CHAPTER IV
RESULTS AND DISCUSSION

4.1 Mixed Matrix Membranes of Silicone Rubber and Polyethylene Glycol

The permeabilities of carbon dioxide, P_{CO2}/d; and nitrogen, P_{N2}/d and the selectivity of carbon dioxide to nitrogen, P_{CO2}/P_{N2} were determined from steady state permeation rates of each gas through the membrane at room temperature. The experimental results are demonstrated in Table 4.1.

Table 4.1 Permeabilities and selectivities of gases through MMM prepared from silicone rubber and PEG

Membrane	Permeability x 10^6 (cm^3/cm^2-sec-cmHg)		Selectivity (P_{CO2}/P_{N2})
	CO_2	N_2	
SIL-PS[1]	14.03	1.29	10.92
10wt%PEG/SIL MMM[2]	8.13	0.23	34.96
20wt%PEG/SIL MMM[3]	6.56	0.13	51.95
30wt%PEG/SIL MMM[4]	6.19	0.09	70.28
20wt%PEG/SIL gly-P MMM[5]	8.56	0.13	65.22

Notes

[1]SIL-PS = Silicone rubber coated on porous polysulfone

[2]10wt%PEG/SIL MMM = 10wt%Polyethylene glycol/silicone rubber coated on porous polysulfone

[3]20wt%PEG/SIL MMM = 20wt%Polyethylene glycol/silicone rubber coated on porous polysulfone

[4]30wt%PEG/SIL MMM = 30wt%Polyethylene glycol/silicone rubber coated on porous polysulfone

[5]20wt%PEG/SILgly-P MMM = 20wt%Polyethylene glycol/silicone rubber coated on glycerol treated porous polysulfone

Silicone rubber is rubber polymer, of which the segments of backbones can rotate freely around their axis; this makes the polymer soft and rubbery. Transport of gas through rubbery polymer is postulated to occur when there is a transient gap of sufficient size to accommodate the penetrant. This transient gap forms and fades throughout the polymer matrix due to thermally induced motion of the polymer segments. In comparison with silicone rubber without PEG membrane, it was found that membranes with PEG exhibit lower gas permeances than membrane without PEG. The added PEG filled up the transient gap between polymer chain and hindered the diffusion path of gas molecules. In this regard, gas molecule permeates slower (Vijitjunya, 2001). 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 and Kulkarni, 1986).

The selectivities of membrane with PEG are significantly improved. PEG enhances solubility coefficient of CO_2 by allowing CO_2 to pass through with a more rapid rate than the membrane without PEG. It was found that the hydroxyl groups, which are present in each of PEG molecules, are the major determiner of solubility of CO_2 into a membrane. The O-H bond is strongly polar. This polarity induces the formation of London force arisen from temporary dipole moment (Serivalsatit, 1999). Hence CO_2 molecules, which are more polar than N_2, selectivity be sorbed into the membrane and diffuse through the polymeric matrix. In addition, the CO_2/N_2 selectivity is observed to increase as the concentration of polar group in PEG increases.

Moreover for the membrane with PEG, the selectivity was further improved when polysulfone was first treated by glycerol. The reason was probably because polysulfone was soaked by glycerol resulting in the swelling porous polysulfone. Although this effect showed a decrease in permeability, the separation factors were enhanced.

4.2 Mixed Matrix Membranes of Silicone Rubber, Activated Carbon with/without Polyethylene Glycol

It was found from a previous work that PEG emulsified silicone rubber mixed matrix membrane, though it has capability of altering selectivity of silicone rubber, lost their stability due to PEG leakage (Vijitjunya, 2001). In this study, activated carbon was used to prevent the leak out of PEG by being incorporated into PEG. Activated carbon was added in the casting solution to form suspended solution before coating on the porous polysulfone support. The permeabilities and selectivities are shown in Table 4.2.

Table 4.2 Permeabilities and selectivities of gases through MMM prepared from silicone rubber, activated carbon with/without PEG

Membrane	Permeability X 10^6 (cm^3/cm^2-sec-cmHg)		Selectivity (P_{CO2}/P_{N2})
	CO_2	N_2	
SIL-PS	14.03	1.29	10.92
10wt%PEG/SIL MMM	8.13	0.23	34.96
20wt%Act.C/SIL MMM[1]	34.78	2.20	15.83
10wt%PEG/20wt%Act.C/SIL MMM[2]	26.23	0.75	34.64

Notes

[1]20wt%Act.C/SIL MMM = 20wt%Activated carbon/silicone rubber coated on porous polysulfone

[2]10wt%PEG/20wt%Act.C/SIL MMM = 10wt%Polyethyleneglycol/ 20wt%activated carbon/silicone rubber coated on porous polysulfone

The activated carbon incorporated silicone rubber membrane exhibits higher permeabilities for both gases than the liquid PEG emulsified silicone rubber membrane since gas seldom diffuses through viscous PEG filled up the gap between polymer chains. Likewise, this reason is contributed to the higher permeabilities of mixed matrix membranes prepared from PEG, activated carbon and silicone rubber, compare to PEG emulsified silicone rubber mixed matrix membrane.

In comparison of activated carbon incorporated silicone rubber membrane with activated carbon incorporated PEG emulsified silicone rubber membrane, the latter is less permeable to both gases due to the presence of PEG on the surface of activated carbon which hindered the path of gas diffusion.

It can be seen that the activated carbon incorporated silicone rubber membrane has the capability of altering selectivity of silicone rubber. The controlling mechanism which is involved in the selectivity enhancement is size selective such that carbon often larger molecules (carbon dioxide, kinetic diameter is 3.94 °A) permeate better than smaller molecules (nitrogen, kinetic diameter is 3.79 ° A), (Soffer and Gilron, 1999).

In comparison of carbon dioxide to nitrogen selectivities of PEG, activated carbon, and silicone rubber membrane and activated carbon incorporated silicone rubber membrane, the previous one shows the higher selectivity. Carbon dioxide passes through the mixed matrix membrane prepared from PEG, activated carbon at a more rapid rate due to the higher solubility of carbon dioxide in PEG and more selective to carbon dioxide in activated carbon compared with nitrogen.

4.3 Mixed Matrix Membranes of Silicone Rubber, K_2CO_3 Impregnated Activated Carbon with/without Polyethylene Glycol

According to the literature (Chen *et at.*, 2001), the selectivity of carbon dioxide over nitrogen of carbonate salt-solvent Immobilized Liquid Membrane (ILMs) can be enhanced by facilitated transport mechanism. Thus, mixed matrix membrane incorporated with K_2CO_3 was used to study in this work. Table 4.3 shows the permeabilities and the selectivities as a function of water content in gas feed stream (%RH) through the mixed matrix membrane of silicone rubber, K_2CO_3 impregnated activated carbon with/without PEG.

Table 4.3 Permeabilities and selectivities of gases through MMM prepared from silicone rubber, K_2CO_3 impregnated activated carbon with/without PEG

Membrane	%RH	Permeability X 10^6 (cm^3/cm^2-sec-cmHg)		Selectivity (P_{CO2}/P_{N2})
		CO_2	N_2	
5wt%K_2CO_3/ 15wt%Act.C./ SIL MMM[1]	30	16.25	0.81	20.04
	60	16.18	0.81	19.89
	70	16.01	0.82	19.63
10wt%PEG/5wt%K_2CO_3/ 15wt%Act.C/ SIL MMM[2]	30	14.37	0.36	40.50
	50	14.48	0.36	40.63
	70	14.46	0.36	40.44

Notes

[1] 5wt%K_2CO_3/15wt%Act.C/SIL MMM = 5wt%K_2CO_3/15wt%activated carbon/silicone rubber coated on porous polysulfone

[2] 10wt%PEG/5wt%K_2CO_3/ 15wt%Act.C/SIL MMM = 10wt%Polyethylene glycol/ 5wt%K_2CO_3/15wt%activated carbon/ silicone rubber coated on porous polysulfone

In comparison of the results from the membranes without K_2CO_3 in Table 4.2 with the membranes with K_2CO_3 in Table 4.3, the permeability of the latter ones were lower. A possible reason may be due to the higher ionic strength of the membranes, the lower the permeabilities of gases (Chen *et al.*, 2001). However, the selectivities of the membrane with K_2CO_3 were higher than those on the membrane without K_2CO_3 because of facilitated transport mechanism.

The chemistry of the CO_2-carbonate/bicarbonate system has been investigated and reviewed by many authors (Chen *et al.*, 2001). The rate controlling reactions for the process are :

$$CO_2 \quad + \quad H_2O \quad \leftrightarrow \quad H_2CO_3 \tag{4.1}$$

$$OH^- \quad + \quad CO_2 \quad \leftrightarrow \quad HCO_3^- \tag{4.2}$$

The following very fast reactions can be assumed to be at equilibrium:

$$H^+ \quad + \quad CO_3^{2-} \quad \leftrightarrow \quad HCO_3^- \tag{4.3}$$

$$H_2O \quad \leftrightarrow \quad H^+ \quad + \quad OH^- \tag{4.4}$$

The hydration reactions produce a bicarbonate ion concentration gradient, which parallels that of the physically dissolved CO_2. The presence of K_2CO_3 leads to appearance of carbonate ions (CO_3^{2-}) that associate with H^+ according to reaction (4.3) and diffuse counter to the bicarbonate ions (HCO_3^-). The overall reaction is thus written as

$$CO_2 \quad + \quad H_2O \quad + \quad CO_3^{2-} \quad \leftrightarrow \quad 2HCO_3^- \tag{4.5}$$

The CO_3^{2-} generated at the lower pressure side of the membrane from the reverse reaction of equation (4.3) diffuses counter to the bicarbonate ions to satisfy the restriction of electroneutrality in the membrane.

The water content (%RH) range of the feed stream investigated was from about 30 to 70%. The results presented in Table 4.3 indicate that %RH did not affect the permeabilities and the selectivities of the mixed matrix membranes composed of K_2CO_3 impregnated activated carbon on neither with nor without PEG. It is believed

that at 30%RH in gas feed stream was adequate to reversibly form a reaction with CO_2 therefore the permeabilities and the selectivities were somewhat constant although %RH was increased.