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Rigorous calculations of permeation in mixed-matrix membranes: Evaluation of interfacial equilibrium effects and permeability-based models

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ABSTRACT

We present rigorous calculations of single-component permeation in mixed-matrix membranes (MMMs), and show their importance in developing a more reliable understanding of MMM permeation behavior. We first develop methods for the construction of detailed and large-scale 3D mixed-matrix membrane (MMM) models, which are then solved by finite-element methods. Our models explicitly account for the effects of matrix-filler interfacial equilibrium in addition to the differences in Fickian diffusivity between the two phases. Analytical equations (*e.g.*, Maxwell model) can only predict the MMM permeability under an implicit assumption that the interfacial equilibrium constant K and the diffusivity ratio of the filler and the matrix (D_f/D_m) can be lumped into a single parameter, the permeability ratio $P_f/P_m = K D_f/D_m$. It is shown here that the individual values of K and D_f/D_m, and not the combined permeability ratio P_f/P_m, determine the MMM permeability. Our simulations also indicate that an ideal MMM shows no significant direct effect of filler particle size. We fit our computational data to an empirical correlation that can be easily and accurately used to calculate ideal MMM permeabilities, given equilibrium and diffusion data for the matrix and filler. We also examine some current issues regarding interpretation of MMM permeation behavior. For example, CO_2 solubilities and diffusivities in representative MOF filler and polymer matrix materials are used to rigorously compare the 'exact' predictions with permeability-based models. The rigorous calculations show non-monotonic behavior of the MMM permeability as a function of the matrix permeability, which cannot be predicted by permeability-based models. Also, the 'apparent' CO_2 permeability of ZIF-8 fillers extracted with Maxwell and Lewis–Nielsen models from the computational MMM permeation data, varies by 3 orders of magnitude depending upon the matrix polymer. Though the ZIF-8 filler maintains a constant permeability of ~ 3000 Barrer, the permeability models would require postulation of (spurious) non-idealities such as matrix-dependent filler behavior or interfacial rigidification to explain the results. Overall, this work provides a method for more reliable use of models to understand and design MMMs, as well as to better interpret the large and growing body of experimental data on these membranes.

1. Introduction

Membranes offer an energy-efficient alternative to traditional thermodynamically-controlled separations [1]. Polymeric membranes provide a range of molecular transport properties, relatively easier processing techniques, and a low membrane fabrication cost per unit membrane area. However, polymeric membranes face an intrinsic trade-off between the permeability and selectivity [2]. A widely-taken approach to overcome this trade-off is to incorporate higher-performance nanoporous particles (zeolites, metal-organic frameworks, or nanoscale materials

such as porous layers or nanotubes) as fillers into polymeric membranes. Such membranes are also referred to as 'mixed-matrix' membranes (MMMs) [3–6]. These membranes have been shown to yield enhanced separation performance (higher permeability, higher selectivity, or both), and can preserve to a large extent the good processibility characteristics of polymeric membranes.

Several analytical models, such as the Maxwell, Bruggeman, Pal, Lewis–Nielsen, and other models, have been developed to understand and predict the effective permeability and selectivity of MMMs. These analytical models are described in detail in previous reviews [7,8]. A significant – yet rarely discussed – limitation of the above models is that none of them consider the effects of the adsorption equilibrium at the polymer/filler interface on the effective permeability. Effectively, they employ the permeabilities of the

two phases (filler and polymer matrix) to describe the overall membrane permeability. The interfacial adsorption equilibrium is only implicitly included in the sense of a 'bulk' quantity, within the filler and matrix permeabilities. As pointed out in a recent work [9], this produces a situation equivalent to assuming an interfacial equilibrium constant $K \sim 1$. This can lead to qualitatively and quantitatively erroneous interpretations of permeability data from MMMs when analyzed with the above 'permeability-based' models, since most polymer/filler interfaces will not have an interfacial equilibrium constant of unity. Furthermore, the models often cannot successfully interpret experimental MMM permeation data, or reconcile data from different sources, without the postulation of 'non-idealities' such as the presence of interfacial voids or rigidified polymeric regions at the interface with the filler. These effects are taken into account by modifications of the permeability-based models to include intermediate regions at the interfaces between the matrix and the filler, as exemplified by investigations of zeolite A/polymer and carbon molecular sieve/polymer MMMs [10–12]. However, these modifications – generally involving the inclusion of an 'interphase' structure between the filler and the matrix [13] – introduce additional fitting parameters into the models such as the interphase thickness and interphase permeability, which are difficult to verify by independent characterization. With the advent of a new class of nanoporous metal-organic framework (MOF) materials as MMM fillers, a large quantity of permeation data is emerging [8] that is increasingly difficult to interpret, *e.g.*, the case of the MOF ZIF-8 [14,15] considered later in this paper.

Although non-idealities may actually exist in several types of MMMs, a reliable assessment of their contribution to the permeation behavior would first require an accurate understanding of the expected intrinsic permeation behavior in an ideal (defect-free) MMM. A fundamental difficulty is that the permeability-based models do not allow one to reliably separate the effects of the ideal permeation behavior from the effects of hypothesized non-idealities. The effective medium theory (EMT) [16,17] explicitly accounts for interfacial equilibrium effects in addition to the Fickian diffusivity in both phases, and has been recently considered in detail [9] to illustrate the importance of matrix-filler interfacial adsorption in MMMs. However, it was also found to have several drawbacks (Section 3.2) that prevent its general use for quantitative predictions or fitting of permeation data from composite membranes [9]. Boom et al. [18] developed a simple 2D numerical simulation of a single filler particle placed in a matrix to qualitatively explain trends in experimentally observed pervaporation behavior of zeolite/polymer MMMs. Although the predictions from that study could not be directly extended to 3D MMMs containing randomly distributed fillers, the simulation results indicated that the filler/matrix interfacial adsorption equilibrium played a large role in determining the permeation behavior in a manner that cannot be explained by the permeability-based analytical models. It has also been found that functional MMMs incorporating MOFs are often free of obvious defects such as interfacial voids or poor dispersion, due to their generally better compatibility with polymeric phases [8]. Hence, it also becomes important to accurately describe the intrinsic effects of interfacial adsorption and diffusion in MMM systems in order to predict and select filler and matrix materials for high performance in target separations. Thus, there is a requirement for 'rigorous' predictions of permeation in ideal MMMs that capture the true dependence of the permeability on the diffusivities of the matrix and filler phases, the polymer/filler interface adsorption equilibrium, and the volume fraction of the filler. Such predictions can then be used for reliable interpretation of MMM data, assessment of the effects of the intrinsic material properties versus those originating from possible non-idealities, and selection of matrix and filler materials for desired separation properties.

Towards the above purpose, the objectives of this paper are three-fold. Firstly, we develop techniques to construct large (up to 30 μm thickness × 225 μm² surface area), three-dimensional (3D), statistically valid, models of MMMs with different spherical particle sizes and loadings, and then obtain single-component transport properties of such membranes *via* computational finite-element methods within the COMSOL Multiphysics simulation package. These predictions can be considered as 'exact' to the limits of accuracy of the numerical simulation methods. Single-component transport is described by Fick's law and the adsorption equilibrium at the filler–matrix interfaces is explicitly invoked as a boundary condition. Secondly, we use our predictions to conduct a detailed investigation of the effective permeability of MMMs as a function of filler loadings, particle size, and the properties of the individual polymeric and filler phases. We compare the 'exact' computational results with those of existing analytical models, and discuss the implications of our findings on the interpretation of MMM permeation data with permeability-based models. This discussion also considers examples of real filler and matrix materials, although a more comprehensive comparison of the 'exact' predictions with experimental data is a study in itself and will be reserved for a separate work. Thirdly, we introduce an empirical correlation that satisfactorily fits our data over a large range of adsorption and diffusion parameters and thereby allows easier application of our results.

2. Computational methods

2.1. Model assumptions and boundary conditions

Finite element modeling of mass transport was employed for a 3D heterogeneous composite membrane system under single-component Fickian diffusion of penetrant molecules and including adsorptive equilibrium at the filler–matrix interfaces. Since a main purpose of the present paper is the direct comparison to analytical permeability-based models, the diffusion coefficients for the filler (D_f) and matrix (D_m) phases were not taken to be functions of the local penetrant concentration in this paper, although the concentration-dependence of the Fickian diffusivity can be incorporated into the computational model without difficulty to describe nanoporous fillers like zeolites or MOFs in more generalized terms. Adsorptive equilibrium was assumed to be established at the matrix–filler interfaces, and was described by a concentration-independent equilibrium constant. Again, this allows ease of definition of the permeabilities and direct comparison with analytical models, although the concentration-dependence of the interface equilibrium can be incorporated into our computational model by a more detailed adsorption isotherm. The objective of the simulation is to calculate the 'effective diffusivity' (D_{eff}) of the MMM. It should be noted that D_{eff} is not a microscopic diffusivity and cannot be used in a differential equation such as Fick's law. It is a macroscopic membrane transport quantity that, when multiplied by a linear concentration gradient between the feed and permeate side, conveniently gives the flux through the MMM in the same manner as the flux calculation for a pure polymeric membrane having a constant diffusivity D_m and the same thickness and concentration differential as the MMM. The ratio of these two fluxes therefore gives D_{eff}/D_m. Considering the macroscopic definition of D_{eff} above, the ratio D_{eff}/D_m exactly equals the permeability ratio P_{eff}/P_m, since the adsorption equilibria are the same for the MMM and the pure polymer membrane at the fluid–membrane interfaces on the feed-side and permeate-side.

The boundary conditions used in our simulations are given in Fig. 1, which is a 2D projection of the matrix–filler system with