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Permeability of gas mixtures in the glassy polymers with and without plasticization

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Abstract: In this research, solubility, permeability and diffusivity of gas mixtures are comprehensively studied through the glassy polymers. Diffusivity of components in the mixture is assumed to be a function of the concentration of all components in the mixture. Then, the permeability of pure species is expanded to the gas mixtures and for checking the validity, the model fitted to the experimental data for permeation of CO₂/CH₄ through different glassy membranes and the parameters of the model are calculated. Afterwards, the obtained parameters are used for predicting permeability of CO₂ and CH₄ in the mixture. The results show that solubility, diffusivity, and also permeability of CO₂ in the glassy polymers are suppressed in the presence of CH₄ as well as plasticization. Moreover, the diffusivity (*D*) for pure CO₂ is significantly pressure dependent in the presence of plasticization whereas with the increase in the CH₄ fraction, this dependency decreases due to the reduction in the plasticization.

Keywords: Gas separation; membrane; plasticization; solubility; diffusivity.

INTRODUCTION

Polymeric membranes are widely used in natural gas separation process. For removal carbon dioxide (CO₂), glassy polymeric membranes are often preferred over rubbery polymeric membranes because of their higher CO₂/CH₄ or CO₂/N₂ selectivity.¹⁻⁶ Although some types of glassy membranes have a good performance in CO₂ separation, the performance of these membranes can be hindered by plasticization phenomenon.⁷⁻¹² Therefore, CO₂ permeability increases with the feed pressure.⁷⁻¹³ On the other hand, permeability of pure inert gases such as CH₄ or N₂ has decreasing trend with the pressure.¹⁴⁻¹⁶ Thus, ideal selectivity of CO₂/N₂ or CO₂/CH₄ increases with feed pressure.¹³⁻¹⁶ However, the behavior of mixed gas feeds is significantly different from pure species. In the presence of the plasticization, both CO₂ and N₂ or CH₄ permeabilities increase. But N₂ or CH₄ generally has larger increase than CO₂, resulting in decreasing selectivity.^{1,10,14,17-18} Thus, the actual selectivity is lower than ideal selectivity at an special pressure.^{1,14,19} Raymond *et al.*¹⁹ reported that for mixed gas feed of

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CO₂ and CH₄ with equal composition, the actual selectivity at 5 atm is well predicted by pure gases, whereas at 20 atm, the actual selectivity was much lower than ideal selectivity. It was due to plasticization of membranes at 20 atm pressure. Also, ideal selectivity of CO₂ and CH₄ for polyimide (6FDA-mPD) was reported about 60 at a feed pressure of 17.5 atm, whereas the actual selectivity for feed with equal composition of these gases was observed about 4.²⁰

Therefore, a proper prediction of transport behavior for gas mixtures especially in the presence of plasticization is essential to accurately represent the experimental results. Then, an accurate and simple model is required to use for all the different behaviors of gaseous in glassy polymers.

Different approaches were developed to describe the solubility and transport of gases and vapors in the glassy polymers. Among these models, Dual Mode Sorption (DMS) and Non-equilibrium lattice fluid (NELF) models are well-known models. It should be mentioned that, although NELF model has been extended for all permeability behavior of gaseous in glassy polymers, it is used less than DMS model because of the complexity and long calculations. DMS, a model with empirical parameters, are widely used mainly due to its remarkable simplicity. Although, different models with different assumption have been developed based on this theory to investigate the permeability of pure and mixed gases in the glassy polymers, less attention has been paid for predicting permeation of mixed gases through glassy polymers in the presence of plasticization. In our previous works, we extended a model for permeation of gas mixtures in glassy polymers based on DMS model with no predictive capability.²¹⁻²² In the present study, a comprehensive model based on DMS model is developed to predict the permeation behavior of mixed gases through glassy polymers with and without plasticization using pure data for solubility and permeability. To achieve this aim, diffusivity of all species in the mixture is assumed to be a function of the concentration of all components in the mixture. Then, for determining the parameters and also evaluation the accuracy of the model, the predictions of the model are compared against the experimental data for permeation of different groups of gas mixture in different glassy polymers.

THEORY AND BACHGROUND

Solubility

Based up on DMS model, two mechanisms of sorption occur in glassy polymers: i) ordinary dissolution based on Henry's law and, ii) "hole-filling" according to Langmuir theory. The equilibrium isotherm for a pure gas A based on DMS model is expressed as:²¹⁻²³

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

where C is the gas concentrations in polymer (cm³ STP / cm³ polymer), C_D is Henry's solubility represents ordinary dissolution, C_H is Langmuir solubility represents sorption in microvoids or holes, k_D is Henry's law solubility coefficient (cm³ STP / cm³ polymer.atm), C'_H is the hole

saturation constant ($\text{cm}^3 \text{ STP} / \text{cm}^3 \text{ polymer}$), b is the hole affinity constant (atm^{-1}) and p is pressure (atm). Solubility coefficient of gas A in polymeric membranes is defined as:²¹⁻²²

$$S_A = C_A / p_A \quad (2)$$

Koros *et al.* extended DMS model for gas mixture systems and the sorption of components A and B of a binary gas mixture is expressed as:²³

$$C_A = k_{DA} p_A + \frac{C'_{HA} b_A p_A}{1 + b_A p_A + b_B p_B} \quad (3)$$

$$C_B = k_{DB} p_B + \frac{C'_{HB} b_B p_B}{1 + b_A p_A + b_B p_B} \quad (4)$$

Permeability

Based on the partial immobilization model (PIM), a fraction F of the sorbed gases in the Langmuir sites are mobile and the remainder $(1-F)$ is immobile whereas the whole gas dissolved in the Henry's region is mobile. The total concentration of mobile part of gas adsorbed is C_m with a diffusion coefficient D . F is the immobilization factor and depends on the nature of penetrant-polymer system as well as the system temperature.²⁴⁻²⁵

The flux (N) of component i is expressed as follows:²¹

$$N_i = -D_i \left(\frac{\partial C_{mi}}{\partial x} \right) \quad (5)$$

where²¹

$$C_{mi} = C_{Di} + F_i C_{Hi} = k_{Di} p_i + F_i \frac{C'_{Hi} b_i p_i}{1 + b_i p_i} \quad (6)$$

For diffusivity of species i , a simple exponential relationship with penetrant mobile concentration was found effective and given by:²⁶⁻²⁷

$$D_i = D_{i0} \exp(\beta_i C_{mi}) \quad (7)$$

where D_{i0} is the diffusion coefficient of pure gas at zero penetrant concentration, and β_i is the plasticization factor.

It should be noted that Eq. (7) can be used for all gases including plasticizer or not. In the absence of plasticization (*i.e.* $\beta_i = 0$), diffusivity will be constant and would not change with pressure.

Then, Eqs. (5)-(7) yield the following expression for the flux of penetrant gas in glassy polymers:

$$N_i = -\frac{D_{i0}}{l} \int_{C_{mi1}}^{C_{mi2}} \exp(\beta_i C_{mi}) dC_{mi} \quad (8)$$

where subscripts 2 and 1 represent the upstream and downstream conditions and when the downstream pressure is considered zero, $C_{mA1}=0$.

As Toni *et al.* study which considered the two mobility coefficients related to the concentration of both penetrants,²⁸ diffusivities for components A and B in the binary gas mixture, are assumed to be related to the concentration of both penetrants and obtained by:

$$D_A = D_{A0} \exp(\beta_A C_{mA} + \beta_B C_{mB}) \quad (9)$$

$$D_B = D_{B0} \exp(\beta_A C_{mA} + \beta_B C_{mB}) \quad (10)$$

where D_{A0} , D_{B0} , β_A and β_B were obtained from pure state, and:

$$C_{mA} = C_{DA} + F_A C_{HA} = \left(k_{DA} p_A + F_A \frac{C'_{HA} b_A p_A}{1 + b_A p_A + b_B p_B} \right) \quad (11)$$

$$C_{mB} = C_{DB} + F_B C_{HB} = \left(k_{DB} p_B + F_B \frac{C'_{HB} b_B p_B}{1 + b_A p_A + b_B p_B} \right) \quad (12)$$

Again combining Eq. (5) and Eqs. (9)-(12) and integrating, yield the following expression for the flux of for components A and B in glassy polymers:

$$N_A = -\frac{D_{A0}}{l} \int_{C_{mA1}}^{C_{mA2}} \exp(\beta_A C_{mA} + \beta_B C_{mB}) dC_{mA} \quad (13)$$

$$N_B = -\frac{D_{B0}}{l} \int_{C_{mB1}}^{C_{mB2}} \exp(\beta_A C_{mA} + \beta_B C_{mB}) dC_{mB} \quad (14)$$

It is worth mentioning that for integrating Eq. (13), C_{mA} and C_{mB} should be written in term p_A and for Eq. (14) should be written in term p_B .

Further, under steady state conditions, the permeability and selectivity are given by:²²

$$P_1 = \frac{N_1 l}{p_{i2} - p_{i1}} \quad (15)$$

where l is the membrane thickness.

RESULTS AND DISCUSSION

Mathematical procedure to predict permeation of mixed gas through glassy polymeric membranes is as follows:

1. Calculation of parameters of DMS model (Eq. (1)) for pure species by fitting this equation on the experimental data of isotherms.
2. Using the obtained parameters from step 1, fitting Eq. (8) on the experimental data for permeability of pure species and calculation parameters β , F and D_0 of pure species.
3. Using the obtained parameters of steps 1 and 3 in conjunction with Eqs. (13) and (14), for prediction of permeability of species in gas mixture.

It is worth noting that the parameters of DMS model and non-linear proposed models are obtained by least squares regression technique using MATLAB software.

To validate the model, comparing with the experimental data for permeation of CO₂/CH₄ mixtures through different glassy membranes including polysulfone (PSf), polyetherimide (PEI), polyhydroxyether (PH), polyarylate (PAr) and cellulose acetate (CA) are investigated.^{15, 29-31}

Solubility

In order to study the permeability behavior of CO₂/CH₄ gaseous mixture, the parameters of the sorption isotherm of pure CO₂ and CH₄ in the glassy polymers

is required. DMS parameters for CO₂ and CH₄ in the different glassy polymers which have been obtained by fitting DMS model on the experimental data are reported in Table I. Afterwards, by consideration the parameters of Table I, and using Eqs. (3) and (4), the solubility of species in the gas mixture are predicted.

Table I. DMS parameters for pure CO₂ and CH₄ in the different glassy polymers at 35 °C

Polymer	Gas	$k_D / \text{cm}^3 \text{ STP} / \text{cm}^3 \cdot \text{atm}$	$C'_H / \text{cm}^3 \text{ STP} / \text{cm}^3$	B / atm^{-1}	Reference
PSf	CO ₂	0.664	17.91	0.326	29
	CH ₄	0.161	9.86	0.070	
PH	CO ₂	0.289	10.01	0.184	29
	CH ₄	0.051	2.70	0.067	
PEI	CO ₂	0.758	25.02	0.366	29
	CH ₄	0.207	7.31	0.136	
PAr	CO ₂	0.631	22.69	0.215	29
	CH ₄	0.181	6.45	0.100	
CA	CO ₂	1.362	22.58	0.248	15
	CH ₄	0.190	2.504	0.132	

As mentioned in our previous work,²¹⁻²² the solubility-pressure isotherm for CO₂ and CH₄ and their mixtures in glassy polymers, at the lower pressures severely increases and with the increase in the pressure, the decrease in the sorption slope is occurred. For higher pressures, almost this slope is constant and the sorption isotherm changes linearly like the sorption of gases in the rubbery polymers. This trend of sorption is due to this fact that at low pressures, gas molecules adsorbed in the Henry and Langmuir sites and for higher pressures Langmuir sites will be occupied. For gas mixtures, the presence of the second component (*i.e.* CH₄) inhibited the sorption of first component (CO₂) by the occupation of some sites of Langmuir portion. Then, the sorption of CO₂ is suppressed by the presence of CH₄ in the mixture (Figure 1).

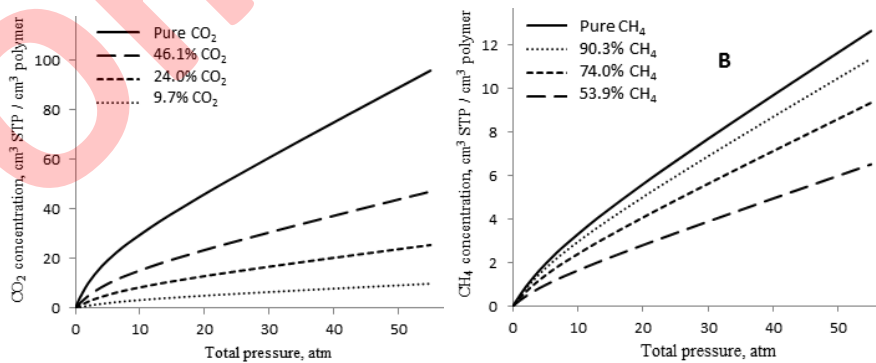


Figure 1. solubility of A) CO₂ and B) CH₄ in CA glassy polymer

Figure 2 shows solubility selectivity of CO₂/CH₄ versus pressure. Solubility selectivity is found to be significantly higher in mixture compared to pure condition. This can be attributed to competitive sorption whereas solubility of CO₂ decreases in the presence of CH₄ as well as CH₄. It should be mentioned that the decrease in CH₄ solubility is more than CO₂ solubility due to higher hole affinity constant of CO₂ ($b_{CO_2} > b_{CH_4}$) resulted in increase in solubility selectivity. As can be observed, the ideal solubility selectivity increases with the increase in CH₄ fraction at constant pressure as reported results by Vopicka *et al.*³²

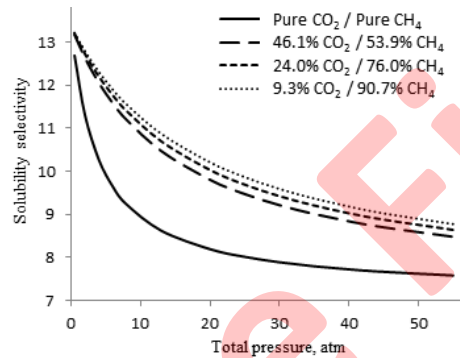


Figure 2. solubility selectivity of CO₂/CH₄ in CA glassy polymer

Permeation without plasticization

Permeability of pure CO₂ and CH₄ in different glassy polymers has been fitted on the experimental data from the literature³⁰ and parameters of the model including β , F and D_0 for CO₂ and CH₄ are reported in Table II (also determined in ref. 30). Permeability-pressure plots have a decreasing and/or constant trend in all cases. In these cases, there is no plasticization ($\beta = 0$), then, diffusivity is constant. In this case which plasticization do not occurred, decreasing and/or constant trends for permeability is related to solubility coefficient and is controlled by immobilization factor (F) which is shown the mobile parts of sorbed gas in the Langmuir region.

Table II. Parameters of Eq. (8) for permeation without plasticization ($\beta=0$) as ref. 30.

Polymer	Gas	β	F	$D_0 \times 10^8 / \text{cm}^2 \text{s}^{-1}$
PSf	CO ₂	0	0.118	4.53
	CH ₄	0	0.174	0.690
PH	CO ₂	0	0.094	0.877
	CH ₄	0	0.072	0.246
PEI	CO ₂	0	0.063	1.14
	CH ₄	0	0.073	0.113
PAr	CO ₂	0	0.126	6.90
	CH ₄	0	0.160	1.30

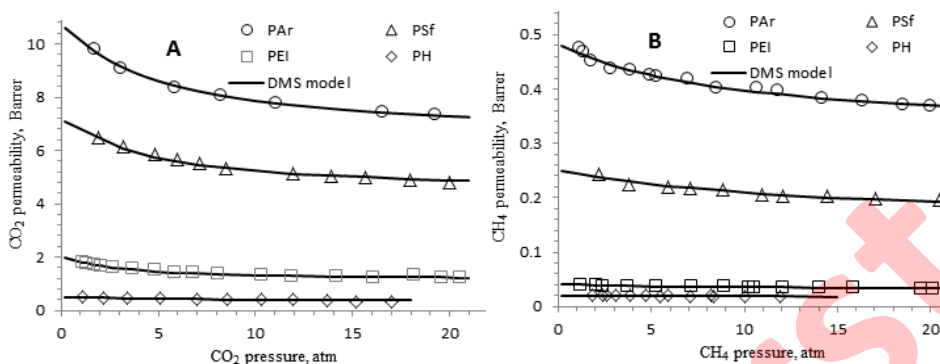


Figure 3. Permeability of pure A) CO₂ and B) CH₄ in different glassy polymers without plasticization (experimental data from ref. 30)

Figures 4a-b show the prediction of model for CO₂ and CH₄ gases of 50/50 vol./vol. mixture in different glassy membranes using Eqs. (13) and (14) compared to the experimental data from Ref. 31. At a glance, almost a little suppression in permeability in gas mixture is observed compared to pure species. As mentioned above, solubility of species in the presence of second component reduces compared to pure species due to occupation of Langmuir sites which has been resulted in the reduction in the diffusivity as well as permeability. An acceptable prediction for all cases can be observed.

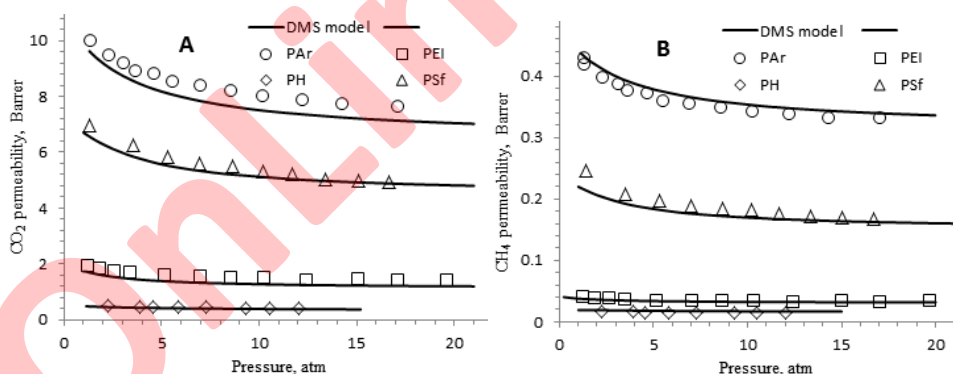


Figure 4. Permeability of A) CO₂ and B) CH₄ gases of 50/50 vol./vol. mixture in different glassy polymers without plasticization (experimental data from ref. 31)

Permeation with plasticization

Permeability

Figs. 5a-b show the permeability behavior of pure CO₂ and CH₄ through the CA membrane, respectively. These figs. present the experimental data of Ref. 15. with the predictions of the model, calculated by Eqs. (8), using parameters β , F and D_0 for CO₂ and CH₄ listed in Table III. For pure CO₂, permeability increases with

the increase in the pressure due to the higher degree of plasticization of the CA membrane. Because of the high sorption of CO₂ which is a condensable gas, polymer matrix swells and the interaction between adjacent segments of the polymer chain reduces. Therefore, due to the increase in segmental mobility and the free volume of polymer matrix, diffusivity increases with the increase in the pressure. On the other hand, solubility coefficient decreases with the increase in the pressure. Since, the increase in the diffusivity overcomes the decrease in solubility coefficient, CO₂ permeability increases with the increase in the pressure. For CH₄ which has low solubility in the membrane, permeability decreases with the increase in the pressure. In this case, plasticization does not occur, and diffusivity is constant. On the other hand, solubility coefficient decreases with the pressure. Then, permeability decreases with the increase in the pressure.

In addition, comparing the experimental data for permeability of CO₂ in the gas mixture feed with different compositions from Ref. 15 and the predictions of the model using parameters of Table II, is shown in Fig. 6.

Table III. Infinite dilution diffusivity and plasticization factor for the various penetrants in CA membrane

Polymer	Gas	β	F	$D_0 \times 10^7 / \text{cm}^2 \text{s}^{-1}$
CA	CO ₂	0.031	0.06	1.45
	CH ₄	0	0.38	0.29

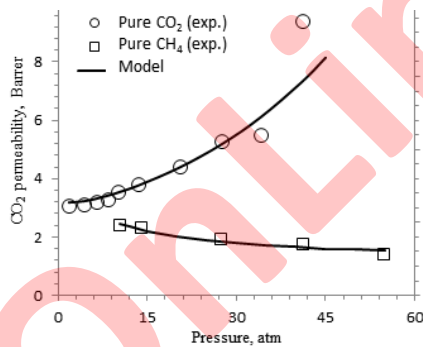


Figure 5: Permeability of pure CO₂ and CH₄ penetrants in the CA membrane (experimental data from Ref. 15)

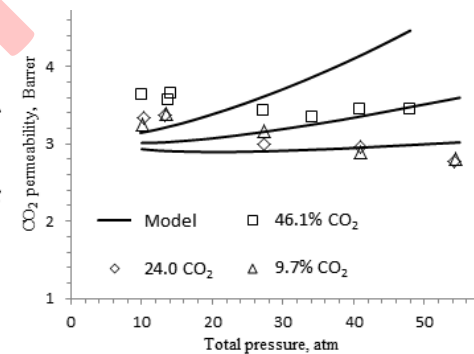


Figure 6: Permeability of CO₂ in the mixture with different compositions versus pressure, comparison between experimental data from Ref. 15 and the model prediction

For feed with 46.1 % CO₂ and the rest CH₄, permeability decreases with the increase in the pressure up to about 30 atm and then increases. 30 atm is called the “plasticization pressure”. Afore mentioned, solubility coefficient decreases with the increase in the pressure and in the presence of CO₂ as a plasticizer component, diffusivity increases with the increase in the pressure. For a feed with

46.1 % CO_2 , at the pressures lower than 30 atm, the decrease in solubility coefficient overcomes the increase in the diffusivity whereas at higher pressures the increase in the diffusivity overcomes. Indeed, by adding CH_4 as the second component to the feed, some sites for sorption of CO_2 are occupied by CH_4 molecules so that the solubility of CO_2 in the mixture declines compared to the pure CO_2 . By the suppression in the CO_2 solubility, diffusivity of CO_2 lowers at a specific pressure, consequently CO_2 -induced plasticization decreases. It means that CH_4 in the feed acts as anti-plasticizer. For higher fractions of CH_4 in the feed, the effect of anti-plasticization increases and the permeability with the increase in the pressure decreases. Therefore, by introducing CH_4 in the feed, CO_2 -induced plasticization suppresses. As can be seen, the prediction of the model for permeability behavior is almost acceptable.

Moreover, Fig. 7 shows comparing the experimental data and the predictions of the model for CH_4 in gas mixture feeds with different compositions using parameters Table II. As observed in this Fig., for feed with 53.9 % CH_4 , permeability of CH_4 passes through a minimum similar to the permeability of CO_2 in Fig. 3. This behavior is due to the presence of CO_2 which causes the membrane to plasticize. Also, for feeds with the higher fractions of CH_4 , plasticization decreases due to the reduction of CO_2 sorption and diffusion, so that for feeds with the fractions higher than 53.9 % of CH_4 , CH_4 permeability decreases and/or is constant with the increase in the pressure. Also, with the increase in CH_4 fraction in the feed, CH_4 permeability at specific pressures reduces following suppression in plasticization.

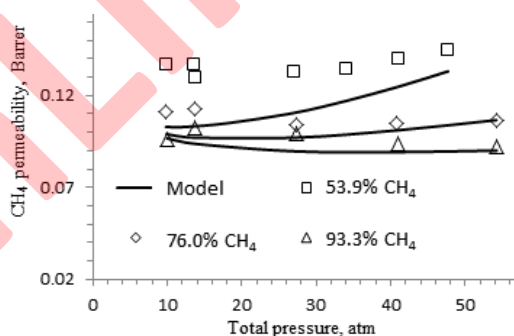


Figure 7. Permeability of CH_4 in the mixture with different compositions versus pressure, comparison between the experimental data from Ref. 15 and the model calculation

Diffusivity

Figs. 8a-b illustrate the estimated diffusivity versus pressure for CO_2 and CH_4 in the pure state and in the gas mixture derived from Eqs. (9) and (10) using parameters Tables I and II. For pure CO_2 , stronger dependency of D to pressure is observed, so that D increases significantly with the increase in the pressure due

to higher degree of plasticization. For feeds with different fractions of CH_4 , because of the reduction in the plasticization, the effect of pressure on D for CO_2 become very weak and the dependency of D with the pressure, decreases with the increase in the CH_4 fraction.

For pure CH_4 , D is constant and do not change with the increase in the pressure. By adding 9.7 % CO_2 to the feed, very weak dependency of D to the pressure is observed and this dependency increases with the increase in the CO_2 fraction due to the increase in the plasticization, so that for feeds with 46.1 % CO_2 , D for CH_4 increases significantly. Also, at a specific pressure, D for CH_4 decreases with the increase in CH_4 fraction. It should be mentioned that although, with the increase in CH_4 fraction in the feed, CH_4 sorption increases, the swelling and the plasticization effect decreases due to reduction in the CO_2 sorption. The latter reason overcomes which results in the reduction in the diffusivity of CH_4 with the increase in CH_4 fraction at a specific pressure.

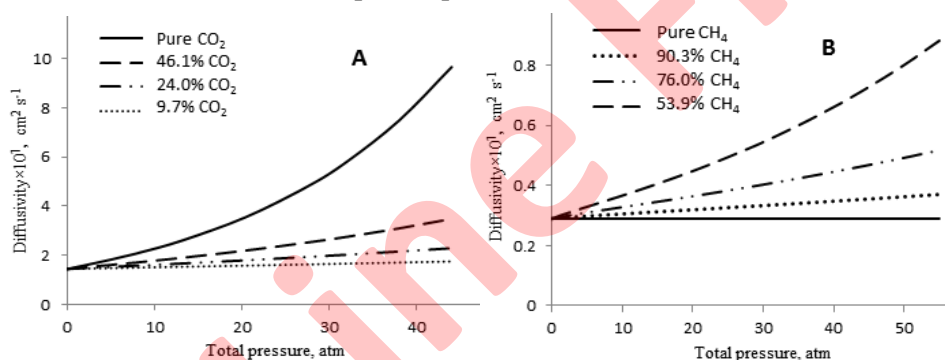


Figure 8. Diffusivity of A) CO_2 and B) CH_4 in the CA membrane at the pure state and the mixture

CONCLUSIONS

Permeation behavior of mixed gases through the glassy membranes is significantly different from pure species, especially in the presence of plasticization phenomenon. The presence of the second component such as CH_4 or N_2 along with CO_2 in the feed, led to the decrease in the CO_2 solubility resulted in the decrease in diffusivity, permeability and also the plasticization effect. This research was focused on the gas mixtures and developed a model for prediction the permeability of species in the mixed gaseous through glassy polymers with and without plasticization. Then, by comparing the proposed model on the experimental data for permeation of pure CO_2 and CH_4 through the different glassy polymer membranes, the parameters of the model calculated. Afterwards, these parameters were used for predicting permeability of gases in the mixture. The results show that the presence of CH_4 in the feed reduces the permeability of CO_2 as well as the plasticization. Also, the results show that D

for pure CO₂ significantly changes with the pressure and by adding CH₄ to the feed, this dependency decreased. For feed with 53.9 % CH₄ (46.1 % CO₂) *D* for CH₄ increased with the increase in the pressure but for higher fractions of CH₄ in the feed this dependency almost disappeared.

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ИЗВОД
ПРОПУСТЉИВОСТ МЕШАВИНА ГАСОВА У ПОЛИМЕРИМА У СТАКЛАСТОМ СТАЊУ
СА И БЕЗ ПЛАСТИФИКАЦИЈЕ

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У овом истраживању проучавана је растворљивост, пропустљивост и дифузивност смеша гасова кроз полимере у стакластом стању. Претоставља се да је дифузивност компонената у мешавини функција концентрације свих компоненти у смеши. Затим се пропустљивост чистих компонената проширује на смеше гасова и за проверу ваљаности се проверава модел фитовањем експерименталних података за пермеабилност CO₂/CH₄ кроз различите мембране у стакластом стању и израчунавају се параметри модела. Након тога, тако добијени параметри се користе за предвиђање пропустљивости CO₂ и CH₄ у смеши. Резултати показују да су растворљивост, дифузивност, а такође и пропустљивост CO₂ кроз полимере у стакластом стању смањени у присуству CH₄ и пластификатора. Штавише, дифузивност (*D*) за чисти CO₂ значајно зависи од притиска у присуству пластификатора док се с повећањем удела CH₄ та зависност смањује због смањења пластификације.

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