CHAPTER IV

RESULTS AND DISCUSSION

## 4.1 Plasticization in Cellulose Acetate Membrane

The permeances of propane, $P_{C_3H_8}$; propylene, $P_{C_3H_6}$; methane, P_{CH_4}; and carbon dioxide, P_{CO_2}, and the selectivities of CO_2/CH_4 and C_3H_6/C_3H_8 are presented in Table 4.1. In order to investigate the plasticization phenomenon in a cellulose acetate (CA) membrane, the gas permeance of carbon dioxide (CO_2) was determined from the steady state permeation rates of individual gas through the membrane at room temperature and in the pressure range of 25-200 psi. Plasticization of the membrane is usually defined as an increase in CO_2 permeance as a function of feed pressure due to dilation of the glassy polymer (Visser *et al.*, 2005). The relationship between pressure and gas permeation rate shown in Figure 4.1 indicates the occurrence of plasticizatioin phenomenon for the studied membrane.

CO_2 permeance increased with increasing pressure. Clearer evidence in supporting the above explanation can be illustrated in that CO_2 sorbed at higher feed pressure may dilate the member since CO_2 had a strong interaction with polar groups of the polymer. These interactions were stronger than the interactions between the chain segments. Thus, CO_2 broke these interactions providing additional diffusion path ways for the gas molecules (Bos *et al.*, 1999). In other words, it was indicative of plasticization. CO_2 acted as a plasticizer to swell the polymer matrix causing an increase in free volume and segmental mobility of the polymer matrix, accelerating the permeation of all gases. That caused the reduction in the selectivity. To confirm the plasticizing effect, the gas permeance of C_3H_8, C_3H_6 and CH_4 was measured after contacting with CO_2 from the first cycle to forth cycle as shown in Table 4.1. The results show an increase in the gas permeance of all gases studied. As a consequence, both C_3H_6/C_3H_8 and CO_2/CH_4 selectivity decreased as increasing in the order of the cycles when the plasticization occurred.

Table 4.1 Observation of plasticizing effect in cellulose acetate membrane

Cycle order	Gas Permeance (GPU) at 100 psi				Selectivity at 100 psi	
	C_3H_8	C_3H_6	CH_4	CO_2	C_3H_6/C_3H_8	CO_2/CH_4
1st	0.1047	0.2269	0.7231	10.2052	2.1662	14.1127
2nd	0.1437	0.2789	1.0317	11.6563	1.9413	11.2986
3rd	0.1580	0.2957	1.4362	13.9816	1.8709	9.7349
4th	0.2143	0.3229	2.2623	18.3557	1.5067	8.1137

* $GPU = 1 \times 10^{-6}$ $cm^3(STP).cm.s^{-1}.cm^{-2}.cmHg$.
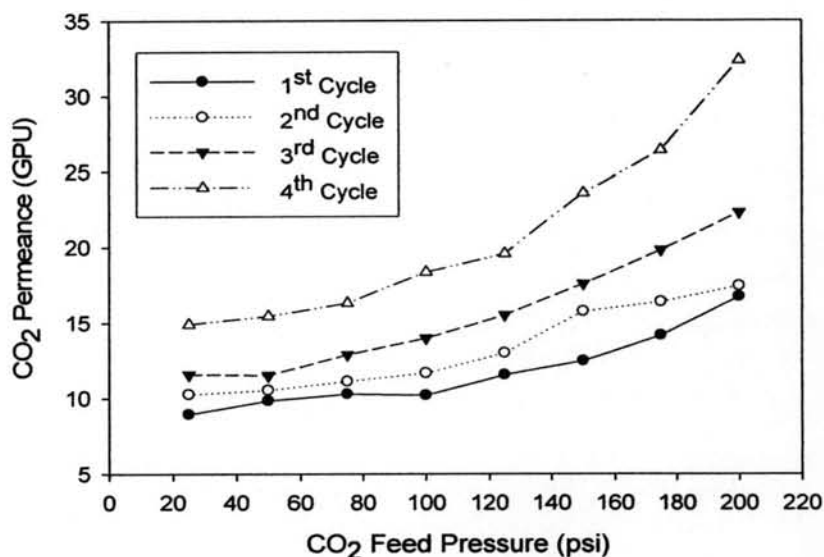
Figure 4.1 Relationship between CO_2 permeance and pressure for CA membrane.

4.2 Plasticization in CA MMMs

To sustain reasonable performance, membreanes with enhanced plasticization resistance are imperative (Sander *et al.*, 1992 and Ismail and Lorna, 2002). One of the goals of this study was to examine the effect of zeolite on the plasticizing suppression of CA MMMs. According to Section 4.1, there is a strong interaction between CO_2 molecules and polymer matrices leading to the inducement

of plasticization. The observed plasticization, caused by the CO_2 molecules was found in the cellulose acetate, not mixed matrix phase, rubbery phase (Soontraratpong, 2005). Furthermore, the incorporation of NaX into polymeric MMMs provided good plasticizing suppression of MMMs for CO_2/CH_4 separation (Sriwasut, 2006). In order to elucidate the plasticizing suppression, various types of adsorbents (NaA, NaX, NaY, CaA, silicalite and PEG-NaX) were incorporated into the polymer phase.

4.2.1 NaA-CA MMMs

Figure 4.2 shows the CO_2 permeation behavior of NaA-CA MMMs. The slope of the graph represents how easy the membrane was plasticized by CO_2 molecules. The higher the value of the slope was, the higher the tendency to be plasticized in the membranes was. The obtained result shows that the incorporation of NaA-zeolite into MMMs reduced the CO_2 permeance which accounts for the declining slope of the CO_2 permeance graphs. This implies that the incorporation had a positive effect in plasticizing suppression. It is feasible that NaA-zeolite can rigidify polymer chains and inhibit polymer chain mobility in MMMs (Chan et al., 2002). This rigidification perception was extended that the polymer region near the polymer-sieve interface was assumed to have reduced permeability due to chain immobilization effects (Mahajan, 2000). This phenomenon is an extension of behavior observed in the semi-crystalline polymer literature. Crystallites appear to inhibit polymer chain mobility within the amorphous near the crystal, resulting in higher activation energy for diffusion through the amorphous phase (Brandrup, 1999 and Mogri and Paul, 2000). However, the slope started to increase when there was a further increase amount of NaA more than 20%. As a result, in MMMs at high NaA content, small channels or microvoids around the zeolite-polymer interface appeared leading to the loosening of MMMs. This result agreed with the experiment by Suer et al. (1994).
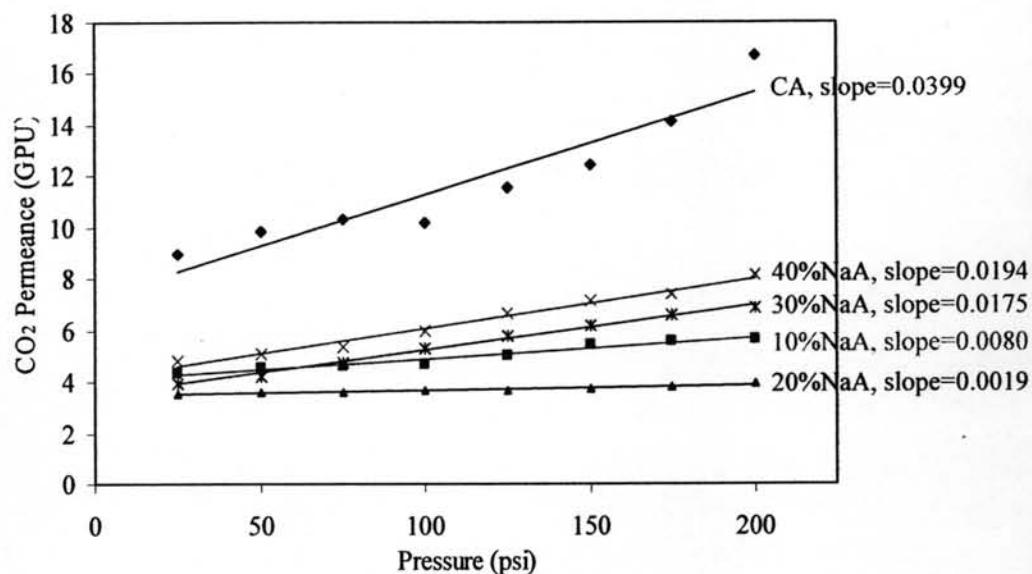
Figure 4.2 Relationship between CO_2 permeance and pressure for NaA-CA MMMs.

4.2.2 NaX-CA MMMs

The relationship of CO_2 permeance to pressure is shown in Figure 4.3. The results show that the slope of the graph decreased when adding NaX-zeolite into MMMs. This means that NaX-zeolite can reduce the plasticizing effect. Nevertheless, the lowest slope was at 10%NaX-zeolite loading. The slope increased with increasing NaX-zeolite loading. The reason for this behavior is that NaX can rigidify the polymer matrices at low content but provide the additional pathways for the gas molecules at high content resulting from the appearance of microvoids around the zeolite-polymer interface.
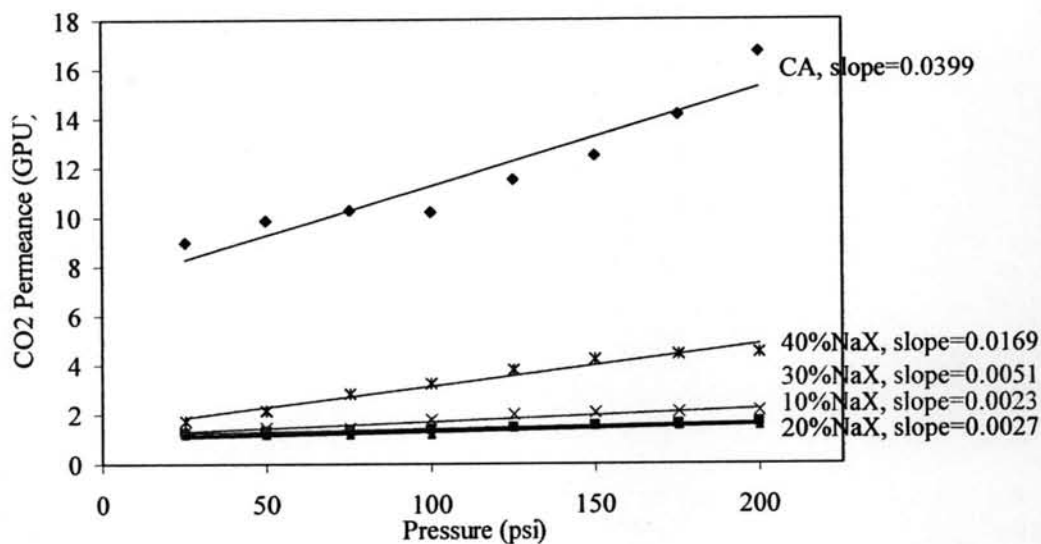
Figure 4.3 Relationship between CO_2 permeance and pressure for NaX-CA MMMs.

4.2.3 NaY-CA MMMs

Figure 4.4 shows the CO_2 permeation behavior of NaY-CA MMMs. Although the results show the same trend as in the case of NaA- and NaX-CA MMMs, it attained a minimum value at 30%NaY content. The explanation can be clearly given that NaY had a positive effect on the plasticization causing from the rigidification and densification of the polymers.
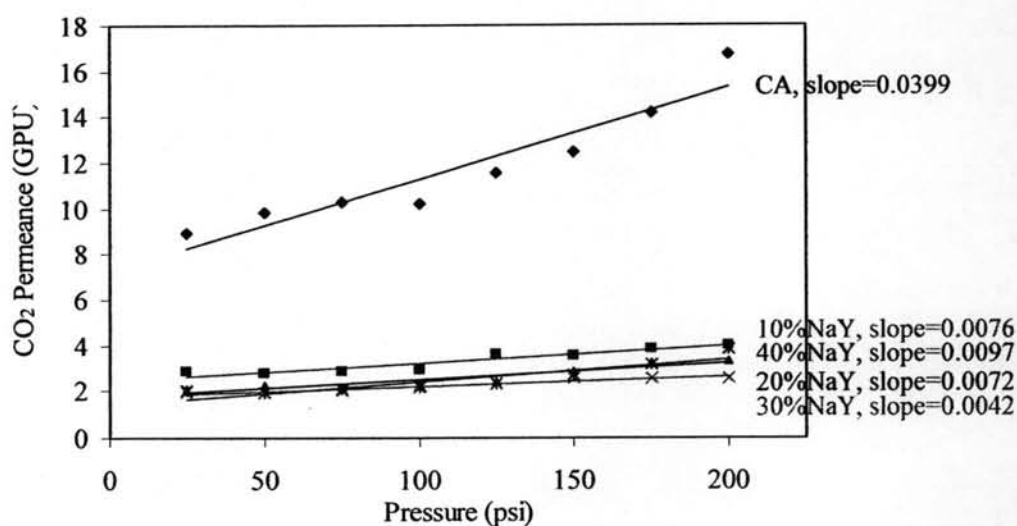

Figure 4.4 Relationship between CO_2 permeance and pressure for NaY-CA MMMs.

4.2.4 CaA-CA MMMs

It can be noticed from Figure 4.5 that the incorporation of CaA-zeolite into MMMs can improve the plasticizing suppression due to the reduction in the value of the slope. It is feasible the CaA can inhibit the chain mobility of the polymers and hinder the diffusion pathway of the CO_2 molecules.
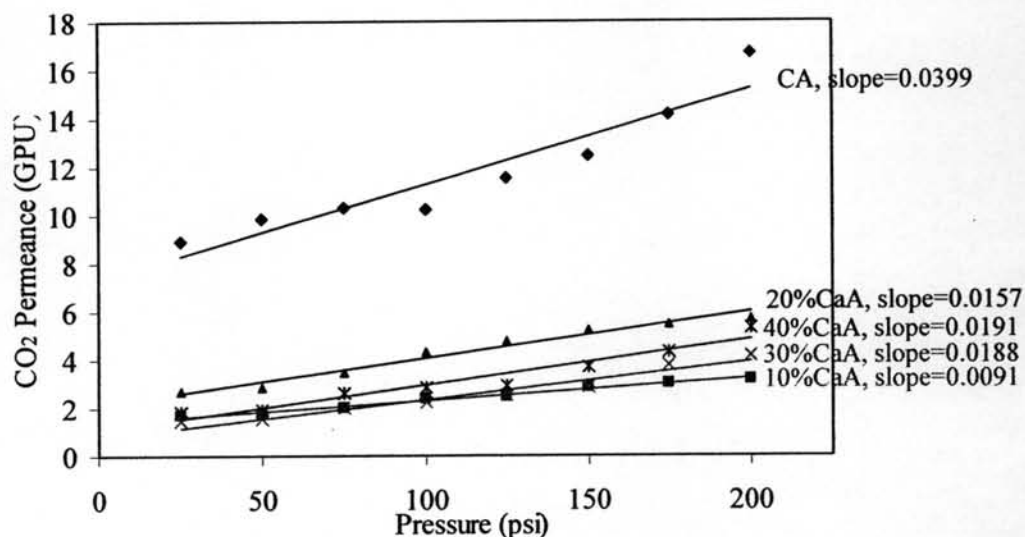

Figure 4.5 Relationship between CO_2 permeance and pressure for CaA-CA MMMs.

4.2.5 Silicalite-CA MMMs

The relation of CO_2 permeance with pressure shows in Figure 4.6. It is clearly seen that silicalite reduced the CO_2 permeance and the value of the slope since silicalite can densify and rigidfy the polymers. As a consequence, the incorporation of silicalite in CA can suppress the plasticization in MMMs.
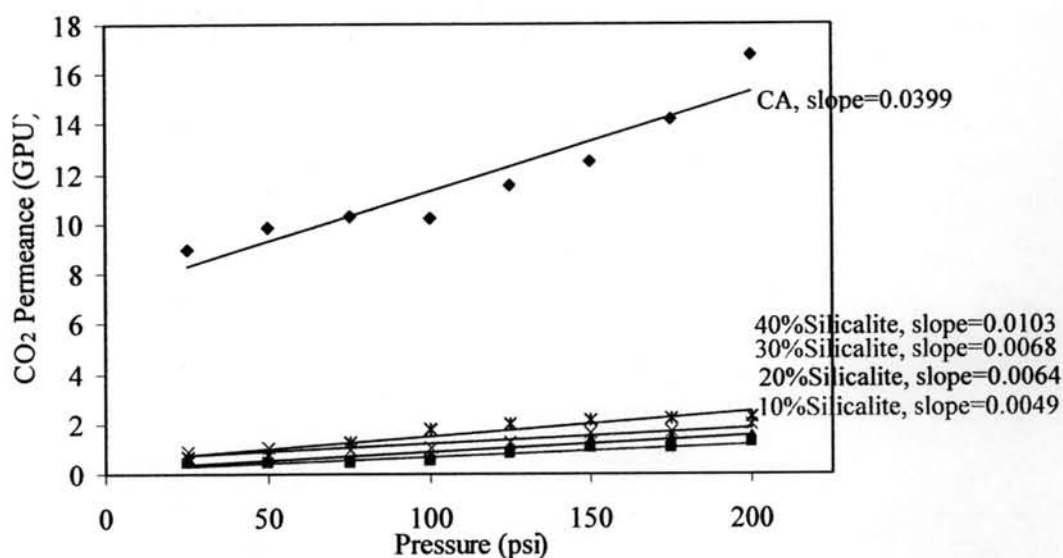
Figure 4.6 Relationship between CO_2 permeance and pressure for Silicalite-CA MMMs.

4.2.6 PEG-NaX-CA MMMs

From Figure 4.7, it can be seen that CO_2 permeance for 30%PEG-NaX-CA MMMs was nearly constant at any pressure. This means that 30%PEG-NaX can suppress the plasticizing effect. It is obvious that PEG adsorbed into NaX-zeolite in MMMs reduced the gas permeance because it replaced the void space. Therefore, the polymer molecules surrounding the inorganic material are fixed at the surface resulting in their segmental mobility being lower, so that the polymers would likely display a lower permeability.
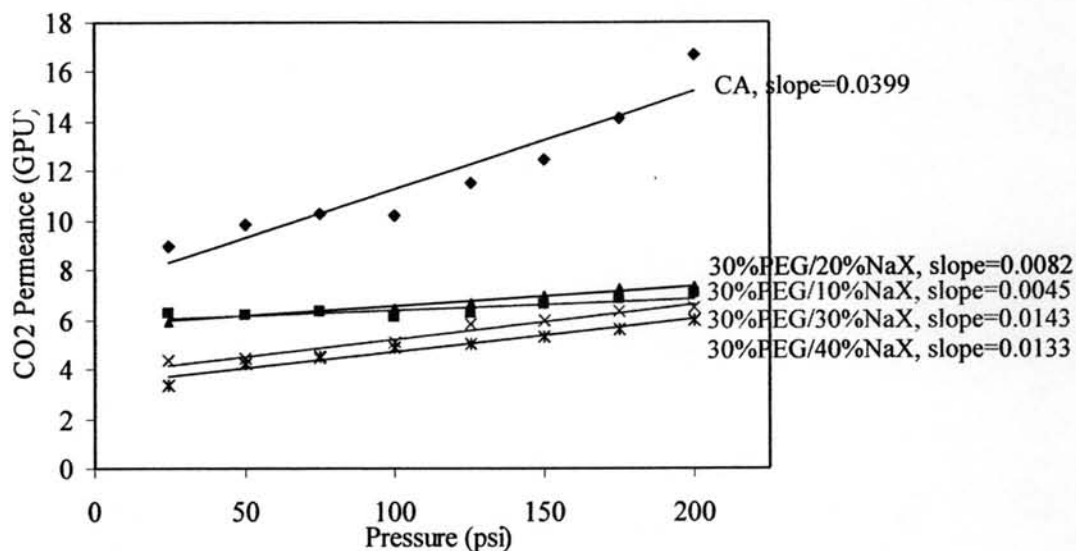
Figure 4.7 Relationship between CO_2 permeance and pressure for 30%PEG-NaX-CA MMMs.

4.3 Selectivity for CA MMMs

There are two terms that control the gas separation, diffusivity and solubility. The diffusivity is usually dominated by the differences in molecular sizes of gas molecules (Orthmer, 1981). In the case of CO_2/CH_4 and C_3H_6/C_3H_8, their molecular sizes are quite similar, so the solubility should be taken into consideration for describing such properties. The solubility of gas in a polymer membrane depends on the penetrant-polymer interaction. CO_2 and C_3H_6 have a higher polarizability of CO_2 molecules and they have a flat configuration due to the presence of the π electrons of olefins (Chan *et al.*, 2002). This means that they are more favorable to be sorbed, possibly in the polymer membrane leading to better interaction between CO_2 or C_3H_6 and CA chain segment. As the results, the CA membrane is selective to CO_2. over CH_4 and C_3H_6 over C_3H_8. Furthermore, the product of these two parameters is permeability which is a measure of the membrane's ability to permeate molecules. In addition, if there are two types of molecules, the ratio of their permeabilities is selectivity, which is the ability of a membrane to separate the molecules.

The incorporation of polyethylene glycol (PEG)-NaX-silicone rubber (SR) into polymeric membranes provided good separation performance of the mixed matrix membranes (MMMs) for CO_2/CH_4 separation. (Soontraratpong, 2005) However, their performances have been developed and applied for other separation processes such as C_3H_6/C_3H_8 separation. In contrast, NaX-zeolite and silicalite showed the reverse performance of Ultem-MMMs for C_3H_6/C_3H_8 separation. (Srisilp, 2004) Therefore, in an attempt to study the performance of CA-MMMs, NaX; NaY; NaA; CaA; Silicalite and 30%PEG/NaX were incorporated into CA MMMs. The maximum adsorbent loading considered in this work was ~40% because of the considerable difficulty in preparing membranes at high loading. The obtained results are shown in Figures 4.8-4.15.

4.3.1 NaA-CA MMMs

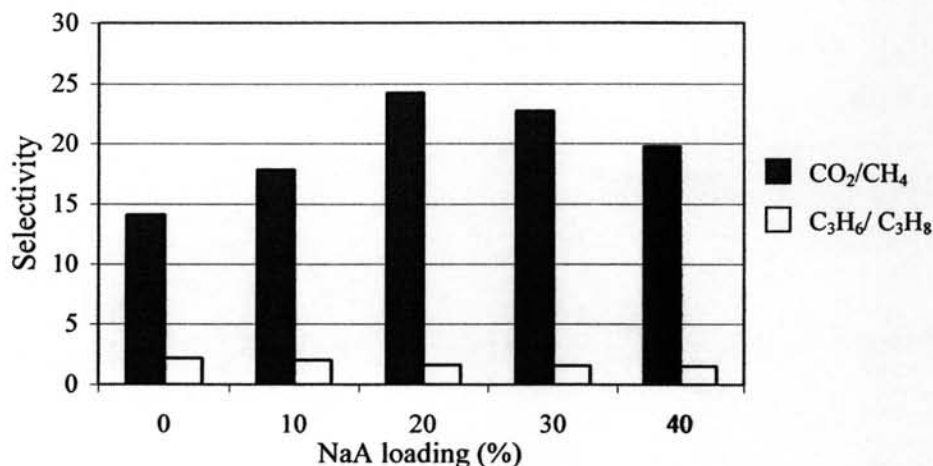The CO_2/CH_4 and C_3H_6/C_3H_8 selectivities for NaA-CA MMMs are shown in Figure 4.8.

Figure 4.8 Ideal CO_2/CH_4 and C_3H_6/C_3H_8 selectivities at 100 psi for NaA-CA MMMs.

This figure shows that the incorporation of NaA-zeolite into the membrane resulted in an increase in CO_2/CH_4 selectivity when compared with that of the CA membrane. It can be said that NaA-zeolite was more selective to CO_2 over CH_4, leading to the high solubility of CO_2. However, its selectivity decreased at high

NaA-zeolite loading. It is believed that CO_2-adsorption of NaA-zeolite is so strong that CO_2 molecules are difficult to desorb. Therefore, the membrane's CO_2/CH_4 selectivity was reduced.

The C_3H_6/C_3H_8 selectivity decreased increasing NaA-zeolite loading. The reason for the reverse selectivity is unclear. However, there are two possible explanations for this phenomenon. First, NaA-zeolite in the polymer matrix played a molecular sieving role in gas separation through the MMMs. In other words, NaA-zeolite was more selective to propane over propylene than cellulose acetate. Another reason is that NaA-zeolite may change the membrane morphology of cellulose acetate. The membrane could prefer propane to propylene (Rattanawong, 2001).

4.2.2 NaX-CA MMMs

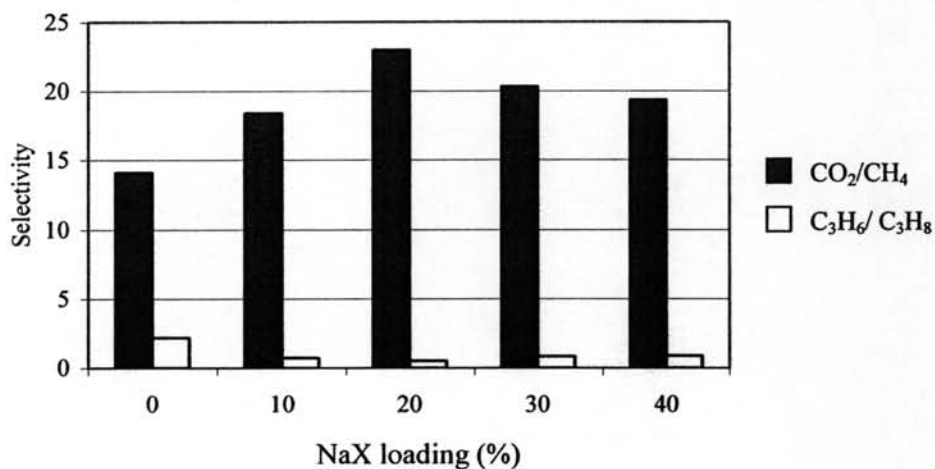The CO_2/CH_4 and C_3H_6/C_3H_8 selectivities for NaX-CA MMMs are shown in Figure 4.9.

Figure 4.9 Ideal CO_2/CH_4 and C_3H_6/C_3H_8 selectivities at 100 psi for NaX-CA MMMs.

The result shows that the CO_2/CH_4 selectivity for NaX-CA MMMs reached a plateau at 20% NaX-zeolite loading. A higher amount of NaX-zeolite loading did not show the originally enhanced properties anymore. These results may be explained by the solubility of the gas molecules.

The C_3H_6/C_3H_8 selectivity decreased when incorporating NaX-zeolite into cellulose acetate. It is worth mentioning that NaX-zeolite affected this separation. C_3H_6 is intrinsically more adsorbed into NaX-zeolite than C_3H_8 by having a strong interaction between the acid site of the NaX and the π electrons of C_3H_6 molecules. However, this effect was subjected to the difficult desorption of C_3H_6 molecules. In other words, a high amount of C_3H_6 molecules adsorbed into the membrane, but they barely desorbed out because of the strong adsorption of NaX-zeolite in the membrane. Therefore, the decreased C_3H_6/C_3H_8 selectivity resulted from the effect of NaX-zeolite on the separation.

4.3.3 NaY-CA MMMs

The CO_2/CH_4 and C_3H_6/C_3H_8 selectivities for NaY-CA MMMs are shown in Figure 4.10.
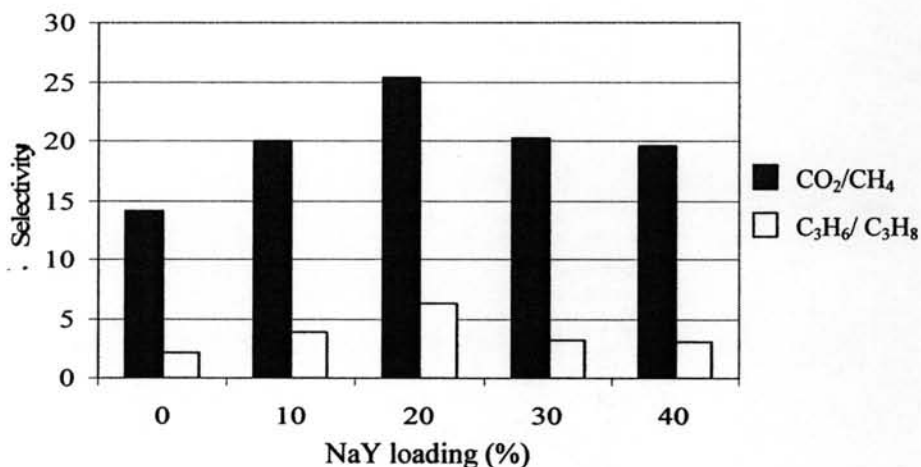

Figure 4.10 Ideal CO_2/CH_4 and C_3H_6/C_3H_8 selectivities at 100 psi for NaY-CA MMMs.

The figure reveals that the incorporation of NaY-zeolite into the membrane resulted in increasing both CO_2/CH_4 and C_3H_6/C_3H_8 selectivity when compared to that of the CA membrane. It is believed that NaY-zeolite is more selective to CO_2 over CH_4 and to C_3H_6 over C_3H_8, leading to the high solubility of CO_2 and C_3H_6. Due to the similar molecular sizes of C_3H_6/C_3H_8 and CO_2/CH_4, NaY-

zeolite can facilitate these molecules passing through the membrane in a similar manner. However, both CO_2/CH_4 and C_3H_6/C_3H_8 selectivities reached a maximum value at 30% NaY loading and then decreased. This is caused by the reduction of CO_2 and C_3H_6 permeance. A possible explanation might be that the excess amount of NaY blocked the transient gap of polymer, since the transport of gas is postulated to occur when there is a transient gap of sufficient size to accommodate the gas penetrants (Charoenpol, 2002). Therefore, the NaY hindered the diffusion path of gas molecules. It can also be stated that the gas diffusion played a dominant role in the gas solubility at high NaY loading.

4.3.4 CaA-CA MMMs

The CO_2/CH_4 and C_3H_6/C_3H_8 selectivities for CaA-CA MMMs are shown in Figure 4.11.

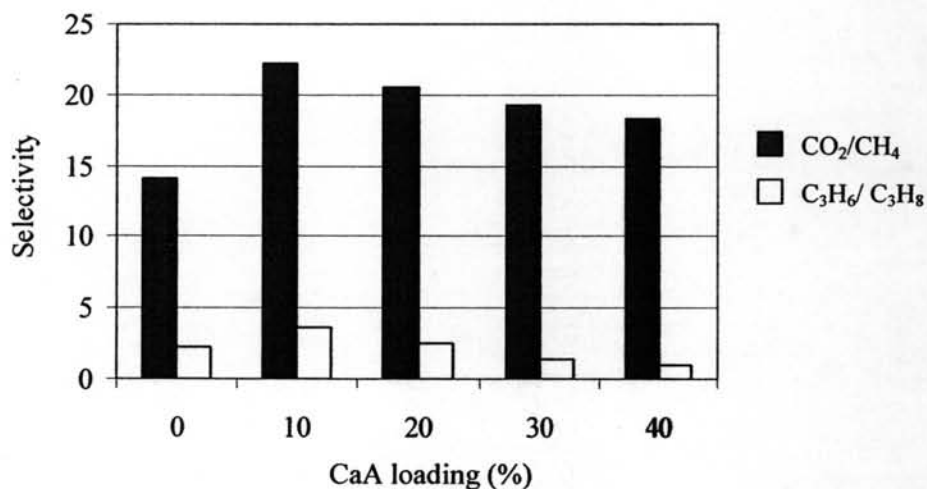**Figure 4.11** Ideal CO_2/CH_4 and C_3H_6/C_3H_8 selectivities at 100 psi for CaA-CA MMMs.

The results indicate that both CO_2/CH_4 and C_3H_6/C_3H_8 selectivity increased when incorporating CaA-zeolite into CA MMMs. In addition, both of them reached a maximum value at 10% CaA loading. For the CO_2/CH_4 selectivity, it believed that the separation was controlled by the solubility of the gas molecules.

However, the molecular sieving mechanism was probably a controlling factor for the C_3H_6/C_3H_8 separation

4.3.5 Silicalite-CA MMMs

The CO_2/CH_4 and C_3H_6/C_3H_8 selectivities for Silicalite-CA MMMs are shown in Figure 4.12.
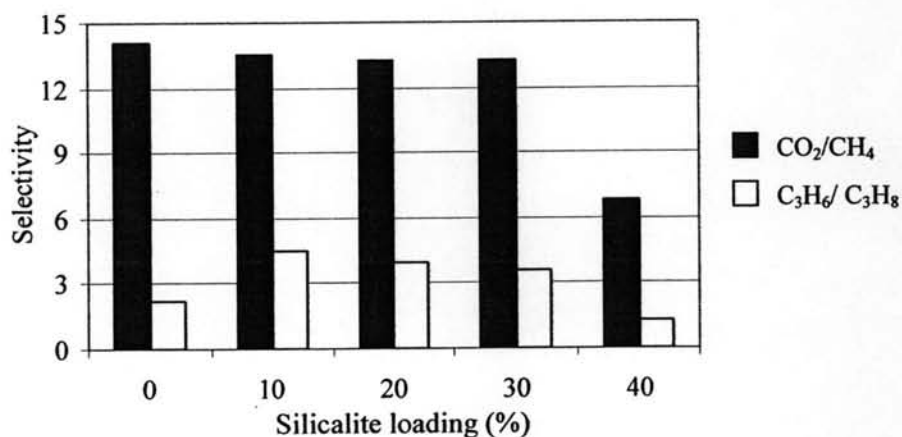

Figure 4.12 Ideal CO_2/CH_4 and C_3H_6/C_3H_8 selectivities at 100 psi for Silicalite-CA MMMs

Figure 4.12 shows that the CO_2/CH_4 selectivity of silicalite-CA MMMs changed insignificantly when compared to the CA membrane. However, CO_2/CH_4 selectivity dramatically dropped at high silicalite loading. It seems reasonable to assume that silicalite in MMMs played a molecular sieve role in gas separation. CH_4 was more soluble in the membrane than CO_2 due to the high hydrophobic nature of silicalite. On the contrary, C_3H_6/C_3H_8 selectivity increased when adding 10% silicalite, due to the higher diffusivity of propylene. It has a smaller effective diameter than propane. The double bond has a greater total bond energy than a single bond and the atoms are held together more tightly. Therefore, olefins have higher diffusivity than paraffins at the same carbon atoms (Chan *et al.*, 2002). Nevertheless, C_3H_6/C_3H_8 selectivity decreased when adding more than 10% of silicalite.

4.3.6 PEG-NaX-CA MMMs

PEG was found to enhance selectivity towards the polar gases on several kinds of membrane separation (US. Pat. No.4,608,060 and 4,737,165). According to previous work (Soontraratpong, 2005), 30%PEG-NaX-SR-supporting CA was the most selective to CO_2 over CH_4. 30% Liquid PEG was additionally adsorbed into NaX and then incorporated into MMMs. The attained results are shown in Figure 4.13
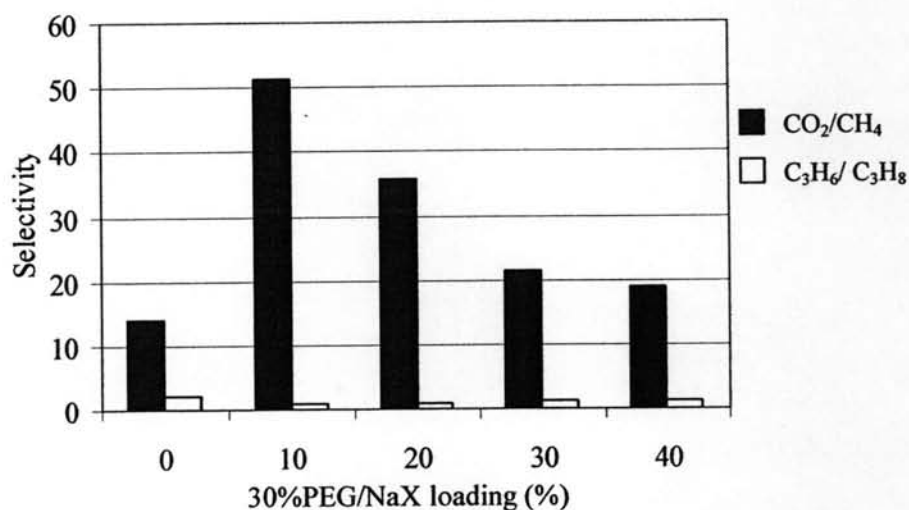

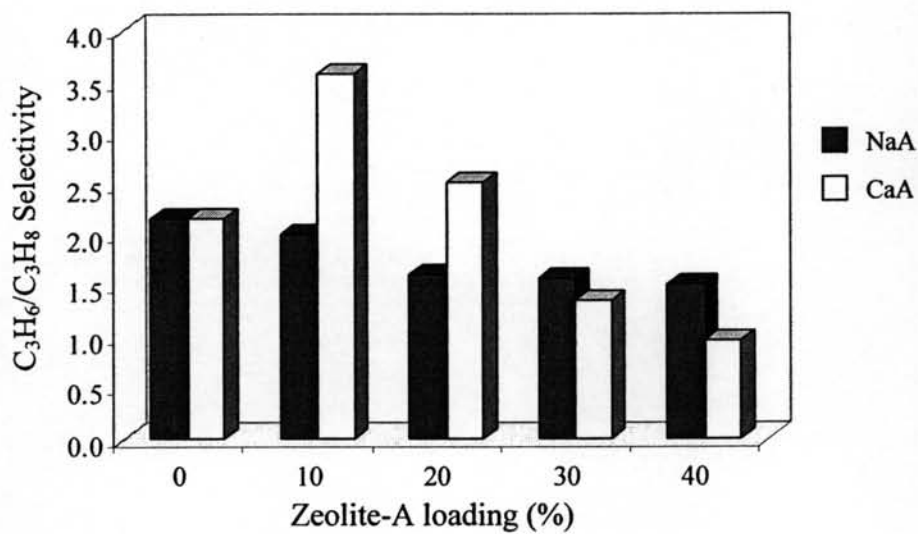**Figure 4.13** Ideal CO_2/CH_4 and C_3H_6/C_3H_8 selectivity at 100 psi for 30%PEG-NaX-CA MMMs.

From Figure 4.13, the CO_2/CH_4 selectivity increased when adding 30%PEG/10%NaX in MMMs. The reason for this would be related to the acid-base interaction between acidic CO_2 and the electron-rich ether oxygen atoms of the PEG molecules. That is probably responsible for the high solubility of CO_2 in PEG (Saha and Chakma, 1994). Therefore 30%PEG-NaX-CA MMMs was selective to CO_2. However, CO_2/CH_4 selectivity after 30%PEG-10%NaX decreased as increasing 30%PEG-NaX loading due to the reduction in CO_2 permeance. There are two possible explanations. First, the pore blockage of zeolites by PEG may play a much more important role in this separation (Li *et al.*, 2005). Another reason is that PEG at high content allowed large penetrants such as CO_2 and CH_4 to diffuse easily because of its flexible main chain, resulting in more improvements in CO_2 and CH_4

permeance (Li *et al.*, 1998). On the contrary, the result shows the reverse C_3H_6/C_3H_8 selectivity on this adsorbent. The finding herein proves that PEG was adsorbed into the pore of NaX. The properties of NaX may change after the adsorption of PEG into NaX.
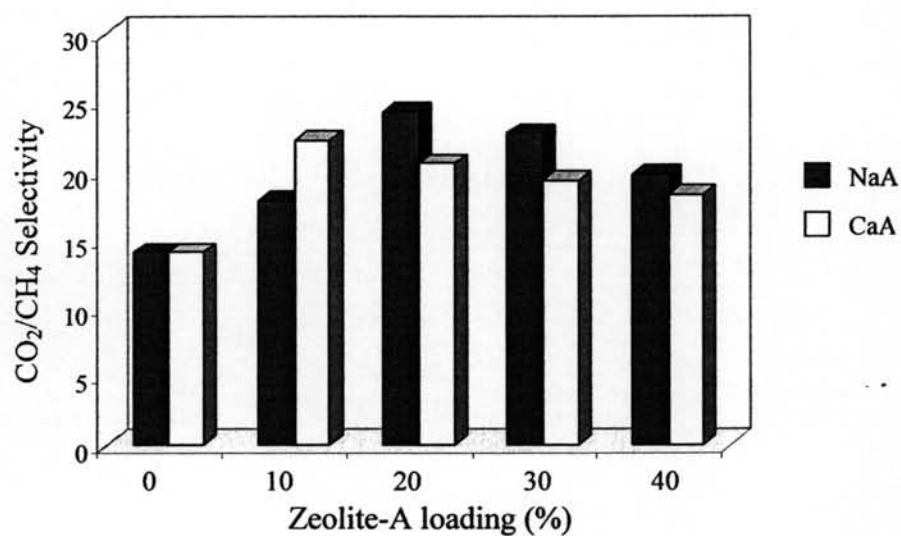
4.3.7 Comparisons of Separation Performance between NaA-CA MMMs and CaA-CA MMMs

In this section, the effect of pore size of zeolite-A on both the CO_2/CH_4 and C_3H_6/C_3H_8 selectivity was studied by individually introducing NaA and CaA into CA MMMs. The kinetic diameters of CO_2, CH_4, C_3H_6 and C_3H_8 are 3.3, 3.8, 4.5 and 4.3 Å, respectively. Furthermore, the pore size of NaA and CaA is 4.1 and 4.7 Å. From these differences, it is believed that both NaA-zeolite and CaA-zeolite in the polymer matrix are better off playing a molecular sieving role in gas separation through MMMs. According to the results (Figure 4.14), there were different effects on the C_3H_6/C_3H_8 selectivity. Due to the pore size effect, NaA-zeolite intrinsically prefers C_3H_8 to C_3H_6 resulting in the reverse selectivity in MMMs. In contrast, the effect of CaA-zeolite at below 20% loading provided good separation. Poor separation performance at high CaA-zeolite loading was discussed in section 4.3.4.

The effect of both types of zeolite on the CO_2/CH_4 selectivity showed the same tendency. It is worth mentioning that this separation was not controlled by the molecular sieve mechanism because both of them have much larger pore size than the kinetic diameters of CO_2 and CH_4. Therefore, the surface property of zeolite is supposed to be the controlling factor. In other words, the gas separation was not dominantly controlled by size selective mechanism, but the solubility played the selective role in determining the separation performance.
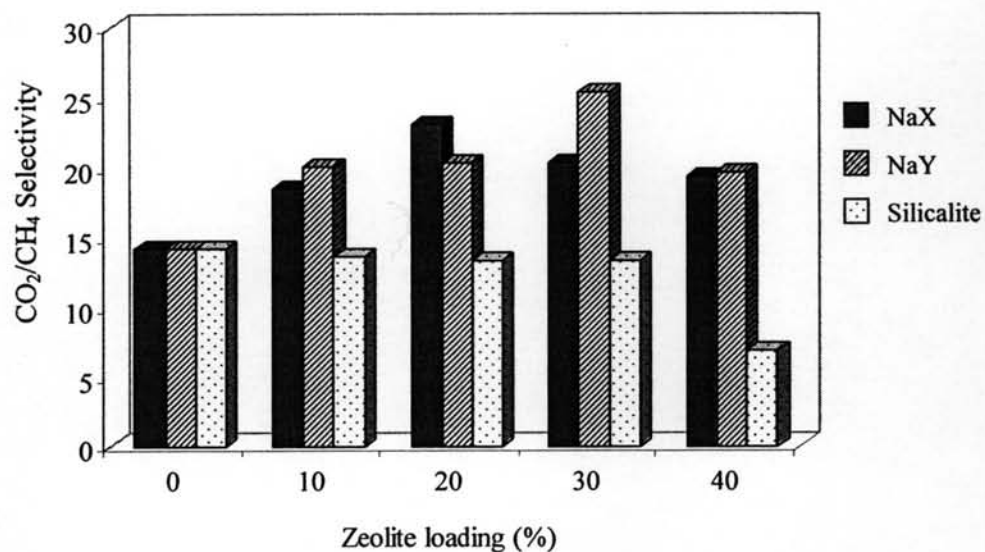
Figure 4.14 Comparison of the ideal selectivity at 100 psi between NaA-CA MMMs and CaA-CA MMMs (a) CO_2/CH_4 selectivity (b) C_3H_6/C_3H_8 selectivity.

4.3.8   Comparisons of Separation Performance through NaX-CA MMMs,
        NaY-CA MMMs and Silicalite-CA MMMs

The comparisons of the CO_2/CH_4 and C_3H_6/C_3H_8 selectivity through NaX-CA MMMs, NaY-CA MMMs and Silicalite-CA MMMs are graphically presented in Figure 4.15. As shown in Figure 4.15 (a), the effect of NaX-CA MMMs and NaY-CA MMMs on CO_2/CH_4 selectivity showed a consistently parallel behavior. However, a different tendency was observed from the result of silicalite-CA MMMs. It was subsequently demonstrated that CO_2 was more adsorbed into NaX-CA MMM and NaY-CA MMM than that into silicalite-CA MMM since silicalite has very high Si/Al ratios, 670, and is very hydrophobic. The NaX and NaY have strongly polar anionic frameworks and strong local electrostatic fields. It might be presumed that electron enriched CO_2 molecules induce the formation of London force that arises from the temporary dipole moment. This led to the enhancement of CO_2 solubility in both NaX-zeolite and NaY-zeolte added in the mixed matrix membranes.

Figure 4.15 (b) shows that the NaX-CA MMMs provided reverse selectivity, but the others expressed enhanced selectivity. It is feasible that NaX-zeolite has more acid sites for adsorbing C_3H_6 than NaY-zeolite and silicalite due to lower Si/Al ratio. This attributed to the stronger interaction and adsorption of C_3H_6. To paraphrase, it was more difficult for C_3H_6 to come out from NaX-CA MMMs when compared with NaY-CA and silicalite-CA MMMs.

(a)
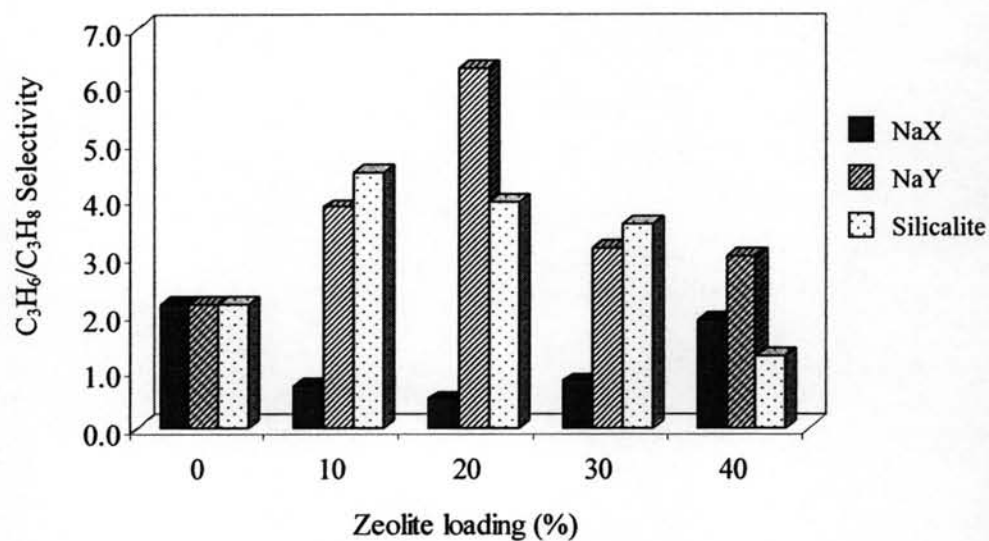
(b)

Figure 4.15 Comparison of the ideal selectivity at 100 psi through NaX-CA MMMs, NaY-CA MMMs and Silicalite-CA MMMs (a) CO_2/CH_4 selectivity (b) C_3H_6/C_3H_8 selectivity.