

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Gas Permeation Rate and Selectivity for Silicone Rubber and Solids/Silicone Rubber MMMs

There are two properties of the membrane which are the critical importance in determining the separation performance. The first property is the solubility (S) of the gas in the membrane, while the second property is the diffusivity (D) of the gas in the membrane material. The solubility depends on the condensability of the gas molecule to the membrane material and the polymer–gas interactions. On the other hand, the diffusivity is determined by packing and motion of the polymer segments and by the size and shape of the gas molecules. The product of these two materials is permeability (P) (Ismail and Lorna, 2001). Due to the similar size of molecular diameter of all three gases; CO₂ 3.94 °A, CH₄ 3.8 °A, and N₂ 3.79 °A, thus; their diffusivity through the membrane are not probably different. Therefore; the gas separation is not dominantly controlled by size selective mechanism, but the solubility plays the selective role in determining the separation performance.

In this section, in order to enhance the gas permeability and selectivity properties of polymeric membranes, the incorporation of various solid components such as activated carbon (AC), NaX or LiX zeolite were added into the matrix phase. The primary motivation for preparing MMMs is to join the adsorption properties of the materials and function of solubility enhancement of a desired gas.

- The permeance or a thickness normalized permeation rate (P/l) of gases; carbon dioxide (CO₂), methane (CH₄) and nitrogen (N₂) and CO₂/CH₄ and CO₂/N₂ selectivities for silicone rubber and solid/silicone rubber MMMs with activated carbon, NaX and LiX individually incorporated at various loadings of 10, 20 and 30 wt % were determined from the steady state permeation rates of each gas through the membrane at room temperature and feed pressure of 50 psia. The calculation of such properties is provided in Appendix A. The obtained results are shown in Table 4.1

Table 4.1 Gas permeation rate and selectivity of CO₂/CH₄ and CO₂/N₂ for SR/CA, AC/SR/CA, NaX/SR/CA and LiX/SR/CA MMMs

MMM	Gas permeance (GPU)			Selectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
CA ¹	176.86	21.12	21.22	8.37	8.34
SR/CA ²	21.58	1.64	1.32	13.17	16.32
10%AC/SR/CA ³	26.54	2.61	1.81	10.19	14.70
20%AC/SR/CA ³	30.06	2.24	1.63	13.44	18.46
30%AC/SR/CA ³	21.29	1.74	1.55	12.26	13.72
10%NaX/SR/CA ³	38.50	2.39	1.49	16.14	25.89
20%NaX/SR/CA ³	19.88	1.68	1.33	11.84	14.97
30%NaX/SR/CA ³	15.48	1.28	1.00	12.09	15.47
10%LiX/SR/CA ³	28.95	1.99	1.46	14.57	19.84
20%LiX/SR/CA ³	20.12	1.68	1.38	12.00	14.59
30%LiX/SR/CA ³	13.72	1.48	1.27	9.26	10.79

Notes

¹CA = Porous cellulose acetate from UOP

²SR/CA = Silicone rubber casted on cellulose acetate

³X% solid/SR/CA = X% solid with silicone rubber casted on cellulose acetate

where X = 10, 20, 30 and solid = activated carbon (AC), NaX, LiX

% solid was calculated respect to the total weight of solid and silicone rubber

GPU = $1 \cdot 10^{-6}$ cm³(STP)/cm².sec.cmHg

4.1.1 AC/SR/CA MMMs

The gas permeation rate and CO_2/CH_4 and CO_2/N_2 selectivities of AC/SR/CA MMMs are shown in Figure 4.1.

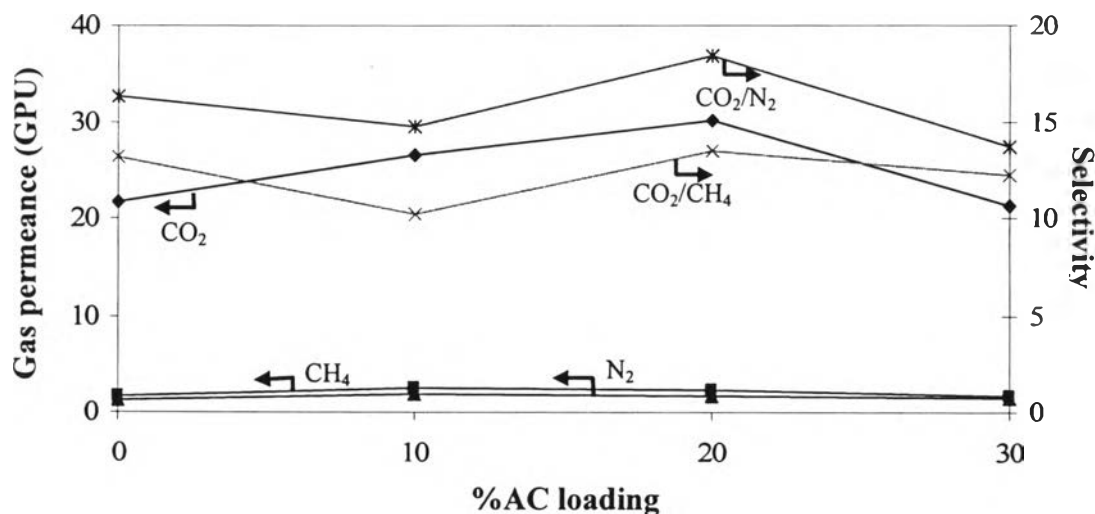


Figure 4.1 Gas permeation rate and CO_2/CH_4 and CO_2/N_2 selectivities of various %AC/SR/CA MMMs.

As can be seen from Figure 4.1, the incorporation of activated carbon into silicone rubber/cellulose acetate membrane primarily effected to CO_2 permeation rate, while those of CH_4 and N_2 were not significantly changed when compared to the membrane without activated carbon. This is the effect of the solubility enhancement which only takes place to CO_2 molecules, therefore this is the reason for unchanging in CH_4 and N_2 permeation. However CO_2 permeance reached the maximum at 20%AC loading and decreased after that. Consequently, the selectivities reached the maximum point at 20%AC loading but it seems to be insignificantly changed. This may infer that 30%AC is the excess amount of activated carbon blocked the transient gap of silicone rubber. Since the transport of gas is postulated to occur when there is a transient gap of sufficient size to accommodate the gas penetrant (Charoenpol, 2002). Therefore, it hindered the diffusion path of gas molecule. In other words, the difficulty of gas diffusion had dominantly played the role over the gas solubility when too excess of activated carbon was added into the matrix phase.

4.1.2 NaX/SR/CA MMMs

The gas permeation rate and CO_2/CH_4 and CO_2/N_2 selectivities of NaX/SR/CA MMMs are shown in Figure 4.2.

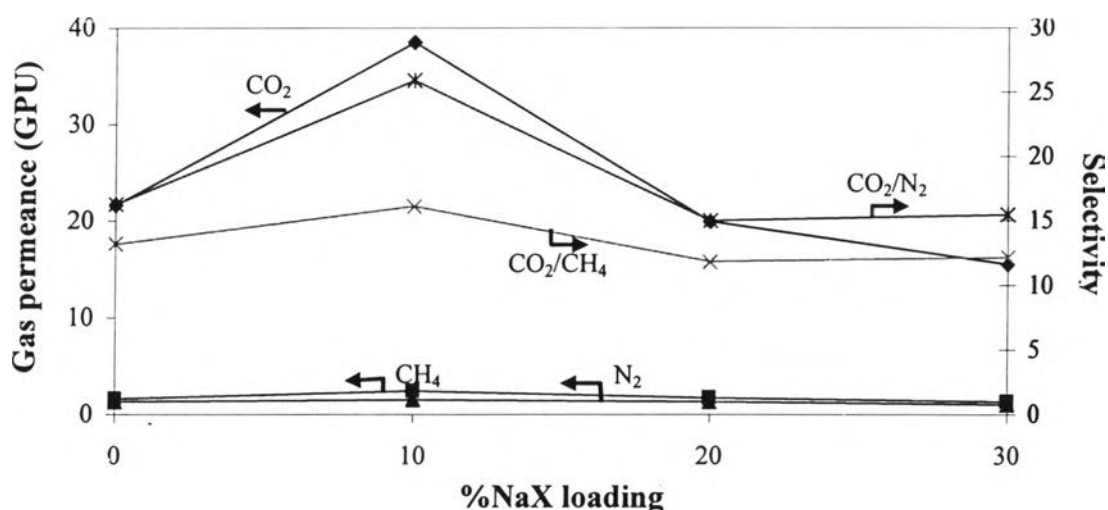


Figure 4.2 Gas permeation rate and CO_2/CH_4 and CO_2/N_2 selectivities of various %NaX/SR/CA MMMs.

From Figure 4.2, the incorporation of NaX into silicone rubber/cellulose acetate membrane primarily affected to CO_2 permeance, while those of CH_4 and N_2 were not significantly changed when compared to the membrane without NaX. The same manner, CO_2 permeance increased as increasing NaX loading; but decreased after a 10%NaX was added. Consequently, the selectivities reached the maximum point at 10%NaX loading. The results obtained could be explained in the same reasons as given for the case of activated carbon.

4.1.3 LiX/SR/CA MMMs

From Figure 4.3 that shows the gas permeation rate and CO_2/CH_4 and CO_2/N_2 selectivity of NaX/SR/CA, the incorporation of LiX into silicone rubber/cellulose acetate membrane primarily effected to CO_2 permeation rate, while those of CH_4 and N_2 were not significantly changed when compared to the membrane without LiX. The same manner, CO_2 permeance increased as increasing LiX

loading; but decreased after a 10%LiX was added. Consequently, the selectivities reached the maximum point at 10%LiX loading. The results obtained could be explained in the same reasons as given in the previous cases.

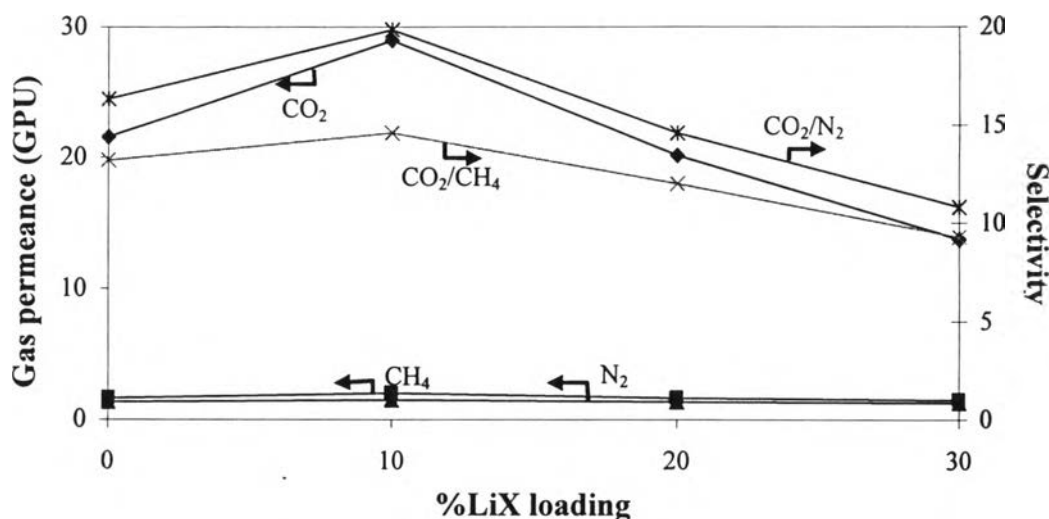


Figure 4.3 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %LiX/SR/CA MMMs.

4.1.4 Comparison of Separation Performance through AC/SR/CA, NaX/SR/CA and LiX/SR/CA MMMs

The comparisons of the gas permeation rate and the CO₂/CH₄ and CO₂/N₂ selectivities through AC/SR/CA MMMs, NaX/SR/CA MMMs and LiX/SR/CA MMMs are graphically presented in Figures 4.4 - 4.5. As can be seen from Figure 4.5, incorporation of solid components into the MMMs exhibited decreases in CO₂, CH₄ and N₂ permeances, as an increase in solid components loading. The selectivities were observed to be independent of the amount of solid component loaded in the membrane matrix as can be seen from Figure 4.5. Interestingly, NaX and LiX zeolites gave the best selectivity at 10% zeolite loading and the higher amount of zeolite could not further enhance the separation anymore. While activated carbon did not significantly enhance the separation for both CO₂/CH₄ and CO₂/N₂.

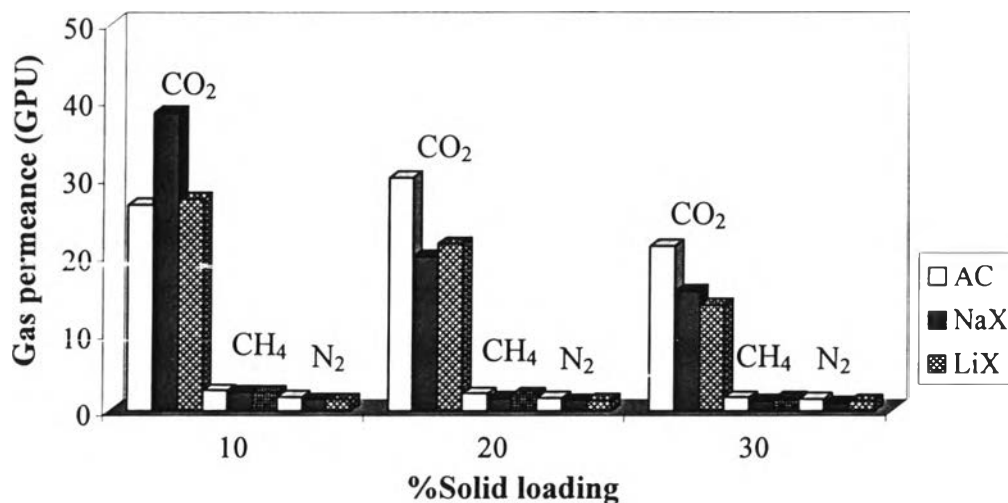


Figure 4.4 The comparison of the gas permeation rate through AC/SR/CA, NaX/SR/CA and LiX/AC/SR/CA MMMs.

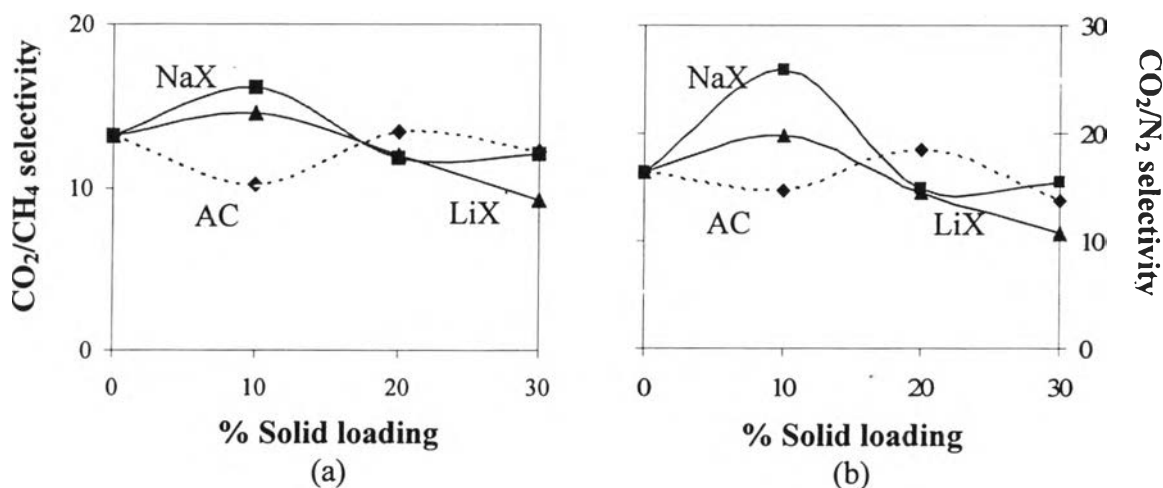


Figure 4.5 The comparison of selectivity through AC/SR/CA, NaX/SR/CA and LiX/SR/CA MMMs (a) CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity.

From the past, many researchers tried to investigate the relationship between adsorption properties and the function of solid components in mixed matrix membrane. No correlation report was found. NaX, AgX zeolites and silicate were widely used in olefin/paraffin adsorption separation process, though they were

reverse selective for olefins over paraffins in mixed matrix membrane separation (Rattanawong, 2001 and Srisilp, 2004). However, possible reason may be given by the effect of induced polarization between gas molecules and solid components. The NaX and LiX zeolites have low Si/Al ratios = 1.1 which have strongly polar anionic frameworks and strong local electrostatic fields. It is believed that electron enriched CO₂ molecules induce the formation of London force that arisen from temporary dipole moment. This is the major determiner of CO₂ solubility enhancement of zeolite added in the mixed matrix membrane. As a result that both NaX and LiX MMMs can show the enhancement properties. On the other hand, activated carbon of which AC MMMs is essentially nonpolar and tends to be hydrophobic. It could not have such that properties, therefore this is the reason for insignificant improvement for AC MMMs. However the higher zeolite loading could not further improve the separation performance due to the harder for gas diffusion which attaining from the densified packing of zeolite in matrix phase.

4.2 Effect of PEG on Gas Permeation Rate and Selectivity

In prior mixed matrix membranes, there have been shown 3 different types of MMMs – those are solid/polymer MMMs, liquid/polymer MMMs and solid/liquid/polymer MMMs. In previous studies, PEG was found to enhance selectivity towards the polar gases on several kinds of membrane separation (US. Pat. Nos. 4,608,060 and 4,737,165). However, the liquid PEG was not stable and diffused out slowly at relative high pressure. In order to overcome the PEG leakage problem and to maintain a selective performance, solid/liquid/polymer MMMs were created by using several kinds of solid as adsorbents for PEG such as activated carbon (AC) (US. Pat. No. 6,726,744B2).

From section 4.1, MMMs that contained 20%AC loading, 10%NaX loading, and 10%LiX loading gave the good result. To further improve the separation performance of MMMs, PEG was incorporated at various loadings of 10, 20 and 30 wt % respect to the weight of solid component into the those MMMs. Additionally, adsorbing liquid PEG into the solid components prior admix into matrix phase is the way to prevent the leakage of PEG liquid.

The permeation rate of three gases and CO_2/CH_4 and CO_2/N_2 selectivities were presented in Table 4.2

Table 4.2 Gas permeation rate and selectivity of CO₂/CH₄ and CO₂/N₂ for PEG/20%AC/SR/CA, PEG/10%NaX/SR/CA and PEG/10%LiX/SR/CA MMMs

MMM	Gas permeance (GPU)			Selectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
20%AC/SR/CA	30.06	2.24	1.63	13.44	18.46
10%PEG/20%AC/SR/CA ⁴	20.97	2.41	1.39	8.72	15.07
20%PEG/20%AC/SR/CA ⁴	17.61	1.12	0.68	15.72	25.91
30%PEG/20%AC/SR/CA ⁴	14.93	0.92	0.49	16.24	30.34
10%NaX/SR/CA	38.50	2.39	1.49	16.14	25.89
10%PEG/10%NaX/SR/CA ⁵	17.06	0.68	0.59	24.97	29.04
20%PEG/10%NaX/SR/CA ⁵	11.47	0.31	0.33	37.27	35.12
30%PEG/10%NaX/SR/CA ⁵	8.69	0.18	0.19	47.38	45.78
10%LiX/SR/CA	28.95	1.99	1.46	14.57	19.84
10%PEG/10%LiX/SR/CA ⁶	14.93	0.64	0.50	23.33	29.96
20%PEG/10%LiX/SR/CA ⁶	9.13	0.26	0.19	34.66	47.61
30%PEG/10%LiX/SR/CA ⁶	8.26	0.19	0.21	42.74	40.00

Notes

⁴X% PEG/20% AC/SR/CA = X% polyethylene glycol/20% activated carbon with silicone rubber casted on cellulose acetate where X = 10, 20, 30

⁵X% PEG/10% NaX/SR/CA = X% polyethylene glycol/10% NaX with silicone rubber casted on cellulose acetate where X = 10, 20, 30

⁶X% PEG/10% LiX/SR/CA = X% polyethylene glycol/10% LiX with silicone rubber casted on cellulose acetate where X = 10, 20, 30

% PEG was calculated respect to the total weight of solid and PEG

% solid was calculated respect to the total weight of silicone rubber and solid

GPU = $1 \cdot 10^{-6}$ cm³(STP)/cm².sec.cmHg

4.2.1 PEG/20%AC/SR/CA MMMs

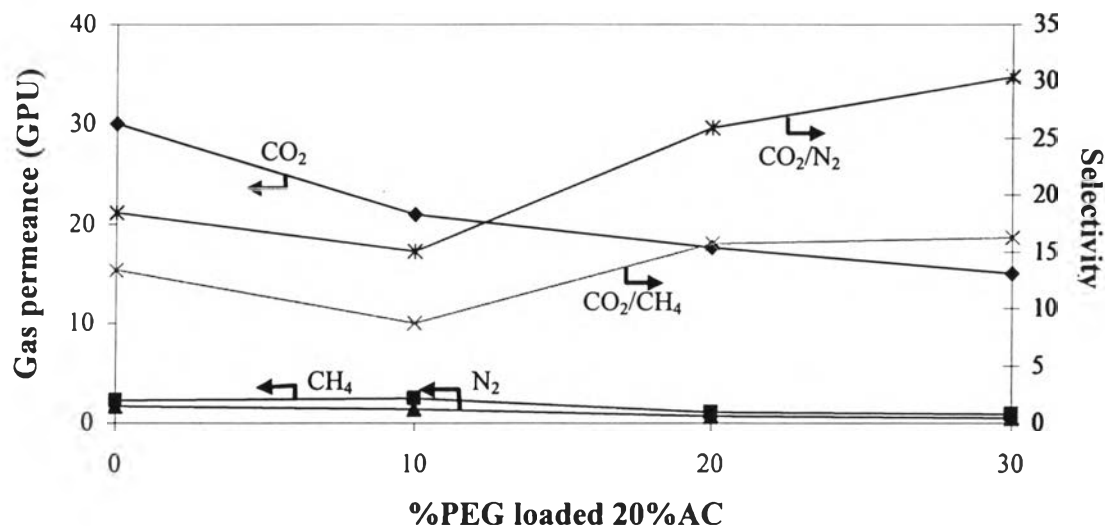


Figure 4.6 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %PEG loaded 20%AC/SR/CA MMMs.

It is clearly seen from Figure 4.6 that the incorporation of PEG into 20%AC/SR/CA resulted in decreases of CO₂, CH₄, and N₂ permeation rates as increasing PEG loading. Due to the dominance of PEG crystallinity (Li et al., 1998), it caused denser in intersegment packing and hindered the gas transport. However CO₂/CH₄ and CO₂/N₂ selectivities decreased when adding 10%PEG and then increased when 20, 30%PEG in activated carbon. Because little amount of PEG at 10% adsorbed in pore of activated carbon so PEG cannot show the effect to enhance selectivity. While 20, 30%PEG was enough to adsorb in pore of activated carbon and the rest was suspended around the surface of activated carbon and the polymer phase. It was found that PEG could enhance the selectivity if the PEG was suspended in the polymer phase (Kalapanulak, 2001).

It seems like hardly to explain the selective mechanism of PEG to the desired permeate gas. It postulated that the acid-base interaction from temporary dipole moments between the acidic CO₂ and the electron-rich ether oxygen atoms of the PEG molecules is probably responsible for the enhanced solubility of CO₂ in PEG (Saha and Chakma, 1994).

With respect to some of the gas separation membranes heretofore known, U.S. Pat. No.6,726,744B2 described the mixed matrix membrane which comprised of polyethylene glycol (PEG), activated carbon (AC), silicone rubber (SR) and polysulfone (PS) exhibited the good separation properties. There are some similarities and some differences between the invention and the study. The studied MMMs contained the same composition but cellulose acetate (CA) was used instead of polysulfone (PS). The solution in the invention is performed by physical mix. On the other hand, in the study PEG was adsorbed into activated carbon (AC) prior mixed in the solution. The compared results are expressed in the Table 4.3.

Table 4.3 Comparison of Gas permeation rate and CO₂/N₂ selectivity for PEG/AC/SR/PS and PEG/AC/SR/CA

MMM	Gas permeance (GPU)		CO ₂ /N ₂ selectivity
	CO ₂	N ₂	
10%PEG/20%AC/SR/PS	26.23	0.75	34.64
10%PEG/20%AC/SR/CA	14.93	0.49	30.34

Notes

10%PEG/20%AC/SR/CA is equivalent to 10%PEG/20%AC/SR/CA which % PEG was calculated respect to the total weight of solid and PEG.

The result showed that MMM with polysulfone (PS) showed a little better separation properties. It exhibited both selectivity and gas permeance higher than that of cellulose acetate (CA). The reason of lower separation performance may come from the difference in preparation method and the intrinsic properties of used material.

4.2.2 PEG/10%NaX/SR/CA MMMs

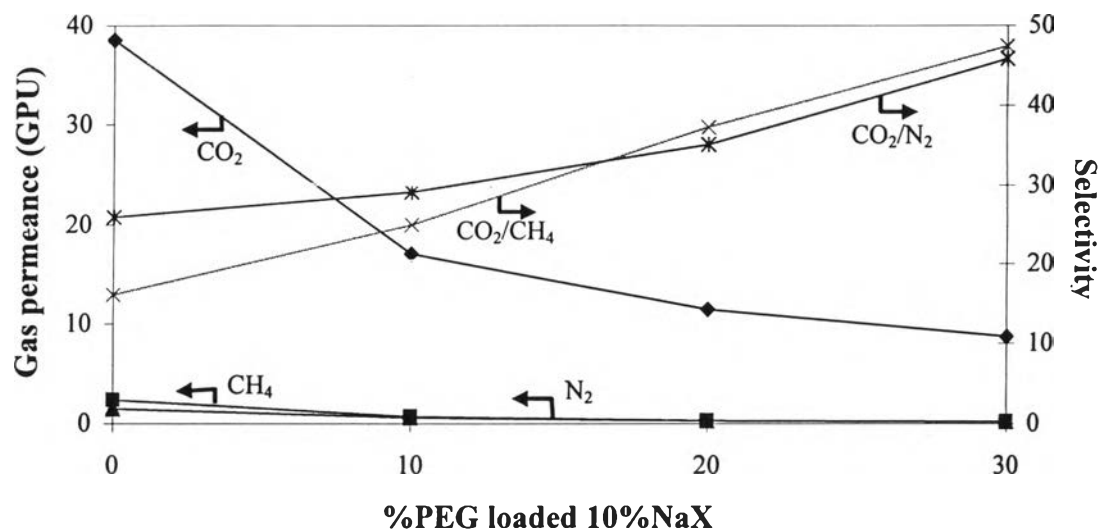


Figure 4.7 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %PEG loaded 10%NaX/SR/CA MMMs.

From Figure 4.7, incorporation of PEG into 10%NaX/SR/CA membrane resulted in decreases in the CO₂, CH₄, and N₂ permeation rates with increasing PEG loading in NaX; however, the CO₂/CH₄ and CO₂/N₂ selectivities were significantly increased with intrinsic properties of PEG. Although PEG filled up the pore of NaX and caused the difficult in gas transport such decreases of gas permeances were found.

4.2.3 PEG/10%LiX/SR/CA MMMs

From Figure 4.8, incorporation of PEG into 10%LiX/SR/CA membrane resulted in decreases in the CO₂, CH₄, and N₂ permeation rates with increasing PEG loading in LiX; however, the CO₂/CH₄ and CO₂/N₂ selectivities were significantly increased. The explanation can be clearly given same as case of NaX.

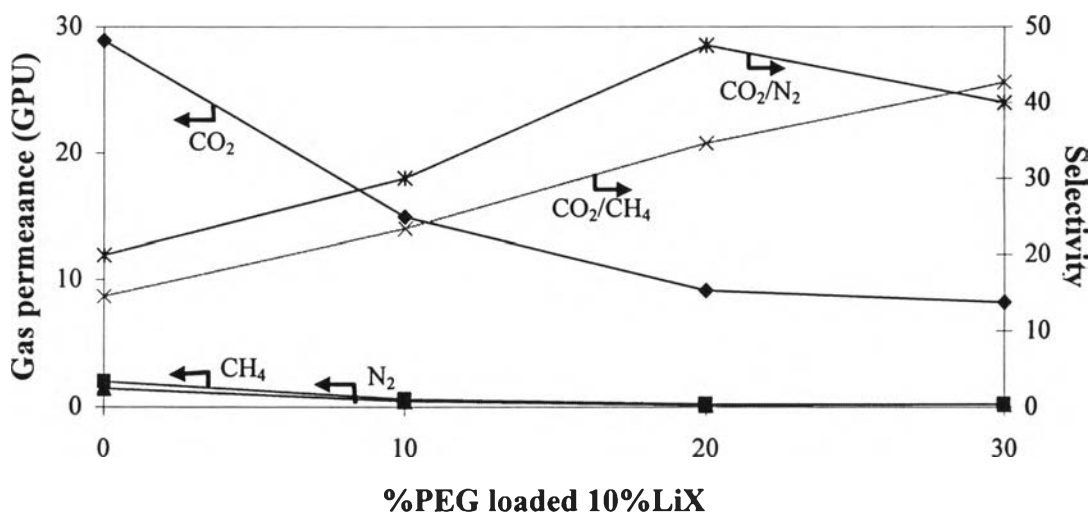


Figure 4.8 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %PEG loaded 10%LiX/SR/CA MMMs.

From section 4.2.2 and 4.2.3, 30%PEG/10%NaX/SR/CA gave the highest CO₂/CH₄ and CO₂/N₂ selectivity, 47.38 and 45.78, respectively among various PEG/10%NaX/SR/CA MMMs, whereas 30%PEG/10%LiX/SR/CA gave the highest CO₂/CH₄ and CO₂/N₂ selectivity, 36.58 and 45.52, respectively among various PEG/10%LiX/SR/CA MMMs. It seems like the higher %PEG loading give the better selectivity. However the saturation of adsorbed PEG into the solids has to be seriously concerned from the PEG leakage. Thus, the attempts to increase the amount of PEG into the MMMs could be done by adding higher amount of 30%PEG/NaX and 30%PEG/LiX which resulted in the increasing both of solids and PEG. The gas permeation rate and selectivity results obtained are shown in Table.4.4.

Table 4.4 Gas permeation rate and selectivity of CO₂/CH₄ and CO₂/N₂ for various PEG/NaX/SR/CA and PEG/LiX/SR/CA MMMs

MMM	Gas permeance (GPU)			Selectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
30%PEG/5%NaX/SR/CA ⁷	6.47	0.15	0.14	43.35	46.69
30%PEG/10%NaX/SR/CA ⁷	8.69	0.17	0.17	52.37	50.09
30%PEG/15%NaX/SR/CA ⁷	8.07	0.13	0.13	64.53	60.65
30%PEG/20%NaX/SR/CA ⁷	3.38	0.09	0.09	36.03	36.03
30%PEG/30%NaX/SR/CA ⁷	1.62	0.10	0.07	17.01	22.54
30%PEG/5%LiX/SR/CA ⁸	9.77	0.24	0.24	40.41	40.14
30%PEG/10%LiX/SR/CA ⁶	8.26	0.19	0.21	42.74	40.00
30%PEG/15%LiX/SR/CA ⁸	5.13	0.14	0.11	36.58	45.52
30%PEG/20%LiX/SR/CA ⁸	3.50	0.17	0.10	20.56	36.01
30%PEG/30%LiX/SR/CA ⁸	3.08	0.16	0.10	19.73	32.37

Notes

⁷30% PEG /X% NaX/SR/CA = 30% polyethylene glycol/X% NaX with silicone rubber casted on cellulose acetate where X = 5, 10, 15, 20, 30

⁸30% PEG /X% LiX/SR/CA = 30% polyethylene glycol/X% LiX with silicone rubber casted on cellulose acetate where X = 5, 10, 15, 20, 30

% PEG was calculated respect to the total weight of solid and PEG

% solid was calculated respect to the total weight of silicone rubber and solid

GPU = $1 \cdot 10^{-6}$ cm³(STP)/cm².seℓ.cmHg

As can be seen from Figures 4.9 - 4.10 which show the CO₂/CH₄ and CO₂/N₂ selectivities through various PEG/NaX/SR/CA MMMs and PEG/LiX/SR/CA MMMs, the selectivity was increased by the intrinsic properties of PEG and zeolite but probably decreased after that. Obviously, to excess amount of zeolites and PEG not only impeded the gas permeabilities, but gas selectivities also

decreased by the effect of viscous PEG liquid and the denser of zeolite in the matrix phase. These contribute to the poor separation performance.

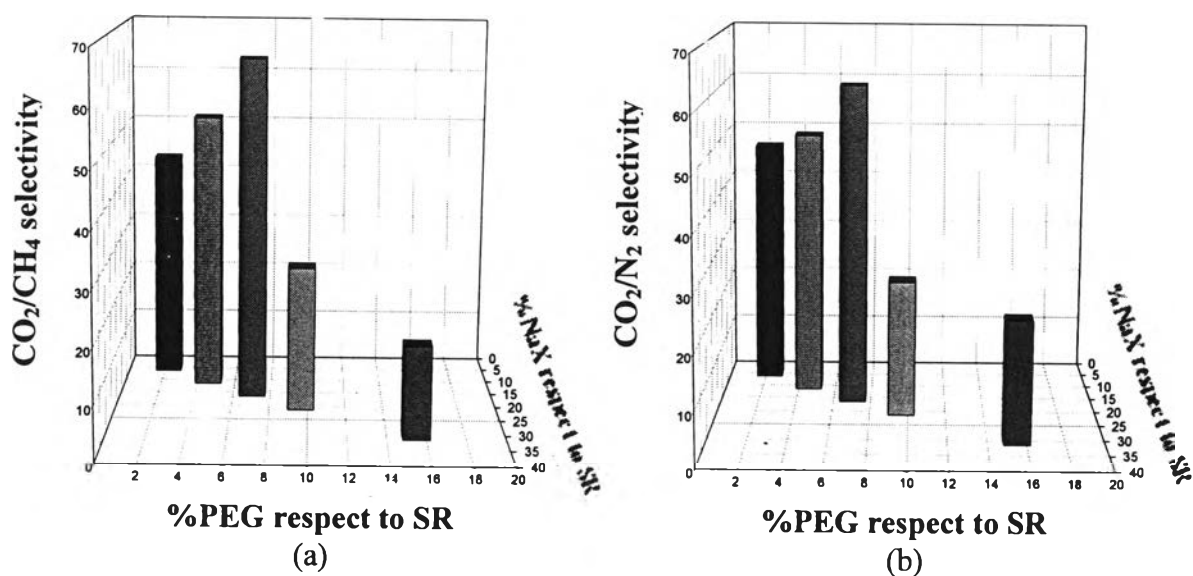


Figure 4.9 The selectivity of various PEG/NaX/SR/CA MMMs (a) CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity.

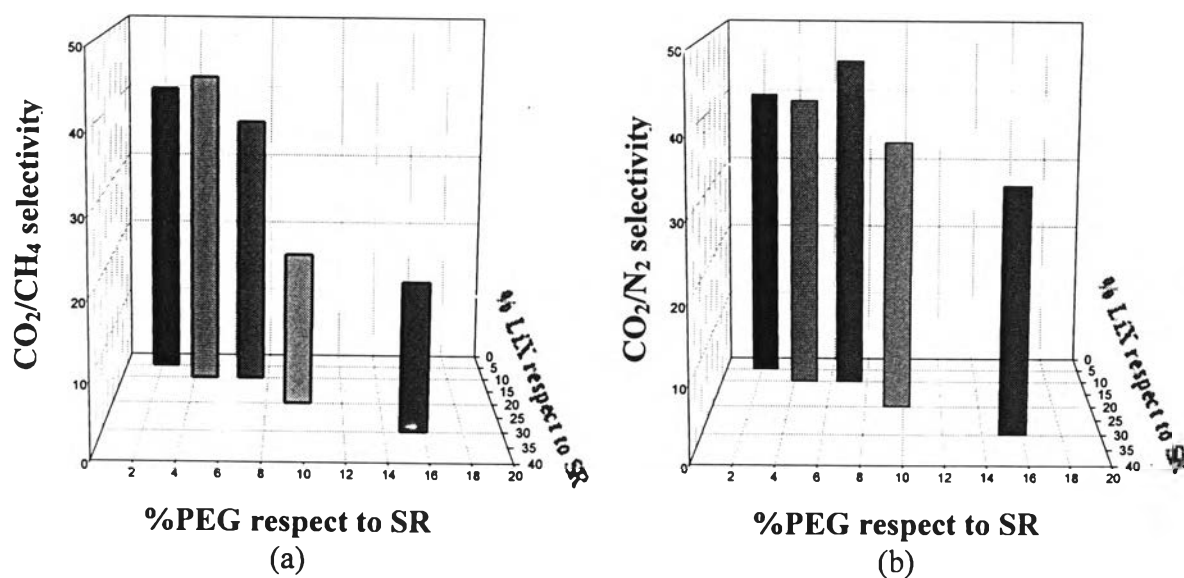


Figure 4.10 The selectivity of various PEG/LiX/SR/CA MMMs (a) CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity.

4.3 Effect of DEA on Gas Permeation Rate and Selectivity

Beside the polymeric membrane based on the solution-diffusion mechanism, another kind of CO₂-selective separation processes is the facilitated transport membrane based on the solution-reaction-diffusion mechanism. In the case of facilitated transport mechanism, the selective liquid reacts reversibly with the diffusing gas and greatly enhances the selectivity by providing higher mass fluxes for the reacting component as compared to the other non-reacting components (Chakma, 1995).

Diethanolamine is a kind of alkanolamine, has been widely used in amine absorption as well as used in facilitated transport membrane for removing CO₂ from undesired gases. In present study also worked on the facilitated transport mechanism of DEA by using activated carbon, NaX and LiX zeolite incorporated at various loading 10, 20, 30%wt of DEA combining in the membrane phase. The gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities are given in Table.4.5.

Table 4.5 Gas permeation rate and selectivity of CO₂/CH₄ and CO₂/N₂ for DEA/20%AC/SR/CA, DEA/10%NaX/SR/CA and DEA/10%LiX/SR/CA MMMs

MMM	Gas permeance (GPU)			Selectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
20%AC/SR/CA	30.06	2.24	1.63	13.44	18.46
10%DEA/20%AC/SR/CA ⁹	24.17	2.73	1.41	8.86	17.18
20%DEA/20%AC/SR/CA ⁹	22.48	2.32	1.30	9.67	17.23
30%DEA/20%AC/SR/CA ⁹	21.51	1.80	1.05	11.98	20.43
10%NaX/SR/CA	38.50	2.39	1.49	16.14	25.89
10%DEA/10%NaX/SR/CA ¹⁰	35.85	2.29	1.62	15.64	22.07
20%DEA/10%NaX/SR/CA ¹⁰	25.44	1.35	1.09	18.78	23.45
30%DEA/10%NaX/SR/CA ¹⁰	23.53	1.02	0.86	23.00	27.50
10%LiX/SR/CA	28.95	1.99	1.46	14.57	19.84
10%DEA/10%LiX/SR/CA ¹¹	28.15	1.00	1.12	28.07	25.22
20%DEA/10%LiX/SR/CA ¹¹	23.29	0.82	0.80	28.53	28.97
30%DEA/10%LiX/SR/CA ¹¹	23.44	0.72	0.75	32.54	31.10

Notes

⁹X% DEA/20% AC/SR/CA = X% diethanolamine/20% activated carbon with silicone rubber casted on cellulose acetate where X = 10, 20, 30

¹⁰X% DEA/10% NaX/SR/CA = X% diethanolamine/10% NaX with silicone rubber casted on cellulose acetate where X = 10, 20, 30

¹¹X% DEA/10% LiX/SR/CA = X% diethanolamine/10% LiX with silicone rubber casted on cellulose acetate where X = 10, 20, 30

% DEA was calculated respect to the total weight of solid and DEA

% solid was calculated respect to the total weight of silicone rubber and solid

GPU = $1 \cdot 10^{-6}$ cm³(STP)/cm².sec.cmHg

4.3.1 DEA/20%AC/SR/CA MMMs

The gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various DEA/20%AC/SR/CA MMMs are shown in Figure 4.11.

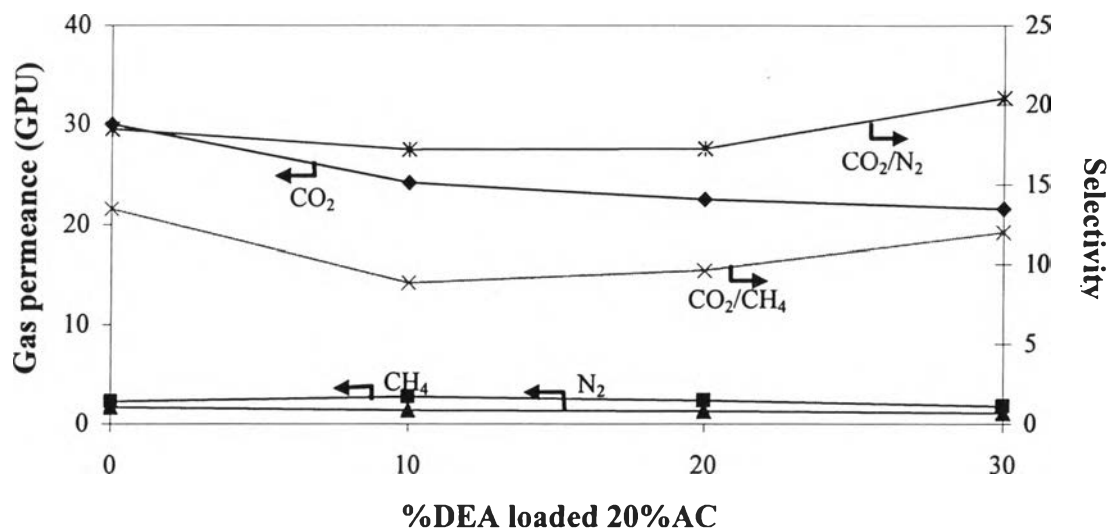


Figure 4.11 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %DEA loaded 20%AC/SR/CA MMMs.

It is clearly seen from Figure 4.11 that the incorporation of DEA into 20%AC/SR/CA resulted in decreases of CO₂, CH₄, and N₂ permeation rate as increasing DEA loading. Such a decrease of gas permeation rate was found to be function of the amount of DEA loaded in the membrane matrix. Probably same explanation similar to the PEG, the reduction in the mobility of gas molecules in denser intersegmental packing lowered the gas flux.

The CO₂/CH₄ and CO₂/N₂ selectivities were probably unchanged and mostly decreased when compared to the 20%AC/SR/CA without DEA. It seems like DEA does not show the separation enhancement by solution-reaction-diffusion mechanism or facilitated transport mechanism.

The chemistry of the CO₂-DEA facilitated mechanism has been proposed as follows (Teramoto *et al.*, 2004). CO₂ reacts with DEA, RRNH, to form carbamate ion and protonated amine.



Then, the overall reaction is expressed by (c), and the maximum value of CO₂ loading, which is defined as the ratio (mol CO₂ adsorbed)/(mol amine), is 0.5:



Since carbamate ion is unstable, it is hydrolyzed to form HCO₃⁻ as expressed by (d)



Therefore, the overall reaction is expressed by (e), and the maximum CO₂ loading is unity:



From the unstable carbamate ion shows that the overall reaction in (c) hardly to be occurred. However the MMMs probably have some moisture left inside from the humidity in working environment; thus once they have some moisture the overall reaction in (e) could be possibly occurred. So the separation performance of DEA in the studied MMMs mainly comes from solution-diffusion mechanism, not solution-reaction-diffusion mechanisms, corresponding to no selectivity improvement.

4.3.2 DEA/10%NaX/SR/CA MMMs

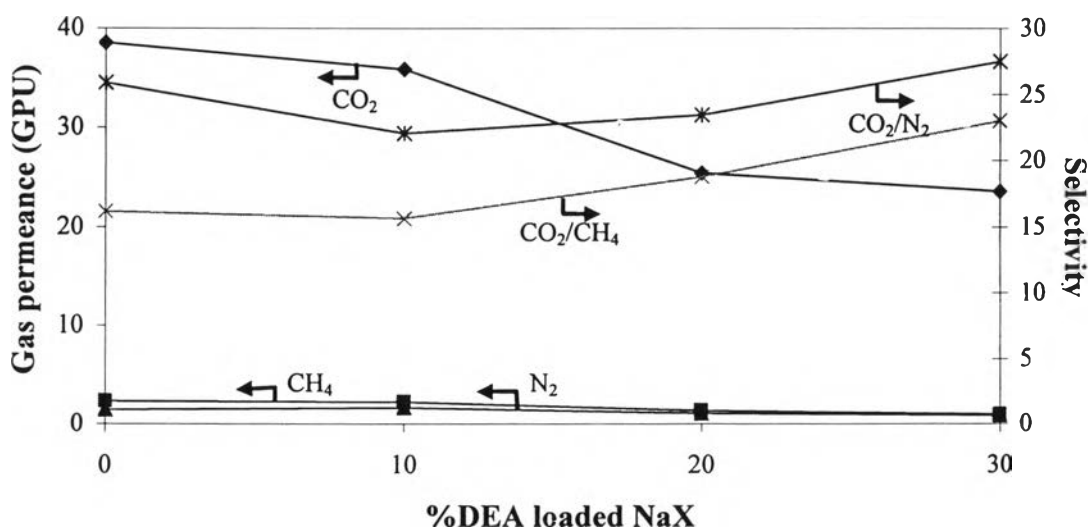


Figure 4.12 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %DEA loaded 10%NaX/SR/CA MMMs.

From Figure 4.12, incorporation of DEA into 10%NaX/SR/CA membrane resulted in decreases in the CO₂, CH₄, and N₂ permeation rates with increasing DEA loading in NaX. However CO₂/CH₄ and CO₂/N₂ selectivities fairly increased. The improvement may come from the intrinsic properties of NaX zeolite that already mentioned in previous part.

4.3.3 DEA/10%LiX/SR/CA MMMs

The gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivity of various DEA/10%LiX/SR/CA MMMs are shown in Figure 4.13.

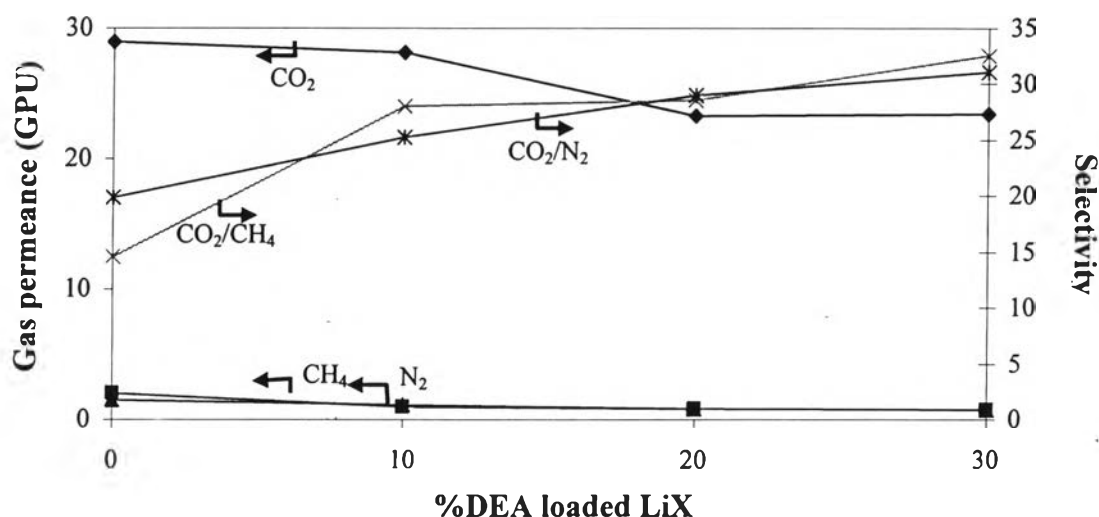


Figure 4.13 Gas permeation rate and CO₂/CH₄ and CO₂/N₂ selectivities of various %DEA loaded 10%LiX/SR/CA MMMs.

From Figure 4.13, incorporation of DEA into 10%LiX/SR/CA membrane resulted in decreases in the CO₂, CH₄, and N₂ permeation rates with increasing DEA loading in LiX. But CO₂/CH₄ and CO₂/N₂ selectivities increased continuously as the amount of DEA loading. Although DEA/LiX gave a different behavior in selectivity improvement, the explanation could be due to the zeolite selective enhancement. Another possible reason is after DEA adsorbed into LiX, it may changed its property to have more affinity to CO₂ that can obviously see from a less of CO₂ permeability reduction.

4.3.4 DEA - Facilitated Transport

DEA is supposed to enhance the separation performance effectively when it has enough water to complete the reaction. The additional test for DEA MMM with water was studied in order to prove the hypothesis. The compared results are given in Table 4.6.

Table 4.6 Gas permeation rate and selectivity of CO₂/CH₄ and CO₂/N₂ for 30%DEA/10%NaX/SR/CA and 30%DEA/10%NaX/SR/CA with water.

MMM	Permeance (GPU)			Selectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
30%DEA/10%NaX/SR/CA	23.53	1.02	0.86	23.00	27.50
30%DEA/10%NaX/SR/CA + H ₂ O	13.85	0.56	0.51	24.93	27.06

The results from the test with water showed lower permeation rate of every gas than that without water but the CO₂/CH₄ and CO₂/N₂ selectivities were almost unchanged. The reasons for no improvement in selectivity may be explained as follows. Water molecules cannot pass through the matrix phase to react with DEA due to its large size. The surface of MMM covered with those water molecules could result in less gas diffusion, corresponding to the lower gas permeation rate. Another possible reason would be that vapor pressure of water is not enough to complete the reaction as can be seen from the ratio of CO₂: DEA: H₂O = 1:1:1 in Equation (e) but the vapor pressure at room temperature (30°C) is only 0.0418 psi which is much less than that of 50 psi of CO₂ pressure. Therefore CO₂ - DEA- facilitated mechanism

- may not be practical to use for MMMs.

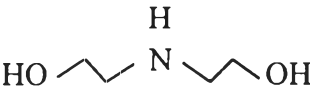
4.4 Comparison of Separation Performance between PEG MMMs and DEA MMMs

A difference of PEG and DEA is a controlled mechanism. PEG is controlled by physical absorption while DEA is controlled by chemical absorption. The advantages of physical solvents over chemical solvents are the absorption capacity is not limited by the stoichiometry of a reaction since no bond formation needed in physical absorption and the physical absorption is easier to reversible than chemical absorption. In order to compare the separation performance between PEG MMMs and DEA MMMs, the obtained results of gas permeation rate and selectivities are graphically compared in Figures 4.14 – 4.16 for comparisons of gas permeation rates and Figures 4.17 – 4.19 for comparisons of gas selectivities.

4.4.1 Comparison of Gas Permeation Rate

By comparing the gas permeation rates through various kinds of PEG MMMs and DEA MMMs in Figures 4.14 - 4.16, it can be clearly seen that MMMs contained PEG have lower permeance of every gas than those of MMMs contained DEA. As can be seen from Table 4.7 that clearly given the physical properties of PEG and DEA, the density and molecular structure would be factors that contributed to the gas diffusion. With the bulkier of long chain of PEG (MW.400) molecule and higher density, the gas transport through PEG molecule would be more difficult than that of DEA.

Table 4.7 Physical properties of PEG and DEA at 20 °C (Saha and Chakma, 1995)

Liquid	Mol.weight (g/mol)	Density (g/ml)	Molecular structure
PEG	400	1.124	$-(\text{CH}_2\text{-CH}_2\text{-O})_n$
DEA	105.14	1.0919	

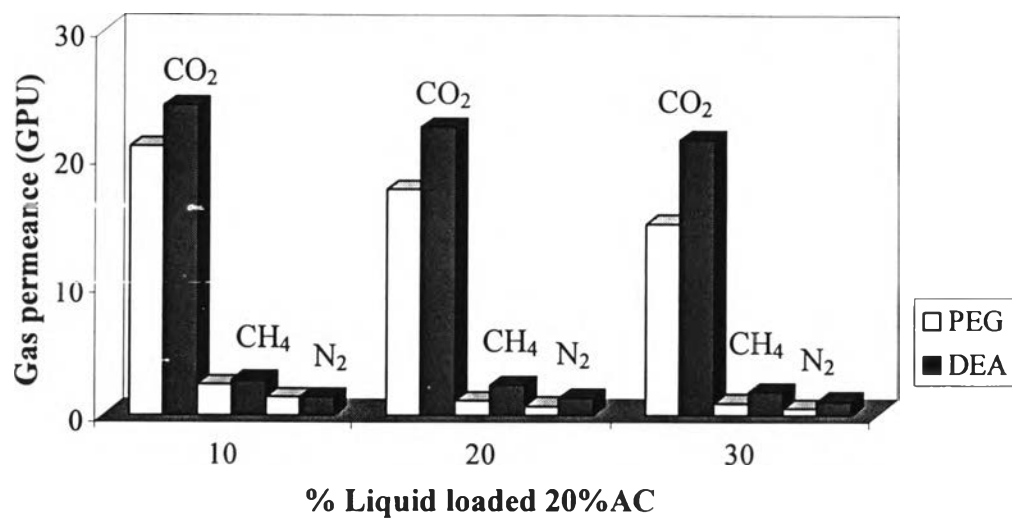


Figure 4.14 The comparison of the gas permeation rate through PEG/20%AC/SR/CA and DEA/20%AC/SR/CA MMMs.

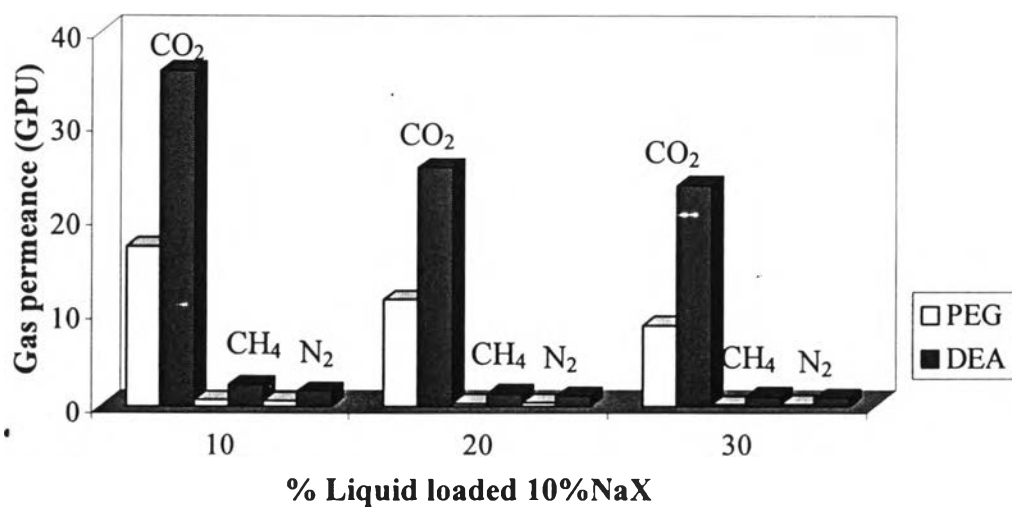


Figure 4.15 The comparison of the gas permeation rate through PEG/10%NaX/SR/CA and DEA/10%NaX/SR/CA MMMs.

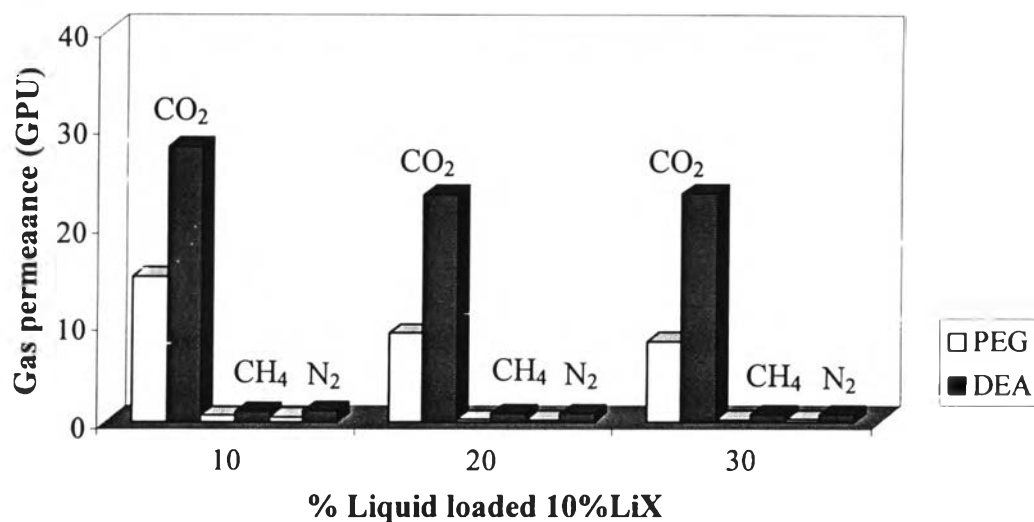


Figure 4.16 The comparison of the gas permeation rate through PEG/10%LiX/SR/CA and DEA/10%LiX/SR/CA MMMs.

4.4.2 Comparison of Selectivity

The CO₂/CH₄ and CO₂/N₂ selectivities through various kind of PEG MMMs and DEA MMMs are shown in Figure 4.17 – 4.19.

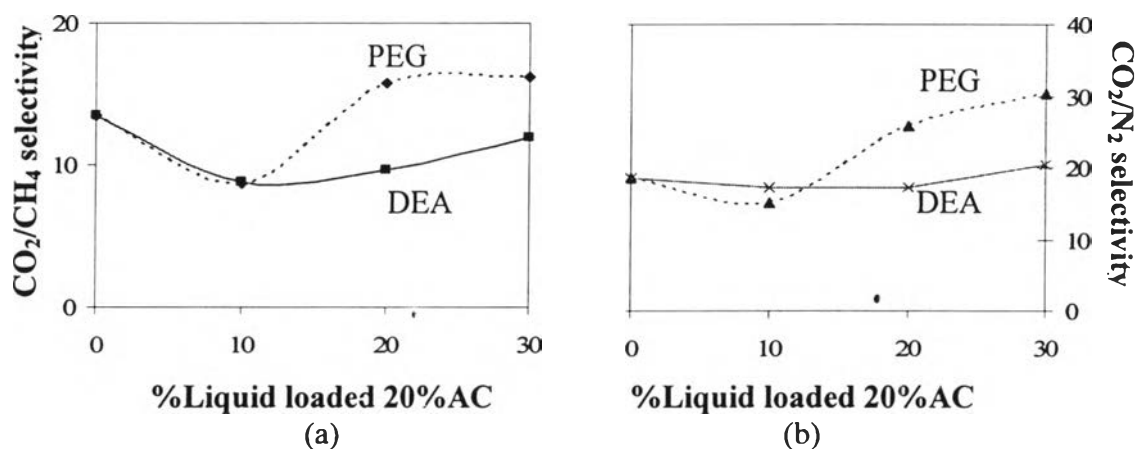


Figure 4.17 The comparison of selectivity through PEG/20%AC/SR/CA and DEA/20%AC/SR/CA MMMs (a) CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity.

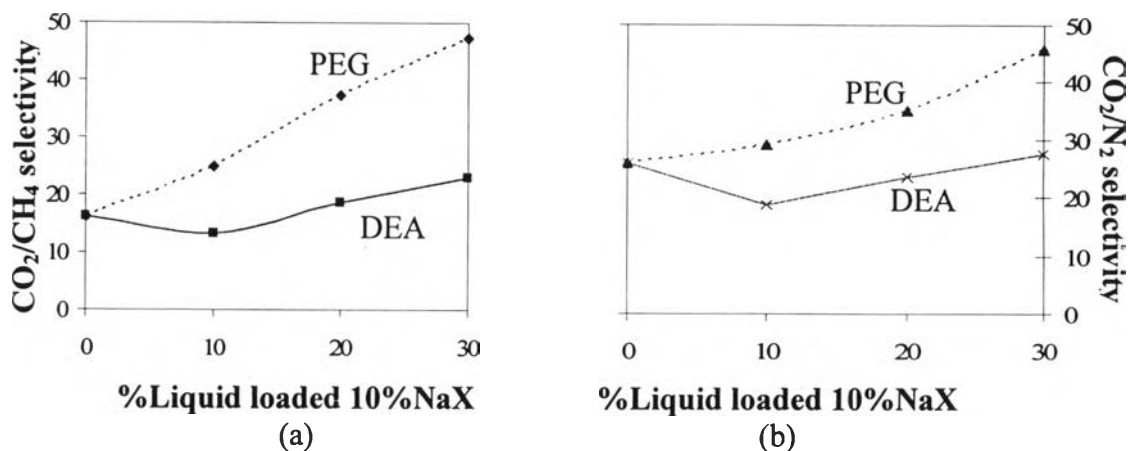


Figure 4.18 The comparison of selectivity through PEG/10%NaX/SR/CA and DEA/10%NaX/SR/CA MMMs (a) CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity.

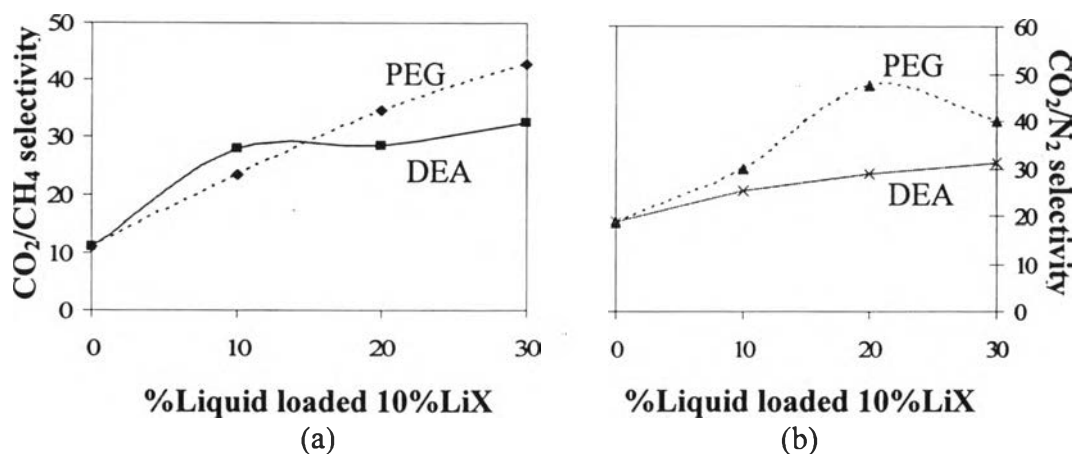


Figure 4.19 The comparison of selectivity through PEG/10%LiX/SR/CA and DEA/10%LiX/SR/CA MMMs (a) CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity.

• It can be clearly seen from Figures 4.17 – 4.19 which are shown the comparisons of the CO₂/CH₄ and CO₂/N₂ selectivities through PEG MMMs and DEA MMMs that PEG mostly gave the better CO₂/CH₄ and CO₂/N₂ selectivities than DEA. Based on the results of this study, it can be concluded that PEG effectively enhance the separation performance of the MMMs by the solution-diffusion mechanism, while DEA is not practical to use due to DEA could not facilitated the gas transport in the MMMs.

4.4.3 Comparison with Commercial Membranes

During the past decade many researchers attempted to develop the membranes that exhibit both high permeability and high selectivity, although gas separation properties of polymer membrane follow distinct tradeoff relations: more permeable polymers are generally less selective and vice versa. Robeson identified the best combinations of permeability and selectivity for important binary gas pairs by graphing the available published data with a basis line. This basis line were constructed on an empirical basis for many particular gas pairs and defined as the upper bound combinations of permeability and selectivity. Materials with the best performance would be in the upper right-hand corner of the figure, however materials such that property are very rare. Moreover glassy polymers generally define the upper bound limit, while rubbery polymers usually have poorer properties and sit in the lower range next to the glassy polymer (Robeson, 1991).

In order to compare the studied MMMs with commercial membranes, the plots of permeability and selectivity had been placed with Robeson's upper bound. As can be seen from the plots with CO_2/CH_4 and CO_2/N_2 Robeson's upper bound as illustrated in Figures 4.21 - 4.22, the data somewhat fitted near the upper bound and showed a typical tradeoff behavior which is consistent with the literature data. Interestingly, most studied MMMs were above the upper bound indicating greater potential in gas separation than commercial membranes.

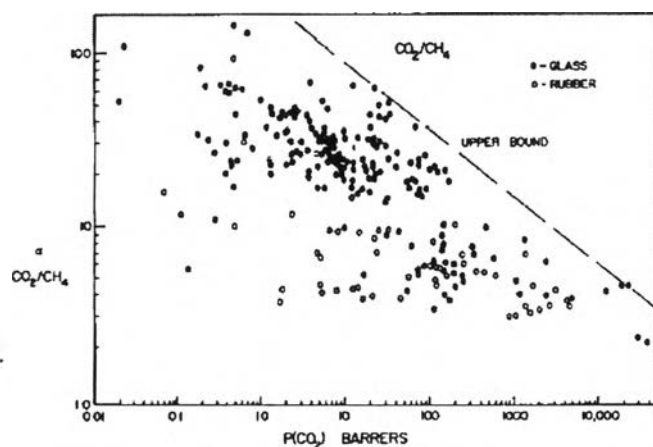


Figure 4.20 Literature data for CO_2/CH_4 separation selectivity versus CO_2 permeability (Robeson, 1991).

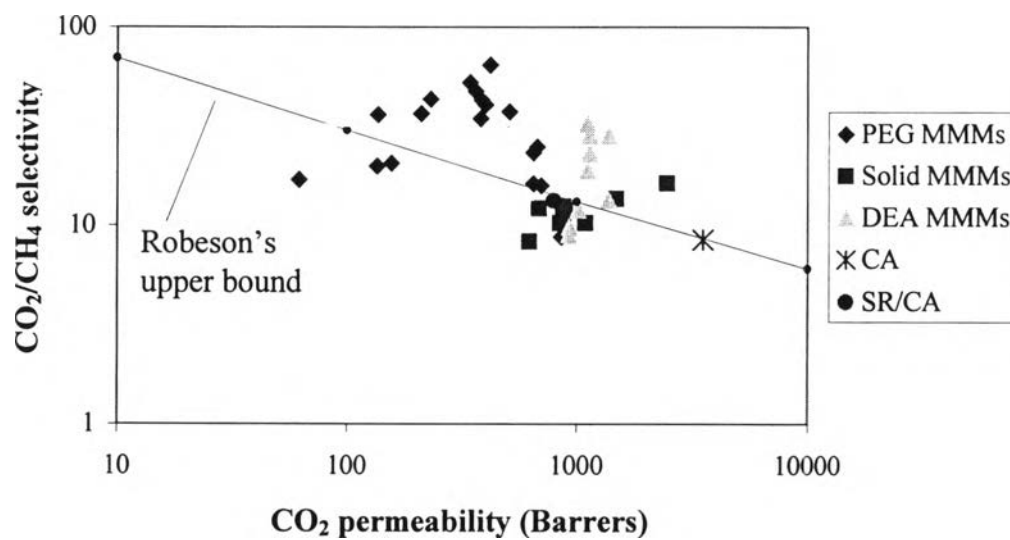


Figure 4.21 The plots between CO_2/CH_4 selectivity and CO_2 permeability with Robeson's upper bound.

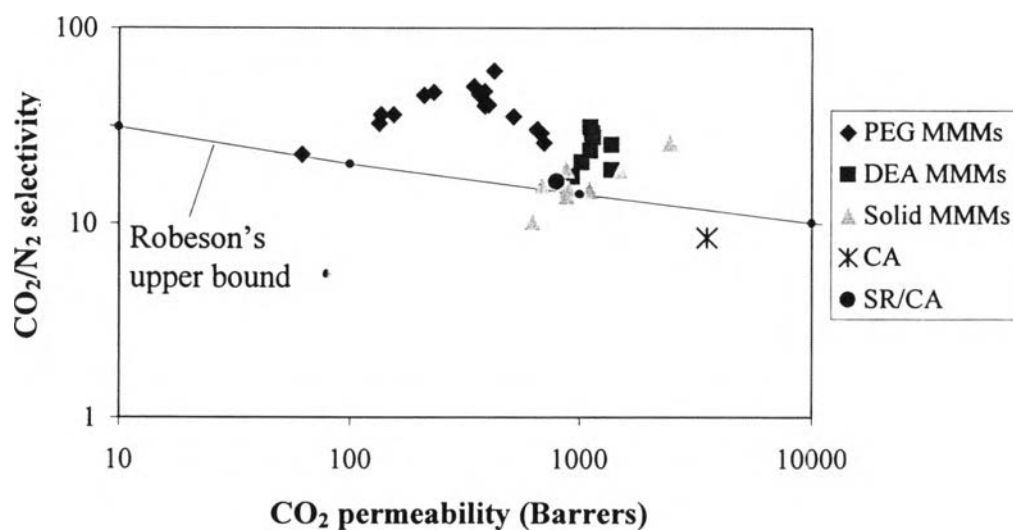


Figure 4.22 The plots between CO_2/N_2 selectivity and CO_2 permeability with Robeson's upper bound.

4.5 Plasticization Study

High permeable and high selective membranes will be meaningless, if those membranes cannot maintain such properties in the presence of plasticizing molecules. CO₂ induced plasticization is seriously concerned for membrane separation.

4.5.1 Plasticization on MMMs

In this study, the gas permeances were determined from the steady state permeation rates of each gas through the membrane at room temperature and varied pressures from 10 to 100 psia to investigate the plasticization phenomenon. The relations between pressure and gas permeation rate of MMMs are shown in Figures 4.23 – 4.32. It is clearly seen from the figures that only CO₂ permeance increased with increasing feed pressure whereas those of CH₄ and N₂ were independent of pressure. From Figures 4.26 – 4.32, the decreases of gas permeances were observed due to the densely packed chains from the solids and liquids added into the matrix phase.

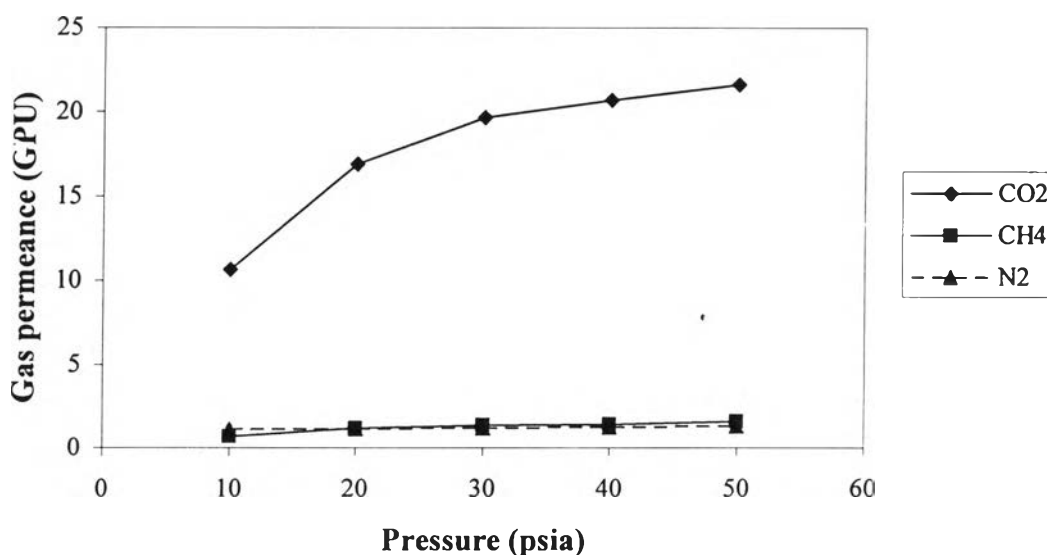


Figure 4.23 Relations between pressure and gas permeation rate for SR/CA.

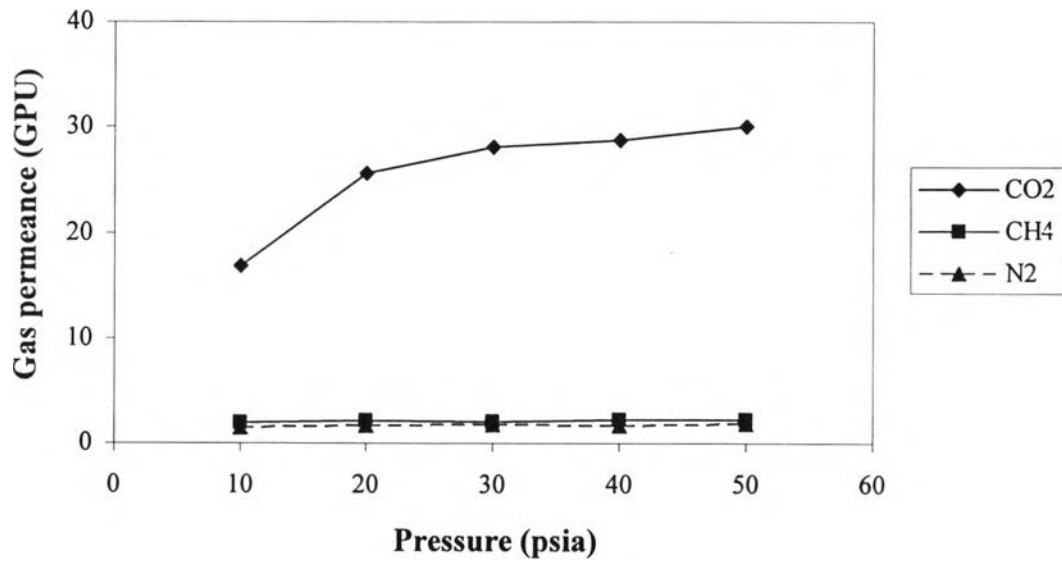


Figure 4.24 Relations between pressure and gas permeation rate for 20%AC/SR/CA.

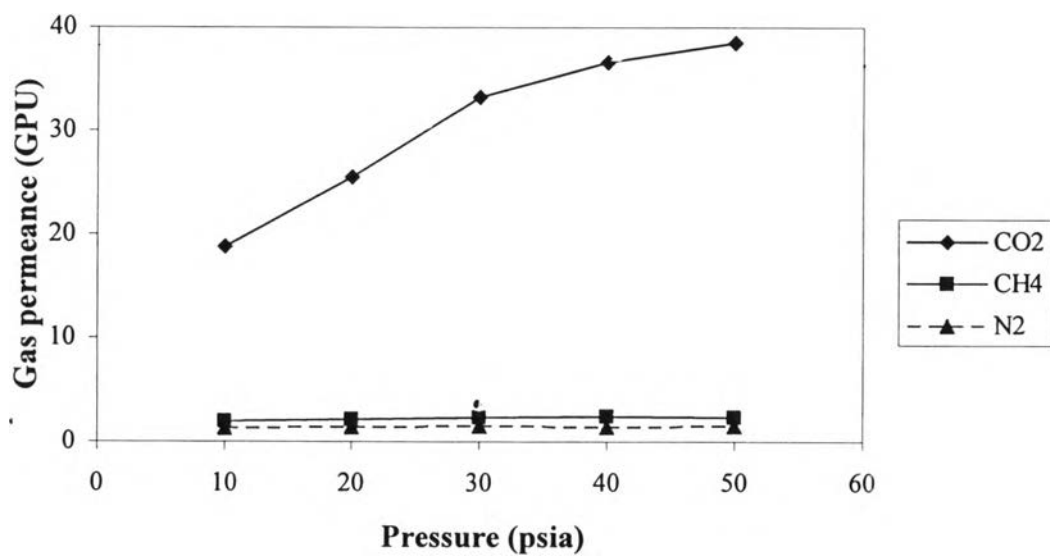


Figure 4.25 Relations between pressure and gas permeation rate for 10%NaX/SR/CA.

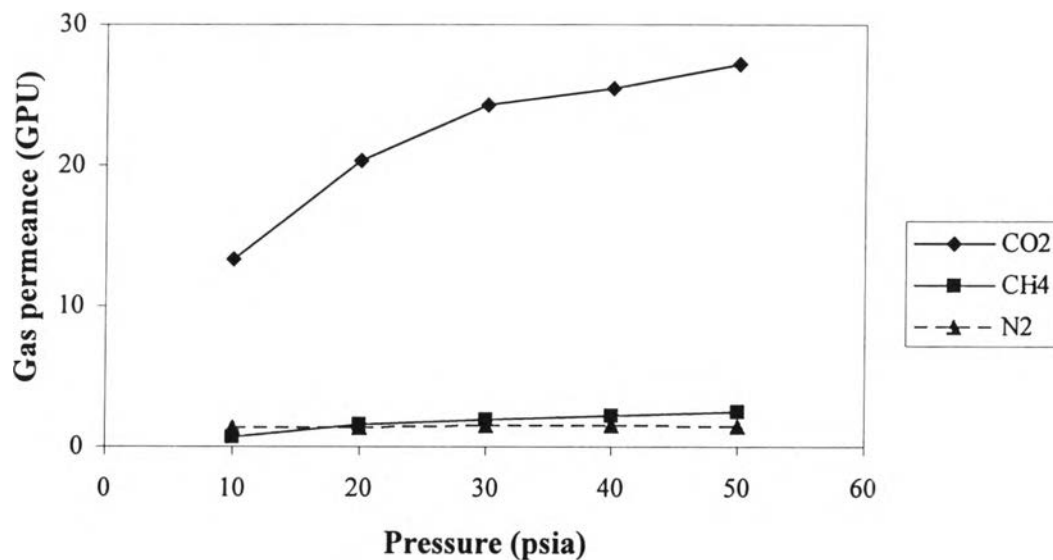


Figure 4.26 Relations between pressure and gas permeation rate for 10%LiX/SR/CA.

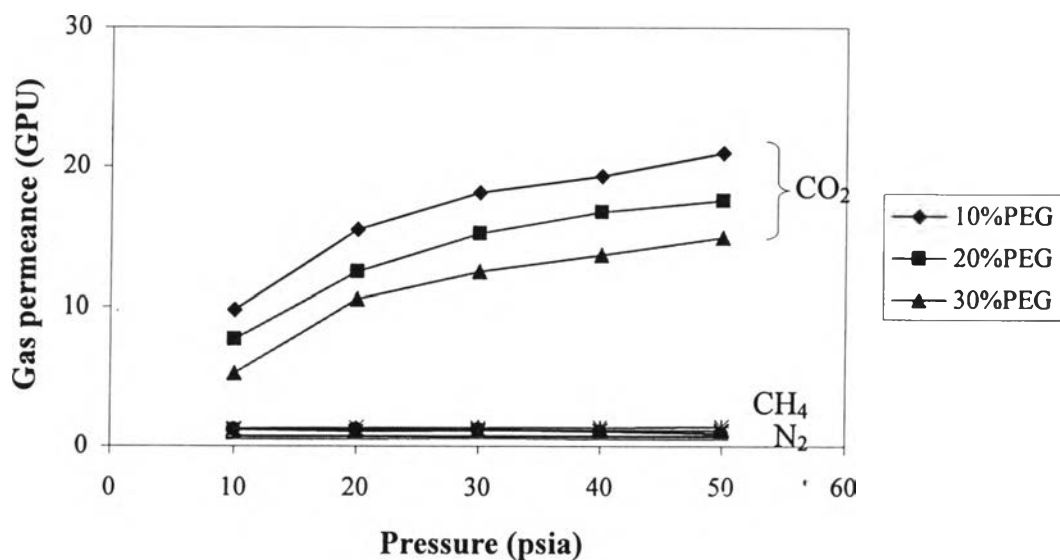


Figure 4.27 Relations between pressure and gas permeation rate for 10, 20, and 30%PEG/20%AC/SR/CA MMMs.

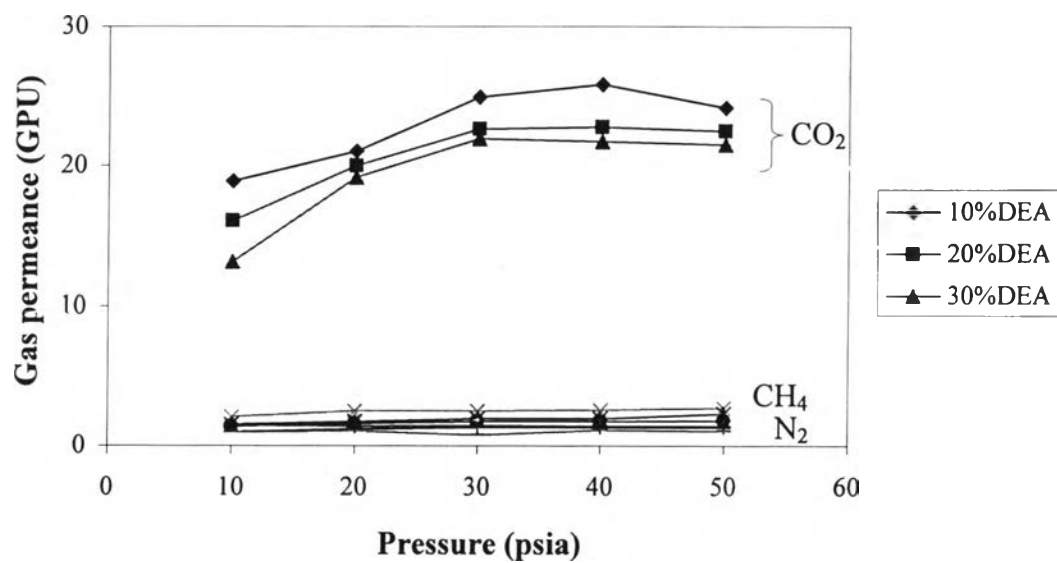


Figure 4.28 Relations between pressure and gas permeation rate in 10, 20, and 30%DEA/20%AC/SR/CA MMMs.

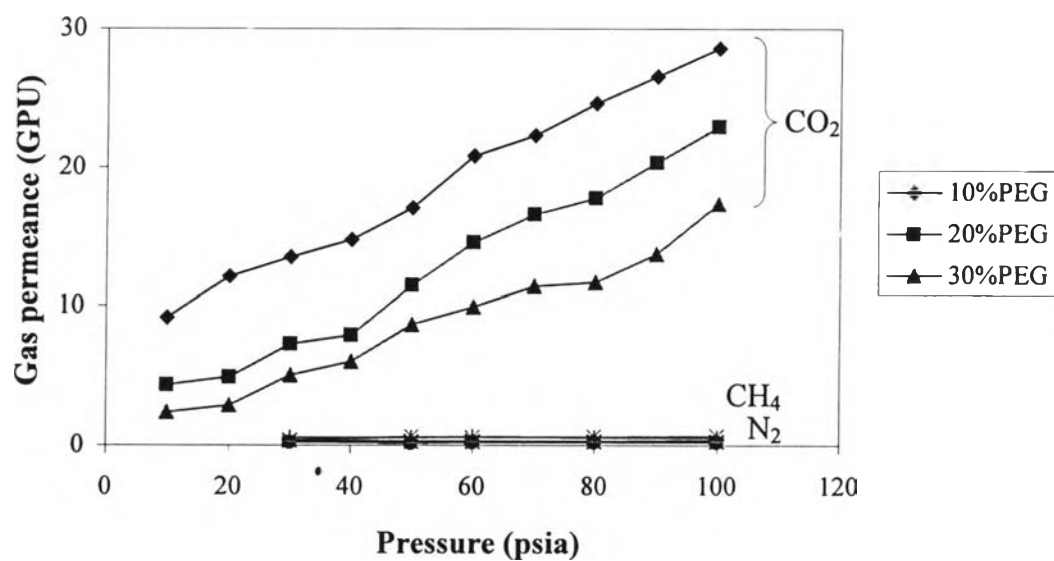


Figure 4.29 Relations between pressure and gas permeation rate in 10, 20, and 30%PEG/10%NaX/SR/CA MMMs.

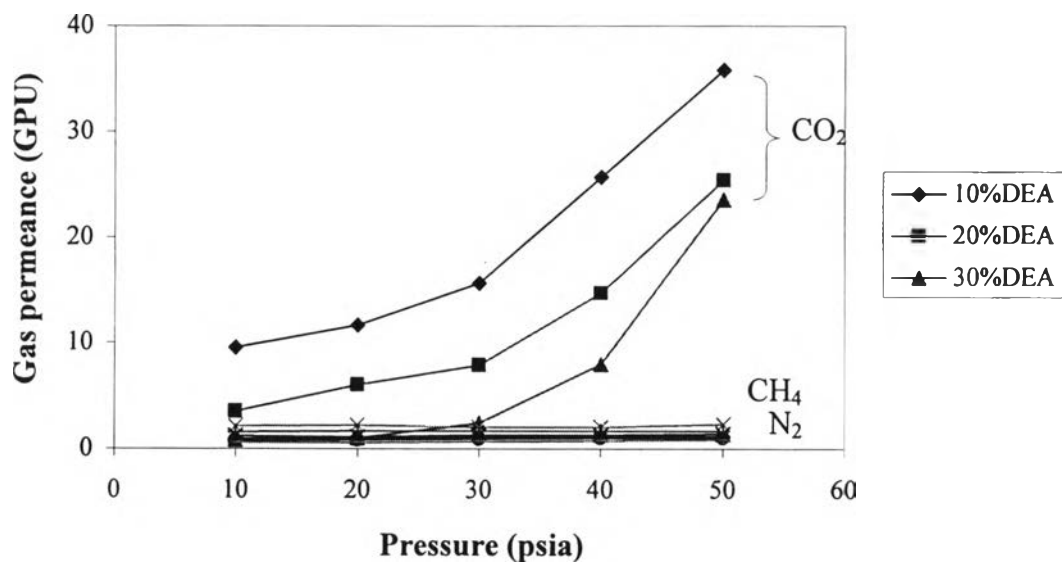


Figure 4.30 Relations between pressure and gas permeation rate in 10, 20, and 30%DEA/10%NaX/SR/CA MMMs.

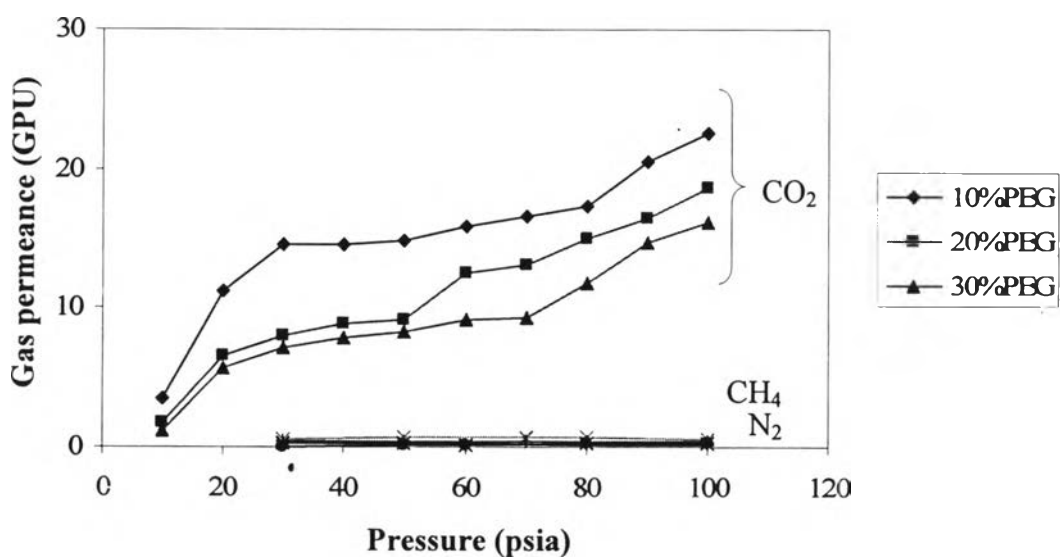


Figure 4.31 Relations between pressure and gas permeation rate in 10, 20, and 30%PEG/10%LiX/SR/CA MMMs.

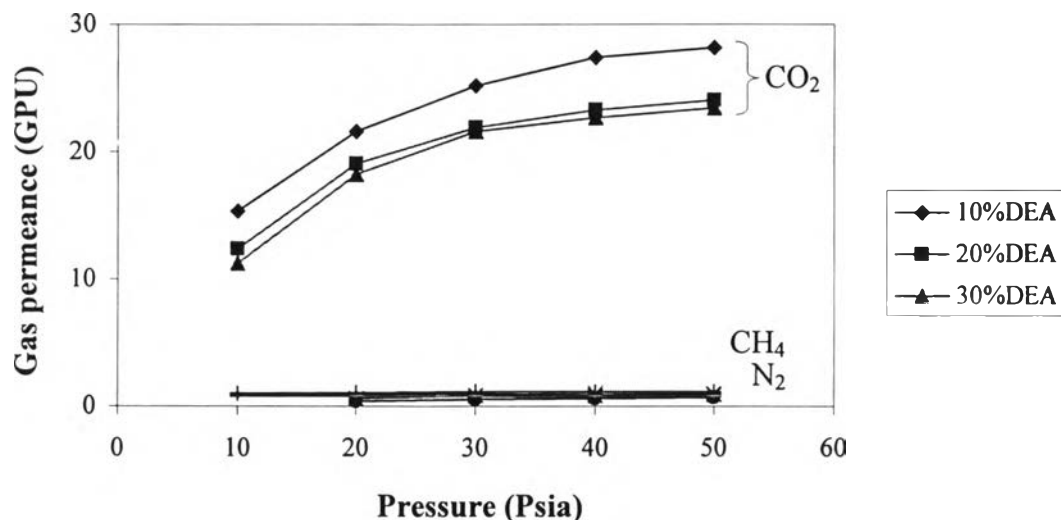


Figure 4.32 Relations between pressure and gas permeation rate for 10, 20, and 30%DEA/10%LiX/SR/CA MMMs.

4.5.2 Plasticization Investigation

Glassy polymer generally undergoes plasticization from high condensable gas molecules like CO_2 , though no plasticization report has been found on rubbery polymer (Hughes and Jiang, 1995). Since the studied MMMs were combined from 2 parts; the cellulose acetate which is glassy polymer and the mixed matrix phase which is rubbery polymer comprised silicone rubber with solid adsorbent and selective liquid.

In this section, Cellulose acetate (CA), silicone rubber (SR), and 30%PEG/10%NaX/SR were selected to be a representative of glassy polymer, rubbery polymer and rubbery mixed matrix phase, respectively, to be individually tested for CO_2 plasticization at feed pressure 10-100 psia. in order to investigate the cause of plasticization. As can be clearly seen from Figure 4.33, only CA membrane had CO_2 plasticization effect as the observed of increase CO_2 permeance with increasing feed pressure. While no observation of significant changes of CO_2 permeances were found on SR and 30%PEG/10%NaX/SR. These results are consistent with literature data. Therefore it can prove that the observed plasticization on the studied MMM undoubtedly caused from cellulose acetate, not a mixed matrix phase, rubbery phase.

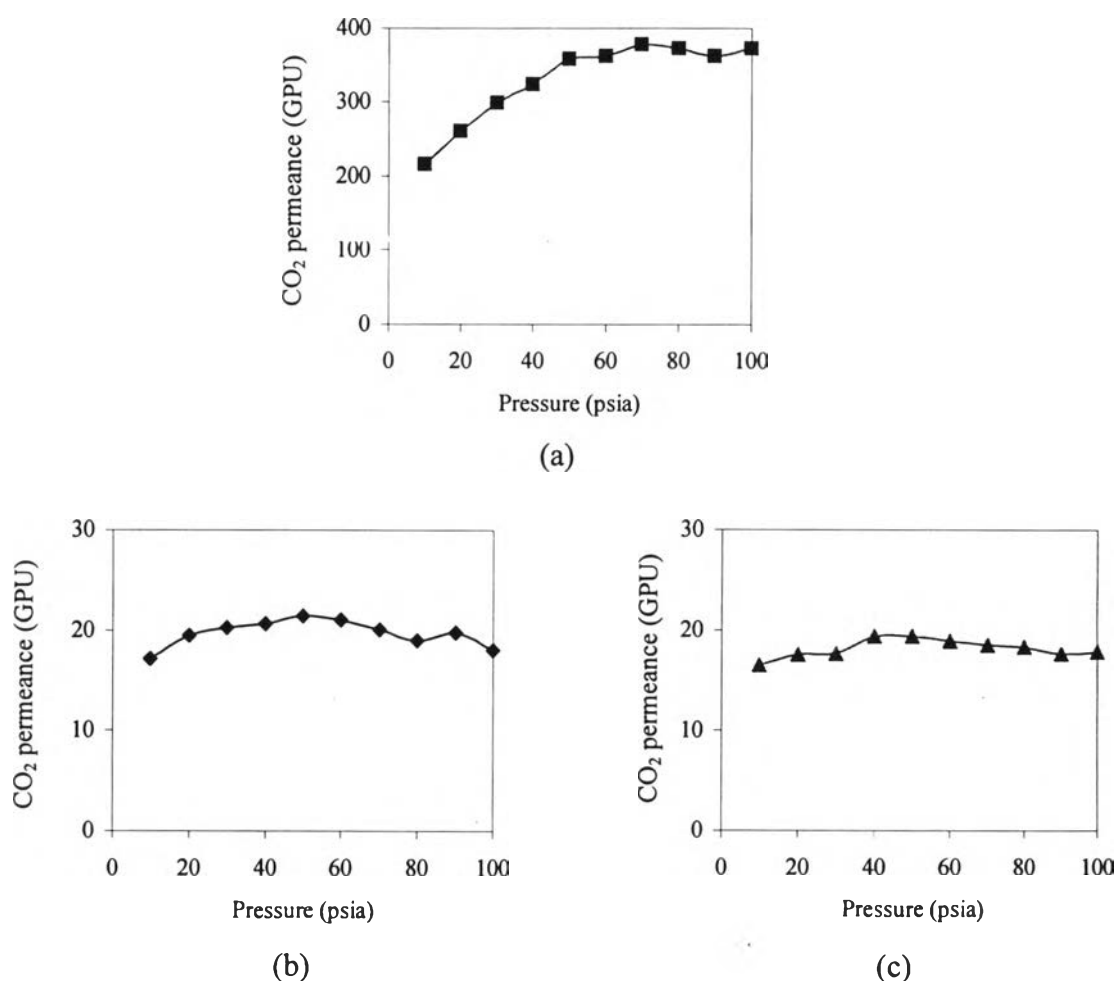


Figure 4.33 Relations between pressure and gas permeation rate for (a) cellulose acetate (CA), (b) silicone rubber and (c) 30%PEG/10%NaX/SR.

Many researchers have studied the effect of CO₂ in polymer. It is well known that sorption of CO₂ can facilitate the local segmental organization of membrane with a reduction in the selectivity. The strong interaction between CO₂ and polymers allow higher degree of segmental mobility which substantially reduces the interchain interactions of polymer chains resulted in an increasing of permeability but reduction in selectivity that is accordance with a consequent increase in free volume of the polymer allow all gases pass through. (Ismail and Lorna, 2001) Several authors indicated that CO₂ has a quadrupole moment and is probable to be more soluble in polymers with a polar matrix (Costello and Koros, 1992).

Furthermore, gases like CO₂ with higher critical temperature are considerably high gas solubilities can attribute to plasticization as well.

By the attempts to study gas separation using single gas measurement may be used to interpret the permeability and selectivity of mixed gas feed measurement. Once the mixed gas system include of CO₂, CH₄ and N₂, the membrane will swell upon the CO₂ plasticization and accelerating the permeation of CH₄ and N₂ as well as CO₂. Finally the swollen membrane will lose its selective properties. In binary mixtures of CO₂-N₂ and CO₂-CH₄, lower permeability is measured for CO₂ than those measured for the pure CO₂ gas. Also, higher permeability is measured for the slower species, N₂ and CH₄, than those for pure N₂ or CH₄ gases (Ettouney and Majeed, 1997). The reduction of permeability is most likely due to the competition between the gas penetrant for adsorption sites in polymer, as the permeation follows the solution-diffusion mechanism (Tin *et al.*, 2003). The presence of CH₄ and N₂ is believed to reduce the solubility coefficient of CO₂, Hence CO₂ permeability is lowered. For the same reason, the presence of CO₂ also decreases the solubility of CH₄ and N₂. However the CO₂ sorption enhances the mobility of intersegment chain of polymer that greatly increases the diffusivity of the gas molecules. Since the permeation dominate by the diffusivity improvement rather than the declined solubility, the CH₄ and N₂ permeabilities will increased as the result of CO₂ plasticization.