CHAPTER-VII

SEPARATION OF CO₂ FROM CO₂/CH₄ MIXTURES THROUGH HYDROXYPROPYLEMETHYLCELLULOSE MEMBRANE

ABSTRACT

Hydroxypropylmethyl cellulose (HPMC) membrane has been prepared by solution casting and solvent evaporation method and tested for its barrier properties for the separation of natural gas mixtures viz., CO₂ and CH₄. Barrier properties have been investigated as a function of feed pressure and composition of the gaseous mixtures of CO₂ and CH₄. The CO₂ permeability was found to increase from 0.87 to 1.91 Barrers for the feed composition varying from 2 to 20-mol % of CO₂, while the corresponding values for methane ranged from 0.08 to 0.39 Barrers. Under the constant operating conditions of feed pressure (40 kg/cm²) and membrane thickness (50 μm), the selectivity values were reduced from 11.6 to 4.87 with increasing feed CO₂ concentration, due to increased membrane swelling and plasticization effect. When the pressure on the feed side was varied from 10 to 40 kg/cm² at a constant feed concentration of 2 % CO₂, the permeability values decreased from 3.52 to 0.87 Barrers, while the selectivity was reduced from 20.87 to 11.6 due to the dual mode sorption effect.

Results of this chapter are communicated to the Journal of Applied Polymer Science (2007).
VII.1. INTRODUCTION

Use of polymeric membranes to selectively remove carbon dioxide (CO\textsubscript{2}) from its mixtures with hydrogen (H\textsubscript{2}), nitrogen (N\textsubscript{2}) and methane (CH\textsubscript{4}) has been industrially important in a wide variety of applications such as syngas processing, flue gas rectification and natural gas separation [1,2]. CO\textsubscript{2} along with carbon monoxide is a known culprit in rising global warming problems. Therefore, the development of environment friendly and energy-saving technologies to recover CO\textsubscript{2} from flue gases is a challenging task [3]. In this pursuit, polymeric membranes have been used. However, despite rapid developments in synthetic polymers, cellulosic polymers still hold prominent positions in process engineering as separating membranes. In the earlier literature, blend membranes of cellulosic polymers have been extensively used [4-9] for a variety of applications including CO\textsubscript{2} separation [10-12]. In this study, hydroxypropyl methylcellulose (HPMC) is investigated as a gas separation membrane to achieve the selective removal of CO\textsubscript{2} from its mixture with CH\textsubscript{4}. Effect of feed concentration and feed pressure on membrane properties has been evaluated.

VII.2. RESULTS AND DISCUSSION

VII.2.1. Effect of feed concentration

The flux, partial pressure difference across the membrane, permeability and selectivity are determined using Equations II.8, II.9, II.10 and II.11 respectively, which are described in Chapter II.

Separation of CO\textsubscript{2} occurs due to the preferential sorption of the gas in the HPMC membrane, which helps to migrate through the barrier by a solution-diffusion mechanism [13]. The CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} selectivity are affected by the concentration of CO\textsubscript{2} in the feed gas mixture. The results are displayed in Table VII.1. Figures VII.1 and VII.2 show that
as CO₂ concentration in the feed increased from 2 to 20 mol %, its permeability also increased significantly from 0.87 to 1.91, but selectivity decreased drastically from 11.6 to 4.87. This could be attributed to the plasticization effect arising from the increasing CO₂ dissolution in the membrane matrix. According to Figures VII.1 and VII.2, permeability increased linearly with increasing concentration of CO₂ in the feed mixture with a corresponding decrease in selectivity. Even though the plasticization effect in polymers has been reported in the earlier literature [14-21], there is still no general rule that can predict whether a polymer will be plasticized by a gaseous penetrant or not. Particularly, during CO₂/CH₄ separation, CO₂ could act as a plasticizer when present in reasonably high concentrations, leading to an increase in free volume, which induces a greater segmental mobility in the polymer chain. Due to polymer swelling, permeation of CH₄ may be accelerated with a loss in selectivity. In order to overcome the loss of methane, polymer plasticization should be minimized. An increase in permeability results from an increase in chain mobility. This can be observed by a depression in Tₑ of the polymer [22-28]. Tₑ value of HPMC ranges from 170 to 198°C. Sanders [14] studied the CO₂-induced changes in polyethersulfone (PES) and observed that PES was highly plasticized by CO₂. Therefore, one could expect an increase in permeability at low CO₂ pressure. However, no increase in CO₂ permeability for PES was found at pressures up to 27 atm. To understand the plasticization effect, a more fundamental study is necessary. However, many plasticization related phenomena are reported in the literature [14,15,16-21], but there is no general rule that can predict whether a polymer is plasticized by a penetrant or not.
Table VII.1. Effect of CO₂ feed concentration on permeability and selectivity

<table>
<thead>
<tr>
<th>CO₂ concentration in feed gas mixture</th>
<th>Permeability (K) in Barrer</th>
<th>Selectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>2%</td>
<td>0.866</td>
<td>0.078</td>
</tr>
<tr>
<td>7%</td>
<td>1.688</td>
<td>0.176</td>
</tr>
<tr>
<td>20%</td>
<td>1.912</td>
<td>0.392</td>
</tr>
</tbody>
</table>

Figure VII.1. Effect of feed concentration of CO₂ on permeability of (●) CO₂ and (■) CH₄.
VII.2.2. Effect of feed pressure

In the present study, we have used the constant feed mixture composition of 2 % CO$_2$ + 98 % CH$_4$ to study the effect of variation of feed pressure. The membrane was pressurized at 10, 20, 30 and 40 kg/cm$^2$; the resultant permeability and selectivity of the HPMC membrane at different feed pressures for 2 % CO$_2$ in CH$_4$ gas mixture are displayed in Figures VII.3 and VII.4. Table VI.2 shows the experimental results of effect of feed pressure. In mixed-gas permeation experiments, one can attempt to provide an insight into the plasticization behavior, especially over long-term CO$_2$ exposure. Figure VII.5 shows the permeation isotherms for HPMC membrane. The minima in these curves correspond to “plasticization pressure”. In the region of 15-25 kg/cm$^2$ feed pressure, an increase in plasticization effect is observed. [29] The membrane selectivity decreased monotonically with increasing feed pressure. At 10 kg/cm$^2$, permeability values are 3.52 and 0.17 Barrers for CO$_2$ and CH$_4$, respectively, while selectivity is 20.87. However, at 40 kg/cm$^2$ pressure, CO$_2$ permeability is 0.87 Barrers and selectivity is 11.6. According to Figure VII.4,
there is a decrease in selectivity at a pressure of 20 kg/cm², while an increase is observed at 30 kg/cm² pressure prior to further reduction in permeability at 40 kg/cm² pressure.

Figure VII.3. Effect of feed pressure on CO₂ and CH₄ permeability. Symbols: (●) CO₂ (■) CH₄.

Figure VII.4. Effect of feed pressure on CO₂ selectivity (■).
Selectivity data are displayed in Figure VII.4. As the pressure is reduced, selectivity of CO₂ increased. These observations are in accordance with the dual mode sorption effect. The membrane consists of crystalline and amorphous phases. Crystalline phases are considered impermeable, whereas amorphous phases allow gas permeation through the sorption process by Henry's as well as Langmuir's modes. [30] Henry's mode of sorption refers to uptake of gas molecules through interaction, whereas Langmuir sorption takes place in the microvoids. At higher pressures, microvoids become constricted or more compact, which would reduce CO₂ permeability. At this juncture, CH₄ molecules permeate competitively with CO₂, resulting in a poor separation.

Table VII.2. Effect of feed pressure on flux, permeability and selectivity

<table>
<thead>
<tr>
<th>Feed pressure kg/cm²</th>
<th>Flux</th>
<th>Permeability in Barrer</th>
<th>Selectivity (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>CH₄</td>
<td>CO₂</td>
</tr>
<tr>
<td>10</td>
<td>15.25</td>
<td>8.52</td>
<td>3.52</td>
</tr>
<tr>
<td>20</td>
<td>8.75</td>
<td>7.89</td>
<td>1.99</td>
</tr>
<tr>
<td>30</td>
<td>11.2</td>
<td>6.24</td>
<td>2.26</td>
</tr>
<tr>
<td>40</td>
<td>9.26</td>
<td>5.98</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The sorbed CO₂ molecules tend to create a hindrance to the transport of CH₄ through the void volume of the membrane matrix; this could result in a lower permeation of CH₄. As the CO₂ concentration in the feed side increased, permeability and selectivity decreased as shown in Figure VII.4 and VII.5, suggesting that CO₂ molecules are sorbed by the membrane matrix due to the plasticization effect.
VII.3. CONCLUSIONS

HPMC membrane was prepared and tested for the separation of CO$_2$ from CO$_2$/CH$_4$ mixture. The membrane of this study exhibited an ability to effectively separate the binary feed mixtures of CO$_2$/CH$_4$, which contained lower concentrations of CO$_2$. Effect of varying feed pressure was also studied. A feed pressure of 10 kg/cm$^2$ was found to be optimum for the selective separation of CO$_2$. The observed plastisization effect is due to increased CO$_2$ sorption at higher feed concentrations, which showed a positive effect on permeability, but a negative impact on selectivity. Dual mode sorption effect could be possible reason for decreasing the CO$_2$ flux and selectivity at higher pressures. For treating actual natural gas mixtures, HPMC membrane could be crosslinked to prevent high swelling at higher CO$_2$ concentrations.
VII.4. REFERENCES