



Predictive simulation of non-steady-state transport of gases through rubbery polymer membranes

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ABSTRACT

A multiscale, physically-based, reaction-diffusion kinetics model is developed for non-steady-state transport of simple gases through a rubbery polymer. Experimental data from the literature, new measurements of non-steady-state permeation and a molecular dynamics simulation of a gas-polymer sticking probability for a typical system are used to construct and validate the model framework. Using no adjustable parameters, the model successfully reproduces time-dependent experimental data for two distinct systems: (1) O₂ quenching of a phosphorescent dye embedded in poly(*n*-butyl(amino)thionylphosphazene), and (2) O₂, N₂, CH₄ and CO₂ transport through poly(dimethyl siloxane). The calculations show that in the pre-steady-state regime, permeation is only correctly described if the sorbed gas concentration in the polymer is dynamically determined by the rise in pressure. The framework is used to predict selectivity targets for two applications involving rubbery membranes: CO₂ capture from air and blocking of methane cross-over in an aged solar fuels device.

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1. Introduction

Permeant transport through a polymer membrane is driven by differences in pressure, concentration, temperature, and, if it is a polyelectrolyte, the electrical potential across it [1]. The most common model is the solution-diffusion model for steady-state, which is defined in terms of the permeability, P_m . The permeability is the product of the Henry's Law solubility, S , and diffusivity, D , i.e. $P_m = S \times D$ [2]. Models with a high level of detail concerning the physical nature of uptake and permeation are not generally available. Such models are valuable for their predictive character and their ability to provide scientific insight. This work builds a foundation for the development and use of these more detailed models in the study of transport through polymers.

Polymeric membrane materials fall into two basic classes, highly permeable rubbers with low glass transition temperatures (T_g) and weakly permeable glasses with high T_g . The solution-diffusion model applies to both. The physical processes that take place in the polymer bulk do not depend on whether the permeant was initially present as a component of a liquid or in the gas phase. The details of the process of uptake into the membrane, on the other hand, are likely to depend on permeant phase. The solution-diffusion model assumes that no matter what the source of the permeant, its rate of uptake at the polymer interface is much faster than diffusion through the polymer bulk [3], and therefore is not rate limiting. Molecular dynamics simulations and kinetics models using parameterized schemes have provided important insights to the detailed nature of uptake and permeation for ion-conducting, phase-separated perfluorosulfonic-acid polymers [4,5]. This level of physical detail, however, is not available for most membrane systems.

Steady-state permeation as described by the solution-diffusion model is relevant to many applications using polymeric membranes such as purification and electrolyzer systems, but not to

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Nomenclature: List of symbols

Symbol	Meaning	Units
A	area	m^2
$B + 1$	ratio of intensities	–
dx	distance in x	m
D	diffusivity	m^2/s
h	Planck constant	J s
I_0	intensity of light emission in absence of O_2	–*
I_{eq}	intensity of light emission at a constant $[O_2]$	–*
$I(t)$	time-dependent light intensity	–*
J	flux through membrane	$mol/(m^2 s)$
k_B	Boltzmann constant	J/K
k_{ads}	pseudo-first order rate constant for adsorption	s^{-1}
k_{bub}	zeroth order rate constant for CH_4 to enter gas phase	$mol/(L s)$
k_{coll}	rate constant for collision of gases with the surface	s^{-1}
k_{des}	rate constant for desorption from a surface	s^{-1}
k_{ex}	pseudo-first order rate constant for excitation of PtOEP	s^{-1}
k_{hyd}	zeroth order rate constant for CH_4 to enter gas phase	$mol/(L s)$
k_{nr}	rate constant for radiative decay of PtOEP	s^{-1}
k_{prod}	zeroth order rate constant for production of CH_4	$mol/(L s)$
k_q	rate constant for quenching of PtOEP by O_2	$L/(mol s)$
k_r	rate constant for emission of photons from PtOEP	s^{-1}
k_{TTA}	rate constant for TTA	$L/(mol s)$
l	thickness of the membrane	m
m_w	molecular mass	kg/mol
n	amount of gas	mol
n_{max}	maximum amount of gas	mol
N_{Av}	Avogadro's number	molecules/mol
P_m	permeability of the membrane	$(mol m)/(m^2 s Pa)$ for gas phase m^2/s for liquid phase
p_{ds}	downstream pressure	Pa
p_{O_2}	external partial pressure of O_2	Pa
p_{up}	upstream pressure	Pa
Δp	difference between upstream and downstream pressures	Pa
r_{sun}	ratio of current sunlight level to maximum sunlight level	–
R	universal gas constant	J/(mol K)
R_{AB}	encounter distance	m
S	solubility	$mol/(L Pa)$ for gas phase $(mol/L)/(mol/L)$ for liquid phase
t	time	s
T	temperature	K
V	volume	m^3
V_{ds}	downstream volume	m^3
x	position	m
Z	collision frequency	s^{-1}
μ	sticking probability	–
ν_L	frequency of exciting light	m
π	pi	–
ρ	mass density	kg/m^3
σ_a	absorption cross section	m^2
τ	lifetime of 3PtOEP in the presence of a constant $[O_2]$	s
τ_0	lifetime of 3PtOEP in the absence of O_2	s
ϕ_P	phosphorescence quantum yield	–
χ	rate	$mol/(L s)$
ω_L	energy density	J/m^2
$[gas_{(p)}]$	concentration of a gas within the polymer	mol/L
$[O_{2(p)}]_{eq}$	concentration of O_2 within the polymer at equilibrium	mol/L
$[O_{2(p)}](x,t)$	concentration of O_2 within the polymer as a function of position and time	mol/L
$[PtOEP]$	total concentration of PtOEP	mol/L
$[^3PtOEP]_{init}$	initial concentration of excited-state PtOEP	mol/L

*All reported intensities are normalized and so unitless.

those in which permeant concentrations and other operating conditions such as temperature vary significantly with time. Examples are gas sensor and intermittent gas separations systems, electrolyzers using electricity from renewable sources, or photo-electrochemical systems that use sunlight to convert components of air and water into fuels. The membrane composition and structure required for each of these applications varies, and at our

current level of understanding the physical details governing time-dependent membrane performance cannot be assumed to be as simple to capture as they are by the solution-diffusion model. To begin to develop a description of membrane behaviors far from steady state, we focus in this study on one extreme – inert gases permeating a rubbery polymer. Our basic model is constructed in a manner that enables it to be extended to more complex situations

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