Modeling of simultaneous competitive mixed gas permeation and CO_2 induced plasticization in glassy polymers

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ABSTRACT

Plasticization behavior of polymeric membranes, in presence of a second component in the feed is different from plasticization of pure CO_2 due to competitive sorption. This study focused on a mathematical model derived for permeation of mixed gases in glassy polymers considering the plasticization case. It was assumed that diffusion coefficient for all components were exclusively a function of plasticizing component. In this study, the partial immobilization model was employed to determine fraction of mobile sorbed gases. This model accurately predicted the permeation behavior of CO2 as plasticizer and N2 in presence of plasticization. The model parameters were calculated by fitting experimental data from literature. Plasticization parameter (β) decreased for both CO_2 and N_2 by increasing fraction of N_2 in the feed. It means that plasticization of glassy polymers was suppressed. This decrease was caused by competitive sorption between CO_2 and N_2. Indeed N_2 in the feed acts as an anti-plasticizer. In addition, permeances of the feed gas components were declined in comparison to pure gases, which might be attributed to reduction of sorption and occupying Langmuir sites with the second component. The proposed model is capable of giving a useful tool to enhance our knowledge related to permeability and selectivity behavior of mixed gas systems in glassy polymeric membranes.

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1. Introduction

Membranes are widely used in separation processes such as waste water treatment, desalination, gas separation, food technology and biotechnology. Many materials including polymers, carbon molecular sieves (CMS), zeolites and ceramics can be used in membrane production. Polymers are the dominant membrane materials used in natural gas separation processes [1]. In order to remove carbon dioxide (CO_2), preferentially glassy polymeric membranes are often applied rather than rubbery polymeric membranes because of their higher CO_2/CH_4 or CO_2/N_2 selectivity [2–5]. However, in high-pressure CO_2/CH_4 or CO_2/N_2 separation, problems arise due to CO_2 induced plasticization. The polymer matrix swells by the highly sorbed CO_2, which results in an increase in permeability of all components at the cost of substantial decrease in selectivity. In permeability vs. pressure curves, the permeability goes through a minimum. This is the minimum CO_2 pressure necessary to induce plasticization, which is known as "*plasticization pressure*" [6–11].

At higher pressures than plasticization pressure, permeability of pure CO_2 in a glassy membrane, increases with pressure, whereas for an inert gas such as N_2 or CH_4, permeability decreases with pressure, therefore, ideal gas selectivity increases with pressure [12]. In many cases, especially in CO_2/CH_4 or CO_2/N_2 separation, the mixed gas permeation behavior in glassy polymers is totally different compared with pure gas separation [12–14]. Staudt–Bickel and Koros [14] reported a mixed gas CO_2/CH_4 selectivity for polyimide (6FDA-mPD) about 4 at a feed pressure of 17.5 atm, whereas the ideal selectivity for this was observed about 60. Also, Bos et al. [15] showed that their Matrimid membranes tested under a mixed gas of CO_2/CH_4, was plasticized and due to swelling of the polymer matrix, selectivity of the membranes decreased with pressure dramatically. Normally, CO_2 swelling and plasticization causes permeability of CH_4 to be increased versus pressure more than CO_2 permeability, therefore, in the case of mixed gas, selectivity decreases rapidly.

Sada et al. [16] demonstrated that the addition of CH_4 to the feed, suppressed the CO_2 permeability in cellulose acetate membranes. Also, Donohue et al. [13] studied on CO_2/CH_4 mixture and reported that the presence of CH_4 not only led to reduction in CO_2 solubility, but also lowered the diffusivity of CO_2 for a given partial pressure, which resulted in lowering the CO_2 permeability in the

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presence of CH_4. On the other hand, they showed that in reference to pure CH_4, presence of CO_2 in the feed decreased CH_4 solubility, whereas due to the higher membrane plasticization by dissolved CO_2, diffusivity of CH_4 increased as well. They reported that the enhancement in CH_4 diffusivity was much greater than the decrease in solubility, which finally led to an increase in CH_4 permeability. Accordingly, unlike ideal selectivity, mixed gas selectivity decreased with pressure due to plasticization.

Furthermore, Visser et al. [12] reported that introducing N_2 or CH_4 to the CO_2 feed mixture apparently suppressed plasticization of asymmetric Polyethersulfone (PES)/Polyimide (PI) hollow fiber membrane. Its effect was more pronounced at higher concentrations of inert gases. Also, it was shown that in presence of inert gas, plasticization was counterbalanced by competitive sorption. By introducing N_2 or CH_4 as the second component to the feed, due to lower sorption of CO_2, permeances of CO_2 was lower than the pure gas one.

Koros et al. [17], based on Dual Mode Sorption (DMS) model of mixed gas system, proposed a model for permeation of mixed gases in polymeric membranes, but they did not consider the effect of plasticization. As a result, their model could not predict the permeation of mixed gases in presence of plasticization [12]. Lee et al. [18] developed a model for permeation of mixed gases in polymeric membranes in presence of plasticization. Based on their model, diffusion coefficient of each component was dependent on other components and assumed that the whole of sorbed gaseous molecules are mobile. Sada et al. [19] investigated permeation of binary gas mixture through glassy polymer membranes with plasticization based on this assumption that the whole of sorbed gaseous molecules are mobile.

In this work, a mathematical model for permeation of mixed gases in glassy polymers in presence of plasticization was developed. A dual sorption model of mixed gases was considered and the concentration dependency of diffusivity was studied. There are major differences between this work and the previous study of Refs. [17–19]:

In Ref. [17], permeation of mixed gaseous without plasticization was investigated whereas in this study permeation of mixed gaseous with plasticization phenomenon was considered. Also, based on the partial immobilization model, in the current work a fraction of the sorbed gases were assumed to be mobile and the rest were immobile, whereas in Refs. [18,19], the whole of sorbed gases was considered as mobile molecules. In Ref. [18] it was assumed that, diffusion coefficient for all the components was exclusively a function of plasticizing component (i.e. CO_2) resulting in a model simpler than the previous one. Also, the resulting relation of the present work for permeation of the second component, is a comprehensive relation which can be used for permeation of the second component with and without plasticization.

Then by using experimental data of CO_2/N_2 permeation in PES/PI asymmetric membranes [12], effect of feed composition on the parameters of the model was investigated. Finally, by the aid of the parameters calculated from the model, permeability of CO_2 and N_2 gases with different compositions in the feed was predicted.

2. Theory and modeling

2.1. Sorption

Polymers in glassy state contain some microvoids or "holes" throughout the polymer matrix, which may act to immobilize a portion of the penetrant molecules by entrapping them [20,21]. Based up on this concept, two mechanisms of sorption occur: (i) ordinary dissolution based on Henry's law and, (ii) "hole-filling" according to Langmuir theory. This type of sorption in glassy polymer is known as Dual Mode Sorption (DMS) model. The equilibrium isotherm for a pure gas "A" is expressed as

$$C_A = C_{DA} + C_{HA} = k_{DA}f_A + \frac{C'_{HA}b_Af_A}{1 + b_Af_A} \tag{1}$$

where C is concentration (cm^3(STP)/cm^3 polymer), C_D is Henry's solubility, C_H is the Langmuir solubility, k_D is Henry's law solubility coefficient (cm^3(STP)/cm^3 polymer.atm), C'_H is the hole saturation constant (cm^3(STP)/cm^3 polymer), b is the hole affinity constant (atm^{-1}) which represents the ratio of the rate constants of gas adsorption and desorption in the microvoids and f is the fugacity (atm). In Eq. (1), the first term represents ordinary dissolution while the second term represents sorption in microvoids or holes [21].

Sorption of two components of a binary gas mixture in Henry's region of a glassy polymer (or in a polymer in its rubbery state) is generally considered to be independent of each other, and the concentration of the sorbed components are usually proportional to the fugacity of each component. Then, for component "A" in the gas mixture, concentration of the sorbed gas is as follows [22]:

$$C_A = k_{DA}f_A \tag{2}$$

That k_{DA} is Henry's law constant, measured for a pure gas in the polymer, and f_A, is fugacity of component "A" [22].

For Langmuir sites in glassy polymers, the gas molecules in the mixture compete for sorption on these sites [22]. The expression for the Langmuir sorption isotherm for component "A" is given by [22]

$$C_{HA} = \frac{C'_{HA}b_Af_A}{1 + b_Af_A + b_Bf_B} \tag{3}$$

Accordingly, the total Henry and Langmuir sorbed concentration of gas A in the glassy polymer will be calculated by Eq. (3) [22]:

$$C_A = k_{DA}f_A + \frac{C'_{HA}b_Af_A}{1 + b_Af_A + b_Bf_B} \tag{4}$$

Similarly, sorption isotherm for component B is given by [22]

$$C_B = k_{DB}f_B + \frac{C'_{HB}b_Bf_B}{1 + b_Af_A + b_Bf_B} \tag{5}$$

where k_{DB} is the Henry's law constant for "B", and the total sorbed gas concentration is

$$C = k_{DA}f_A + k_{DB}f_B + \frac{C'_{HA}b_Af_A + C'_{HB}b_Bf_B}{1 + b_Af_A + b_Bf_B} \tag{6}$$

Obviously, when either f_A or f_B approaches zero, Eq. (6) reduces to the pure gas relation i.e. Eq. (1).

2.2. Permeation

Based on partial immobilization sorption [23], all the gas dissolved in the Henry region is mobile, whereas for the Langmuir sites, a fraction (F) of the adsorbed gas molecules, is mobile and the balance ($1-F$) is immobile. F is usually called the immobilization factor which depends on the nature of penetrant–polymer system as well as the temperature [24,25]. This factor represents the ratio of the diffusivity through the microvoids to that through the polymeric matrix.

By assuming that concentration of the mobile part of sorbed gas in the glassy polymer is C_m with diffusion coefficient D, and the remainder ($C-C_m$) is totally immobilized, the flux (N) of component A of two components system is expressed as [23,26]