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Modeling of gas solubility and permeability in glassy and rubbery membranes using lattice fluid theory

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ABSTRACT

In this study, the lattice fluid (LF) and non-equilibrium lattice fluid (NELF) theories combined with the modified Fick's law and free volume theory were employed to develop mass transfer models for the prediction of gas sorption and permeation in glassy and rubbery membranes in a wide range of temperature and pressure. The finite element method using COMSOL multi-physics software was used to solve the governing transport equations. The gas sorption into the glassy membranes shows a non-equilibrium behavior in spite of the rubbery membranes in which the gas sorption is in the equilibrium state. The results indicated that the membranes with higher fractional free volume show higher solubility and diffusion coefficients. The proposed model can predict satisfactory the gas solubility and permeability in the glassy and rubbery membranes and determine the influence of operating pressure and temperature on the transport properties of the membranes without need of any adjustable parameters.

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1. Introduction

Membrane gas separation technology has been given particular attention during the past few decades for various applications like air separation, hydrogen recovery and purification, recovery of volatile organic compounds (VOCs) and natural gas processing [1–3]. The efficiency of the membrane gas separation process is determined by the properties of membrane and gas mixture as well as by the operating variables including pressure, temperature and concentration. Although a large number of studies have been conducted on the development of appropriate membranes and examining the performance of the gas separation process for various applications, there are limited researches on the mass transfer mechanism and mathematical modeling. The reliable and comprehensive mathematical models are necessary to predict the influence of the main operating parameters, scale up the experimental results, design new equipment and improve the performance of the gas separation process. Generally, the permeation of gaseous components through the dense polymeric membranes is described based on the solution-diffusion mechanism [4]. According to this mechanism, the transport of permeating components across the membrane occurs through three seriate steps: i) selective sorption gas into the membrane at the high pressure-side, ii) selective diffusion of the gas in the membrane and iii) desorption of permeated components from the low pressure-side of the membrane. The third step is very fast in comparison to other steps. It means that the components sorption into the membrane along with their diffusion through the membrane is the most important mass transport steps in the membrane gas separation process. Generally, the solubility and diffusivity of gases through the membranes which characterized the permeation behavior depend mainly on the basic properties of the permeating components and membrane as well as on the operating parameters.

Sorption is a thermodynamic phenomenon and the interactions between the gas molecules and membrane straightforwardly determine the gas solubility into the membrane. The gas sorption into the rubbery membranes which are at the equilibrium state can be predicted using equation-of-state and activity-coefficient relations. Henry's law has been satisfactorily employed to describe the sorption isotherm in the rubbery membranes at relatively low pressures [5]. The thermodynamic properties of a gas/glassy polymer system are affected by temperature, composition and deformation histories, and a pseudo-equilibrium condition rather than the true thermodynamic equilibrium condition reached by the

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system. Therefore, the gas sorption behavior of the glassy membranes is more complicated. The sorption isotherm of the gas into the glassy membranes is widely described by the dual-mode sorption model [6]. Moreover, thermodynamic models like Flory-Huggins theory [7], Flory-Rehner theory [8] and Sanchez-Lacombe equation-of-state [9] have been used to describe gas sorption behavior into the rubbery membranes and thermodynamic models such as the non-equilibrium lattice fluid (NELF) model [10], the non-equilibrium perturbed-hardspheres-chain (NE-PHSC) theory [11] and the non-equilibrium statistical-associating-fluid theory (NE-SAFT) [12] have been employed to model the gas sorption into the glassy membranes. Recently, Galizia et al. [13] used the lattice fluid models, i.e. the NELF and Sanchez–Lacombe models, for prediction of solubility isotherms of hydrogen and helium in both glassy and rubbery polymers.

Diffusion is a kinetics phenomenon related to the rate at which the gaseous components go across the membrane down a driving force which is the concentration gradient. Estimation of the diffusion coefficient for the permeating components in the membrane is also critical to develop a mass transfer model for the membrane gas separation. Various approaches including constant diffusion coefficient [14], empirical models [15], free volume theory [16], activated state theory [17] and molecular dynamic simulation [18] have been used to estimate the gas diffusion coefficient. For example, Dhingra and Marand [14] employed Fick's law with the constant diffusion coefficient to model the permeation of CO_2/CH_4 binary gas through the polydimethylsiloxane (PDMS) as a rubbery membrane and the thermoplastic polyimide (TPI) membrane as a glassy membrane. The gas diffusion coefficient in the polymeric membrane can be also defined based on the fractional free volume (FFV) method [19]. Nabati Shoghl et al. [20] recently employed the Doolittle relation to determine the gas diffusion coefficient in the glassy membrane using the fractional free volume of the polymer.

The computational fluid dynamics (CFD) technique has been previously applied to solve the transport equations in the membrane gas separation process. For example, the CFD was applied by Takab and Nakao [21] to model the hydrogen separation from its mixture with carbon dioxide using a ceramic membrane. Coroneo et al. [22] used the CFD technique for modeling of hydrogen purification using the Pd-Ag membrane. They observed how hydrogen permeation is related to the mass transfer resistance in the membrane. Shehni et al. [23] considered unsteady state permeation of gas mixtures in the PDMS membrane using the CFD technique. A predictive mass transport model based on the NELF theory in conjunction with the modified Fick's law and the free volume theory was developed by Nabati Shoghl et al. [20] and the governing equations were solved numerically using the CFD technique.

It is obvious that the gas separation using the polymeric membranes has important industrial applications, thus it is necessary to develop a predictive model for the solubility, diffusivity and permeability of gases in these types of membranes. This work will provide insight into the effect of operating parameters in conjunction with the gas composition on the gas separation performance of the rubbery and glassy polymeric membranes. The model was considered on the sorption of gases such as O_2, N_2, CH_4 and CO_2 in the glassy and rubbery membranes like hexafluoro polycarbonate (HFPC), polycarbonate (PC), tetramethyl polycarbonate (TMPC), polysulfone (PSf) and PDMS. By modifying the lattice fluid (LF) theory, a new method was developed for the calculation of the gas permeation based on the solution-diffusion mechanism and the finite element method using COMSOL multiphysics software was used to solve the governing equations. Finally, the developed model was validated with the experimental data reported in the literature. The main innovative aspect of this study is the use of LF and NELF theories for description of the gas sorption into both glassy and rubbery membranes. Another important contribution is the investigation of effect of the operating temperature and pressure, especially at high pressures, on the gas sorption and permeation of various membranes.

2. Mathematical modeling procedure

In order to develop a mass transport model for predication of the gas permeability into the dense polymeric membrane, we applied the solution-diffusion mechanism in a plate and frame membrane module. Based on this mechanism, the components from the feed solution must first be sorbed into the membrane and then transport across the membrane by diffusion. Therefore, the permeability coefficient can be expressed as a product of the sorption and diffusion coefficients:

$$P = S_o \times D \tag{1}$$

where P, S_o and D are the gas permeability, solubility and diffusion coefficients, respectively.

As shown in Fig. 1, three domains including feed side, membrane and permeate side were considered in this study. For the suitable model prediction, the model must be developed based on the accurate assumption, thus the following assumptions are considered in order to derive the governing equations: i) the steady state and isothermal condition are assumed for mass transport through the membrane, ii) the one-dimensional gas permeation through the membrane is considered, iii) negligible concentration polarization and iv) the effect of pressure on membrane deformation is negligible.

In this work, the gas sorption in the rubbery membranes is estimated based on the convenient equilibrium lattice fluid while the NELF model is utilized for the penetrant sorption in the glassy membrane. Also, the transport of gaseous components through the membrane is described by the generalized Fick's law. In the following, the theoretical background and procedure used to develop the mass transport model are presented.

2.1. Gas flow in the feed side

The flow and mass transport through the feed side of the membrane module were modeled by the aid of the conservation equation of momentum and mass. By applying the proposed assumptions, the conservation equation of momentum for the feed side is simplified as follows:

$$\rho u_y \frac{\partial u_y}{\partial y} = -\frac{\partial p}{\partial y} + \eta \frac{\partial^2 u_y}{\partial y^2} \tag{2}$$

where u is the velocity, p is the pressure, ρ is the density and η is the viscosity.

Furthermore, the simplified conservation equation of mass for component i based on the proposed assumptions is [24]:

$$\rho_i u_y \frac{\partial c_i}{\partial y} = -\frac{\partial J_i}{\partial x} \tag{3}$$

where c_i is the concentration and J_i is the molar flux. In this study, Fick's law is applied in order to calculate the molar flux:

$$J_i = -D_i \frac{\partial c_i}{\partial x} \tag{4}$$

hence D_i is the gas diffusion coefficient. The gas diffusion coefficient in the feed side is estimated using the following equation:

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