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# The effect of ethane on the performance of commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes in $CO_2/CH_4$ separation applications

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**Abstract**−Impurities such as hydrogen sulfide, water vapor and heavy hydrocarbons in natural gas have considerable effects on the membrane performance. Small amounts of condensable and polymer soluble components in the feed gas cause swelling or plasticization of glassy membranes, leading to a reduction in membrane selectivity. In the present research the influence of ethane was investigated on the permeance and selectivity of two commercially available hollow fiber membranes, namely Cardo-type polyimide and PPO hollow fibers for $CO_2/CH_4$ separations. It was concluded that the gas mixture permeation rate was increased in the presence of $C_2H_6$. However, the $CO_2/CH_4$ separation factors remained almost the same in the presence and absence of the $C_2H_6$.

Key words: Membrane Gas Separation, Natural Gas, Gas Sweetening, Ethane, Hollow Fiber

## INTRODUCTION

One of the important factors affecting the gas separation properties of membranes in industrial applications for natural gas processing is the presence of impurities such as carbon dioxide, hydrogen sulfide, water vapor and heavy hydrocarbons in feed gas streams. Impurities such as water vapor have considerable effect on membrane performance [1]. Even after removing water vapor (dehumidification) and residual liquids, natural gas may contain minute amounts of more than 500 paraffinic or aromatic hydrocarbons. It seems that even minute amounts of condensable and polymer soluble components, especially aromatics and heavy hydrocarbons, could seriously affect the performance of polymeric membranes. In most cases the presence of these components causes swelling or plasticization of glassy membranes leading to a reduction in the membrane selectivity.

From an industrial point of view, removal of heavy hydrocarbons from natural gas is necessary to facilitate transmission in the pipeline and distribution systems and its use in common gas flares and cogeneration (combined heat and power). Furthermore, recovery of heavy hydrocarbons from natural gas is favorable for the following reasons.

- The higher value of heavy hydrocarbons.
- Elimination of problems caused by condensation of higher hydrocarbons which results in softness or partial dissolution of plastic pipes and measuring instruments.
- Increase in methane number. Methane numbers smaller than 70-80 may cause difficulties in gas ignition in hybrid engines.
- Since the flares bear a limited amount of Wobb index, the control of this index is very important, because heavy hydrocarbons cause substantial variation in this index.

The hard and vigorous structure of polymeric glassy membranes helps the gas separation performance, whereas the same characteristics promote adsorption of condensable components on the surface of membrane resulting in a reduction in their performance. The decrease in performance is very crucial in industrial applications and real gas mixture separation. Vu et al. [2] have investigated the effect of condensable impurities on the performance of carbon molecular sieve hollow-fiber membranes in $CO_2/CH_4$ separation applications. In this context, the experimental studies by Koros et al. [3] suggested that competition of permeating components for Langmuir adsorption locations (or free volumes) in glassy membranes will mainly end up in a decrease in their permeability, selectivity and increased cost of operation. As for cellulose acetate membranes, it was observed that the $CO_2/CH_4$ selectivity remained constant in the presence of aromatics such as benzene and toluene, while flux decreased up to 97% [4]. Nevertheless, inherent selectivity of cellulose acetate is lower than that of other polymers such as polyimides. Studies on polymeric flat membranes, such as glassy polyimide, stated that the selectivity of membranes decreased nearly 50% when toluene or normal hexane was present in a $CO_2/CH_4$ feed at saturation concentrations. This kind of effect on selectivity was deemed to be induced by plasticization [5].

A similar work using concentrations of 100 and 300 ppm of toluene and normal hexane, respectively, in $CH_4$ gas stream containing 10% $CO_2$ showed that selectivity of asymmetric hollow fiber polyimide membranes decreased by 30 to 50% [6]. Tanihara et al. [7] also studied the effect of higher concentrations of more than 1,600 to 7,600 ppm of toluene in the equimolar $CH_4/H_2$ mixture. It was

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stated that permeation rate of $H_2$ decreased up to 80+% and 47%, respectively, in the presence of toluene vapor ranging from 1,600 to 7,600 ppm. It was postulated that toluene sorbed caused plasticization of the active skin layer on the polyimide membrane resulting in the loss of selectivity. It was concluded that the polyimide membranes with high selectivity are highly sensitive to the presence of heavy hydrocarbons in the feed. The separation performance of these membranes compared to cellulose acetate is mostly based on the difference in permeability through their dense layers. Therefore, any decline in the polymeric chain movement due to the presence of condensable components could severely deteriorate the performance of the polymers. According to Lokhandwala and Baker [8,9], polysulfone performance is superior to cellulose acetate in the presence of heavy hydrocarbons due to its stability at higher temperatures (200 °F). This is especially important when the natural gas stream is heated to prevent condensation of heavy hydrocarbons in the course of removing $CO_2$. The high temperature also improves the permeability of membranes. Because the inherent selectivity of polysulfone membrane is lower than cellulose acetate, the loss of methane would be higher, which dictates the need for further processing. The useful technique in this case is cooling the feed gas to liquefy heavy hydrocarbons and then heating the gas back to its initial temperature before it is transmitted to the membrane unit.

Vu et al. [10-12] have also investigated the effects of condensable impurities on the performance of $CO_2/CH_4$ separation of hollow fiber molecular sieve membranes. Their results were compared with the results obtained from polyimide polymeric membranes. They used gas streams containing 10% $CO_2$ in $CH_4$ and including toluene and heptane as aromatic and paraffinic impurities, respectively. Their results showed that the carbon membrane selectivity remained constant in the presence of these impurities, whereas the permeability of gas components decreased by 20%. The same research group showed that by applying a simple recovery method with the aid of dry nitrogen gas at medium temperatures (70 to 90 °C), the performance of membranes could be recovered. They concluded that carbon membranes offer considerable advantages over polyimides under similar conditions where impurities are present.

Recently Visser et al. [13-15] studied the auto and mutual plasticization, mixed gas plasticization behavior in asymmetric glassy membranes and the kinetic sorption behavior of pure gases in glassy polymers. To obtain deeper discussions on plasticization and sorption, references [13-15] can be referred.

Since common processes for removal of heavy hydrocarbons, such as cryogenics or adsorption by active carbon, are expensive, efforts have been focused on finding alternative processes.

Shultz and Peinemann [16] have examined more than 40 different polymers for n-$C_4/CH_4$ separation. They have shown that except for polyoctylmethyl siloxane (POMS) and poly(trimethylsilylpropyne) (PTMSP), the selectivity of other polymers was less than 10, which is not economically feasible. The n-$C_4/CH_4$ selectivity obtained for POMS and PTMSP was 12 and 27, respectively. Arruebo et al. [17] studied the hydrocarbon selectivity from natural gas by using silicalite membrane. They used a concentration of butane (normal butane plus iso-butane) equal to 0.65%. They observed that the normal butane shows higher permeability as compared to $CH_4$ due to high adsorption capacity of butane in the membrane, which at the same time prevents permeation of $CH_4$. Interesting point in this study is gaining of highest performance in $C_4/CH_4$ separation under similar pressures on both sides of membrane and using sweeping gas flow. The other important point is membrane fouling, which causes substantial decrease in permeability in continuous performance.

Among the glassy polymers, Cardo-type polyimide and PPO possess excellent separation properties that make them suitable candidates for gas separation. The polyimide hollow fiber membranes that were developed for $CO_2/N_2$ separation by the Research Institute of Innovative Technology for the Earth (RITE, Japan) proved to be good candidates for $CO_2/CH_4$ separation as well due to their high selectivities in comparison with other glassy membranes [18]. On the other hand, polyphenelene oxide (PPO) membrane is a suitable candidate for a wide range of industrial gas separation applications. PPO is a linear amorphous thermoplastic with glass transition temperature ($T_g$) ranging from 212 to 218 °C. Due to the presence of the phenyl rings, PPO is hydrophobic and has excellent resistance to water, acids, alcohols, steam and bases [19]. It has been reported that, amongst all glassy polymers, PPO shows one of the highest permeabilities to gases [20-24]. The high permeability has been attributed to the absence of polar groups in the main chain of PPO [24]. The results of $CO_2/CH_4$ separation using PI and PPO membranes including the affects of $CO_2$ and stage-cut on the separation performance of the experimental membranes have been previously reported by the authors [18].

While ethane is present as a major impurity in natural gas our understanding of its effect on the separation properties of membranes is limited. The present study is designed to investigate the performance of Cardo-type polyimide and PPO membranes for separation of $CO_2/CH_4$ mixtures containing ethane. The performance is evaluated based on the permeances and selectivities of these hollow fiber membranes for the mentioned feed.

## EXPERIMENTAL

### 1. Materials & Modules

The Cardo-type polyimide (PI) hollow fiber module was generously supplied by RITE, Japan. The inside and outside diameters of fibers were 370 and 500 μm, respectively. The commercially available PPO hollow fibers were generously supplied by Aquilo Gas Separation B.V. (Parker Filtration and Separation B.V., The Netherlands). The inside and outside diameters of hollow fibers were 370 and 520 μm, respectively. The PPO modules were assembled by loading a bundle of 10 fibers in a shell and tube structure. Although the dense selective layer of PPO hollow fibers was on the

**Table 1. Specifications of Cardo-type polyimide and PPO hollow fibers**

| Module type | Hollow fiber parameters | | Module specifications | |
|---|---|---|---|---|
| | Inside diameter (μm) | Outside diameter (μm) | Number of fibers | Permeation area ($cm^2$) |
| Cardo-type PI | 370 | 500 | 135 | 416 |
| PPO#1 | 370 | 520 | 10 | 51 |
| PPO#2 | 370 | 520 | 10 | 49 |

**Table 2. Compositions of gas mixtures containing $C_2H_6$**

| Module type | Gas mixture | $CH_4$ volume percent | $CO_2$ volume percent | $C_2H_6$ volume percent |
|---|---|---|---|---|
| Cardo-type PI | $CH_4$-$C_2H_6$ | 94.8 | --- | 5.2 |
| | $CH_4$-$C_2H_6$-$CO_2$ | 89.7 | 4.8 | 5.5 |
| PPO#2 | $CH_4$-$C_2H_6$ | 92.8 | --- | 7.2 |
| | $CH_4$-$C_2H_6$-$CO_2$ | 88.0 | 4.7 | 7.3 |

outside, in this study, the feed gas was introduced inside the fibers and permeate was collected in the shell side. The permeances, however, were calculated based on the outer surface area of the hollow fibers. Cardo-type polyimide and PPO modules and hollow fibers specifications are shown in Table 1. Ultra high purity $CO_2$, $CH_4$, $C_2H_6$ (99.8%) and $CO_2$/$CH_4$ gas mixture (5% $CO_2$-balance $CH_4$) were purchased from Praxair Distribution Inc., Canada. The maximum impurities accompanying $C_2H_6$, which is reported by $C_2H_6$ gas Provider Company, Praxair Distribution Inc., Canada, was 1,972 ppm of which 1,760 ppm was ethylene.

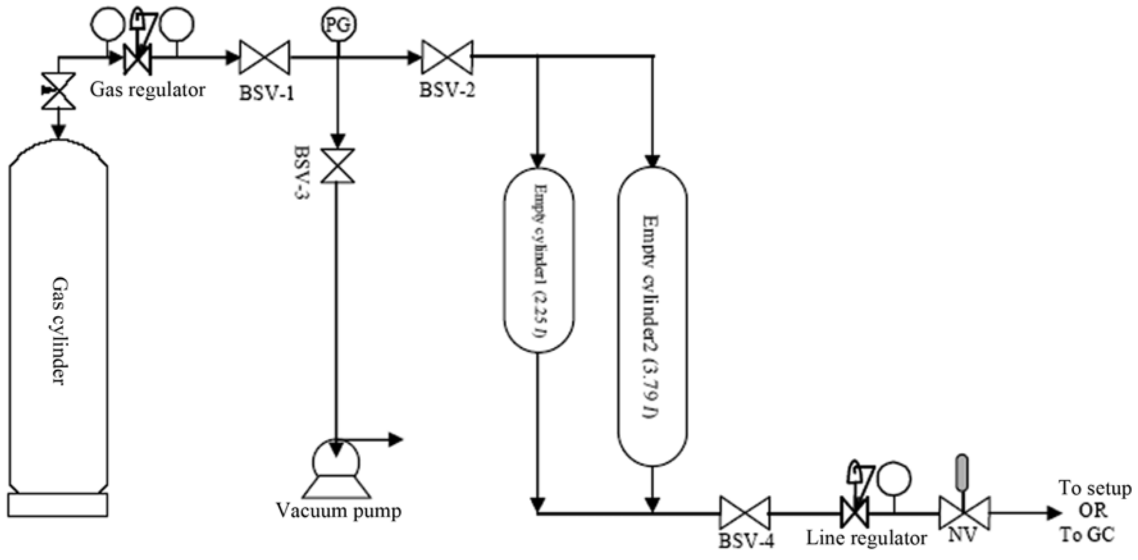
The concentrations of the feed gas mixtures used in different experiments are shown in Table 2. Binary $CH_4$-$C_2H_6$ and tertiary $CH_4$-$C_2H_6$-$CO_2$ gas mixtures were prepared using an experimental setup presented in Fig. 1. The required composition of the gas mixtures was prepared based on the components' partial pressure in the gas mixture. For example, to prepare binary $CH_4$-$C_2H_6$ gas mixtures, the two cylinders (as shown in Fig. 1) were evacuated. The pure ethane cylinder was connected to the evacuated cylinders with its outlet pressure set at a predefined pressure, $p_1$. Then, both valves (BSV-1 and BSV-2) were opened and ethane was gradually introduced to the empty cylinders. When the pressure of the empty cylinders reached $p_1$, BSV-1, and BSV-2 were closed and the ethane cylinder was replaced by a pure methane cylinder. Methane was fed to the cylinder containing pure ethane until the pressure reached the predefined value of $p_2$. The pressures $p_1$ and $p_2$ were selected high enough to attain the required amount of gas mixture concentration while providing a supply of feed gas for at least two hours of operation. Finally, the system was set to rest for two days in order to attain a homogeneous gas mixture.

The experiments were conducted by connecting the gas mixture cylinders to the membrane separation setup and a GC (Varian 3400). The GC was equipped with a thermal conductivity detector (TCD) and a "HayeSep Q" column. The GC readings were corrected using thermal response factors (TRFs) that were carefully calculated for each gas following Dietz's method [25]. At the beginning of each set of experiments the exact composition of the feed gas mixtures was determined by passing a sample of each mixture through the GC. This exercise was repeated several times during each experiment and the analytical results were compared with the mass balance calculations to ensure the accuracy of the results. The concentrations of the permeate and retentate were also determined by the GC. The details of the gas separation experimental setup are described in an earlier publication [1].

The tertiary $CH_4$-$C_2H_6$-$CO_2$ gas mixtures were prepared by mixing pure ethane with the purchased $CO_2$/$CH_4$ gas mixture (5% $CO_2$-balance $CH_4$) following the same procedure as described above.

### 2. Gas Permeation Experiments

The experiments were conducted at 7.9 bar absolute feed pressure (100 psig) and room temperature of 23±0.2 °C. In the first step the ethane plasticization effect was investigated by comparing the pure methane permeance at 7.9 bar absolute feed pressure before and after the membrane was exposed to pure ethane at the same feed pressure. Subsequently, the effect of ethane on separation of $CH_4$-$CO_2$ was studied. The experiments were carried out in the following order: pure methane, $CH_4$-$C_2H_6$ mixture, pure methane, $CH_4$-$CO_2$ mixture, $CH_4$-$C_2H_6$-$CO_2$ mixture, and finally the repetition of $CH_4$-$C_2H_6$ mixture. The experiments were carried out with a stage-cut of 5%. After each experiment the membrane modules were flushed with pure nitrogen in order to purge any remaining hydrocarbon.



BSV: Below Seal Valve, NV: Needle Valve, PG: Pressure gauge

**Fig. 1. Schematic of the prepared experimental setup for making gas mixtures containing $C_2H_6$.**

The membranes were then left to rest for 24 hours before the next experiment. This procedure was done to make sure that the membranes returned to their original forms. Each experiment was repeated at least three times and the readings at steady-state were averaged. The steady-state was usually reached in approximately two hours.

## RESULTS AND DISCUSSIONS

Although the partial pressures of the impurities in ethane were minute in the final feed gas mixture, it was speculated that their presence in the feed might influence the performance of the membranes with unsaturated bonds in their monomers [1]. For example, ethylene can be strongly sorbed at the sorption sites limiting the sorption of methane and ethane. Therefore, in the following discussion on the effect of $C_2H_6$, naturally the possible effect of these impurities will be considered.

The permeances *[GPU (gas permeation unit); 1GPU=*$10^{-6}$ *cm*$^3$ *(STP) cm*$^{-2}$ *s*$^{-1}$ *(cmHg)*$^{-1}$*]* of pure $C_2H_6$ and $CH_4$ for Cardo-type PI and PPO membranes are shown in Figs. 2 and 3. The PPO membrane allowed for larger permeances for both gases compared to Cardo-type PI. The permselectivities of both membranes, however, were similar and close to unity, suggesting that little separation between methane and ethane was achieved. Because of the larger size of ethane compared to methane a lower diffusion rate through polymeric membranes and ultimately, a lower permeance of this gas was expected. The similar permeances of the two gases could be attributed to the plasticization effect and/or condensability of ethane.

To investigate the $C_2H_6$ plasticization effect, pure $CH_4$ permeation experiments were conducted at 7.9 bar absolute feed pressure before and after pure $C_2H_6$ permeation tests through both membranes. The results are shown in Figs. 4 and 5. Permeation of methane through both membranes increased by approximately 30% after the membranes were exposed to ethane. The initial large increase was followed by a gradual decline before reaching a steady-state after a few hours. Although the trend was suggestive of a diminishing plasticization effect, the permeance did not return to the original level within the experimental time period of 30 hours. This observation was suggestive of a possible permanent change in the membrane performance which could be due to an alteration in the physical structures of the membranes.

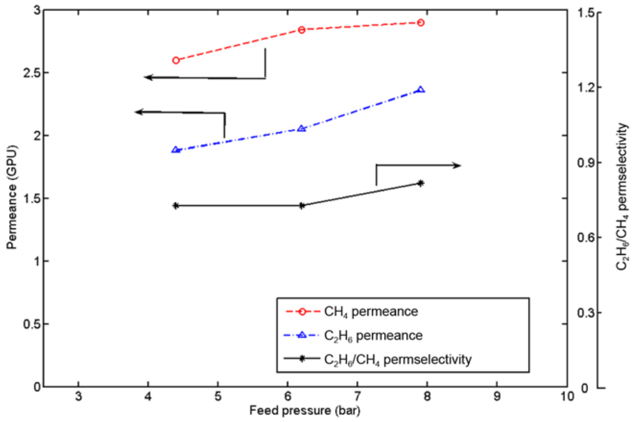


**Fig. 2. $C_2H_6$, $CH_4$ permeances and $C_2H_6/CH_4$ permselectivity (the permeance ratio of two gases) vs. feed pressure. Cardo-type polyimide module.**

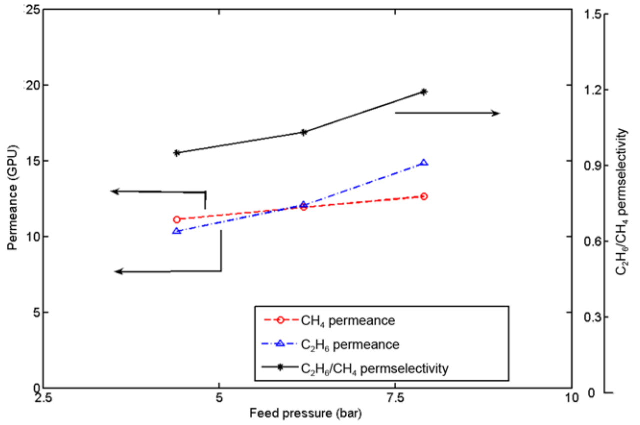


**Fig. 3. $C_2H_6$, $CH_4$ permeances and $C_2H_6/CH_4$ permselectivity vs. feed pressure. PPO#2 module.**

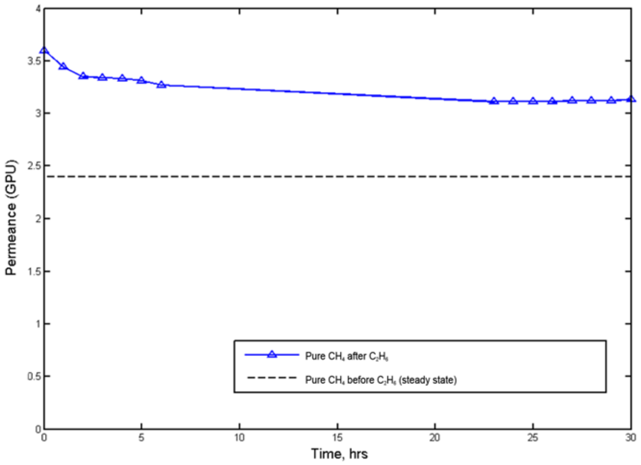


**Fig. 4. $CH_4$ permeances before and after $C_2H_6$ experiment, Cardo-type polyimide module: feed pressure, 7.9 bar (100 psig).**

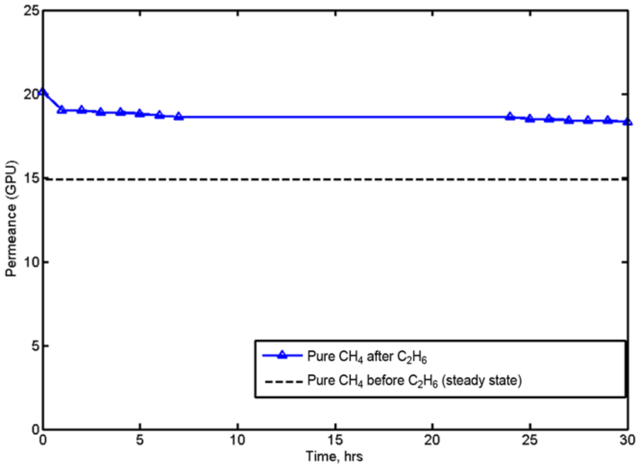


**Fig. 5. $CH_4$ permeances before and after $C_2H_6$ experiment, PPO#1 module: feed pressure, 7.9 bar (100 psig).**

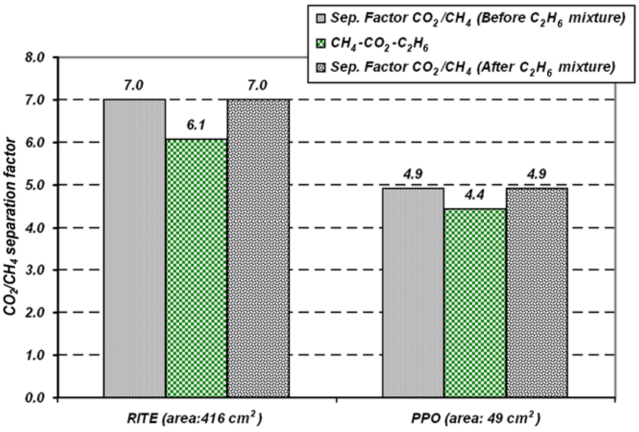


**Fig. 6. Separation factors of $CO_2/CH_4$ and $CO_2/CH_4/C_2H_6$ gas mixtures at 7.9 bar absolute feed pressure (100 psig). Cardo-type polyimide and PPO#2 modules.**

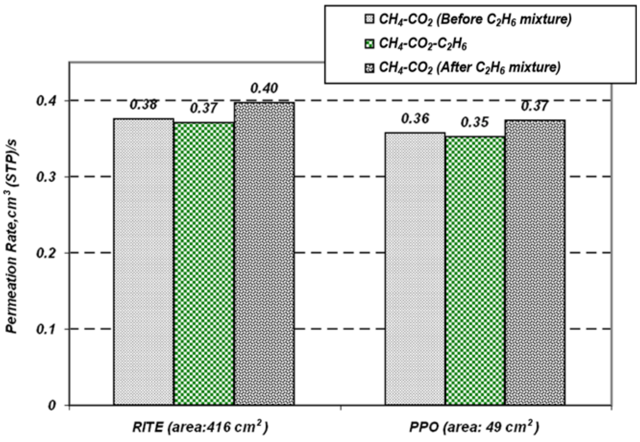


**Fig. 7. Permeation rates in $CO_2/CH_4$ and $CO_2/CH_4/C_2H_6$ gas separation at 7.9 bar absolute feed pressure (100 psig). Cardo-type polyimide and PPO#2 modules.**

The plasticization effect of ethane was further investigated on the separation of gas mixtures. For this purpose, separation of methane/carbon dioxide was studied in the presence and absence of ethane. The experiments were carried out with two and three component mixtures containing $CH_4$, $C_2H_6$ and $CO_2$ at room temperature, a stage cut of 5%, and feed pressure of 7.9 bar. The compositions of the experimental gas mixtures are shown in Table 2. The results are shown in Figs. 6 and 7. Fig. 6 compares the separation factors of the two membranes before and after ethane was introduced into the feed. As shown, the separation factors of both membranes slightly decreased in the presence of ethane, but were recovered when this gas was removed from the feed. The permeation rates, as shown in Fig. 7, negligibly declined in the presence of ethane, but surpassed and remained above the initial value when ethane was removed from the feed. These results are consistent with those previously obtained in the binary mixture experiments as shown in Figs. 4 and 5. It should be noted that the decline of $CO_2$ concentration as a result of introduction of a third component (ethane) was not expected to influence the results. That is because, although the partial pressure of this gas was reduced with the introduction of ethane, the ratio of partial pressures of $CO_2$ to $CH_4$ was maintained at a constant value of 0.053 in all the mixtures.

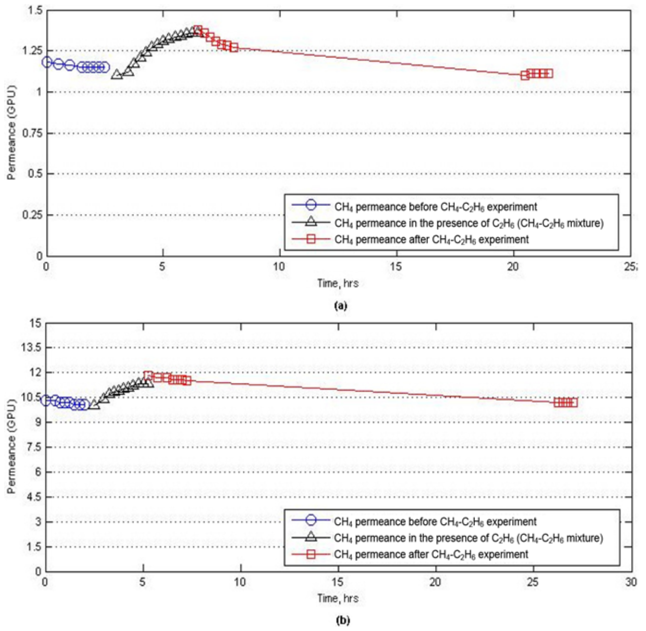


**Fig. 8. $CH_4$ permeance before and after $CH_4/C_2H_6$ separation experiment at 7.9 bar absolute feed pressure (100 psig): (a) Cardo-type polyimide and (b) PPO#2 modules.**

Finally, the effect of $C_2H_6$ on $CH_4$ permeance was studied. The results are shown in Figs. 8(a) and (b). In these experiments the permeation rates of pure $CH_4$ and $CH_4/C_2H_6$ mixtures were measured at 7.9 bar absolute feed pressure and room temperature for the two membranes. The compositions of the gas mixtures are given in Table 2. As shown in Figs. 8(a) and (b) the plot of permeance versus time can be divided into three segments. The first segment includes the permeance of pure methane, followed by the permeance of $CH_4/C_2H_6$ mixture, and finally permeance of pure methane again. It is clear from both figures that the permeance of methane increased considerably when 5% to 7% ethane was introduced into the feed. The increased permeance was clearly a result of plasticization of the membranes by the addition of ethane to the feed. A steady-state was expected at approximately 50% higher value of permeance compared to pure methane. In the end, the gas mixture was stopped and pure methane was fed into the system again. A sudden small jump in the permeance was observed at this point, which was followed by a gradual decrease that ended in a plateau at a level similar to the original pure methane permeance. The sudden jump can be explained by a small increase in the partial pressure of methane. The gradual decline in the permeance is then attributed to the diminishing plasticization effect of ethane. These observations confirm the previous results as discussed above and presented in Figs. 2 to 7. A comparison of the results in Figs. 8(a) and (b) with those presented in Figs. 4 and 5 indicated that the extent of plasticization effect of ethane depends on its concentration in the feed. Pure ethane irreversibly altered the performance of both membranes within the experimental time frame of the experiments as shown in Figs. 4 and 5, while, 5% to 7% ethane in the feed only temporarily exhibited the same effect.

## CONCLUSIONS

Neither of the two experimental membranes was found selective between methane and ethane. However, ethane exhibited plasticization effects on both membranes. The effect was observed in both small concentrations of ethane as well as pure ethane. The permeance of methane increased when the membranes were exposed to small or large concentrations of ethane. The increase was reversible at low concentrations of 5.2% to 7.2% ethane and the permeance of methane returned to its initial levels after 21 to 27 hours. However, when the membranes were exposed to pure ethane, the methane permeance increased irreversibly within the experimental time frame of 30 hours.

The plasticization effect was also observed when ternary mixtures of $CH_4/CO_2/C_2H_6$ were used. In this set of experiments the concentration of ethane was maintained between 5.5% and 7.3% with $CO_2$ concentration at 4.7% to 4.8%. A decline in the $CO_2/CH_4$ selectivity of the membranes was obvious when ethane was introduced to the binary feed mixture, but the variation in the permeation rates of the two experimental membranes was insignificant.

The industrial importance of the present study stems from the fact that ethane is present at different concentrations in natural gas sources. The presence of ethane in natural gas contributes to the plasticization effects of carbon dioxide and heavy hydrocarbons also present in such streams. The combined effects of these impurities count for the reduced selectivity of commercial membranes in natural gas treatment applications.

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