Modeling of CO_2/CH_4 gas mixture permeation and CO_2 induced plasticization through asymmetric cellulose acetate membrane

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Abstract

The target of this study is derivation of a mathematical model for permeability and effective diffusivity of mixed gases in glassy polymeric membranes in presence of plasticization. Diffusion coefficients for all components were assumed to be a function of plasticizing component. The partial immobilization model was employed to determine fraction of mobile sorbed gases. The model accurately predicted the mixed gas permeation behavior of CO_2 as plasticizer and CH_4 as a second component through the asymmetric cellulose acetate membrane in presence of plasticization. The model parameters were calculated by fitting experimental data from literature. Plasticization parameter (β) decreased for both CO_2 and CH_4 by increasing fraction of CH_4 in the feed. It means that plasticization of glassy polymers was suppressed. This decrease was caused by competitive sorption between CO_2 and CH_4. Indeed CH_4 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. Also, immobilization factor (F) for CO_2 and CH_4 decreased with increase in CH_4 fraction due to reduction of plasticization. D_{eff}/l for pure CO_2 was significantly pressure dependent. However with increasing fraction of CH_4 in the feed, this dependency almost disappeared. Finally, the model predicted decreasing trend of separation factor for CO_2/CH_4 mixed gases with pressure accurately. Therefore presented model is capable of giving a useful tool to enhance our knowledge related to permeation behavior of mixed gas systems through glassy polymeric membranes in presence of plasticization.

Keywords: Competitive sorption; Glassy polymer; Mixed gas; Permeance; Effective diffusivity; Plasticization

1. Introduction

Membranes with different organic and inorganic materials such as polymers, carbon molecular sieves (CMS), zeolites, ceramics, and graphene sheets are widely used in gas separation processes[1-5]. In addition, nano-structure materials such as silica nanoparticles, metal oxide nanoparticles, carbon nanotubes (CNTs), and metal−organic frameworks (MOFs) have also been

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used to produce mixed matrix membranes (MMMs) for gas separation.[1] However, polymers are the dominant membrane materials used in natural gas separation processes.[3,4] 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.[4,6-9] It is well known that most of rubbery polymers exhibit high permeability but at the cost of low selectivity.[9] Although some types of glassy membranes have a good performance in CO_2 separation, at high-pressure CO_2/CH_4 or CO_2/N_2 separation, performance of this membranes can be hindered by plasticization phenomenon.[7-11] Polymeric matrix usually swells by the highly sorbed CO_2 as a condensable gas. Then interaction between adjacent segments of polymer chain reduces, and glass transition temperature suppres.[8,10,11] Therefore, it will cause an increase in segmental mobility and free volume of polymeric matrix.[8,10,11] Then, diffusivity as well as permeability of sorbed gases increases with pressure which, eventually the membrane loses its selectivity.[8,10] In permeability vs. pressure curves, the permeability goes through a minimum, which is known as "*plasticization pressure*". This is the minimum CO_2 pressure necessary to induce plasticization.[10,12-16] In some cases which membranes have thin skin (especially asymmetric membranes with thin skin layer) there is not a minimum pressure and permeances increases with pressure monotonously,[11,17] which means plasticization pressure decreases with decrease in thickness.[18]

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.[19] The mixed gas permeation behavior in glassy polymers, especially in CO_2/CH_4 or CO_2/N_2 separation, is significantly different compared with pure gas separation.[19-21] For example, mixed gas CO_2/CH_4 selectivity for polyimide (6FDA-mPD) reported about 4 at a feed pressure of 17.5 atm, whereas the ideal selectivity for this was observed about 60.[21] Also, permeation behavior of matrimid membranes under a mixed gas of CO_2/CH_4 showed that the selectivity of the membranes plasticized by CO_2 decreased with pressure dramatically. Normally, CO_2 swelling and plasticization causes permeability of CH_4 versus pressure to be increased more than CO_2 permeability, therefore, in contrast to pure gas, the selectivity of the mixture of gases, decreases rapidly.[22,23] Also, Donohue *et al.*[20] reported that unlike ideal selectivity, mixed gas selectivity of CO_2/CH_4 mixture in cellulose acetate membrane decreased with pressure due to plasticization.

They interpreted that the presence of CH_4 not only reduces 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 presence of CH_4. On the other hand, presence of CO_2 in the feed decreased CH_4 solubility in reference to pure CH_4, whereas due to the 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**.**

Furthermore, Visser *et al.*[19] demonstrated 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. By introducing N_2 or CH_4 as a second component to the feed, due to lower sorption of CO_2, permeances of CO_2 were less than the pure gas one.

As a first study, Koros *et al.*[24] developed a model for permeation of mixed gases in polymeric membranes based on Dual Mode Sorption (DMS) model of mixed gas system[23], but they did not consider plasticization case. As a result, their model could not predict the permeation of mixed gases when plasticization phenomenon occurs.[19] Lee *et al.*[26] 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 all of the other components and the whole of sorbed gases was considered as mobile molecules.

Although permeation behavior of mixed gases is significantly different from pure gases due to competitive sorption, less attention has been taken into consideration of mixed gas permeation. Therefore, a simple and comprehensive model is required to simulate this behavior.

In a previous work,[27] a mathematical model for permeation of mixed gases in glassy polymeric membranes in presence of plasticization was developed by us. In this work, a model for effective diffusivity for gas component in mixed gas feed based up on Fick's first law was obtained. Then, permeation behavior of CO_2/CH_4 mixed gas in asymmetric cellulose acetate membrane[18] was studied and parameters of model were calculated and discussed.

2. Theory and modeling

2.1. Sorption

Based up on the concept that polymers in glassy state contain some microvoids or "holes" throughout the polymer matrix, two mechanisms of sorption occur in these polymers: i) ordinary dissolution based on Henry's law and, ii) "hole-filling" according to Langmuir theory. This type of sorption is known as Dual Mode Sorption (DMS) model.[28,29] The equilibrium isotherm for a pure gas "*A*" is expressed as:

$$\boldsymbol{C_A = C_{DA} + C_{HA} = k_{DA}p_A + \frac{C'_{HA}b_Ap_A}{1+b_Ap_A}} \quad \textbf{(1)}$$

Where *C* is the gas concentration in polymer (cm^3(STP)/cm^{3}polymer), C_D is Henry's solubility, C_H is Langmuir solubility, k_D is Henry's law solubility coefficient (cm^3(STP)/cm^3 polymer.kPa), C'_H is the hole saturation constant (cm^3(STP)/cm^3 polymer), *b* is the hole affinity constant (kPa^{-1}) which represents the ratio of the rate constants of gas adsorption and desorption in the microvoids and *p* is pressure (kPa). In Eq. (1), the first term represents ordinary dissolution while the second term represents sorption in microvoids or holes[27]. Solubility of gas "*A*" in polymeric membranes is defined as:[30,31]

$$\boldsymbol{S_A = C_A/p_A} \quad \textbf{(2)}$$

Koros *et al.*[25] extended DMS model for mixed gas component systems to consider competitive sorption effect. Based on their assumption, components of a gas mixture in the Henry's region of a glassy polymer is sorbed independent of each other whereas the gas molecules in the mixture compete for sorption on Langmuir sites. The concentration of gas "*A*" of a binary mixture is obtained by:[25]

$$\boldsymbol{C_A = k_{DA}p_A + \frac{C'_{HA}b_Ap_A}{1+b_Ap_A+b_Bp_B}} \quad \textbf{(3)}$$

Similarly, sorption isotherm for component "*B*" is given by:[25]

$$\boldsymbol{C_B = k_{DB}p_B + \frac{C'_{HB}b_Bp_B}{1+b_Ap_A+b_Bp_B}} \quad \textbf{(4)}$$

And the total sorbed gas concentration is:

$$\boldsymbol{C = k_{DA}p_A + k_{DB}p_B + \frac{C'_{HA}b_Ap_A+C'_{HB}b_Bp_B}{1+b_Ap_A+b_Bp_B}} \quad \textbf{(5)}$$

Obviously, when either p_A or p_B approaches zero, Eq. (5) reduces to the pure gas relation i.e. Eq. (1).

2.2. Permeation

Based on partial immobilization model, the total concentration of sorbed gas in glassy polymers is divided into a mobile part with a diffusion coefficient D and concentration C_m while the balance (C-C_m) is totally immobilized. This means that all the gas dissolved in the Henry's region is mobile, whereas for the Langmuir sites, a fraction (F) of the adsorbed gas molecules, is mobile and the remainder ($1-F$) is immobile.[32,33] F is usually called the immobilization factor which depends on the nature of penetrant-polymer system as well as the system temperature.[18,34] This factor represents the ratio of the diffusivity through the microvoids to that through the polymeric matrix ($F = \frac{D_H}{D_D}$).[33]

Then, the flux (N) of component "A" of two components system is expressed as follows:[32, 35, 36]

$$\boldsymbol{N_A = -D_A\left(\frac{\partial C_{mA}}{\partial x}\right)} \quad \textbf{(6)}$$

Where[27]

$$\boldsymbol{C_{mA} = C_{DA} + F_A C_{HA} = \left(k_{DA}p_A + \frac{F_A C'_{HA} b_A p_A}{1+b_A p_A + b_B p_B}\right)} \quad \textbf{(7)}$$

And, diffusivity of component "A" in the presence of plasticization is given by:[27,35]

$$\boldsymbol{D_A(C_{mA}) = D_{A0}\, exp\,(\beta_A C_{mA})} \quad \textbf{(8)}$$

Where D_{A0} is the diffusion coefficient of pure gas in the limit $C_{mA} \rightarrow 0$, and β_A is an empirical constant that depends on the nature of penetrant-polymer system, temperature and membrane thickness, which is known as plasticization parameter indicating the penetrant plasticizing capability.[18,34,35]

Then Eqs. (6)-(8) yield the following expression for the flux of penetrant gas in glassy polymers:

$$N_A = \boldsymbol{D_{eff,A}\frac{\partial C_A}{\partial x} = D_{A0}\, exp\left[\beta_A\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A p_{A2} + b_B p_{B2}}\right)p_{A2}\right]\left[\frac{k_{DA} + \frac{F_A C'_{HA} b_A}{(1+b_A p_{A2}+b_B p_{B2})^2}}{k_{DA} + \frac{C'_{HA} b_A}{(1+b_A p_{A2}+b_B p_{B2})^2}}\right]\frac{\partial C_A}{\partial x}} \quad \textbf{(9)}$$

Then, effective diffusivity from Eq. (9) is calculated as follows:

$$\boldsymbol{D_{eff,A} = D_{A0}\, exp\left[\beta_A\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A p_{A2} + b_B p_{B2}}\right)p_{A2}\right]\left[\frac{k_{DA} + \frac{F_A C'_{HA} b_A}{(1+b_A p_{A2}+b_B p_{B2})^2}}{k_{DA} + \frac{C'_{HA} b_A}{(1+b_A p_{A2}+b_B p_{B2})^2}}\right]} \quad \textbf{(10)}$$

Further, under steady state conditions, the permeability "A" (P_A) can be defined as:[37,38]

$$\boldsymbol{P_A = \frac{N_A l}{p_{A2} - p_{A1}}} \quad \textbf{(11)}$$

Where subscripts 2 and 1 represent the upstream and downstream conditions, respectively.

By substituting Eq. (8) in Eq. (6), then integrating and combining with Eq. (11), permeability of component "*A*" in a binary mixture through glassy polymers in presence of plasticization is expressed as follows:[27]

$$\boldsymbol{P_A = \frac{D_{A0}}{\beta_A p_{A2}}\left\{exp\ \left[\beta_A\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A p_{A2}+b_B p_{B2}}\right)p_{A2}\right] - 1\right\}} \quad \textbf{(12)}$$

It should be noted that negligible downstream pressure of component "*A*" (p_{A1}=0) was assumed in derivation Eq. (12).

For component "*B*" in a binary mixture diffusivity is given by Eq. (13):[27]

$$\boldsymbol{D_B(C_{mA}) = D_{B0} exp\ (\beta_B C_{mA})} \quad \textbf{(13)}$$

Also, concentration of the mobile part of component "*B*" is calculated by:

$$\boldsymbol{C_{mB} = C_{DB} + F_B C_{HB} = \left(k_{DB} p_B + \frac{F_B C'_{HB} b_B p_B}{1+b_A p_A+b_B p_B}\right)} \quad \textbf{(14)}$$

Again, combining Eqs. (6), (13), (14) and (11) obtained permeability of component "*B*" as follows:[27]

$$\boldsymbol{P_B = D_{B0}\left\{exp\left[\beta_B p_{A2}\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A p_{A2}+b_B p_{B2}}\right)\right]\left(k_{DB} + \frac{F_B C'_{HB} b_B}{1+b_A p_{A2}+b_B p_{B2}}\right)\right\}} \quad \textbf{(15)}$$

Again, downstream pressure of components was assumed zero.

Also, by writing Eq. (9) for component "*B*", effective diffusivity for component "*B*" is given by:

$$\boldsymbol{D_{eff,B} = D_{B0}\, exp\left[\beta_B\left(k_{DA} + \frac{F_A C'_{HA} b_A}{1+b_A p_{A2}+b_B p_{B2}}\right)p_{A2}\right]\left[\frac{k_{DB}+\frac{F_B C'_{HB} b_B}{(1+b_A p_{A2}+b_B p_{B2})^2}}{k_{DB}+\frac{C'_{HB} b_B}{(1+b_A p_{A2}+b_B p_{B2})^2}}\right]} \quad \textbf{(16)}$$

It is worth mentioning that permeability for component "*i*" in polymeric membranes is defined as the product of diffusivity and solubility:[31,39,40]

$$\boldsymbol{P_i = D_{ave,i} \times S_i} \quad \textbf{(17)}$$

For a two component system, selectivity of membrane is defined as the ratio of their permeability coefficients, which is given by Eq. (18):[39,41]

$$\boldsymbol{\alpha_{A/B} = \frac{P_A}{P_B}} \quad \textbf{(18)}$$

3. Results and discussion

3.1. Model validation and mathematical procedure

To validate the model, the predictions of the proposed model compared against the permeation of CO_2/CH_4 mixture with different compositions in a cellulose acetate membrane.[20] Mathematical procedure to predict permeation of mixed gas in cellulose acetate membrane was as follows:

i. Calculation of parameters of DMS model (Eq. (1)) for pure CO_2 and CH_4 by fitting this Eq. using sorption experimental data.

ii. Parameters obtained from step i were combined with Eq. (12) and fitted against experimental data for permeation of CO_2 to compute parameters β, F and D_0/l for CO_2.

iii. Parameters obtained from steps i and ii (F_{CO2}) were combined with Eqs. (15) and fitted against experimental data for permeation of CH_4 to compute parameters β, F and D_0/l for CH_4.

It should be noted that the parameters of DMS model and non-linear proposed models for permeation of CO_2 and CH_4 were obtained by least squares regression technique.

3.2. Sorption

In order to study permeation of a mixed gas system in cellulose acetate membrane, first it was necessary to estimate the sorption isotherm of the pure gases in the membrane. Then, by using the results of pure gas sorption, combined with the dual mode sorption model for mixed gas systems (Eqs. (3, 4)), the mixed gas sorption in the membrane was predicted. Using experimental data, parameters of dual sorption model (Eq. (1)) for pure CO_2 and CH_4 were calculated as shown in Table 1.[20] Figs. 1a and 1b show the solubility of pure CO_2, pure CH_4 and also concentration of CO_2 and CH_4 in the mixed gas (CO_2/CH_4) with different compositions versus pressure in the membrane. For the sorption of gases in the membrane, at lower pressures solubility severely decreases, however, for higher pressures due to occupation Langmuir sites decline in solubility slope was occurred. For the sorption of CO_2 in presence of CH_4, CO_2 was sorbed in Henry's part of the glassy membrane independent of the second component, while in Langmuir sites, a competitive sorption occurred and a part of these sites were occupied by CH_4 molecules. Then, the sorption of CH_4 in Langmuir sites caused less CO_2 to be sorbed in these sites at a specific pressure, hence the solubility of CO_2 sorbed in the presence of CH_4 in the polymer decreased relative to pure CO_2. By increasing composition of CH_4 in the feed, more

CH_4 was sorbed in Langmuir sites, and then more reduction of CO_2 sorption in polymer was experienced. Also, competitive sorption was occurred for CH_4 and with increase in CO_2 fraction in the feed, solubility of CH_4 was decreased.

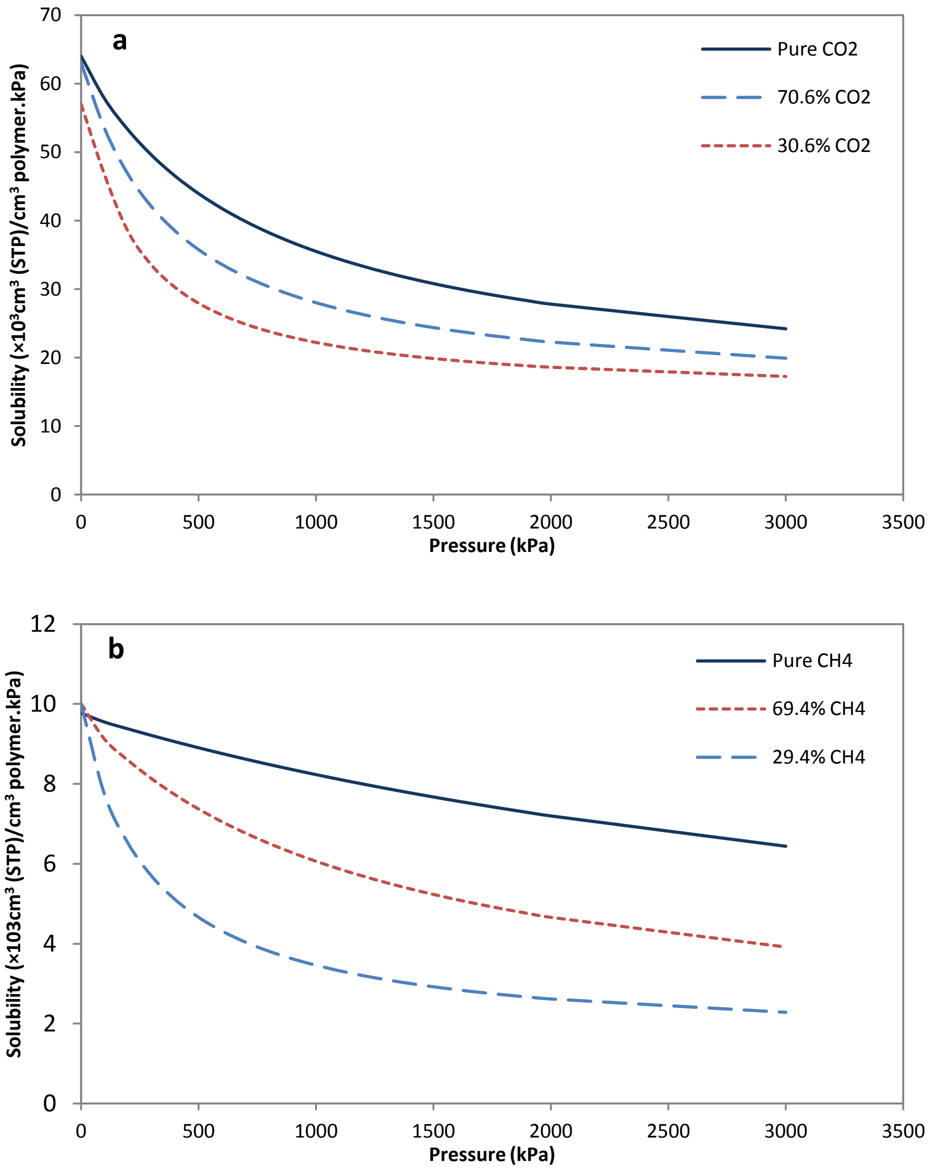

Figure 1: CO_2 and CH_4 sorption isotherm in cellulose acetate membrane as a function pressure.

Table 1: DMS parameters for CO_2 and CH_4 in cellulose acetate membrane.[20]

Component	$k_D(cm^3(STP)/cm^3.kPa)$	$C'_H(cm^3(STP)/cm^3)$	$b(kPa^{-1})$
CO_2	1.43×10^{-2}	37.29	1.32×10^{-3}
CH_4	1.51×10^{-3}	37	2.22×10^{-4}

3.3. Permeation

Fig. 2 shows the effect of feed composition on the CO_2 permeances in cellulose acetate membrane in binary mixture of CO_2/CH_4. This figure compares the experimental data of Donohue *et al.*[20] with the predictions of the proposed model, calculated by Eq. (12), using parameters of CO_2 and CH_4 depicted in Tables 1 and 2. Considering pure CO_2, permeance increases with pressure due to plasticization. This trend was due to thin skin of asymmetric membranes which permeances increases with pressure monotonously.[19,20] The presence of CH_4 in the feed decreases sorption of CO_2 due to competitive sorption, and this decrease in solubility lowers the diffusivity of CO_2 for a given pressure and also suppresses plasticization, consequently reducing the CO_2 permeance.[20] This depression trend was increased with increase in CH_4 fraction. Also, permeances of CO_2 with different amount of CH_4 in the feed, was increased with pressure with lower slope rather than pure CO_2 which means by introducing CH_4 in the feed, CO_2-induced plasticization was suppressed dramatically. It should be mentioned that although solubility decreased with pressure, diffusivity increased due to plasticization. This increase overcomes decrease in solubility then permeance increased with pressure for all cases. It was apparent that the model predictions showed a good agreement with respect to the experimental points.

As mentioned above, parameters of Eq. (12) (β, D_0/l and F) were calculated using sorption parameters of pure CO_2 and CH_4 and also the experimental data[20] for CO_2 permeances with different fractions in the feed in cellulose acetate membrane, as shown in Tables 2. As can be seen, these parameters are strongly dependent on the feed composition. It is worth mentioning that the experimental data are for asymmetric membrane and the reported results for permeation are permeability per thickness (permeance in GPU which 1 GPU = 10^{-6} cm^3(STP) cm^{-2} $cmHg^{-1}$). Then, D_0/l and D/l were reported in the present work.

For β_{CO2} with increasing CH_4 fraction in the feed, competitive sorption caused less CO_2 to be sorbed in the polymer at a specific pressure, hence plasticization and β_{CO2} which showed the plasticization ability, decreased. Also, with increasing fraction of CH_4 in the feed, sorption of CO_2 in the membrane and also plasticization decreases.

Diffusion coefficient of CO_2 at zero penetrant concentration per unit membrane thickness ($D_{0,CO_2}/l$), decreased with CO_2 fraction. With increasing CH_4 fraction in the feed and decrease in plasticization, D_0/l for CO_2 increases. This trend is consistent with the work of Duthie *et al.*[34] and Okamoto *et al.*[42] that reported D_0 increases with decreasing plasticization.

Immobilization factor for CO_2 (F_{CO2}) was decreased with increasing CH_4 (decreasing CO_2 fraction) in the feed as shown in table 2. This means that the diffusivity of CO_2 through the microvoids (Langmuir sites) decreased in comparison to the diffusion through the polymer matrix (Henry's part). This happens due to occupation of part of Langmuir sites by CH_4 molecules, therefore, CO_2 molecules having fewer sites for sorption, while sorption of CO_2 through the polymer matrix was independent of CH_4. The second major reason for decreasing in F_{CO2}, was reduction of mobility of CO_2 molecules due to suppression of plasticization.

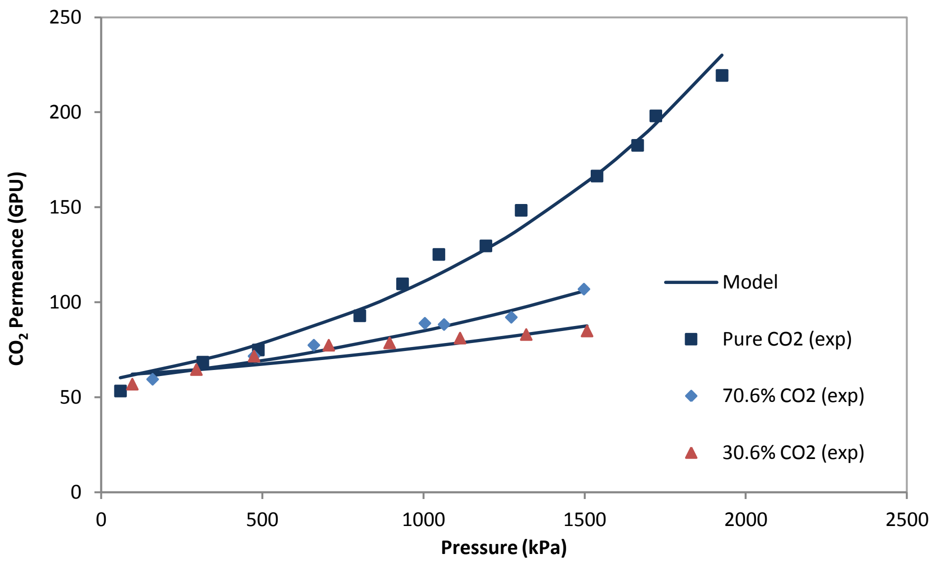

Figure 2: CO_2 permeance in cellulose acetate membrane as a function of pressure with different compositions of the feed.[20]

Table 2: Parameters of Eq. (12) for permeation CO_2 in cellulose acetate membrane.

Composition	β_{CO_2}	F_{CO_2}	$D_{0,CO_2}/l$	R^2
Pure CO_2	0.086	0.06	0.00253528	0.987
70.6% CO_2	0.055	0.039	0.0027093	0.967
30.6% CO_2	0.036	0.028	0.00293148	0.842

The effect of feed composition on the CH_4 permeances in cellulose acetate membrane in binary mixture of CO_2/CH_4 was showed in Fig. 3. This figure compares the experimental data of Donohue *et al.*[20] with the predictions of the proposed model, calculated by Eq. (15), using parameters of CO_2 and CH_4 depicted in Tables 1, 2 and 3. Permeances of CH_4 with different fraction of CO_2 increased with pressure, and at higher fraction of CH_4, increasing trend had lower slope. This was resulted from higher sorption of CH_4 in the membrane which led to decrease in plasticization. Also, at specific pressures, permeances of higher fractions of CH_4 in the feed, due to higher sorption of CH_4, was higher than the lower fractions.

Again, parameters of Eq. (15) (β, D_0/l and F) were calculated using sorption parameters of pure CO_2 and CH_4, immobilization factor for CO_2 (F_{CO2}) and also the experimental data[20] for CH_4 permeances with different fractions in the feed in cellulose acetate membrane, as shown in Tables 3. As was seen in table 3, similar to plasticization ability of CO_2, β_{CH4} decreased as its fraction increased due to suppression in plasticization. $D_{0,CH4}/l$, also increases with CH_4 fraction.

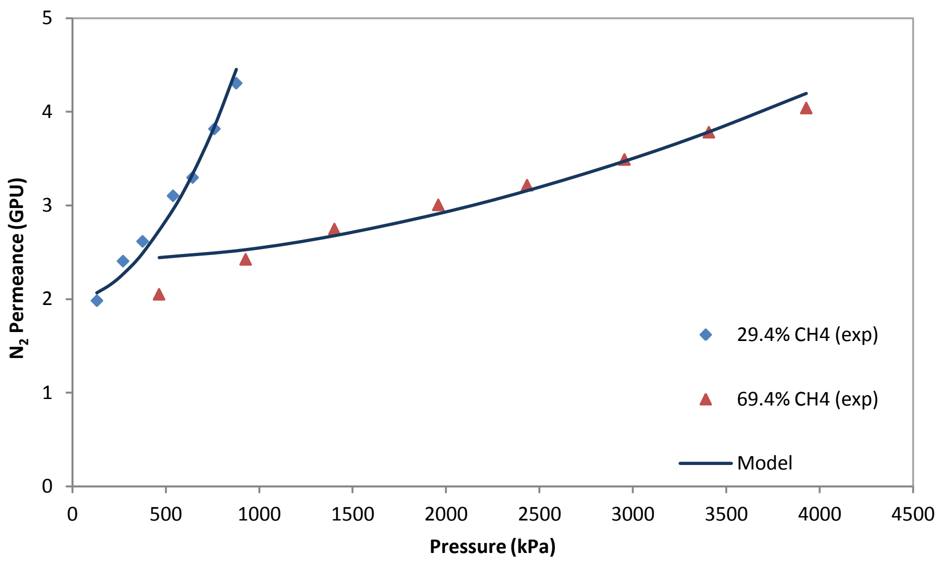

Figure 3: CH_4 permeance in cellulose acetate membrane as a function of pressure with different compositions of the feed.[20]

Table 3: Parameters of Eq. (15) for permeation of CH_4 in cellulose acetate membrane.

Composition	β_{CH_4}	F_{CH_4}	$D_{0,CH_4}/l$	R^2
29.4% CH_4	0.043	0.24	0.0004369	0.978
69.4% CH_4	0.036	0.13	0.0007152	0.942

Also, immobilization factor for CH_4 (F_{CH4}), decreases with fraction of CH_4 in the feed. In this case, although with an increase in CH_4 fraction in the feed, Langmuir sites occupied by CH_4

was enhanced, plasticization and then mobility of CH_4 molecules was reduced. This in turn caused a decrease in F_{CH4}.

3.4. Diffusion

Figs. 4 and 5 respectively illustrate the estimated effective diffusivity per unit membrane thickness (D_{eff}/l) versus pressure for CO_2 and CH_4 derived from Eqs. (10) and (16) utilizing parameters from tables 1, 2 and 3. Although D_0/l increased as a function of CH_4 fraction, variation of effective diffusivity for CO_2 with pressure is rapidly overwhelmed by the higher degree of plasticization at lower fractions of CH_4, so that the effective diffusivity at higher pressures decreases significantly with increasing CH_4 fraction. For pure CO_2, stronger dependency of D_{eff}/l to pressure was observed and D_{eff}/l was increased with increasing pressure due to plasticization. Generally, for feeds containing different fractions of CH_4, the effect of plasticization decreased and the influence of pressure on D_{eff}/l for CO_2 became negligible in comparison to the case with pure CO_2. By increasing CH_4 in the feed, because of less sorption of CO_2 and decrease in plasticization, dependency of D_{eff}/l for CO_2 to pressure, was more reduced. As can be seen in Fig. 5, D_{eff}/l for CH_4 in the feed enhanced as a result of an increase in pressure due to plasticization. Also, for feeds with higher fractions of CH_4, because of higher sorption of CH_4, D_{eff}/l was higher than the cases with lower fractions.

3.5. Separation Factor

Based on Eq. (18), separation factor for a binary gas mixture is the ratio of their permeability coefficients. In Fig. 6, experimental separation factor for CO_2/CH_4 was compared with the predictions of the model by using permeances of CO_2 and CH_4 calculated in section 3.3. According to this figure, the separation factor of the mixed CO_2/CH_4 with different compositions, decreased with increasing pressure and the model showed accurately this trend. As is observed in Figs. 2 and 3, permeances of CO_2 and CH_4 were increased with pressure, but increase in CH_4 permeances were more than that of CO_2, and separation factor decreased with pressure. Also, separation factor for mixed gas feed at specific pressures was decreased with increasing CH_4 fraction. The presence of CH_4 led to CO_2 permeance reduction with increasing CH_4 fraction in the feed at a specific pressure. On the other hand, permeance of CH_4, was increased with increasing CH_4 fraction in the feed. Therefore, with increase in CH_4 fraction at a specific pressure, CO_2/CH_4 separation factor was decreased.

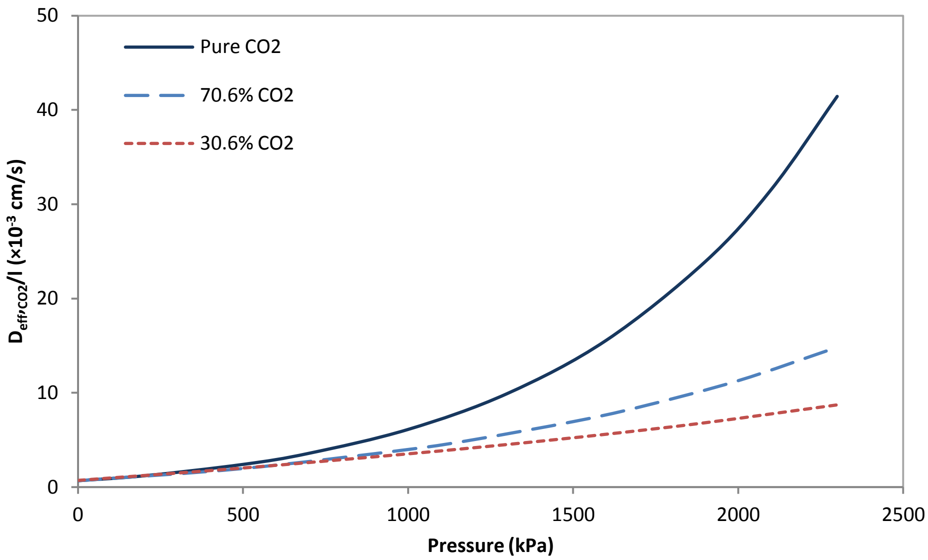

Figure 4: Effective diffusivity per unit membrane thickness (D_{eff}/l) for CO_2 versus pressure.

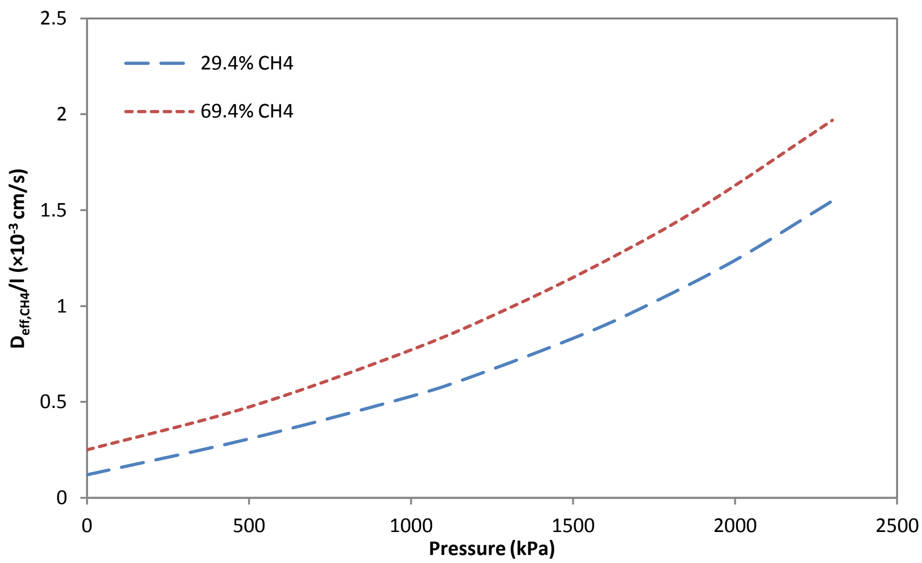

Figure 5: Effective diffusivity per unit membrane thickness (D_{eff}/l) for CH_4 versus pressure.

4. Conclusion

In the current study, a mathematical model was developed to predict permeation behavior of mixed gases through glassy polymeric membranes in presence of plasticization. Parameters of the model (β, F, D_0/l) were obtained by using the experimental data for permeation of CO_2/CH_4 mixture feed with different compositions through asymmetric cellulose acetate membrane. It was shown that these parameters were strongly depended on the feed composition. The observations revealed that β and F for CO_2 and CH_4 declined with increasing CH_4 fraction in the feed due to reduction in plasticization. D_0/l for CO_2 and CH_4 rose with increasing CH_4 fraction. D_{eff}/l for pure CO_2 was significantly pressure dependence, however with increasing fraction of CH_4 in the feed, this dependency almost disappeared. Also, D_{eff}/l for CH_4 increased with pressure due to plasticization. Separation factor for CO_2/CH_4 with different fractions decreased with pressure and the model showed this trend accurately. Also, with increase in CH_4 fraction in the feed, separation factor decreased at specific pressure. In conclusion, presence of the second component along with CO_2 resulted in reduction of sorption of CO_2 due to competitive sorption which eventually, led to decrease in plasticization. The presented model was capable of giving a useful tool to enhance our knowledge related to permeation behavior of mixed gas systems through glassy polymeric membranes in presence of plasticization.

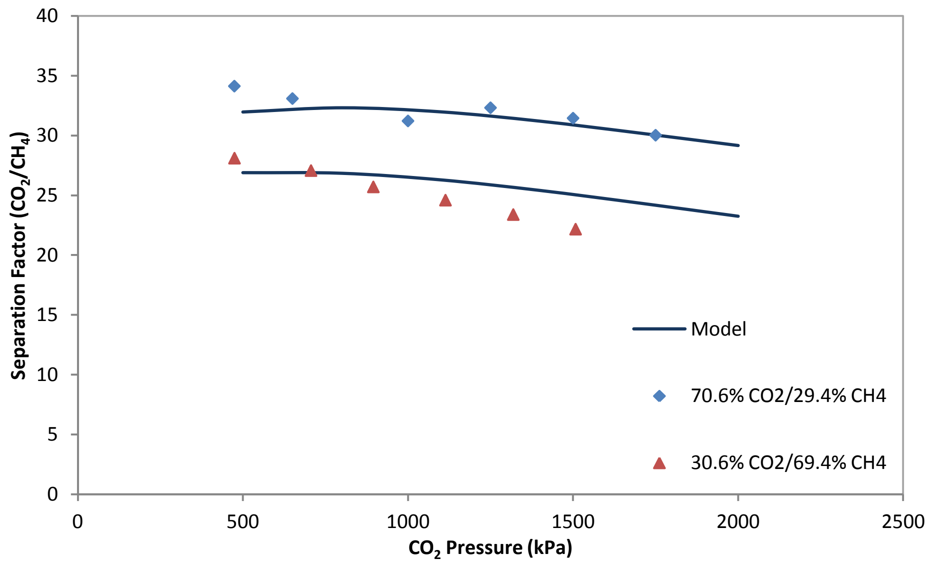

Figure 6: Separation factor for CO_2/CH_4 mixed gas with different compositions versus pressure.

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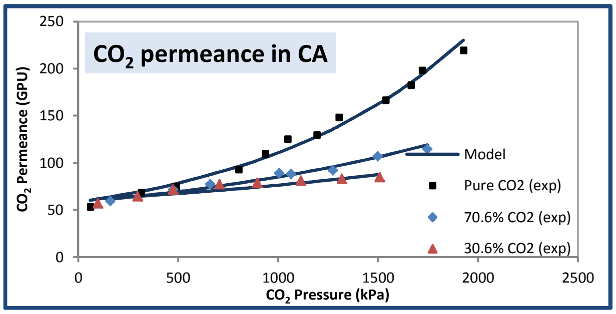

A mathematical model for permeation and diffusion of mixed gases in glassy polymeric membranes in presence of plasticization was derived.