CHAPTER IV
RESULTS AND DISCUSSION

4.1 Silicone Rubber/Poly (ethylene glycol) on Porous Polysulfone Support

The permeabilities of ethylene, P_{C2H4}; ethane, P_{C2H6} and nitrogen, P_{N2} and the selectivity of ethylene to ethane, P_{C2H4}/ P_{C2H6} on SR/PS, SR/PEG/PS and SR/PEG-PS are presented in Table 4.1.

Table 4.1 The permeability and selectivity of gases on SR/PS, SR/PEG/PS and SR/PEG-PS

Membrane Type	Selectivity	Permeability ($cm^3STP/(cm^2$-s-cmHg))		
	$P_{(C2H4)}/P_{(C2H6)}$	$P_{(C2H4)}/\delta*10^6$	$P_{(C2H6)}/\delta*10^6$	$P_{(N2)}/\delta*10^7$
SR/PS	0.86	7.19±0.152	8.34±0.07	9.86±0.391
SR/PEG/PS	1.7	0.79±0.010	0.47±0.003	0.44±0.017
SR/PEG-PS	2.38	0.4±0.02	0.17±0.002	0.22±0.318

The obtained results showed the permeability of three gases in all types of membrane. The permeabilities of gases are both controlled by the gas solubility and the gas diffusivity. Silicone rubber membrane exhibits high permeability for C_2H_6 due to both high solubility and high gas diffusivity. The solubility of gas depends on its critical temperature. Due to the similar size of ethylene and ethane, their diffusion through membrane are not different. Then, the olefin/paraffin separation is not caused by diffusion mechanism. The separation should be controlled by solubility mechanism.

It can be seen that both membranes which contained PEG had higher selectivity for olefin as compared to the silicone rubber membrane. The selectivity of two membranes was significantly improved when PEG was added. In the previous work, it was believed that PEG not only had the capacity of altering the permeability of silicone rubber, but also acted on the polymeric support material (SR) by softening it and cause its pore to shrink (Kulprathipanja, 1988). For this study, the results indicated the effect of PEG to olefin through the high solubility of olefin in PEG. PEG enhances the solubility coefficient of C_2H_4 by passing C_2H_4 with a higher rate than the membrane without polyethylene glycol. These can be seen by the higher permeability of gas through SR/PS than SR/PEG/PS. Besides solubility, PEG also swelled PS. Although this effect showed a decrease in permeability, the separation factors were enhanced when PEG was added to the membrane.

4.2 Silicone Rubber/Ag-zeolite on Porous Polysulfone Support

Ag-zeolite was added in the casting solution to form suspended solution before coating on the porous polysulfone support. The permeability and selectivity are shown in Table 4.2.

Table 4.2 The permeability and selectivity of gases on SR/PS and SR/Ag-zeolite/PS

Membrane Type	Selectivity	Permeability ($cm^3STP/(cm^2$-s-cmHg))		
	$P_{(C2H4)}/P_{(C2H6)}$	$P_{(C2H4)}/\delta*10^6$	$P_{(C2H6)}/\delta*10^6$	$P_{(N2)}/\delta*10^7$
SR/PS	0.86	7.19±0.152	8.34±0.07	9.86±0.391
SR/Ag-LZ/PS	0.84	4.14±0.042	4.9±0.07	5.14±0.077
SR/Ag-A/PS	0.87	4.87±0.047	5.6±0.032	6.05±0.099
SR/Ag-X/PS	0.88	3.78±0.083	4.32±0.067	4.13±0.083

This table showed the comparison of SR with three types of SR/Ag-zeolite/PS membrane. However, all three types of Ag-zeolite showed the same selectivity as SR. There was no any selectivity enhancement from three types of Ag-zeolite. The reason was probably because SR with the very good physical and chemical properties had the highest gas permeability for both olefin and paraffin (Yang and Hsiue, 1997). When a gas passes through the membrane, Ag^+ can reversibly form complex with olefin, the transport mechanism could be describe as:

$$Ag^+(s) + Olefin(g) \Leftrightarrow Ag^+Olefin(s) \tag{4.1}$$

Ag^+ helping the olefin to transport across the membrane. Paraffin can be transferred across the membrane only by a simple physical dissolution-diffusion phenomenon. Because of the high gas permeability of both olefin and paraffin on SR phase, olefin passes through the membrane without forming any complex with another Ag^+. This prevents the reverse reaction of Ag ion and olefin.

The selectivity of SR/Ag-zeolite/PS is the same as SR/PS because Ag-zeolite was saturated by the permeate gas and cause the time lag in reaching steady state of the membrane. Hence, the membrane selective was the same as when the Ag-zeolite was not present (Kulprathipanja *et al.,* 1986). It cannot be seen any effect of Ag-zeolite on olefin and paraffin separation. The facilitated transport of olefin and paraffin with Ag^+ on porous polysulfone support is shown in Figure 4.1.

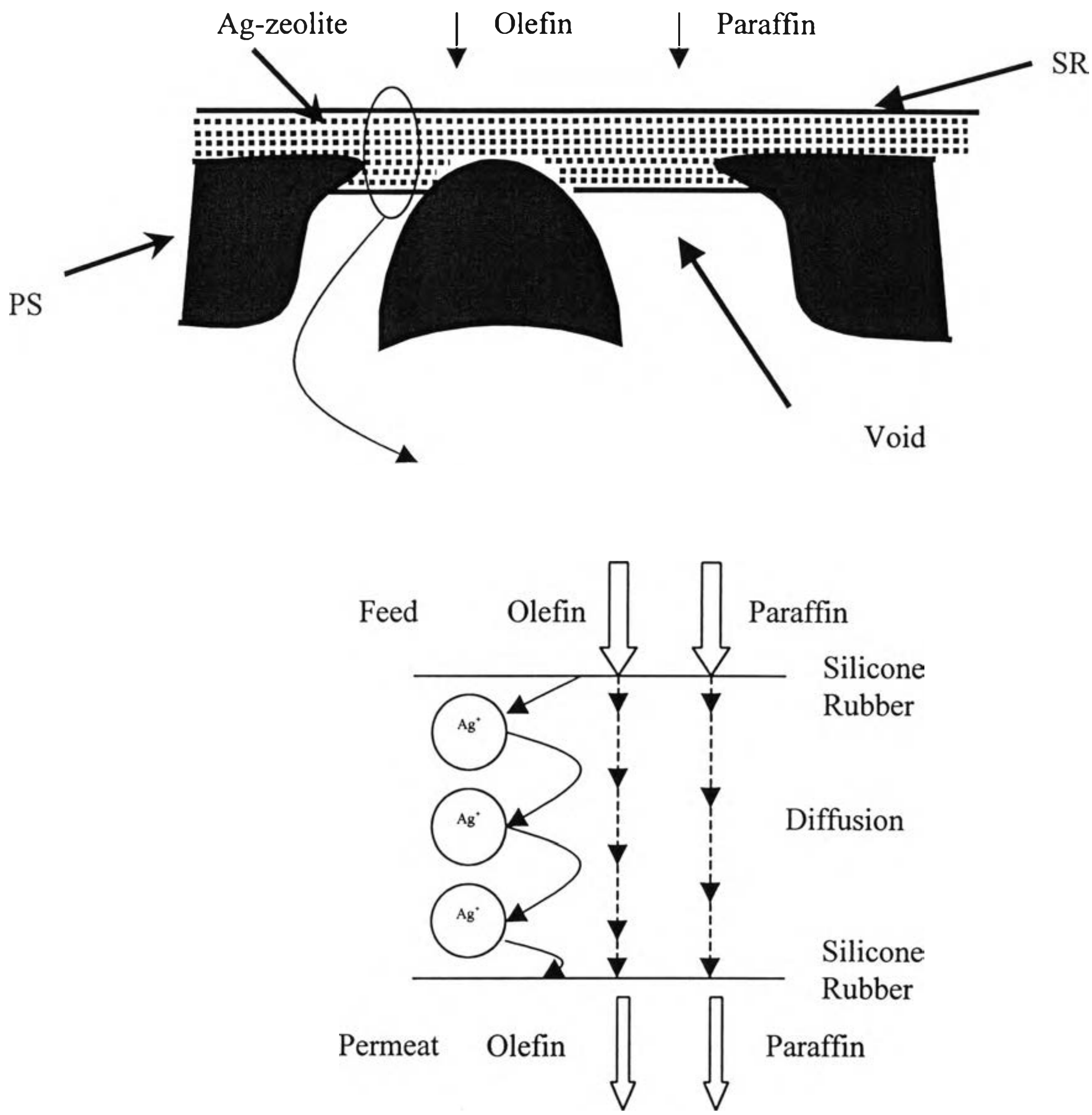

Figure 4.1 Facilitated transport of olefin and paraffin with Ag^+ on porous polysulfone membrane (SR/Ag-zeolite/PS).

From the results, the permeability of SR/Ag-zeolite/PS in all gases decreased when compared to the membrane that did not contain Ag-zeolite. Referring to Eq. 2.3 and Eq. 2.4, the permeability is inversely proportional of the membrane thickness. If the thickness of membrane increases, the permeability decreases. In this case, the permeability is decreased by Ag-zeolite. But the selectivity did not improve due to the strong effect of silicone rubber in the membrane. These indicated that Ag-zeolite on porous polysulfone membrane did not enhance olefin and paraffin separation.

When PEG was treated on porous polysulfone support, the permeability and selectivity of C_2H_4, C_2H_6 and N_2 are shown in Table 4.3.

Table 4.3 The permeability and selectivity of gases on SR/PEG-PS and SR/Ag-zeolite/PEG-PS

Membrane Type	Selectivity	Permeability ($cm^3STP/(cm^2$-s-cmHg))		
	$P_{(C2H4)}/P_{(C2H6)}$	$P_{(C2H4)}/\delta*10^6$	$P_{(C2H6)}/\delta*10^6$	$P_{(N2)}/\delta*10^7$
SR/PEG-PS	2.38	0.4±0.02	0.17±0.002	0.22±0.318
SR/Ag-LZ/PEG-PS	1.89	1.56±0.033	0.81±0.002	0.79±0.188
SR/Ag-A/PEG-PS	1.91	0.56±0.004	0.29±0.002	0.35±0.007
SR/Ag-X/PEG-PS	2	1.16±0.023	0.58±0.008	0.68±0.086

The selectivity of C_2H_4 to C_2H_6 on SR/Ag-zeolite/PEG-PS and SR/PEG-PS is very comparable. Ag-zeolite added in the membrane does not increase the olefin and paraffin selectivity due to the strong effect of PEG in the membrane. Olefin has high permeability due to the high solubility of olefin in PEG since the critical temperature is the scaling factor for the solubility. We treated the porous polysulfone with PEG before coating. Porous polysulfone was soak by PEG and PEG also swelled the porous polysulfone. And then casting solution was coated on the top layer of treated polysulfone. After curing the membrane in hot air for 1 hour, we got second layers on the porous polysulfone membrane. First layer is SR/Ag-zeolite and second layer is PEG-PS.

First, a gas was passed to the first layer (SR/Ag-zeolite) by the facilitated transport of Ag^+ in the membrane. Ag^+ helped the olefin move across the membrane. The facilitated transport of olefin and paraffin with Ag^+

on treated polysulfone membrane (SR/Ag-zeolite/PEG-PS) are shown in Figure 4.2.

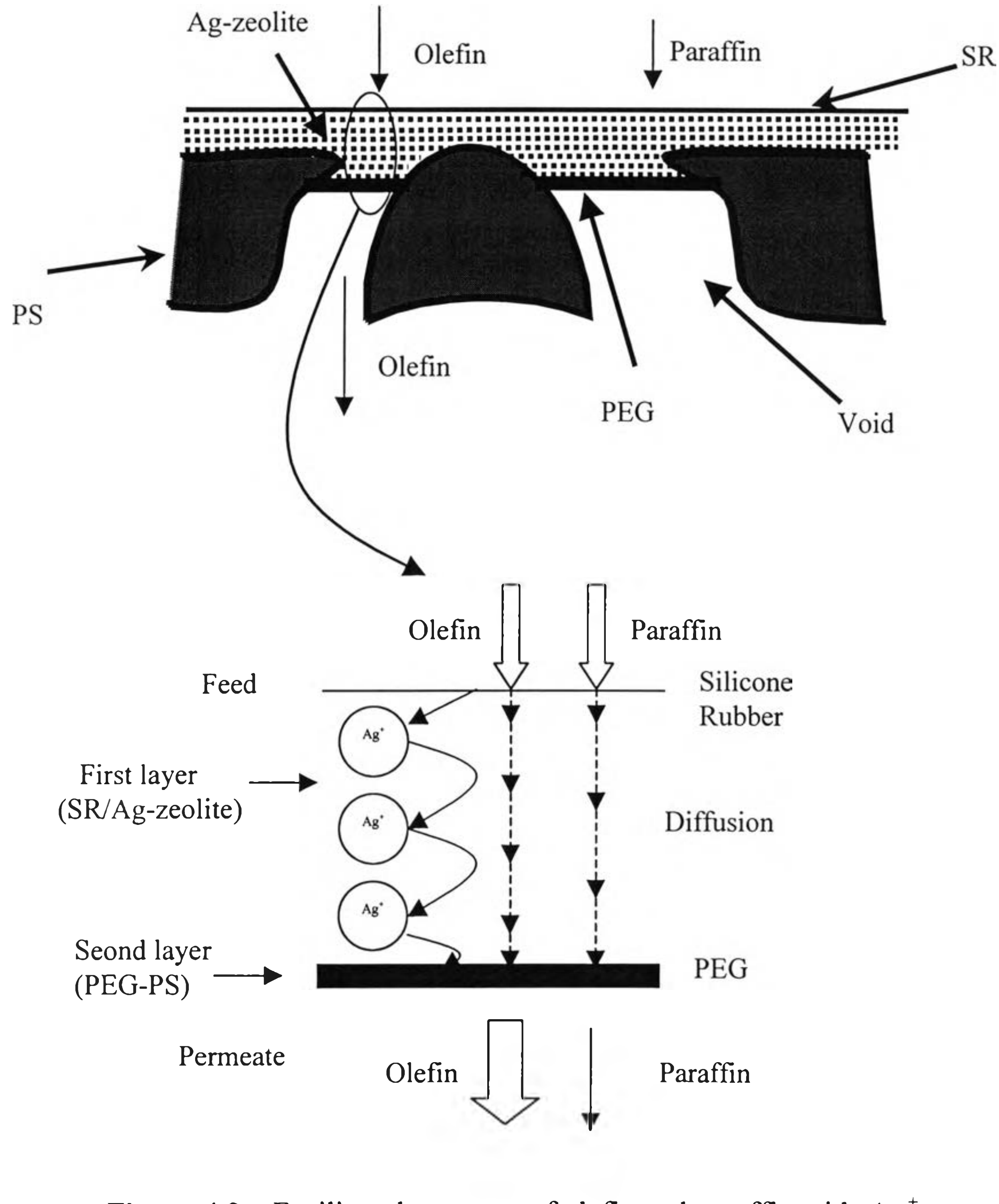

Figure 4.2 Facilitated transport of olefin and paraffin with Ag^+ on treated polysulfone membrane (SR/Ag-zeolite/PEG-PS).

Second, the permeate gas caught the Ag-zeolite to form olefin-silver (I) ion complex after that Ag-zeolite was not affected for the separation at all due to the Ag-zeolite was saturated with the permeate gas. Then, the membrane selectivity of SR/Ag-zeolite/PEG-PS was the same as without Ag-zeolite. Third, gas was passed through the second layer (PEG-PS) by dissolution-diffusion phenomenon. In this layer, PEG swelled the pores of the porous polysulfone. This can be seen by the decrease in permeability of both gases when compared to silicone rubber alone. These again showed the effect of PEG on SR/Ag-zeolite/PEG-PS.

For the next 3 membranes, water and Ag-zeolite were added in the casting solution before coating to obtain SR/Ag-zeolite(H_2O)/PEG-PS. The permeability and selectivity are shown in Table 4.4.

Table 4.4 The permeability and selectivity of gases on SR/PEG-PS and SR/Ag-zeolite (H_2O)/PEG-PS

Membrane Type	Selectivity	Permeability ($cm^3STP/(cm^2$-s-cmHg))		
	$P_{(C2H4)}/P_{(C2H6)}$	$P_{(C2H4)}/\delta*10^6$	$P_{(C2H6)}/\delta*10^6$	$P_{(N2)}/\delta*10^7$
SR/PEG-PS	2.38	0.4±0.02	0.17±0.002	0.22±0.318
SR/Ag-LZ(H_2O)/PEG-PS	1.77	1.66±0.011	0.94±0.006	1.1±0.159
SR/Ag-A(H_2O)/PEG-PS	2	1.24±0.009	0.62±0.003	0.61±0.045
SR/Ag-X(H_2O)/PEG-PS	1.69	1.69±0.042	1.01±0.018	1.47±0.088

For this study, water molecules were added in the SR/Ag-zeolite/PEG-PS membrane. In general, when water is added in the membrane, water molecules may substitute for olefin in the olefin-silver (I) ion complex. The membrane allows olefin to rapidly diffuse through and form a complex with another silver (I) ion. And then the silver (I) ion diffuses back to the feed side and forms a complex with other olefin molecules. These mechanisms explain how water in the membrane helps the olefin move across the membrane and increase the olefin and paraffin separation. In this works, water did not have this ability. The reason was probably because silicone rubber had the high gas permeability for both olefin and paraffin. Olefin could form a complex with silver (I) ion in the membrane for a long period of time and then olefin silver (I) ion complex diffused to the permeate side. This mechanism prevented the reverse reaction of olefin-silver (I) ion complex. Paraffin can transfer across the membrane only by the simple physical dissolution-diffusion phenomenon. The results showed the permeability and selectivity of both olefin and paraffin were the same as the membrane without water. From this reason, the effect of water and Ag-zeolite on SR/Ag-zeolite(H_2O)/PS membrane was not observed. The only effect for olefin and paraffin separation came from PEG. Because PEG had the high solubility for olefin and PEG also desifined the porous polysulfone membrane. This can be seen by the permeability of olefin and paraffin was decreased and the selectivity was significantly improved when compared to the SR alone.

Table 4.5 shows the comparison of $AgNO_3$, Na-X, and Ag-X incorporated in silicone rubber on treated polysulfone membrane.

Table 4.5 The permeability and selectivity of gases on SR/PEG-PS, SR/$AgNO_3$/PEG-PS, SR/Na-X/PEG-PS and SR/Ag-X/PEG-PS

Membrane Type	Selectivity	Permeability (cm^3STP/(cm^2-s-cmHg))		
	$P_{(C2H4)}/P_{(C2H6)}$	$P_{(C2H4)}/\delta*10^6$	$P_{(C2H6)}/\delta*10^6$	$P_{(N2)}/\delta*10^7$
SR/PEG-PS	2.38	0.4±0.02	0.17±0.002	0.22±0.318
SR/$AgNO_3$/PEG-PS	1.91	0.99±0.006	0.52±0.782	3.1±0.052
SR/Na-X/PEG-PS	1.48	0.81±0.006	0.55±0.004	1.66±0.095
SR/Ag-X/PEG-PS	2	1.16±0.023	0.58±0.008	0.68±0.086

The results of the selectivities of SR/$AgNO_3$/PEG-PS, SR/Na-X/PEG-PS and SR/Ag-X/PEG-PS were not considerably different. Although the hydrophilic Na-X is selective to olefin, the enhancement of olefin separation is mostly attributed to PEG. Because PEG is high soluble for olefin and swells porous polysulfone.

Selectivity of $AgNO_3$ is not different from selectivity of Ag-X. As in previous discussion, PEG has more effect than Ag^+. Another reason is that $AgNO_3$, Ag-X, Ag-LZ and Ag-A were added in casting solution in order to provide Ag^+ ion as a carrier, so the forms of silver compound do not have any effect on selectivity. Moreover, the similar selectivity of Ag-X and Na-X confirm the great effect of PEG on olefin and paraffin separation.