by the DM/PI nor EMT models.

The decrease of both $C_3H_6$ and $C_3H_8$ permeability with increase of $C_3H_8$ molar concentration in Figure 6(a) and (b) leads to a decrease of the mixture $\alpha_p$ with increase of $y_{B1}$, as depicted in Figure 6(c) and (d) for each membrane system. Here, both DM/PI and EMT models over-predict the perm-selectivity in the polymer membrane and MMM, with deviations of 44.6% 50.0%, respectively. Further, while both DM/PI and EMT models have been hypothesized to account for competitive adsorption effects through the extended dual-model and Langmuir models (c.f. Section 2), the models’ large deviations in Figure 6(c) and (d) suggest that they are not appropriate when adsorbate-adsorbate interactions are significant on the mixture transport. Moreover, these models predict an increase of the perm-selectivity with increase of $y_{B1}$, which is inconsistent with experimental perm-selectivities and misleading if they were to be used as reference in practical applications.

In Figure 6(c) and (d), simulations results well-match the experimental perm-selectivities, with percentage deviations of 12.9% 8.4%, respectively. Here, the steep decrease of about 50% in $\alpha_p$ between single-gas at $y_{B1} = 0$ and mixed-gas perm-selectivities at $y_{B1} = 0.05$, suggest that permeant interactions have a strong effect on the membrane separation performance, even when $y_{B1} \to 0$ in the mixture. This is because while both $C_3H_6$ and $C_3H_8$ have been shown [17,46,128] to have similar solubilities in polymers; they exhibit large differences in their diffusion coefficients, of least one order
of magnitude, leading to a significant increase of the C$_3$H$_8$ diffusivity in the mixture; and arising from friction between C$_3$H$_6$ and C$_3$H$_8$ molecules due to their large velocity differences. Here, gas mixtures having C$_3$H$_8$ molar fraction in the range 0 < $y_{B_1}$ ≤ 0.5 display comparable perm-selectivities, with $\alpha_p$ only decreasing about 13% in this range. This tendency suggests that $\alpha_p$ is weakly sensitive to increase of the C$_3$H$_8$ molar fraction for the C$_3$H$_6$/C$_3$H$_8$ mixture with 0 < $y_{B_1}$ ≤ 0.5.

Finally, while we recognize that mixed-gas experimental permeabilities and perm-selectivities are only available at $y_{B_1} = 0.5$ in Figure 6 for this membrane system, it has been shown in similar systems (e.g. ZIF-8/6FDA-DAM MMMs and pure 6FDA-DAM membranes) that C$_3$H$_6$/C$_3$H$_8$ perm-selectivity decrease under mixture conditions [7,48]. Thus, this tendency highlights the applicability of our simulation technique as a tool for optimizing membrane-based separations, especially because available experimental studies on the C$_3$H$_6$/C$_3$H$_8$ separation in polymer membranes and MMMs are largely limited to pure gases and/or their mixtures with fixed feeding composition [7,18,27,37,40,46,48]

4.5. **Comparison of single-gas and mixed gas local transport properties**

The main feature of our simulation approach is the consideration of the non-uniformity of driving force (i.e. pressure gradient) in the permeability calculation. Thus, Figure 7 depicts a comparison of single and mixed-gas simulation predictions (using MLT) of the local partial pressure, $\bar{p}_i(x) = \bar{C}_{bi}(x)R_yT_y$, transport diffusivity, $\bar{D}_i(x)$, and adsorbed concentration, $\bar{C}_i$, profiles across the membrane to those based on the DM/PI and EMT models. Here, we consider $y_{B_1} = 0.5$ and $p_A = 1$ bar in the polymer membrane and MMM, and $\rho = 0.160$ and $\langle \phi \rangle = 0.3$ in the MMM. Further, closed symbols in Figure 7 correspond to single-gas data while open symbols corresponds to that of the mixed-gas.
Figure 7. Comparison of simulation and DM/PI and EMT model predictions of the single and mixed-gas position-dependent profiles at $|\Delta p| = 1$ bar, for the partial pressure in (a) PIM-6FDA-OH membrane and (b) ZIF-8/PIM-6FDA-OH MMM, transport diffusivity in (c) PIM-6FDA-OH membrane and (d) ZIF-8/PIM-6FDA-OH MMM, adsorbed concentration in (e) PIM-6FDA-OH membrane and (f) ZIF-8/PIM-6FDA-OH MMM. The MMM has $\phi = 0.3$ and $\rho = 0.160$, and mixture simulations use MLT.
First, Figure 7(a) depicts $\bar{p}_i(x) = \bar{C}_{h_i}(x)R_gT$ profiles in the polymer membrane while Figure 7(b) those in the MMM, with the simulation-based partial pressure profiles based on mean local pseudo-bulk concentration, $\bar{C}_{h_i}(x)$, following Eq. (37). Here, the linear partial pressure profiles in Figure 7(a) and (b) correspond to predictions based on DM/PI and EMT models for both single and mixed-gas, as both of these models consider a constant driving force (i.e. pressure gradient) across the membrane (c.f. Section 2). Here, the simulation-based $C_3H_8$ mixed-gas partial pressure profiles closely match those of the pure gas in both membranes. While this tendency is expected for any ideal equimolar gas mixture, it is evident that $C_3H_8$ partial pressure profiles are nonlinear in both membranes. This nonlinear tendency is associated with the consideration of nonlinear adsorption equilibrium in the simulations.

In the inset of Figure 7(a), both simulation-based single and mixed-gas $C_3H_8$ partial pressure profiles are nearly linear with a minor convex curvature while those in inset of Figure 7(b) are nonlinear with a symmetric curvature near the membrane ends. This tendency suggest that $C_3H_8$ partial pressure is weakly sensitive to isotherm nonlinearity in the polymer phase. In Figure 7(b), the curvature change in the $\bar{p}_i$ profiles in the regions neighboring the MMM ends is associated with increase of volume density of the polymer phase in these regions, arising from decrease of the lower-resistance filler phase in the same regions [66]. Consequently, although both DM/PI and EMT models attempt to consider isotherm nonlinearity in the MMM individual phases phase via Eq. (4), they fail to predict the permeability when the gas transport is sensitive to isotherm nonlinearity and particle size is not negligible in the system [45,67]. This is because they consider a constant pressure gradient across the membrane.

Second, we compare the mean position-dependent diffusivity of the single-gas and a mixed-gas with $y_{b1} = 0.5$ at $|\Delta p| = 1$ bar in Figure 7(c) and (d). Here, we calculate the mean local transport diffusivity of species $i$, $\bar{D}_i(x)$, across the membrane as
\[
\bar{D}_i(x) = \frac{J_{i,x}}{(-d\bar{C}_{bi}/dx)}
\]  

(38)

where the steady-state flux through the membrane, \( J_{i,x} \), is given by Eq. (36) and mean local pseudo-bulk concentration gradient, \( d\bar{C}_{bi}/dx \), by Eq. (37). Further, the dashed and continuous profiles in Figure 7(c) and (d) correspond to single-gas predictions of the DM/PI model and EMT model, respectively. Alternatively, the dotted and dashed-dotted profiles corresponds to mixed-gas predictions of the DM/PI model and EMT model, respectively.

In Figure 7(c) and (d), simulation-based \( C_3H_6 \) diffusivities are 30–40% lower in the mixture than those of the pure \( C_3H_6 \) in both membranes. Similarly, simulation-based \( C_3H_8 \) diffusivities are about 40–50% greater in the mixture than those of pure \( C_3H_8 \). Both tendencies are in agreement with the decrease of about 30–40% between the single and mixed-gas perm-selectivity in Figure 6(c) and (d). Further, both DM/PI and EMT models predict a decrease of only 5–15% between single and mixed-gas \( \bar{D}_i/D'_i \), with these profiles being constant across the membrane thickness due the assumption of linear partial pressures across the membrane (c.f. Figure 7(a) and (b)). Alternatively, the simulation-based \( \bar{D}_i/D'_i \) are nonlinear for both membranes, with this tendency suggesting that both local permeant diffusivities are strongly sensitive to isotherm nonlinearity. Similar to Figure 7(b), the decrease of both single and mixed-gas diffusivities in the regions neighboring the membrane ends in Figure 7(d) is due to the finite character of the MMMs, as filler particle concentration decreases in these regions in a finite membrane. This decrease is associated with an exclusion region of thickness equal to the particle radius, in which no particle centers can lie [45,66,67].

Third, Figure 7(e) and (f) depict a comparison of single and mixed-gas local adsorbed concentration, \( \bar{\chi}_i \), profiles for \( y_{B1} = 0.5 \) and \( p_d = 1 \) bar. Here, the simulation-based mean \( C_3H_6 \) and \( C_3H_8 \) adsorbed concentrations are calculated via Eq. (37) and those based on the EMT model are calculated as the
volume-weighted average adsorbed concentration via \( \bar{c}_i = \bar{c}_f(\bar{p}_i)(\bar{\phi}) + \bar{c}_{ei}(\bar{p}_i)[1 - (\bar{\phi})], \) with \( \bar{c}_f \) and \( \bar{c}_{ei} \) accordingly following the Langmuir and dual-mode models, respectively. In Figure 7(e), the DM/PI model predictions of \( \text{C}_3\text{H}_8 \) adsorbed concentrations deviate from those of simulation in the region \( 0.2 \leq x/\ell \leq 1 \), with this deviation associated with the DM/PI model assumption of constant driving force across the membrane (c.f. Section 2). Consequently, because the \( \text{C}_3\text{H}_8 \) partial pressure profile is nearly linear in the inset of Figure 7(a), the DM/PI model closely match simulation-based \( \bar{c}_b \) profiles in the inset of Figure 7(e). Here, the decrease of \( \bar{c}_i \) between the single-gas and mixed-gas is greater in magnitude for \( \text{C}_3\text{H}_8 \) than \( \text{C}_3\text{H}_6 \), leading to an increase of the solubility selectivity, with this tendency suggesting that the perm-selectivity is more sensitive to effects of permeant diffusion interactions than those of competitive adsorption. This is because even though solubility selectivity increases under mixture conditions, the perm-selectivity decreases (c.f. Figure 6(c) and (d)) due to significant decrease of the diffusion selectivity.

In Figure 7(f), predictions of EMT model for both \( \text{C}_3\text{H}_6 \) and \( \text{C}_3\text{H}_8 \) adsorbed concentrations profile deviate from those of simulation in the region \( 0 \leq x/\ell \leq 0.3 \), with the model unable to mimic the decrease of \( \bar{c}_i \) associated with the depletion of the lower-resistance filler phase in this region. Further, while the steep decrease of \( \bar{c}_i \) in \( 0 \leq x/\ell \leq 0.3 \) under both single and mixed-gas conditions in our simulations is associated with the effect of finite finite particle size relative to membrane thickness \( (\rho = 0.160) \) in the membrane system \([45,66]\), ignored in the EMT model \([44]\), the model deviations in the \( \text{C}_3\text{H}_8 \) adsorbed concentration profiles also extend beyond this region \( 0 \leq x/\ell \leq 0.8 \). This tendency suggests that \( \text{C}_3\text{H}_8 \) profiles are more sensitive to increase of relative particle size than that of \( \text{C}_3\text{H}_6 \). However, because the magnitude of the decrease between the single and mixed-gas \( \bar{c}_i \) is comparable for both gases, solubility selectivities in the MMM are also comparable under both single and mixed-gas conditions. Thus, this
tendency suggest that particle size has a weak effect on the MMM perm-selectivity and corroborates that
decrease of $\alpha_p$ in Figure 6(d) is due to strong permeant diffusion interaction.

4.6. Effect of particle size on the selectivity

For single-gas transport through MMMs, the effective permeability has been shown to decrease with
increase of the relative particle size in the MMM [45,66], with this tendency also shown here in Figure
3 for pure C$_3$H$_6$ and C$_3$H$_8$ in ZIF-8/PIM-6FDA-OH MMMs. For mixed-gas transport, Figure 8 depicts
a comparison of the predicted (i.e. simulation and EMT model) and experimental mixed-gas C$_3$H$_6$
permeability, $P_{A}$, profiles with increase of mean filler volume fraction, $\langle \phi \rangle$. Here, the inset in Figure 8
depicts the mixed-gas C$_3$H$_8$ permeability ($P_{B}$) profiles with increase of mean filler volume fraction, $\langle \phi \rangle$
. In both cases, we consider two filler relative particle sizes ($\rho = r_{c}/\ell$) in our simulations, with
$\rho = 0.080$ and $\rho = 0.160$. Similar to Figure 3, the dotted line at $\langle \phi \rangle = \phi_c(1-2\rho) = 0.439$ in Figure 8
corresponds to the random close-packed limit for a semi-infinite MMM having particles with a relative
size of $\rho = 0.160$.

Figure 8. Comparison between mixed-gas permeability predictions of simulation and EMT models with
increase of the mean filler volume fraction with the experimental C$_3$H$_6$ and C$_3$H$_8$ permeabilities in
ZIF-8/PIM-6FDA-OH MMMs [27], with simulation considering MLT.
In Figure 8, the EMT model over-predicts the experimental $C_3H_6$ permeabilities and under-predicts the experimental $C_3H_8$ permeabilities, having percentage deviations of 64.4% and 22.1%, respectively. By comparing the theoretical profiles in Figure 3 with those in Figure 8, it is evident that the EMT model also predicts a significant increase of $C_3H_6$ permeability and a slight decrease of $C_3H_8$ permeability under mixture conditions. This tendency is inconsistent with both experimental and simulation permeability profiles in Figure 6, which suggests that diffusion interaction effects slow-down the fast gas and speed-up the slow one. Similar to Figure 3, only the simulated MMMs with $\rho = 0.160$ closely match both experimental $C_3H_6$ and $C_3H_8$ permeabilities in Figure 8, with the mixed-gas permeabilities decreasing with increase of the relative particle size in agreement with the single-gas permeabilities in Figure 3.

Finally, Figure 9 depicts a comparison of the single and mixed-gas predictions of simulation and EMT model for the separation performance, $\alpha_p$, with increase of the mean filler volume fraction, $\langle \phi \rangle$, in the MMM. For both single and mixed-gas, we consider $|\Delta p| = 1$ bar in both EMT model and simulations, with the simulations considering two filler relative particle sizes (i.e. $\rho = 0.080$ and $\rho = 0.160$). In any case, closed symbols corresponds to single-gas permeation profiles while open symbols to those of the mixed-gas. Further, the continuous line in Figure 9 corresponds to the Burns and Koros’ experimentally observed single-gas upper bound for the $C_3H_6/C_3H_8$ in polymer membranes [17].

In Figure 9, increase of the mean filler volume fraction leads to an increase of the perm-selectivity under both single and mixed-gas permeation conditions, with the simulations predicting an increase in the perm-selectivity of about 15% between $0 \leq \langle \phi \rangle \leq 0.5$. While this increase of $\alpha_p$ with increase of $\langle \phi \rangle$ is expected, only the MMMs with $\langle \phi \rangle \geq 0.3$ surpass Burns and Koros’ upper bound under mixed-gas conditions [17]. Here, the simulation-based mixed-gas $\alpha_p$ profiles are about 50% lower than those of the pure-gas while the EMT model predictions are only 10% lower than those of the single-gas. This
tendency suggest that the use of early DM/PI and EMT models to estimate mixture-based permeabilities leads to large over-prediction of the MMM perm-selectivity. Furthermore, our simulations suggest that the MMM perm-selectivity, under both single and mixed-gas conditions, is weakly dependent on the relative particle size, as our simulation-based $\alpha_p$ profiles for $\rho = 0.160$ are only very slightly lower than those of $\rho = 0.080$ in Figure 9 when $\langle \phi \rangle \leq 0.3$. We associate this tendency with comparable decrease of the individual gas permeabilities with increase of particle size at fixed mean filler volume fraction (c.f. Figure 3 and Figure 8), so that the perm-selectivity is only very slightly affected by particle size.

Figure 9. Comparison of simulation and EMT model single and mixed-gas predictions of the perm-selectivity with increase of the mean filler particle size at $|\Delta p| = 1$ bar, with simulations considering two filler relative particle sizes ($\rho = 0.080$ and $\rho = 0.160$) and MLT.

CONCLUSIONS

We extended the Maxwell-Stefan (M-S) formulation to describe multicomponent gas transport in pure glassy polymer membranes and MMMs through solution of the 3-d transport equations in full-scale MMMs via the finite-element method (FEM). Here, a key achievement of our approach is the consideration of non-uniform pressure gradient across the membrane, disregarded in earlier approaches, leading to non-uniform position-dependent transport diffusivities across the membrane system. In our M-S formulation, we generalized the DM/PI theory to describe multicomponent transport in glassy
polymer membranes and MMMs, considering the contribution of two parallel diffusion (i.e. Henry or Langmuir) environments in the matrix for the permeant fluxes calculation. Until now, the M-S approach has been always applied considering only a single diffusion mode in the calculation of the permeant fluxes.

The new simulation technique was validated using permeation data for the separation of $\text{C}_3\text{H}_8$ and $\text{C}_3\text{H}_8$ in PIM-6FDA-OH membranes and ZIF-8/PIM-6FDA-OH MMMs. Here, we show that our simulations closely match the experimental permeabilities in each one of these membrane system, with percentage deviations of only about $10–20\%$ in comparison to earlier models shown here to have large deviations ($50–120\%$). Further, we showed that these early models fail to predict mixed-gas permeabilities because they largely disregard effects of intrinsic membrane properties, such as nonlinear permeant adsorption, competitive adsorption, diffusional friction and finite filler particle size, on the transport. Here, our simulation technique accommodates all these intrinsic membrane properties without introduction of fitting parameters in the flux calculation, only requiring single-gas adsorption and permeation data on the individual MMM constituent phases to describe the mixture transport in the MMM as a whole.

Finally, our rigorous simulation predictions suggest the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ perm-selectivity is weakly sensitive to the increase of the $\text{C}_3\text{H}_8$ feed molar fraction in the range $0 < y_{\text{C}_3\text{H}_8} \leq 0.5$ (only decreasing about $13\%$ in this range), with earlier EMT approaches, predicting an opposite tendency, unable to mimic this behavior. Besides, simulations indicate that perm-selectivities decrease about $50\%$ under mixture conditions (for a $50/50$ $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixture), with such a decrease associated with the strong permeant diffusion interaction. Here, we found both single and mixed-gas permeabilities to decrease with increase of particle size in the MMM, with this effect associated with increase of the volume density of the polymer near the membrane ends for a finite MMM. Alternatively, the perm-selectivity under both single
and mixed-gas conditions is found much less sensitive to increase of particle size in the MMM, and only weakly decreasing with increase of particle size for MMMs with $\langle \phi \rangle \geq 0.3$.

3 Acknowledgments

This research has been supported by a grant (No. DP150101996) from the Australian Research Council, through the Discovery scheme.
## Appendix A. Parameter values used in the simulations and theoretical models

### Table A-1. Parameter values for C$_6$H$_6$/C$_7$H$_8$ separation in ZIF-8/ PIM-6FDA-OH MMMs [71,107].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value(s)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{ha2}$</td>
<td>0</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$C_{hb2}$</td>
<td>0</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$c_{sA}^s$</td>
<td>$1.128 \times 10^3 (25.28)$</td>
<td>mol/m$^3$ (cm$^3$STP/cm$^3$)</td>
</tr>
<tr>
<td>$c_{sB}^s$</td>
<td>$1.253 \times 10^3 (28.08)$</td>
<td>mol/m$^3$ (cm$^3$STP/cm$^3$)</td>
</tr>
<tr>
<td>$c_{fA}^s$</td>
<td>$6.058 \times 10^3 (135.8)$</td>
<td>mol/m$^3$ (cm$^3$STP/cm$^3$)</td>
</tr>
<tr>
<td>$c_{fB}^s$</td>
<td>$5.377 \times 10^3 (120.5)$</td>
<td>mol/m$^3$ (cm$^3$STP/cm$^3$)</td>
</tr>
<tr>
<td>$D_A^{\perp}$</td>
<td>$5.6 \times 10^{-12}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_B^{\perp}$</td>
<td>$4.3 \times 10^{-14}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_A^{\parallel}$</td>
<td>$4.8 \times 10^{-13}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_B^{\parallel}$</td>
<td>$4.2 \times 10^{-14}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_A^{</td>
<td></td>
<td>}$</td>
</tr>
<tr>
<td>$D_B^{</td>
<td></td>
<td>}$</td>
</tr>
<tr>
<td>$D_A^{\parallel }$</td>
<td>$1.2 \times 10^{-15}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_B^{\parallel }$</td>
<td>$2.9 \times 10^{-12}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_A^{\parallel }$</td>
<td>$2.0 \times 10^{-14}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_B^{\parallel }$</td>
<td>$3.6 \times 10^{-13}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_A^{\parallel }$</td>
<td>$3.6 \times 10^{-14}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_B^{\parallel }$</td>
<td>$2.9 \times 10^{-14}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$k_{sA}$</td>
<td>$2.091 \times 10^{-3} (5.626 \times 10^{-1})$</td>
<td>m$^3$/mol (psia$^{-1}$)</td>
</tr>
<tr>
<td>$k_{sB}$</td>
<td>$4.068 \times 10^{-2} (1.095 \times 10^{-1})$</td>
<td>m$^3$/mol (psia$^{-1}$)</td>
</tr>
<tr>
<td>$k_{fA}$</td>
<td>$4.340 \times 10^{-2} (1.168 \times 10^{-1})$</td>
<td>m$^3$/mol (psia$^{-1}$)</td>
</tr>
<tr>
<td>$k_{fB}$</td>
<td>$6.505 \times 10^{-2} (1.751 \times 10^{-1})$</td>
<td>m$^3$/mol (psia$^{-1}$)</td>
</tr>
<tr>
<td>$k_{MA}$</td>
<td>$5.188 (3.129 \times 10^{-1})$</td>
<td>dimensionless (cm$^3$ (STP)/cm$^3$psia)</td>
</tr>
<tr>
<td>$k_{AB}$</td>
<td>$1.979 (1.193 \times 10^{-1})$</td>
<td>dimensionless (cm$^3$ (STP)/cm$^3$psia)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$20, 25, 30$</td>
<td>um</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$0.05, 0.2, 0.4$</td>
<td>um</td>
</tr>
<tr>
<td>$R_g$</td>
<td>$8.3144622$</td>
<td>m$^3$Pa/mol K</td>
</tr>
<tr>
<td>$T_g$</td>
<td>$308.15$</td>
<td>K (°C)</td>
</tr>
<tr>
<td>$T_c$</td>
<td>$20, 25$</td>
<td>um</td>
</tr>
<tr>
<td>$\rho = r_o / \ell$</td>
<td>$0.002, 0.080, 0.160$</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>

$^1$ Fitted with Eq. (6) considering $n = 1$ using single-gas experimental data from [107] (permeabilities based on kinetic uptake rate measurements). $^2$ Fitted with Eq. (7) considering $n = 1$ using single-gas
experimental permeation data from [71]. § Fitted with Eq. (31) using single-gas experimental permeation data from (permeabilities based on kinetic uptake rate measurements) [107]. †Fitted with Eq. (32) using single-gas experimental permeation data from [71].
REFERENCES


[14] B. Zornoza, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential,


