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Survey

SURVEY

Permeability of gas mixtures in glassy polymers with and without plasticization

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Abstract: In this research, the solubility, permeability and diffusivity of gas mixtures through glassy polymers were comprehensively studied. The diffusivity of the components in the mixture was assumed to be a function of the concentration of all components in the mixture. Then, the permeability of pure species was expanded to the gas mixtures and to check the validity, the model was fitted to the experimental data for permeation of CO_2/CH_4 through different glassy membranes and the parameters of the model were calculated. Afterwards, the obtained parameters were used for predicting the permeability of CO_2 and CH_4 in the mixture. The results showed that the solubility, diffusivity, and the permeability of CO_2 in the glassy polymers are suppressed in the presence of CH_4 as well as plasticization. Moreover, the diffusivity (*D*) for pure CO_2 is significantly pressure dependent in the presence of plasticization whereas with the increase in the CH_4 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 the natural gas separation process. For removal of carbon dioxide (CO_2), glassy polymeric membranes are often preferred over rubbery polymeric membranes because of their higher CO_2/CH_4 or CO_2/N_2 selectivity.[1–6] Although some types of glassy membranes have a good performance in CO_2 separation, the performance of these membranes can be hindered by the plasticization phenomenon.[7–12] Therefore, CO_2 permeability increases with the feed pressure.[7–13] On the other hand, permeability of pure inert gases, such as CH_4 or N_2, has a decreasing trend with the pressure.[14–16] Thus, the ideal selectivity of CO_2/N_2 or CO_2/CH_4 increases with feed pressure.[13–16] However, the behavior of mixed gas feeds is significantly different from pure

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species. In the presence of plasticization, the permeabilities of both CO_2 and N_2 or CH_4 increase. But N_2 or CH_4 generally have larger increases than CO_2, resulting in decreasing selectivity.[1,10,14,17,18] Thus, the actual selectivity is lower than ideal selectivity at a special pressure.[1,14,19] Raymond *et al.*[19] reported that for mixed gas feed of CO_2 and CH_4 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. In addition, ideal selectivity of CO_2 and CH_4 for polyimide (6FDA-mPD) was reported to be 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, for a proper prediction of transport behavior for gas mixtures, especially in the presence of plasticization, it is essential to represent accurately the experimental results. Then, an accurate and simple model is required to be used for all the different behaviors of gases in glassy polymers.

Different approaches were developed to describe the solubility and transport of gases and vapors in glassy polymers. Among these models, the 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 the DMS model because of its complexity and long calculation times. DMS, a model with empirical parameters, is widely used mainly due to its remarkable simplicity. Although, different models with different assumptions have been developed based on this theory to investigate the permeability of pure and mixed gases in 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 the DMS model was 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, the 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 evaluation of the accuracy of the model, the predictions of the model were compared against experimental data for the permeation of different groups of gas mixture in different glassy polymers.

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* 1 atm = 101325 Pa

THEORY AND BACKGROUND

Solubility

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

$$C_{\mathrm{A}} = C_{\mathrm{DA}} + C_{\mathrm{HA}} = k_{\mathrm{DA}} p_{\mathrm{A}} + C'_{\mathrm{HA}} b_{\mathrm{A}} p_{\mathrm{A}} / (1 + b_{\mathrm{A}} p_{\mathrm{A}}) \tag{1}$$

where C is the gas concentrations in the polymer (cm^3 STP/cm^3 polymer), C_{D} is the 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 (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}) and p is pressure (atm). The solubility coefficient of gas A in polymeric membranes is defined as:[21,22]

$$S_{\mathrm{A}} = C_{\mathrm{A}}/p_{\mathrm{A}} \tag{2}$$

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

$$C_{\mathrm{A}} = k_{\mathrm{DA}} p_{\mathrm{A}} + C'_{\mathrm{HA}} b_{\mathrm{A}} p_{\mathrm{A}} / (1 + b_{\mathrm{A}} p_{\mathrm{A}} + b_{\mathrm{B}} p_{\mathrm{B}}) \tag{3}$$

$$C_{\mathrm{B}} = k_{\mathrm{DB}} p_{\mathrm{B}} + C'_{\mathrm{HB}} b_{\mathrm{B}} p_{\mathrm{B}} / (1 + b_{\mathrm{A}} p_{\mathrm{A}} + b_{\mathrm{B}} p_{\mathrm{B}}) \tag{4}$$

Permeability

Based on the partial immobilization model (PIM), a fraction F of the sorbed gases in the Langmuir sites are mobile and the remainder ($1-F$) are immobile whereas the whole gas dissolved in the Henry's region is mobile. The total concentration of the mobile part of the adsorbed gas 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]

$$N_{\mathrm{i}} = -D_{\mathrm{i}} \left(\frac{\partial C_{\mathrm{mi}}}{\partial x}\right) \tag{5}$$

where:[21]

$$C_{\mathrm{mi}} = C_{\mathrm{Di}} + F_{\mathrm{i}} C_{\mathrm{Hi}} = k_{\mathrm{Di}} p_{\mathrm{i}} + F_{\mathrm{i}} C'_{\mathrm{Hi}} b_{\mathrm{i}} p_{\mathrm{i}} / (1 + b_{\mathrm{i}} p_{\mathrm{i}}) \tag{6}$$

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

$$D_i = D_{i0} \exp(\beta_i C_{\mathrm{m}i}) \tag{7}$$

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) could 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 the penetrant gas in glassy polymers:

$$N_i = -\frac{D_{i0}}{l} \int_{C_{\mathrm{m}i1}}^{C_{\mathrm{m}i2}} \exp\left(\beta_i C_{\mathrm{m}i}\right) \mathrm{d}C_{\mathrm{m}i} \tag{8}$$

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

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

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

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

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

$$C_{mA} = C_{DA} + F_A C_{HA} = k_{DA} p_A + F_A C'_{HA} b_A p_A / (1 + b_A p_A + b_B p_B) \tag{11}$$

$$C_{mB} = C_{DB} + F_B C_{HB} = k_{DB} p_B + F_B C'_{HB} b_B p_B / (1 + b_A p_A + b_B p_B) \tag{12}$$

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

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

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

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.

Furthermore, under steady state conditions, the permeability and selectivity are given by:[22]

$$P_i = \frac{N_i l}{p_{i2} - p_{i1}} \tag{15}$$

where l is the membrane thickness.

RESULTS AND DISCUSSION

The mathematical procedure to predict the permeation of mixed gas through glassy polymeric membranes is as follows:

1. Calculation of parameters of the DMS model (Eq. (1)) for pure species by fitting this equation to the experimental data of the isotherms.

2. Using the obtained parameters from step 1, fitting Eq. (8) to the experimental data for permeability of pure species and the calculation of parameters β, F and D_0 for the pure species.

3. Using the obtained parameters of steps 1 and 2 in conjunction with Eqs. (13) and (14), for the prediction of the permeability of the species in the gas mixture.

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

To validate the model, comparing with the experimental data for the permeation of CO_2/CH_4 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 CO_2/CH_4 gaseous mixture, the parameters of the sorption isotherm of pure CO_2 and CH_4 in the glassy polymers is required. The DMS parameters for CO_2 and CH_4 in the different glassy polymers, which were obtained by fitting the DMS model to the experimental data, are reported in Table I. Then, by consideration the parameters of Table I, and using Eqs. (3) and (4), the solubility of the species in the gas mixture were predicted.

TABLE I. DMS parameters for pure CO_2 and CH_4 in the different glassy polymers at 35 °C

Polymer	Gas	k_D / (cm^3 STP/(cm^3 atm))	C'_H / (cm^3 STP/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 a previous work,[21,22] the solubility–pressure isotherm for CO_2 and CH_4 and their mixtures in glassy polymers, at lower pressures severely increases and with increasing pressure, a decrease in the sorption slope occurred. For higher pressures, this slope is almost constant and the sorption isotherm changes linearly, like the sorption of gases in rubbery polymers. This trend of sorption is because 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.*, CH_4) inhibited the sorption of first component (CO_2) by occupation of some sites of the Langmuir portion. Then, the sorption of CO_2 is suppressed by the presence of CH_4 in the mixture (Fig. 1).

The solubility selectivity of CO_2/CH_4 *vs*. pressure is shown in Fig. 2. Solubility selectivity is found to be significantly higher in mixtures compared to the pure condition. This could be attributed to competitive sorption whereby the solubility of CO_2 decreases in the presence of CH_4 as well as CH_4. It should be mentioned that the decrease in CH_4 solubility is more than that of CO_2 solubility due to higher hole affinity constant of CO_2 ($b_{CO_2} > b_{CH_4}$) resulting in an increase in the solubility selectivity. As could be observed, the ideal solubility selectivity increases with increasing CH_4 fraction at constant pressure as reported by Vopicka *et al.*[20]

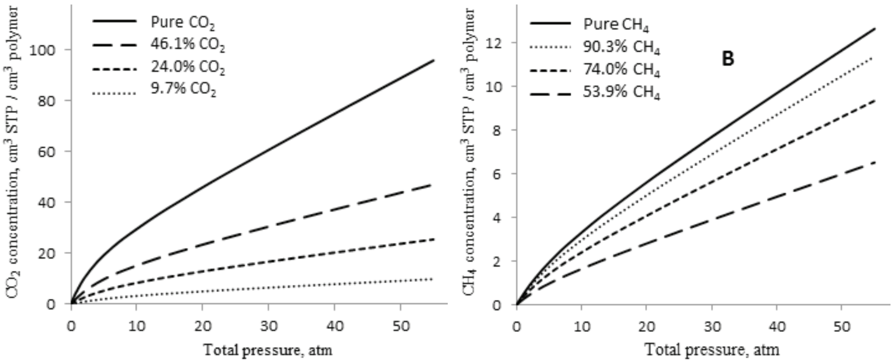

Fig. 1. Solubility of: A) CO_2 and B) CH_4 in CA glassy polymer.

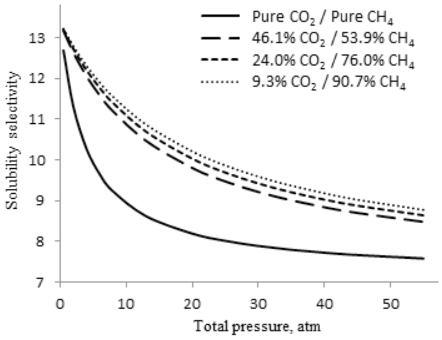

Fig. 2. Solubility selectivity of CO_2/CH_4 in CA glassy polymer.

Permeation without plasticization

The permeability of pure CO_2 and CH_4 in different glassy polymers was fitted using experimental data from the literature[30] and the parameters of the model, including β, F and D_0 for CO_2 and CH_4, are reported in Table II (also determined in the literature[30]). The permeability–pressure plots have a decreasing and/or constant trend in all cases. In these cases, there is no plasticization ($\beta = 0$), then, the diffusivity is constant. In this case when there was no plasticization, the decreasing and/or constant trends for permeability is related to the solubility coefficient and is controlled by the immobilization factor (F), which shows the mobile parts of the sorbed gas in the Langmuir region.

The predictions of the model for CO_2 and CH_4 gases of 50/50 volume ratio mixture in different glassy membranes using Eqs. (13) and (14) compared to the experimental data from the literature[31] are shown in Fig. 4a and b. At a glance, almost a small suppression in permeability in gas mixture is observed compared to the pure species. As mentioned above, solubility of species in the presence of second component is reduced compared to pure species due to occupation of Langmuir sites, which resulted in a reduction in the diffusivity as well as permeability. An acceptable prediction for all cases could be observed.

TABLE II. Parameters of Eq. (8) for permeation without plasticization ($\beta = 0$)[30]

Polymer	Gas	F	$D_0\times10^8$ / cm^2 s^{-1}
PSf	CO_2	0.118	4.53
	CH_4	0.174	0.690
PH	CO_2	0.094	0.877
	CH_4	0.072	0.246
PEI	CO_2	0.063	1.14
	CH_4	0.073	0.113
PAr	CO_2	0.126	6.90
	CH_4	0.160	1.30

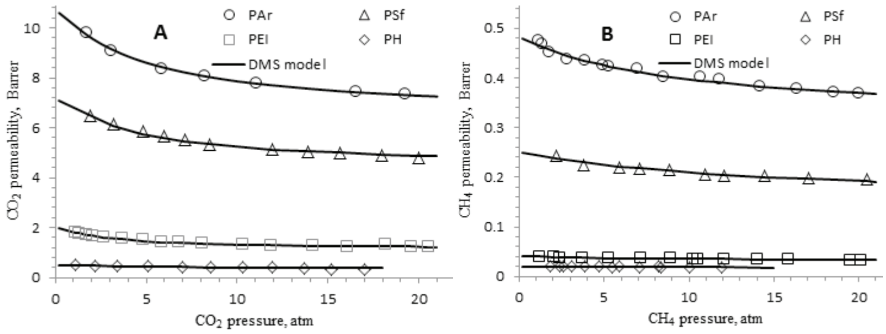

Fig. 3. Permeability of pure: A) CO_2 and B) CH_4 in different glassy polymers without plasticization (experimental data from the literature[30]).

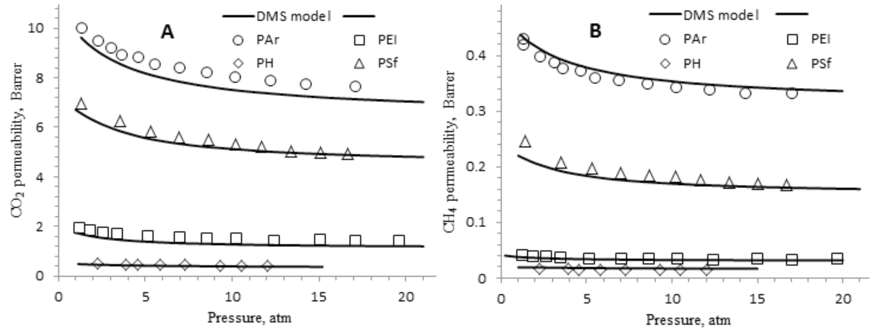

Fig. 4. Permeability of: A) CO_2 and B) CH_4 gases of 50/50 volume ratio mixture in different glassy polymers without plasticization (experimental data from the literature[31]).

Permeation with plasticization

Permeability. The permeability behavior of pure CO_2 and CH_4 through the CA membrane is shown in Fig. 5. These figures present experimental data from the literature[15] with predictions of the model, calculated by Eq. (8), using the parameters β, F and D_0 for CO_2 and CH_4 listed in Table III. For pure CO_2, the permeability increases with increasing pressure due to the higher degree of plasticization of the CA membrane. Due to the high sorption of CO_2, which is a condensable gas, the 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, the diffusivity increases with increasing pressure. On the other hand, the solubility coefficient decreases with increasing pressure. Since, the increase in the diffusivity overcomes the decrease in solubility coefficient, CO_2 permeability increases with increasing pressure. For CH_4, which has low solubility in the membrane, the permeability decreases with increasing pressure. In this case, plasticization does not occur, and diffusivity is constant. On the other hand, the solubility coefficient decreases with pressure. Then, the permeability decreases with increasing pressure.

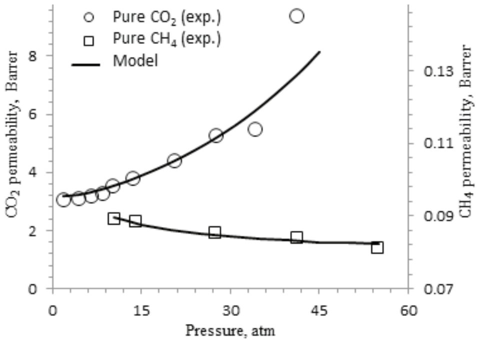

Fig. 5. Permeability of pure CO_2 and CH_4 penetrants in the CA membrane (experimental data from the literature[15]).

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

Polymer	Gas	β	F	$D_0 \times 10^7$ / $cm^2 s^{-1}$
CA	CO_2	0.031	0.06	1.45
	CH_4	0	0.38	0.29

In addition, comparing the experimental data for the permeability of CO_2 in the gas mixture feed with different compositions from the literature[15] and the predictions of the model using parameters from Table II is shown in Fig. 6.

For a feed with 46.1 % CO_2 and the rest CH_4, the permeability decreases with increasing pressure up to about 30 atm and then increases and 30 atm is called the "plasticization pressure". The aforementioned solubility coefficient decreases with increasing pressure and in the presence of CO_2 as a plasticizer component, the diffusivity increases with increasing pressure. For a feed with 46.1 % CO_2, at pressures lower than 30 atm, the decrease in the solubility coefficient overcomes the increase in the diffusivity whereas at higher pressures, the increase in the diffusivity dominates. 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 pure CO_2. By 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 to the feed, CO_2-induced plasticization is suppressed. As can be seen, the prediction of the model for permeability behavior is almost acceptable.

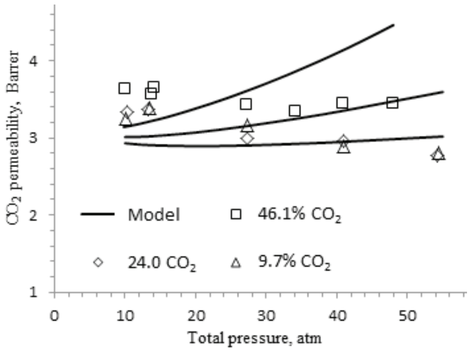

Fig. 6. Permeability of CO_2 in mixtures with different compositions *vs*. pressure, comparison between the experimental data from the literature[15] and the model prediction.

Moreover, the experimental data and the predictions of the model for CH_4 in gas mixture feeds with different compositions using parameters in Table II are compared in Fig. 7. As observed, for a feed with 53.9 % CH_4, the 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. In addition, for feeds with higher fractions of CH_4, plasticization decreases due to the reduction of CO_2 sorption and diffusion, and hence, for feeds with the fractions higher than 53.9 % of CH_4, the CH_4 permeability decreases and/or is constant with increasing in pressure. Furthermore, with increasing CH_4 fraction in the feed, the CH_4 permeability at specific pressures is reduced following suppression

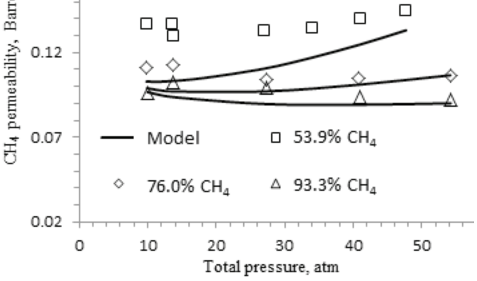

Fig. 7. Permeability of CH_4 in mixtures of different compositions *vs*. pressure, comparison between the experimental data from the literature[15] and the model calculation.

of plasticization.

Diffusivity

The estimated diffusivity *vs*. pressure for CO_2 and CH_4 in the pure state and in the gas mixture derived from Eqs. (9) and (10) using parameters from Tables I and II is illustrated in Fig. 8a and b. For pure CO_2, stronger dependency of D on pressure was observed, so that D increases significantly with increasing 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 became very weak and the dependency of D on pressure decreases with increasing CH_4 fraction.

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

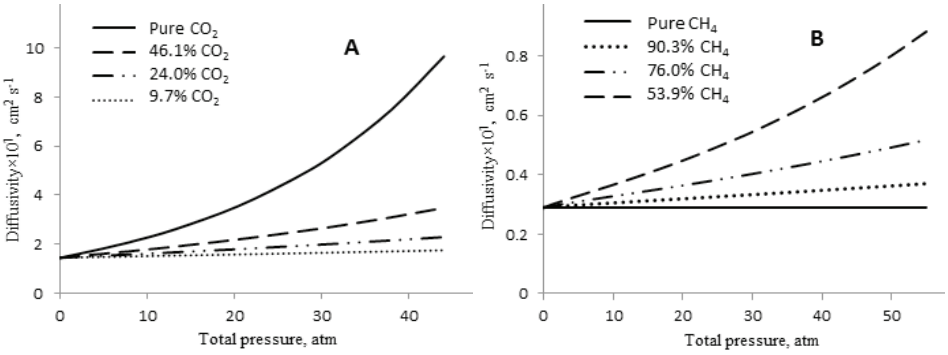

Fig. 8. Diffusivity of: A) CO_2 and B) CH_4 in the pure state and as mixtures in the CA membrane.

CONCLUSIONS

The permeation behavior of mixed gases through glassy membranes was significantly different from pure species, especially in the presence of the plasticizeation phenomenon. The presence of the second component, such as CH_4 or N_2, along with CO_2 in the feed led to a decrease in the CO_2 solubility resulting in a decrease in diffusivity, permeability and the plasticization effect. This research was focused on gas mixtures and a model was developed for the prediction the permeability of the species in mixed gases through glassy polymers with and without plasticization. Then, by comparing the proposed model for the experimental data of permeation of pure CO_2 and CH_4 through the different glassy polymer membranes, the parameters of the model were calculated. Then, these parameters were used for predicting the permeability of gases in the mixtures. The results showed that the presence of CH_4 in the feed reduces the permeability of CO_2 as well as the plasticization. Moreover, the results show that *D* for pure CO_2 significantly changes with pressure and with the addition of CH_4 to the feed, this dependency decreased. For a feed with 53.9 % CH_4 (46.1 % CO_2) the *D* value for CH_4 increased with increasing pressure but for higher fractions of CH_4 in the feed, this dependency almost disappeared.

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ИЗВОД

ПРОПУСТЉИВОСТ СМЕШЕ ГАСОВА КРОЗ ПОЛИМЕРЕ У СТАКЛАСТОМ СТАЊУ СА ПЛАСТИФИКАЦИЈОМ И БЕЗ ЊЕ

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У овом истраживању проучавана је растворљивост, пропустљивост и дифузивност смеша гасова кроз полимере у стакластом стању. Претпоставља 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 CO_2/CH_4 кроз различите мембране у стакластом стању и израчунавају се параметри модела. Након тога, тако добијени параметри се користе за предвиђање пропустљивости CO_2 и CH_4 у смеши. Резултати показују да су растворљивост, дифузивност, а такође и пропустљивост CO_2 кроз полимере у стакластом стању смањени у присуству CH_4 и пластификатора. Штавише, дифузивност за чисти CO_2 значајно зависи од притиска у присуству пластификатора док се с повећањем удела CH_4 та зависност смањује због смањења пластификације.

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