

## CHAPTER IV RESULTS AND DISCUSSION



### 4.1 Silicone Rubber Membrane

Permeances were determined from steady-state permeation rates of CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub> and N<sub>2</sub> through the multicomponent membranes. The permeation rate measurements were made with all gases at room temperature and calculated using Equation 2.1. The properties of gas studied are presented in Table 4.1 and the experimental results are presented in Table 4.2.

Table 4.1 Gas Properties

	Critical temperature (K)	Kinetic diameter (Å)
C <sub>2</sub> H <sub>6</sub>	305.4	4.443
CO <sub>2</sub>	304.2	3.941
N <sub>2</sub>	126.2	3.798
H <sub>2</sub>	33.3	2.827

Table 4.2 Gas Permeance for Silicone Rubber Membrane

Backing	Permeance <sup>a</sup>			
	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub>	N <sub>2</sub>
Ultem-1000	4.46	1.45	1.05	0.35
20% wt polyacrylonitrile	5.17	1.55	1.07	0.45
17% wt polyacrylonitrile	4.49	1.3	0.84	0.38
Polysulfone	1.27	0.78	0.39	0.13
6F-Polysulfone with silicone	6.07	1.87	1.21	0.5

<sup>a</sup> \* 10<sup>-5</sup> (cm<sup>3</sup>STP / cm<sup>2</sup>-sec-cm Hg)

It is seen that the values of permeance for the penetrant gases in all membranes decrease in the order: CO<sub>2</sub> > C<sub>2</sub>H<sub>6</sub> > H<sub>2</sub> > N<sub>2</sub>. The values of permeance for the above mentioned four gases do not correlated either with the kinetic diameter of the gas molecules, or with the critical temperature of these gases. This indicates that the permeance of silicone rubber to four gases studied is not controlled either by the gas diffusivity or the gas solubility in the polymer, but depends to different extents on both the diffusivity and solubility. Silicone rubber membrane exhibits a markedly higher permeance to CO<sub>2</sub> than to the other three gases. CO<sub>2</sub> has a high critical temperature and hence the high solubility in the silicone rubber membrane. The high permeance of silicone rubber membrane to CO<sub>2</sub> is due primarily to the high solubility of this gas in the silicone rubber membrane, since T<sub>c</sub> is a scaling factor for the solubility

(Shah *et al.*, 1986). In contrast, the high permeance of silicone rubber membrane to  $H_2$  is due to the small kinetic diameter of  $H_2$ . The solubility of  $H_2$  in silicone rubber membrane is very low, as is expected from its low critical temperature, and therefore it contributes only little to the permeance of silicone rubber membrane to this gas. The permeance of silicone rubber to  $C_2H_6$  and  $N_2$  appears to depend more on the solubility than on the diffusivity of these gases.

These results showed membranes that were more permeable to larger penetrant gases than to smaller penetrant. In general, increasing penetrant size results in lower diffusion coefficient that is in contrast with solubility coefficient. The solubility coefficients increase with penetrant size because large molecule are normally more condensable than smaller ones. This is probable due to their higher critical temperature and lower vapor pressure at ambient condition, which made them more susceptible to exist as liquids.

For comparison, selectivities, calculated by using Equation 2.3, of multicomponent membrane are presented in Table 4.3.

Table 4.3 Gas Selectivity for Silicone Rubber Membrane

Backing	Selectivity of $\text{CO}_2/\text{N}_2$	Selectivity of $\text{CO}_2/\text{H}_2$	Selectivity of $\text{CO}_2/\text{C}_2\text{H}_6$
Ultem-1000	12.59	4.25	3.07
20% wt polyacrylonitrile	11.45	4.85	3.34
17% wt polyacrylonitrile	11.94	5.36	3.46
Polysulfone	9.59	3.24	1.60
6F-Polysulfone with silicone	12.12	5.01	3.24

The obtained results showed the selectivities for  $\text{CO}_2/\text{N}_2$  were greater than  $\text{CO}_2/\text{H}_2$  and  $\text{CO}_2/\text{C}_2\text{H}_6$ , respectively. The selectivities of these membranes were improved when compared with porous support alone having no separation at all. It is found that the selectivities of all membranes are almost the same. This implied that there was no interaction between silicone rubber and backing and selectivity of the multicomponent was mainly controlled by the thin selective surface layer of silicone rubber on porous support.

## 4.2 Mixed Matrix Membrane of Silicone Rubber and Polyethylene Glycol

The gas permeances decrease in the following order of  $\text{CO}_2 > \text{C}_2\text{H}_6 > \text{H}_2 > \text{N}_2$  as illustrated in Table 4.4. In comparison with silicone rubber without PEG membrane, it is found that membranes with PEG exhibit lower gas permeances than membranes without PEG. This may be believed that PEG normally being plasticizer not only has the capacity of altering the permeability of silicone rubber with which it is mixed. but it also acts on the polymeric support material by softening it and causing its pore to shrink (Kulprathipanja, 1986).

Table 4.4 Gas Permeance for Mixed Matrix Membrane of Silicone Rubber and Polyethylene Glycol

Backing	Permeance <sup>a</sup>			
	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub>	N <sub>2</sub>
Ultem-1000	1.34	0.51	0.25	0.03
20% wt polyacrylonitrile	1.38	0.54	0.22	0.04
17% wt polyacrylonitrile	1.40	0.32	0.14	0.03
Polysulfone	0.42	0.09	0.04	0.01
6F-Polysulfone with silicone	2.15	0.55	0.22	0.08

<sup>a</sup> \* 10<sup>-5</sup> (cm<sup>3</sup>STP / cm<sup>2</sup>-sec-cm Hg)

The selectivities of membrane with PEG are presented in Table 4.5. It can be seen that the selectivities are significantly improved. For this study, polyethylene glycol enhances solubility coefficient by passing CO<sub>2</sub> in more rapid rate than membrane without polyethylene glycol. It is found that the hydroxyl groups, which present in each of the polyethylene glycol molecules, is the major determiner of solubility of CO<sub>2</sub> into a membrane. The O-H bond is strongly polar. This polarity induces the formation of London force arised from temporary dipole moment. Hence CO<sub>2</sub> molecules, which are more polar with relatively large molecule than H<sub>2</sub>, selectivity be sorbed into the membrane and diffuse through the polymeric matrix. This is in contrast with the gas permeation characteristic of the most membrane where relatively small molecules of a gas is selectively permeated from high to low pressure side.

Table 4.5 Gas Selectivity for Mixed Matrix Membrane of Silicone Rubber and Polyethylene Glycol

Backing	Selectivity of CO <sub>2</sub> /N <sub>2</sub>	Selectivity of CO <sub>2</sub> /H <sub>2</sub>	Selectivity of CO <sub>2</sub> /C <sub>2</sub> H <sub>6</sub>
Ultem-1000	47.82	5.41	2.64
20% wt polyacrylonitrile	35.91	6.39	2.53
17% wt polyacrylonitrile	42.27	10.09	4.35
Polysulfone	42.35	10.36	4.51
6F-Polysulfone with silicone	25.50	9.66	3.89

### 4.3 The Dependence of Selectivity on Polyethylene Glycol Composition

The CO<sub>2</sub>/H<sub>2</sub> selectivity and CO<sub>2</sub>/N<sub>2</sub> selectivity for polysulfone and 20% weight polyacrylonitrile backing are shown in Figures 4.1 – 4.2. It is found that the CO<sub>2</sub>/H<sub>2</sub> selectivity and CO<sub>2</sub>/N<sub>2</sub> selectivity is similar for both backings. The CO<sub>2</sub>/N<sub>2</sub> selectivity is presented as a function of percent weight of PEG while the CO<sub>2</sub>/H<sub>2</sub> selectivity is quite constant. The CO<sub>2</sub>/N<sub>2</sub> selectivity is observed to increase as the concentration of polar group in PEG increases. This is probably due to dipole-induced dipole interaction between polar group and CO<sub>2</sub>. CO<sub>2</sub>, polar molecule, can favor in this interaction while N<sub>2</sub>, being non-polar, cannot.

In case of the CO<sub>2</sub>/H<sub>2</sub> selectivity, we may consider in terms of diffusivity selectivity and solubility selectivity. Diffusion coefficient decreases

with increasing penetrant size. Therefore, for a polar-non-polar gas separation, diffusivity selectivity is always less than 1 (Diffusivity of CO<sub>2</sub>/Diffusivity of H<sub>2</sub> < 1). For overall selectivity to be greater than 1, the solubility selectivity must be significantly greater than one to offset the unfavorable diffusivity selectivity. This indicates that PEG not only enhances solubility of CO<sub>2</sub> but also makes polymer soften resulting in higher diffusivity for H<sub>2</sub>.



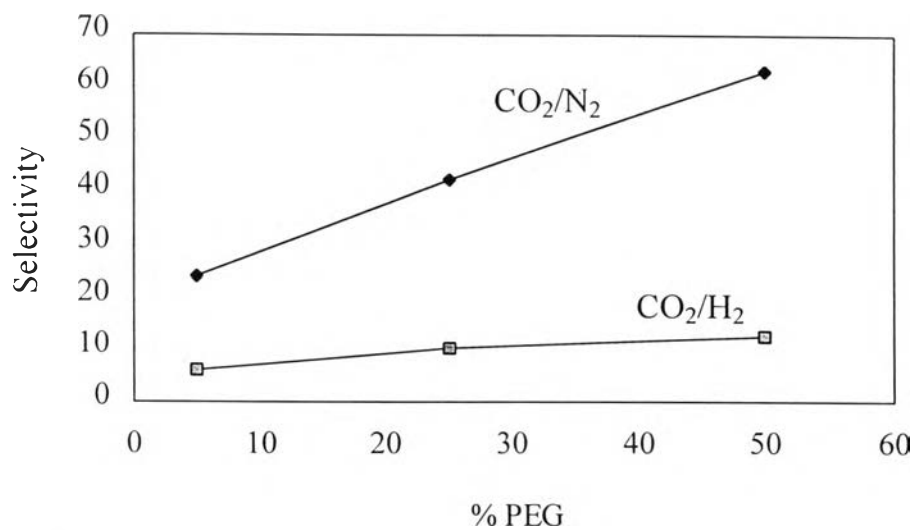


Figure 4.1 The Dependence of Selectivity on PEG Composition for Polysulfone

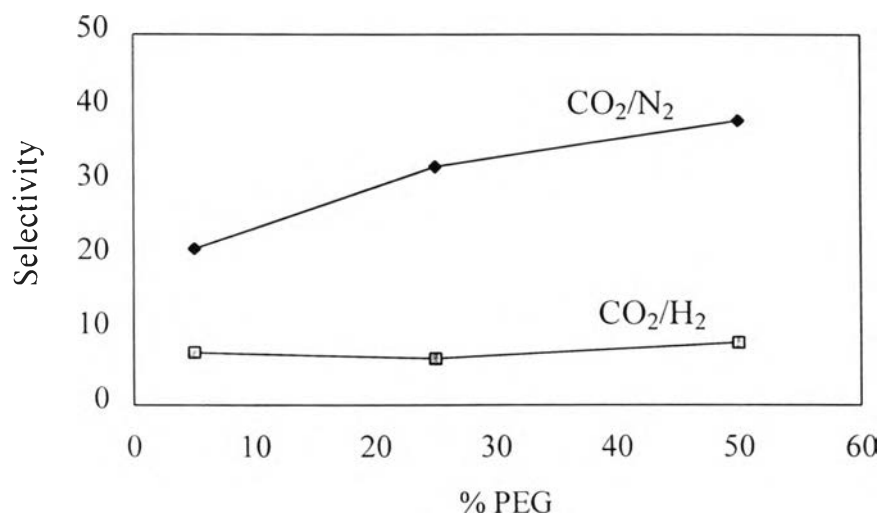


Figure 4.2 The Dependence of Selectivity on PEG Composition for 20% Weight Polyacrylonitrile