A predictive model for the permeability of gas mixtures in glassy polymers

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ABSTRACT

The transport of gaseous mixtures in glassy polymers is analyzed by means of a thermodynamic based model, which is applied to describe the permeability of CO_2/CH_4 50/50 binary mixtures in various glassy polymeric membranes. The approach relies on the description of the solubility behavior of penetrant/polymer mixtures provided by the nonequilibrium thermodynamics for glassy polymers (NET-GP), and considers the gradient in penetrant chemical potential of each species as the actual driving force of the diffusive mass fluxes. Such an approach is specialized to dilute solutions conditions, as it is typically of interest for the transport of light gas (e.g. CO_2, N_2, CH_4, O_2) in glassy polymeric membranes; that allows for the simple and successful prediction of the gas permeability of gas mixtures based on single component transport data, with no additional parameters required.

The NET-GP model is used in combination with an equation of state (lattice fluid theory by Sanchez and Lacombe) to obtain the solubility of pure and mixed gases at various pressures and compositions, as well as the thermodynamic factors accounting for the dependence of chemical potentials of the solutes on the concentrations of both penetrants. An exponential dependence on penetrant concentration is used to describe the mobility coefficient behavior, so that only two adjustable parameters are required for the pure penetrant case (infinite dilution mobility and plasticization factor). A simple but effective linear mixing rule is considered to describe transport in the binary mixture case, which does not introduce any additional adjustable parameter due to the presence of a second penetrating species. The comparison with permeation data of gas mixtures in different polymers shows the good predictive ability of the model.

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1. Introduction

Sorption and transport of low molecular weight species (gases, vapors, and liquids) in polymers represent some of the most significant properties for various applications of actual industrial relevance, such as those based on membranes separation processes [1,2], among the others [3–6]. The experimental analysis of gas solubility and permeability in polymeric membranes is a basic requirement for the complete understanding of the fundamental mechanisms involved; their description by means of appropriate and accurate models is also required for the proper development and the design of membrane systems and processes.

The permeability P_i of a gaseous species i measures the transport rate of the penetrant molecules through the polymer membrane under steady state conditions, and it is defined as follows:

$$P_i = \frac{J_i \, l}{p_i^{up} - p_i^d} \tag{1}$$

in which J_i is the steady state diffusive molar flux of species i, l is the membrane thickness, and the partial pressure difference across the membrane $p_i^{up} - p_i^d$ represents the external driving force of the process.

The separation performance is represented by the selectivity factor $\alpha_{i,j}^{sep}$ between gases i and j. If the downstream partial pressure of the two key components is negligibly small, as it is typically the case in membrane gas separations, the selectivity factor is simply given by the ratio of the two permeability values:

$$\alpha_{i,j}^{sep} = \frac{y_i^d / y_j^d}{y_i^{up} / y_j^{up}} \cong \frac{P_i}{P_j} \tag{2}$$

Most often, the estimation of membrane selectivity is given only on the basis of pure penetrant permeability data, in spite of the fact that mixed gas effects are present and may be relevant; on the other hand, few and very time-consuming procedures have been developed for the proper experimental determination of mixed gas solubility [7–11] and permeability [12–17].

The results of the available experimental mixed gas campaigns reveal that the presence of a second (or a third) component in the feed stream induces a significant effect on the permeability of all species, and that has to be considered for the proper evaluation of membrane performance [18–24]. Thus, there is the clear need of a proper and accurate modeling description of the transport behavior of gases and gaseous mixtures in the glassy polymeric membranes used for gas separations.

Few modeling approaches have been devoted to the analysis of penetrant sorption and transport in rubbery systems, either for pure substances or for mixtures [25–27], while the case of glassy phases requires a more complex examination in view of their peculiar nonequilibrium behavior [28–31]. The approach commonly considered to describe gas transport in glassy polymers is the Dual Mode Sorption model [32,33], empirical in character, which has been first developed to describe the sorption and transport of pure penetrants [34,35], and later extended to the representation of gaseous mixtures [36,37]. The DMS model relies on the assumption that two different penetrant populations are present and diffuse in the glassy polymer, one dissolved in the polymer (Henry's mode) and the other adsorbed onto the surface of microvoids assumed to be present in the glassy phase (Langmuir mode). However, this approach faces severe limitations being intrinsically unable to describe some observed sorption behaviors, such as convex or S-shape isotherms [38–40], as well as the observed increase in permeability as upstream pressure increases, which is documented in different common cases [41,42]. For this reason, the nonmonotonuos permeability trends, typically observed for swelling penetrants (such as CO_2) in high free volume polymers, are out of reach for the DMS model [43].

A simple and effective transport model has been recently developed by Minelli and Sarti for the description of the permeability of gases and vapors in glassy polymers [44]. The model is based on a fundamental approach for penetrant diffusion in multicomponent systems: it considers the diffusion coefficient as the product of a purely kinetic factor, the mobility coefficient, and a thermodynamic factor, accounting for the penetrant chemical potential dependence on its concentration in the membrane [45]. This approach takes advantage of the use of the thermodynamics for glassy polymers (NET-GP) [46,47], able to evaluate penetrant solubility and thermodynamic factor, required for the determination of penetrant permeability.

The transport model has been already successfully applied to describe the permeability dependence on penetrant upstream pressure and temperature for different penetrants in a variety of glassy polymers, including conventional glassy polymers [44,48–50], blends and copolymers [51], semicrystalline phases [52], and high free volume glassy membranes [53]. That approach has been also applied to the development of an a priori procedure for the prediction of the gas permeability in glassy polymers [54].

The fundamental basis of the approach allows a straightforward extension to the case of multicomponent diffusion, for which a model is thus derived starting from a generalized Fick's law [55,56]. The general model is simplified to the case of dilute solution conditions, leading to a significant reduction of the number of model parameters required, still keeping the ability to describe well the transport behavior, and allowing for an a priori estimation of the mixed gas permeability.

This work is devoted to the analysis and modeling of the permeability of binary CO_2/CH_4 gaseous mixtures in different glassy polymers, i.e. polyarylate (PAr), polyetherimide (PEI), polyhydroxyether (PH) and polysulfone (PSf); more general and detailed analysis would be required to describe diffusion in concentrated solutions, as for instance the case of hydrocarbon or vapor separation, or multisolvent polymer solutions [57,58].

The experimental data available in the literature for pure gas solubility and permeability are considered first. By using the predictive ability of the NET-GP approach to represent the thermodynamics of multicomponent mixtures [59,60], the pure gas information will be used to calculate the permeability in the polymer of each component of the gaseous mixture. The focus of this analysis is mainly on conventional glassy polymers, widely characterized from many different points of view, for which CO_2 and CH_4 mixed gas transport data are available.

2. Theoretical background

2.1. Transport model

The standard transport model proposed by Minelli and Sarti considers glassy polymers as uniform nonequilibrium phases, in which the actual driving force for isothermal diffusion is the negative chemical potential gradient [45], so that the molar flux for a single penetrating species i can be described as:

$$\underline{J}_i = -\rho L_i \, \omega_i \, \nabla \left(\frac{\mu_i}{RT} \right)_{T,P} \tag{3}$$

in which $\underline{J}_i$ is the diffusive mass flux of penetrant i, ρ is the mixture density, ω_i the mass fraction of solute i in the mixture, while L_i is the mobility coefficient of penetrant i in the solute/polymer mixture.

In case of a ternary mixtures, which is of interest in membrane gas separations, composed of two gaseous penetrants, 1 and 2, and one polymer species p, the diffusive mechanism requires in general to account for three different driving forces [61]:

$$
\begin{aligned}
d_1 &= -\rho \omega_1 \, \nabla \left(\frac{\mu_1}{RT} \right)_{T,p} \\
d_2 &= -\rho \omega_2 \, \nabla \left(\frac{\mu_2}{RT} \right)_{T,p} \\
d_p &= -\rho \omega_p \, \nabla \left(\frac{\mu_p}{RT} \right)_{T,p}
\end{aligned}
\tag{4}
$$

Hence, the general constitutive equations for the isothermal diffusive fluxes are as follows:

$$
\begin{aligned}
J_1 &= L_{11} \, d_1 + L_{12} \, d_2 + L_{1p} \, d_p \\
J_2 &= L_{21} \, d_1 + L_{22} \, d_2 + L_{2p} \, d_p \\
J_p &= L_{p1} \, d_1 + L_{p2} \, d_2 + L_{pp} \, d_p
\end{aligned}
\tag{5}
$$

The three driving forces are related to one another in order to satisfy the Gibbs–Duhem equation:

$$0 = d_1 + d_2 + d_p \tag{6}$$

After substitution of Eq. (6) in Eq. (5) one has:

$$
\begin{aligned}
J_1 &= (L_{11} - L_{12}) d_1 + (L_{1p} - L_{12}) d_p \\
J_2 &= (L_{22} - L_{21}) d_2 + (L_{2p} - L_{21}) d_p
\end{aligned}
\tag{7}
$$

Thus, the resolution of the general problem can result quite