# CHAPTER IV
# RESULTS AND DISCUSSION

## 4.1 Base Material Property Studies

Cellulose acetate polymer, NaX-zeolite, AgX-zeolite and silicalite were studied for the selectivity of olefin to paraffin to select these materials for making mixed matrix membranes.

### 4.1.1 Cellulose Acetate (CA)

Cellulose acetate, glassy polymer, remains a membrane polymer of practical significance to gas separation technology. It is encountered in the form of asymmetric integrally skinned bi-layers composed of skin active layer without voids and porous support layer. Cellulose acetate is prepared from cellulose by acetylation with acetic anhydride, acetic acid, and a catalyst such as sulfuric acid. These commercial materials are usually characterized by "acetic acid yield" or by " acetyl content" (Kesting and Fritzsche, 1993). For this study, cellulose acetate with 39.5% of acetyl content was selected because it is generally preferred for the preparation of fibers and films of membranes. Cellulose acetate membrane was measured the fluxes of ethylene, ethane, propylene, propane and nitrogen at the room temperature. Then, these gas fluxes were calculated using equations 2.1 and 2.3 to obtain the permeabilities of ethylene, $P_{C2H4}/\delta$; ethane, $P_{C2H6}/\delta$; propylene, $P_{C3H6}/\delta$; propane, $P_{C3H8}/\delta$ and nitrogen, $P_{N2}/\delta$ and the selectivity of ethylene to ethane, $P_{C2H4}/P_{C2H6}$ and propylene to propane, $P_{C3H6}/P_{C3H8}$. The values of the permeability and selectivity are presented in Table 4.1.

**Table 4.1** Base material properties.

| Materials | Permeability, P /δ $10^8$(cm$^3$*STP/ cm$^2$*sec* cmHg) | | | | | Selectivity | | |
|---|---|---|---|---|---|---|---|---|
| | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $N_2$ | $P_{C2H4}$ /$P_{C2H6}$ | $P_{C3H6}$ /$P_{C3H8}$ | $C_6H_{12}$ /$C_6H_{14}$ |
| CA | 1.93 ± 0.03 | 1.56 ± 0.03 | 0.83 ± 0.01 | 0.47 ± 0.01 | 3.30 ± 0.06 | 1.23 | 1.77 | - |
| NaX | - | - | - | - | - | | - | 16.23 |
| AgX | - | - | - | - | - | | - | 48.90 |
| Silicalite | - | - | - | - | - | | - | 1.27 |

The obtained results demonstrate the values of the permeability of all gases through the pure cellulose acetate membrane, which was controlled by both the gas solubility and the gas diffusivity. The results exhibit lower permeabilities of all gases because it had previously been found that the permeation of these gases through a glassy polymer, such as cellulose acetate, are generally too low to measure (Ito and Hwang, 1989). However, the permeability of nitrogen, $P_{N2}$ is the highest because in glassy polymer, unlike in rubber polymer, the diffusivity term is usually dominant, the permeability falls with increasing permeant size and smaller molecules permeate preferentially (Othmer, 1981). Therefore nitrogen is the smallest molecular size or kinetic diameter and quite different from the kinetic diameter of ethane, ethylene, propane and propylene (Kesting and Fritzsche, 1993), its permeability was the highest through cellulose acetate membrane. In cases of ethane, ethylene, propane and propylene, their molecular sizes are similar therefore they could not be only explained by the diffusivity term but be also acted in the role of solubility term for ethylene/ethane and propylene/propane separations. The solubility can be affected by polymer-penetrant interaction (Bungay *et al.*, 1983) in permeation through cellulose acetate membrane. Since ethylene and propylene are more polar than ethane and propane, they interacted with the acetyl group of cellulose acetate (Kesting and Fritzsche, 1993). Consequently, cellulose acetate membrane was selective for ethylene over ethane and propylene over propane. This result agrees with the experimental results by Ito and Hwang (1989) and by Sridhar and Khan (1999). Moreover, the selectivity of propylene to propane was more than selectivity of ethylene to ethane.

### 4.1.2 Adsorptive Fillers

The use of adsorbents such as zeolites and silicalite in separating components from fluid mixtures is also long known. In the adsorption separation process, the adsorbent exhibits selectivity of one mixture component over another (Kulprathipanja *et al*, 1988b). In the present work, the zeolites- NaX, AgX and silicalite were used as the adsorptive filler incorporated into cellulose acetate polymeric matrices since they were also selective for olefin over n-paraffin such as hexene over hexane with testing equilibrium adsorption process. The results of the equilibrium selectivities of NaX , AgX and silicalite are also presented in Table 4.1 and the method of equilibrium selectivity calculation is explained in Appendix.

## 4.2 Material Characterization

### 4.2.1 Zeolites/Cellulose Acetate Mixed Matrix Membranes

AgX-zeolite /cellulose acetate mixed matrix membrane was tested for the porous support layer of membrane morphology by scanning electron microscopy (SEM) to determination of the presence of the incorporated zeolites in the cellulose acetate matrix. This was done at UOP. The micrograph of cross sectional view obtained from SEM study is shown in Figure 4.1

In cases of NaX-zeolite/cellulose acetate and silicalite/cellulose acetate mixed matrix membranes, materials of NaX-zeolite and silicalite are similar to AgX-zeolite therefore the porous support layer morphologies of these adsorptive fillers in the same polymer matrix should be similarity as shown in Figure 4.1.

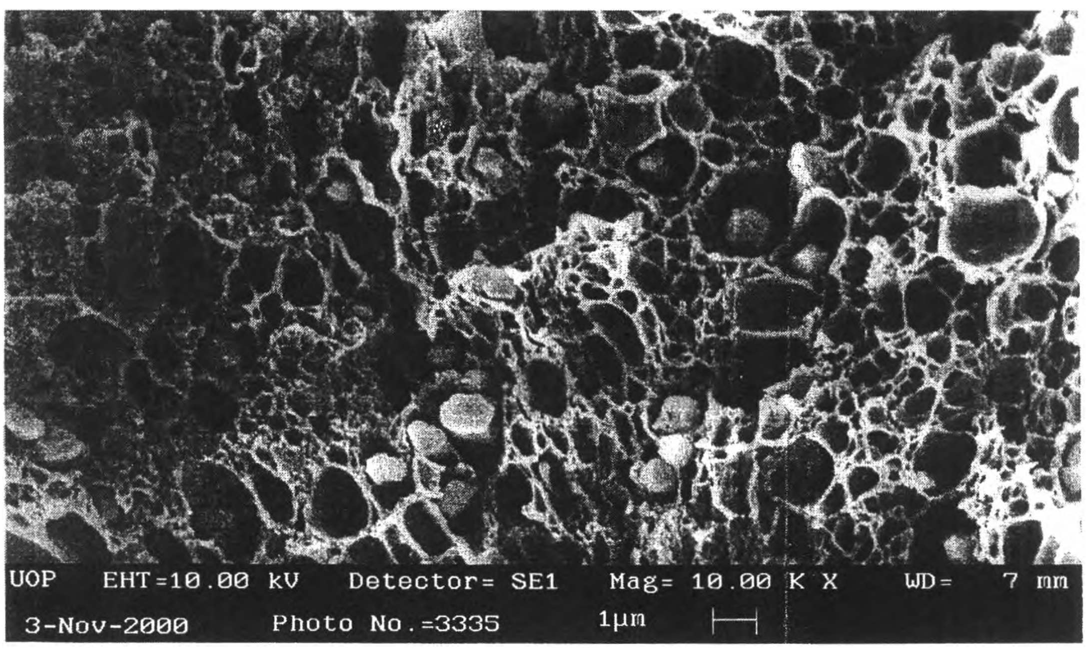


**Figure 4.1** The morphology of AgX/cellulose acetate mixed matrix membrane

Figure 4.1 shows that zeolite particles incorporation in cellulose acetate polymer on the porous support layer-not active skin layer appeared small channels or microvoids around zeolite-polymer surfaces as a result of partial incompatibility between the polymer chains and the zeolitic framework on the support layer of the MMMs. This result agreed with the experimental by Suer *et al*. (1994).

4.2.2 Cellulose Acetate Membrane

The porous support layer morphology of cellulose acetate membrane in Figure 4.2 was characterized by SEM (Sawyer and Grubb, 1996) to compare with the porous support layer morphologies of zeolites/cellulose acetate mixed matrix membrane.

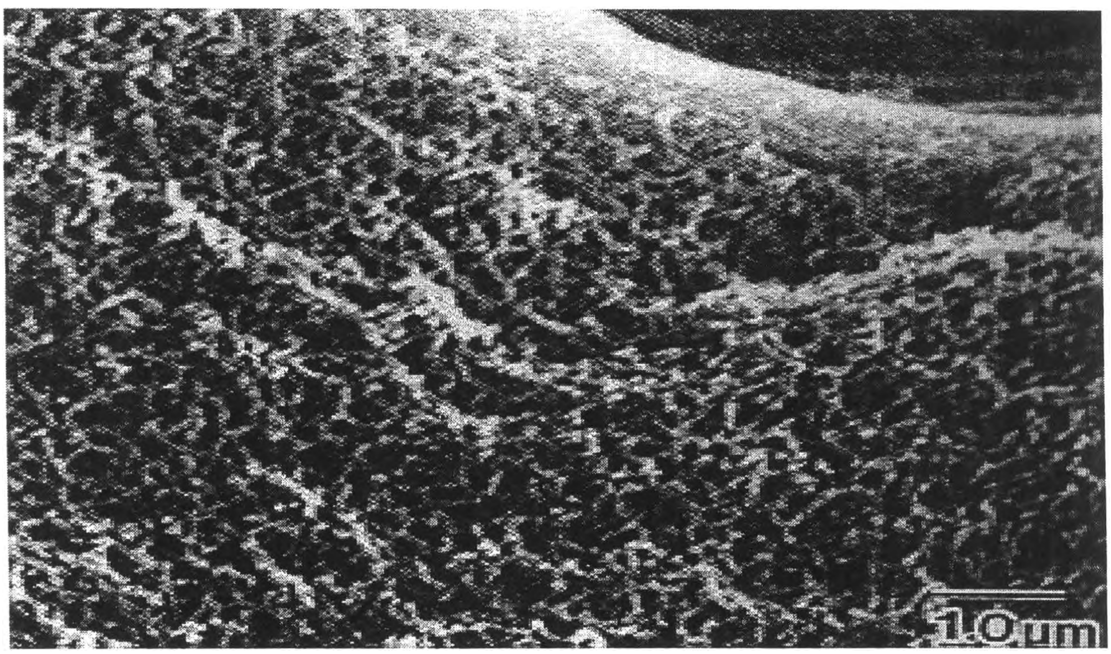


**Figure 4.2** The porous support layer morphology of asymmetric cellulose acetate membrane

## 4.3 The Permeability and Selectivity of Gases on Mixed Matrix Membranes

The results in Table 4.1 demonstrate that NaX-zeolite, AgX-zeolite and silicalite have the same selectivity for olefins over paraffins as cellulose acetate so that these adsorptive fillers were used to incorporate with cellulose acetate to develop the permeability and selectivity of gas through the mixed matrix membranes.

### 4.3.1 NaX-Zeolite/Cellulose Acetate Mixed Matrix Membranes

#### *4.3.1.1 Transport Gases of Ethylene, Ethane and Nitrogen*

The permeabilities of ethylene, $P_{C2H4}/\delta$; ethane, $P_{C2H6}/\delta$ and nitrogen, $P_{N2}/\delta$ and the calculated selectivity of ethylene to ethane, $P_{C2H4}/P_{C2H6}$ of NaX-zeolite/cellulose acetate mixed matrix membranes comprising of NaX at 10 and 20 wt% in comparison to pure cellulose acetate membrane are summerized in Table 4.2.

**Tabel 4.2** The permeability and selectivity of gases on cellulose acetate membrane and on NaX at 10 and 20 wt% /cellulose acetate mixed matrix membrane for $C_2H_4/C_2H_6$ separation.

| **Membrane Type** | **Selectivity, $P_i/P_j$** | | | **Permeability, $P/\delta$ $10^{-8}$( $cm^3$*STP/ $cm^2$*sec*cmHg)** | | |
|---|---|---|---|---|---|---|
| | $C_2H_4/C_2H_6$ | $C_2H_4/N_2$ | $C_2H_6/N_2$ | $C_2H_4$ | $C_2H_6$ | $N_2$ |
| CA | 1.23 | 0.58 | 0.47 | 1.93 ± 0.03 | 1.56 ± 0.03 | 3.30 ± 0.06 |
| 10wt% NaX/CA | 0.95 | 0.33 | 0.35 | 1.80 ± 0.02 | 1.91 ± 0.01 | 5.44 ± 0.01 |
| 20wt% NaX/CA | 0.42 | 0.30 | 0.71 | 2.30 ± 0.07 | 5.45 ± 0.09 | 7.66 ± 0.17 |

The result in Table 4.2 shows that the permeability of ethylene, $P_{C2H4}/\delta$ on cellulose acetate membrane was higher than the permeability of ethane, $P_{C2H6}/\delta$. It was selective for ethylene over ethane. However, in cases of NaX/cellulose acetate mixed matrix membranes, the permeability of ethylene was lower than the permeability of ethane. In addition, the permeabilty of nitrogen was highest for both 10 and 20 wt% NaX/cellulose acetate mixed matrix membranes in comparison to the permeabilities of ethylene and ethane. A possible reason may be due to the fact that the smaller molecule of $N_2$ may easily diffuse and pass through the small channels created around zeolite-polymer surfaces in the support layer as confirmed by SEM result in Figure 4.1 Therefore, zeolite particles could induce a cave-like porous structure into which they may fit. When the channel network created may mature and connect separate cave-like voids to provide an alternate path for smaller molecules (Suer *et al.*, 1993).

However, the 10 and 20 wt% NaX/Cellulose acetate mixed matrix membranes exhibited reverse selectivity of ethylene to ethane in comparison to the pure cellulose acetate membrane since the selectivity of ethylene to ethane was lower than one. The reason of reverse selectivity was not clear understanding of the mechanism. However, two possible reasons of this reverse selectivity may be given as follows: NaX-zeolite and cellulose acetate polymers do not have compatible permeability coefficients. Besides, NaX are more selective for ethylene over ethane than cellulose acetate. Another, NaX-zeolite may change the membrane morphology of cellulose acetate. This change could enhance the selective membrane for ethane over ethylene-decreasing the selectivity of ethylene to ethane. This change is found to be dependent on the amount of NaX loaded in the membrane matrix. This effect can be illustrated in Figure 4.3.

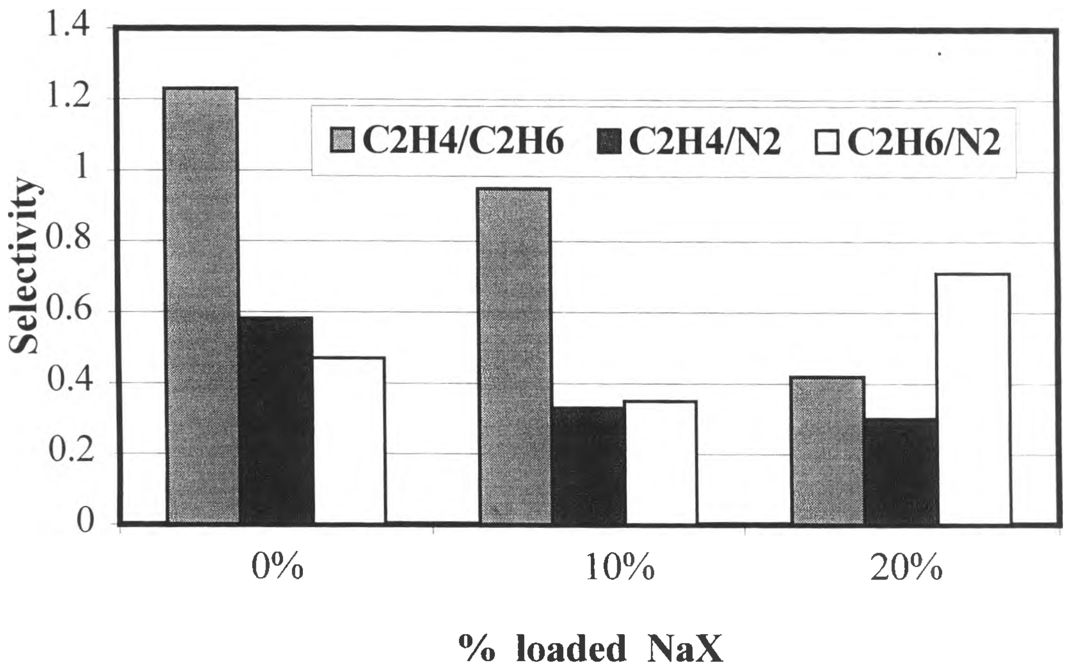


**Figure 4.3** Selectivity of ethylene to ethane vs % loaded NaX of NaX-zeolite/cellulose acetate mixed matrix membrane

*4.3.1.2 Transport Gases of Propylene, Propane and Nitrogen*

The permeabilities of propylene, $P_{C3H6}/\delta$; propane, $P_{C3H8}/\delta$ and nitrogen , $P_{N2}/\delta$ and the calculated selectivity of propylene to propane, $P_{C3H6}/ P_{C3H8}$ on NaX-zeolite/cellulose acetate mixed matrix membranes comprising of NaX at 5, 10 and 20 wt% in comparison to pure cellulose acetate membrane are summarized in Table 4.3.

**Tabel 4.3** The permeability and selectivity of gases on cellulose acetate membrane and on NaX at 5 , 10 and 20 wt% /cellulose acetate mixed matrix membrane for $C_3H_6/C_3H_8$ separation.

| Membrane Type | Selectivity, $P_i/P_j$ | | | Permeability, P/δ $10^8$(cm$^3$*STP/cm$^2$*sec*cmHg) | | |
|---|---|---|---|---|---|---|
| | $C_3H_6/C_3H_8$ | $C_3H_6/N_2$ | $C_3H_8/N_2$ | $C_3H_6$ | $C_3H_8$ | $N_2$ |
| CA | 1.77 | 0.25 | 0.14 | 0.83 ± 0.01 | 0.47 ± 0.01 | 3.30 ± 0.06 |
| 5 wt% NaX/CA | 0.91 | 0.47 | 0.51 | 1.86 ±0.003 | 2.04 ±0.005 | 3.93 ± 0.06 |
| 10wt% NaX/CA | 0.63 | 0.56 | 0.89 | 2.25 ± 0.05 | 3.60 ± 0.06 | 4.02 ± 0.08 |
| 20wt% NaX/CA | 0.58 | 0.70 | 1.21 | 5.66 ± 0.04 | 9.76 ± 0.1 | 8.09 ± 0.03 |

The result in Table 4.3 shows that the permeability of propylene, $P_{C3H6}/\delta$ on cellulose acetate membrane was higher than the permeability of propane, $P_{C3H8}/\delta$. It was selective for propylene over propane. However, in cases of NaX/cellulose acetate mixed matrix membranes, the permeability of propylene was lower than the permeability of propane and the Figure 4.4 shows that the selectivity of propylene to propane was dependent on the amount of NaX-zeolite loaded on the membrane matrix and lower than one. It means that NaX-zeolite affected reverse selectivity of propylene to propane. The reasons of reverse selectivity of propylene to propane were similar to in the case of ethylene/ethane separation in the previous result.

Furthermore, the permeabilities of propylene, propane and nitrogen through NaX-zeolite/cellulose acetate mixed matrix membranes increased in comparison to cellulose acetate membrane. The reason of this result could be given as follows: the spaces or the voids between the polymer and zeolite phases in the support layer in Figure 4.1 could allow the gases to pass easier and the active skin layer of the mixed matrix membranes could be thinner than cellulose acetate membrane.

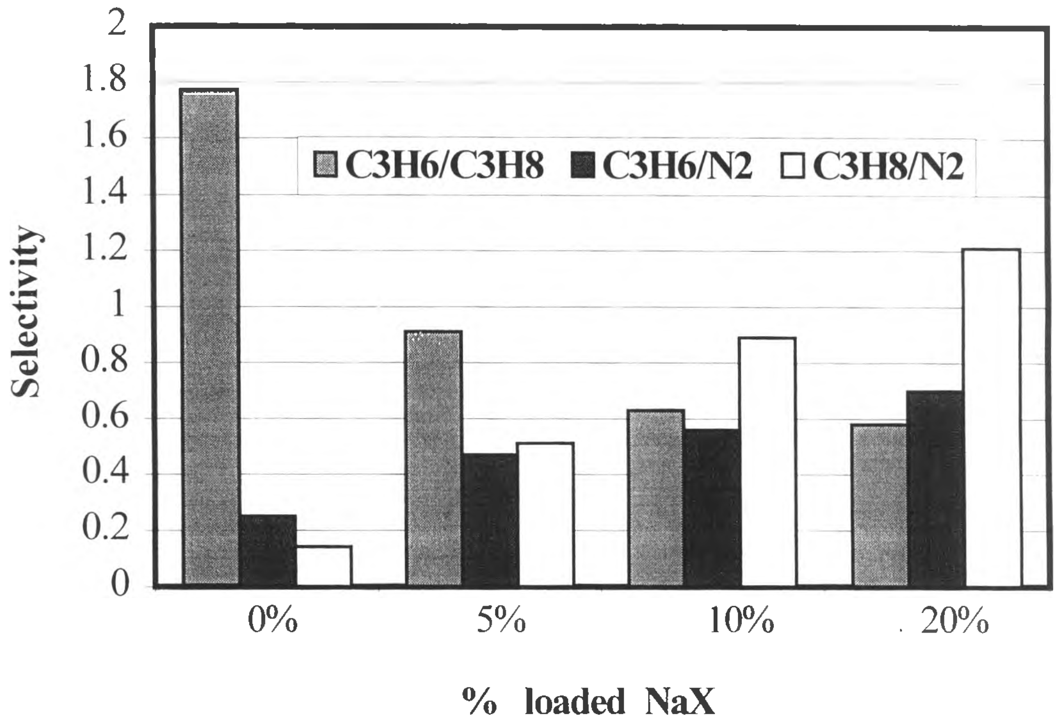


**Figure 4.4** Selectivity of propylene to propane vs % loaded NaX of NaX-zeolite/cellulose acetate mixed matrix membrane

4.3.2 AgX-Zeolite/Cellulose Acetate Mixed Matrix Membranes

Many studies from literatures using silver ion ($Ag^+$) incorporated into polymer matrices showed that the permeability of gases and selectivity for separation were enhanced by the facilitated transport mechanism. Therefore, AgX-zeolite was used as the adsorptive filler incorporated into cellulose acetate polymer matrices.

**Tabel 4.4** The permeability and selectivity of gases on cellulose acetate membrane and AgX at 5 , 10 and 20 wt% /cellulose acetate mixed matrix membrane for $C_3H_6/C_3H_8$ separation.

| Membrane Type | Selectivity, $P_i/P_j$ | | | Permeability, $P/\delta$ $10^8(cm^3*STP/cm^2*sec*cmHg)$ | | |
|---|---|---|---|---|---|---|
| | $C_3H_6$ /$C_3H_8$ | $C_3H_6$ /$N_2$ | $C_3H_8$ /$N_2$ | $C_3H_6$ | $C_3H_8$ | $N_2$ |
| CA | 1.77 | 0.25 | 0.14 | 0.83 ± 0.01 | 0.47 ± 0.01 | 3.30 ± 0.06 |
| 5 wt% AgX/CA | 0.49 | 0.40 | 0.83 | 1.48 ± 0.009 | 3.04 ± 0.006 | 3.67 ± 0.02 |
| 10wt% AgX/CA | 0.47 | 0.52 | 1.11 | 1.79 ± 0.02 | 3.83 ± 0.05 | 3.46 ± 0.06 |
| 20wt% AgX/CA | 0.34 | 0.56 | 1.62 | 2.01 ± 0.008 | 5.85 ± 0.03 | 3.61 ± 0.02 |

The results as shown in Table 4.4 illustrate that the permeability of propylene was lower than the permeability of propane. They were reverse selective for propylene over propane. In addition, Figure 4.5 shows that the selectivity of propylene to propane on AgX-zeolite/cellulose acetate mixed matrix membranes was dependent on the amount of AgX-zeolite loaded on the membrane matrix and lower than one. It meant that the AgX-zeolite affected reverse selectivity of propylene to propane in comparison to cellulose acetate membrane. The reason of reverse selectivity was not clear understanding of the mechanism. However, this would be explained similarity as NaX-zeolite/cellulose acetate mixed matrix membrane. Furthermore, the permeabilities of propylene, propane and nitrogen through AgX-zeolite/cellulose acetate mixed matrix membranes also increased as NaX-zeolite/cellulose acetate mixed matrix membranes in comparison to cellulose acetate membrane. The reason of this result could be given similarity as NaX-zeolite/cellulose acetate mixed matrix membranes.

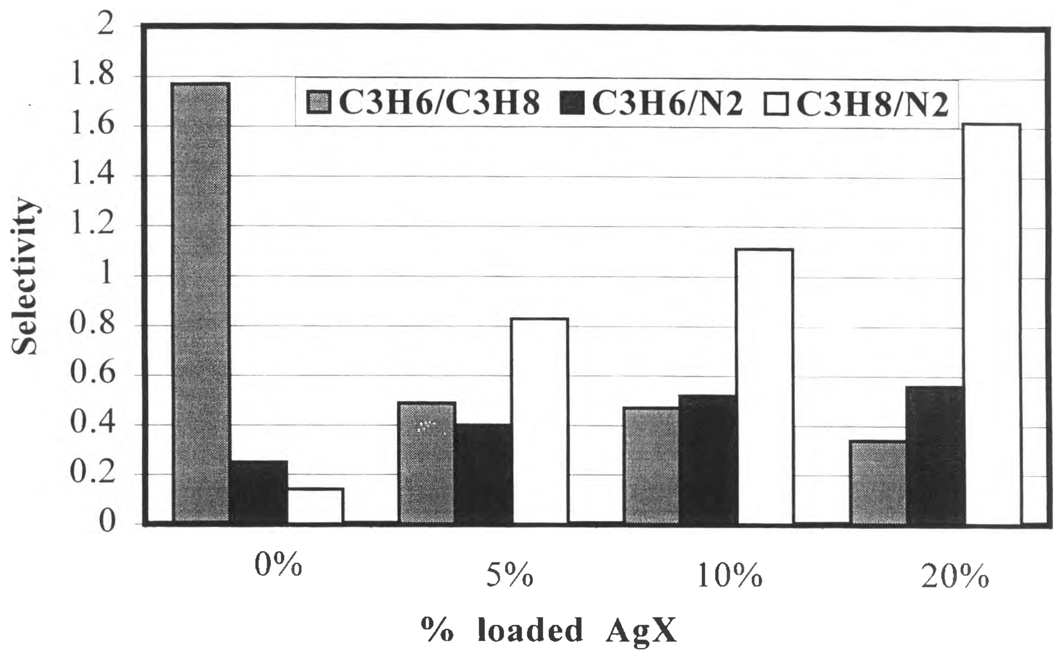


**Figure 4.5** Selectivity of propylene to propane vs % loaded AgX of AgX-zeolite/cellulose acetate mixed matrix membrane

4.3.3 Silicalite/Cellulose Acetate Mixed Matrix Membranes

Silicalite, like NaX-zeolite and AgX-zeolite , was also used as the adsorptive filler incorporated into cellulose acetate polymer matrices since the previous study by Kulprathipanja *et al.* (1988b and 1992) showed that this type of mixed matrix membrane could enhance the selectivity for $O_2/N_2$ separation in comparison to the pure cellulose acetate membrane. Furthermore, the present study from Table 4.1 shows that it was also a little selective for olefin-hexene over paraffin-n-hexane.

**Tabel 4.5** The permeability and selectivity of gases on cellulose acetate membrane and slicalite at 5 , 10 and 20 wt% /cellulose acetate mixed matrix membrane for $C_3H_6/C_3H_8$ separation.

| Membrane Type | Selectivity, $P_i/P_j$ | | | Permeability, P/δ $10^8(cm^3*STP/cm^2*sec*cmHg)$ | | |
|---|---|---|---|---|---|---|
| | $C_3H_6$ $/C_3H_8$ | $C_3H_6$ $/N_2$ | $C_3H_8$ $/N_2$ | $C_3H_6$ | $C_3H_8$ | $N_2$ |
| CA | 1.77 | 0.25 | 0.14 | 0.83 ± 0.01 | 0.47 ± 0.01 | 3.30 ± 0.06 |
| 5 wt% Silicalite/CA | 0.9 | 0.69 | 0.77 | 8.11 ±0.016 | 9.00 ± 0.02 | 11.67 ± 0.01 |
| 10wt% Silicalite/CA | 0.83 | 0.52 | 0.63 | 5.96 ± 0.04 | 7.22 ± 0.05 | 11.46 ± 0.008 |
| 20wt% Silicalite/CA | 2.29 | 0.47 | 0.21 | 3.56 ± 0.004 | 1.56 ± 0.003 | 7.52 ± 0.1 |

Table 4.5 shows that silicalite, unlike NaX-zeolite and AgX-zeolite, had effect to distinct decreasing of the permeabilities of gases when the amount of loaded silicalite was increased from 5 wt% to 20 wt%. Although the permeabilities of gases decreased when the amount of silicalite increased, their permeabilities were higher than through pure cellulose acetate.

Furthermore, it was very interesting on the 20 wt% silicalite/cellulose acetate mixed matrix membrane. The permeability of propylene to propane was higher than the permeability of propane. They were selective for propylene to propane. The selectivity of propylene to propane was enhanced in comparison to pure cellulose acetate membrane as shown in Figure 4.6. However, this result was different in cases of 5 and 10 %wt silicalite/cellulose acetate mixed matrix membrane. The permeability of propylene was close to the permeability of propane.

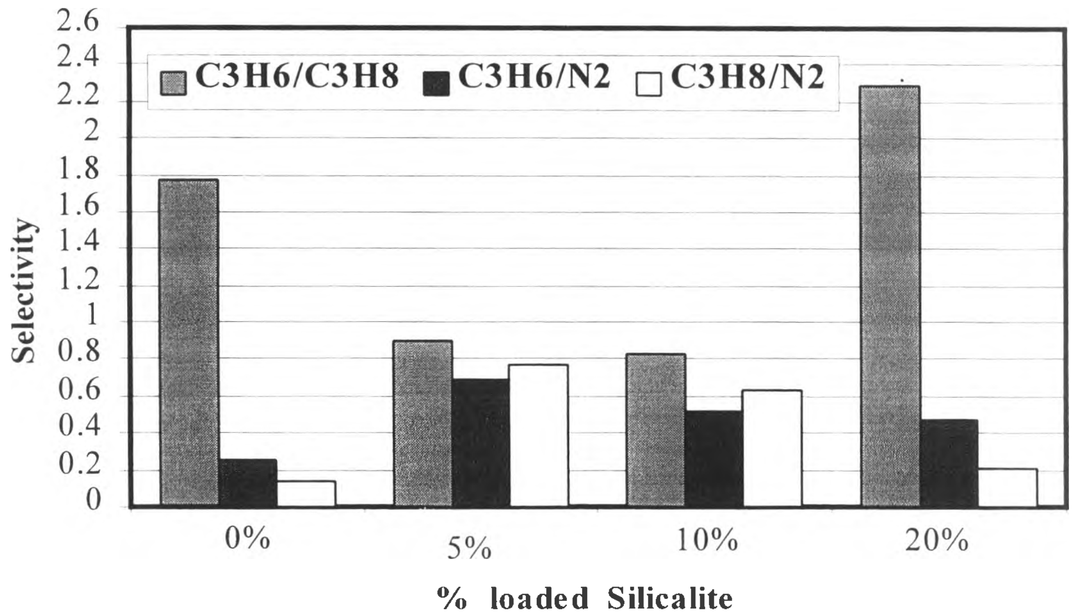


**Figure 4.6** Selectivity of propylene to propane vs % loaded silicalite of silicalite/cellulose acetate mixed matrix membrane

The reason of enhancement in selectivities may be given as follows: silicalite, unlike NaX-zeolite and AgX-zeolite, are hydrophobic polymer and is slightly selective for olefin over paraffin as the results shown in Table 4.1 in comparison to NaX-zeolite and AgX-zeolite. This property might affect the interaction between cellulose acetate polymer and silicalite or permeate gases and silicalite when the amount of loaded silicalite was sufficient. On the other hand, 5 wt% and 10 wt% of silicalite/cellulose acetate mixed matrix membranes show that they were not selective for propylene over propane and their selectivities were nearly one therefore no the separation occurred. The reasons of differential selectivity of propylene to propane between 20 wt% silicalite/cellulose acetate mixed matrix membrane and 5 and 10 wt%/cellulose acetate mixed matrix membranes may be given as follows: since silicalite was slightly selective for olefin as the results shown in Table 4.1, it might not affect the interaction between permeate gases and silicalite. Furthermore, the amount of loaded silicalite at 5 and 10 wt% in cellulose acetate was not enough to have effect on interaction as 20 wt% silicalite/cellulose acetate mixed matrix membrane.