

## Removal of hydrogen sulfide from methane using commercial polyphenylene oxide and Cardo-type polyimide hollow fiber membranes

Mahdi Pourafshari Chenar\*, Houman Savoji\*\*\*, Mohammad Soltanieh\*\*†,  
Takeshi Matsuura\*\*\*, and Shahram Tabe\*\*\*

\*Chemical Engineering Department, Ferdowsi University of Mashhad, Mashhad, P. O. Box 91775-1111, I. R. Iran

\*\*Department of Chemical and Petroleum Engineering, Sharif University of Technology,  
Tehran, P. O. Box 11365-9465, I. R. Iran

(Received 24 February 2010 • accepted 24 September 2010)

**Abstract**—The performance of commercially available poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) and Cardo-type polyimide (PI) hollow fiber membranes was investigated in removing hydrogen sulfide from methane in a series of bench-scale experiments. It was observed that in the concentration range of hydrogen sulfide in methane from 101 to 401 ppm, the methane permeability decreased in the presence of hydrogen sulfide for Cardo-type polyimide hollow fiber membranes, whereas the PPO membrane performance was not affected. The separation coefficients of hydrogen sulfide/methane were 6 and 4 for PI and PPO membranes, respectively. Effects of temperature on the performance of PI and PPO membranes were investigated. It was observed that the permeabilities of both components of the mixture increased by increasing temperature, whereas the selectivities remained constant.

Key words: Polyphenylene Oxide Membrane, Polyimide Membrane, Natural Gas Sweetening, Hydrogen Sulfide, Hollow Fiber

### INTRODUCTION

Natural gas resources around the world contain different levels of acid gases, mainly hydrogen sulfide and carbon dioxide, as impurities. Samples of Iranian raw natural gas have H<sub>2</sub>S contents from 66.2 ppm to 3.27 mol% in different gas fields. Due to the toxic and corrosive properties of this gas, it should be removed from natural gas in order to meet the pipeline specifications.

While absorption processes are the main treatment for the removal of acidic gas from natural gas, polymeric membranes have gained momentum during the past few decades.

The advantages of membranes compared with the competing processes are their lower energy and capital costs as well as operation simplicity, easy scale up, and smaller carbon footprint. Commercialization of membranes for natural gas sweetening started around 1979-80 [1].

Although a significant number of studies have been focused on the removal of CO<sub>2</sub> from CH<sub>4</sub>, the permeation behavior of H<sub>2</sub>S in membranes has been investigated to a lesser extent. The main reason for this is the high toxic and corrosive properties of this gas. In fact, only a few researches have been carried out on the separation of H<sub>2</sub>S from CH<sub>4</sub>, notably the studies reported by Stern [2-7], Baker [8,9], and Klass and Landahl [10], in which the H<sub>2</sub>S/CH<sub>4</sub> selectivities have been reported. Most results presented in these researches were related to cellulose acetate (CA) [3,8], polyimide [6], poly-

urethane [5,7] and PEBAX [7,8] membranes.

Among the glassy polymers, Cardo-type polyimide (PI) and polyphenylene oxide (PPO) possess excellent separation properties that make them suitable candidates for gas separation. The polyimide hollow fiber membranes that were developed for CO<sub>2</sub>/N<sub>2</sub> separation by “Research Institute of Innovative Technology for the Earth” (RITE, Japan) proved to be good candidates for CO<sub>2</sub>/CH<sub>4</sub> separation due to their high selectivities in comparison with other glassy membranes [11].

PPO has also been proven a suitable candidate for a wide range of industrial gas separation applications. It is a linear amorphous thermoplastic with glass transition temperature (T<sub>g</sub>) ranging from 212 to 218 °C. Because of the presence of the phenyl rings, PPO is hydrophobic and has excellent resistance to water, acids, alcohols, steam and bases. It has been reported that, among all glassy polymers, PPO shows one of the highest permeabilities to gases [12-16]. The high permeability has been attributed to the absence of polar groups in the main chain of PPO [16]. An important factor governing the separation properties of any industrial application of membrane is the presence of other contaminants in the stream.

Bhide and Stern [3] presented the effect of H<sub>2</sub>S on the performance of CA membranes in removing acid gases from CH<sub>4</sub>. They indicated that at concentrations greater than 1% H<sub>2</sub>S in a tertiary mixture of CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>S, not only CO<sub>2</sub>, but also H<sub>2</sub>S shows plasticization effects. The group showed that the combined effects of the two gases reduced the selectivities of the membranes.

Lee et al. [17] studied the effect of H<sub>2</sub>S impurity on the performance of the CA membrane and observed that in the presence of water vapor the plasticization effect of H<sub>2</sub>S is magnified mainly in terms of permeation velocity. They proposed that membrane treatment of gases containing both H<sub>2</sub>S and water vapor should be avoided,

†To whom correspondence should be addressed.

E-mail: msoltanieh@sharif.edu

‡Present address: Industrial Membrane Research Institute, Department of Chemical & Biological Engineering, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

especially at relatively high concentrations of H<sub>2</sub>S.

Cooley and Coady [18] also reached a similar conclusion by suggesting that for an effective removal of H<sub>2</sub>S from natural gas using CA membranes, the feed should already be free of water vapor.

In the case of (PI) membranes, it is reported that unlike their higher CO<sub>2</sub>/CH<sub>4</sub> selectivity compared with CA membranes, their H<sub>2</sub>S/CH<sub>4</sub> selectivity is relatively low. For this reason, these membranes are not capable of economically removing H<sub>2</sub>S from natural gas in an industrial application. Stern et al. [6] studied the separation properties of PI membrane based on 6FDA (hexafluoropropane dianhydride). They tried to remove CO<sub>2</sub> from a tertiary mixture of CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>S at high H<sub>2</sub>S concentrations (2.8 to 8%). The group concluded that the selectivity of membranes improved in the presence of H<sub>2</sub>S. While they pointed out that this phenomenon was unpredictable, they did not offer any explanation for their observations.

Klass and Landahl [10] studied the separation of H<sub>2</sub>S and CO<sub>2</sub> from CH<sub>4</sub> with membranes such as Nylon 6, Nylon 6.6 (polyamide), polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) and also rubbery membranes. Although they achieved H<sub>2</sub>S/CH<sub>4</sub> selectivities in the vicinity of 200, the permeabilities of these membranes were very low.

Chatterjee et al. [7] studied the permeation properties of the membranes made of a group of polyurethanes (PU) and polyurethaneureas (PUU). According to their findings, there was a direct correlation between permeabilities of the experimental gases and their critical temperatures. Furthermore, because critical temperature directly affects solubility of gases into rubbery polymers, they concluded that the permeation of the experimental gases was controlled by their solubilities. It was also shown that PUU had better H<sub>2</sub>S/CH<sub>4</sub> selectivity than PU.

Bhide and Stern [2,3] and Bhide et al. [4] showed that H<sub>2</sub>S removal by membranes is an important constraint in system selection affecting the economics of the process. The above authors and Lee et al. [17] pointed out that most existing commercial membranes are not capable of economically reducing the concentration of H<sub>2</sub>S from 5,000 ppm or more to 4 ppm, and that a hybrid system including absorption would be the preferred process. It should be mentioned that the cost of the hybrid process is independent of concentration of H<sub>2</sub>S, and perhaps for the same reason the studies were mainly carried out without taking into account the separation of H<sub>2</sub>S from CH<sub>4</sub> by membranes. At lower feed concentrations of H<sub>2</sub>S where the concentration of H<sub>2</sub>S in the product can be reduced easily by absorption, the concentration of H<sub>2</sub>S in the feed is not a determining parameter in the process design. However, as mentioned before, care must be taken where the presence of small amount of H<sub>2</sub>S along with other components could have a negative effect on the performance of membranes for separation of other gases.

In most studies it is assumed that the plasticization effects and permeabilities of H<sub>2</sub>S and CO<sub>2</sub> in gas mixtures are the same. For example, Kaldis et al. [19] substituted CO<sub>2</sub> for H<sub>2</sub>S in a series of experiments using commercial Ube polyimide membrane, assuming similar permeabilities of these two gases. It should be mentioned that in a few studies this assumption has been confirmed using a gas mixture containing 1% H<sub>2</sub>S. For example, Bhide et al. [4] reported a selectivity of 19 for H<sub>2</sub>S/CH<sub>4</sub> and 21 for CO<sub>2</sub>/CH<sub>4</sub>.

Lokhandwala and Baker [20] studied H<sub>2</sub>S and CO<sub>2</sub> separation from CH<sub>4</sub> by membrane. They proposed a two-step membrane pro-

cess in which the first step contains an H<sub>2</sub>S selective module and the other a CO<sub>2</sub>-selective one. For instance, if the natural gas contains water vapor, it is better to feed it first to the H<sub>2</sub>S-selective module because such membrane would not be damaged by water vapor and the moisture would be transported along with H<sub>2</sub>S to the permeate side. After examining a number of different membrane materials for CO<sub>2</sub> removal, they recommended cellulose acetate and its derivatives as the preferred material for this application. They also recommended copolymers of polyimidepolyether as the most suitable membrane material for H<sub>2</sub>S removal. The latter polymers are currently marketed under PEBAX and Vestamid trade names by Atochem Inc. and Noudex Inc., respectively. The CA membrane used in the study showed a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 20 and H<sub>2</sub>S/CH<sub>4</sub> selectivity of 25. A research group (Lokhandwala and Baker [20]) examined three membrane configurations in the study: single-membrane system with high H<sub>2</sub>S/CH<sub>4</sub> selectivity, single-membrane system with high CO<sub>2</sub>/CH<sub>4</sub> selectivity, and double-membrane system as explained above.

Ismail and Lorna [21] reviewed penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane. They presented an overview of the plasticization phenomenon and the alteration of physical properties resulting from the polymer plasticization by the sorbed penetrant molecules. They also reviewed the plasticization suppression methods in polymeric membrane for gas separation and the future direction of research in this area.

Merkel [22] compared transport properties of H<sub>2</sub>S in fluorinated and nonfluorinated polymers. They showed that nonideal behavior occurred for poly dimethylsiloxane (PDMS), a rubbery polymeric membrane, where the permeability increases with increasing pressure. This behavior indicates that Henry's Law is not applicable for H<sub>2</sub>S at low pressures, even when it is for N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>.

Lin et al. [23] studied plasticization-enhanced H<sub>2</sub> purification using polymeric membranes. They introduced highly permeable, reverse-selective membrane materials, as exemplified by molecularly engineered, highly branched, cross-linked poly ethylene oxide. In contrast to the performance of conventional materials, they demonstrated that plasticization can be harnessed to improve separation performance.

Kanehashi et al. [24] studied the effects of CO<sub>2</sub> induced plasticization on the gas transport properties of glassy polyimide membranes. They investigated the time dependence of CO<sub>2</sub> transport properties, such as permeability, solubility and diffusivity, in glassy PI membranes in terms of membrane preparation protocols (i.e., casting solvent and thermal treatment). The time dependence of CO<sub>2</sub> permeability in the as-cast 6FDA-TeMPD membranes prepared from tetrahydrofuran and dichloromethane showed typical CO<sub>2</sub>-induced plasticization at pressures over 10 atm. The critical plasticization pressure at which CO<sub>2</sub>-induced plasticization begins to affect the gas permeability shifted from nearly 10 atm to 30 atm after heat treatment. The increase in CO<sub>2</sub> permeability upon plasticization is mostly caused by an increase in CO<sub>2</sub> diffusivity. Furthermore, they found that regardless of the membrane preparation protocol, there is a critical CO<sub>2</sub> diffusivity of  $73 \pm 5 \times 10^8$  cm<sup>2</sup>/s at the plasticization pressure in 6FDA-TeMPD membranes.

Visser et al. [25] studied the materials' dependence of mixed gas plasticization behavior in asymmetric membranes. They performed a systematic analysis for five different asymmetric membranes including pure Matrimid, blends of Matrimid with polyethersulfone,

Matrimid with a polyimide P84, cellulose acetate and polyphenylene-oxide PPO with respect to the balance between competitive sorption and plasticization. They reported that a subtle balance exists between competitive sorption and plasticization effects for all asymmetric membranes investigated. The magnitude of competition or plasticization effects varies depending on the materials investigated. Different levels of CO<sub>2</sub>-concentration are required to reach the point where plasticization starts to dominate the separation performance of a certain material. They also reported that the blend of Matrimid with P84 shows the highest mixed gas selectivity and is very resistant against plasticization without any further chemical modification.

Xiao et al. [26] reviewed the strategies of molecular architecture and modification of polyimide-based membranes for CO<sub>2</sub> removal from natural gas. They reported that in addition to good gas separation performance, the durability and the lifetime of the polyimide membranes are also important. Aging and plasticization phenomena create undesirable time-dependency of the gas separation performance for polyimide membranes. To improve the stability of membrane, thermal annealing, polymer blending and cross-linking can be employed. However, for successful commercial application of membrane-based natural gas treatment using polyimides, hollow fiber processing and the overall costs must be adequately tuned.

Scholes et al. [27] reviewed the effects of minor components such as SO<sub>x</sub>, NO<sub>x</sub>, CO, H<sub>2</sub>S, NH<sub>3</sub>, as well as condensable water and hydrocarbons in terms of their permeability through polymeric membranes relative to CO<sub>2</sub>, as well as their plasticization and aging effects on membrane separation performance in both pre- and post-combustion for CO<sub>2</sub> capture. They concluded that many minor components can affect performance both through competitive sorption and plasticization, but much remains unknown. This limits the selection process for membranes in this application.

In another study, Scholes et al. [28] investigated the effect of H<sub>2</sub>S, CO and water on the performance of a PDMS membrane in CO<sub>2</sub>/N<sub>2</sub> separation. The permeability of CO<sub>2</sub> through PDMS is reduced upon exposure to CO, H<sub>2</sub>S and water, due to competitive sorption of these gases into the polymeric matrix.

Meanwhile, the same authors studied [29] the plasticization of ultra-thin polysulfone membranes by CO<sub>2</sub>. They concluded that the plasticization potential of CO<sub>2</sub> increases with decreasing membrane thickness, correlating with the plasticization pressure behavior. Furthermore, the plasticization potential decreased with temperature, implying that CO<sub>2</sub> ability to plasticize the polysulfone membrane reduced at higher temperature.

Basu et al. [30] examined the performance and stability of membranes based on Matrimid, PSf and their blends as a function of temperature, pressure, feed composition and time for more realistic

CO<sub>2</sub>/CH<sub>4</sub> binary gas mixtures and through asymmetric membranes with higher fluxes. PSf was chosen as it is a cheap material, resistant to highly sorbing gases and CO<sub>2</sub>-induced plasticization (>50 bar). They showed that blending appropriate polymers with Matrimid increased critical plasticization pressure. The membrane prepared from a 3 : 1 (Matrimid : PSf) blend ratio showed consistent increase in selectivity at high CO<sub>2</sub> feed composition (up to 90 vol%), elevated temperature (up to 95 °C) and pressure (up to 14 bar). On the contrary, unblended Matrimid membrane performance deteriorated under operating conditions above 90 vol% CO<sub>2</sub> feed composition, 65 °C and 12 bar. Moreover, the prepared asymmetric membranes showed much higher permeances than corresponding dense membranes without too much compromising selectivity.

Omole et al. [31] reported the effects of CO<sub>2</sub> on a high performance hollow-fiber membrane for natural gas purification. They prepared 6FDA-based, cross-linkable polyimide in the form of a defect-free asymmetric hollow-fiber membrane and tested for natural gas purification in the presence of high CO<sub>2</sub> partial pressures. The cross-linked membrane material showed high intrinsic separation performance for CO<sub>2</sub> and CH<sub>4</sub> (selectivity ~49, CO<sub>2</sub> permeability ~161 barrer, with a feed at 65 psia, 35 °C, and 10% CO<sub>2</sub>). Cross-linked asymmetric hollow-fiber membranes made from the material showed good resistance to CO<sub>2</sub>-induced plasticization. These researchers performed the experiments in CO<sub>2</sub> partial pressures as high as ~400 psia, and they showed that the membrane was promisingly stable under these aggressive conditions. The performance of the membrane was also analyzed using the dual-mode sorption/transport model.

In the present study, the removal of H<sub>2</sub>S from methane was studied using commercial Cardo-type polyimide and PPO membranes under different experimental conditions.

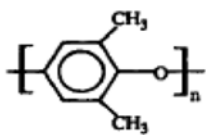
## MATERIALS AND METHODS

### 1. Materials

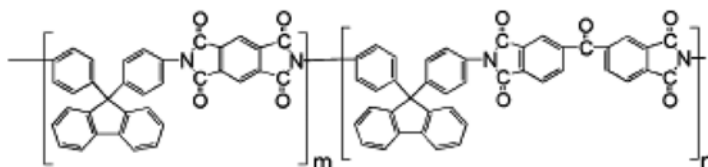
The Cardo-type polyimide hollow fiber module was generously supplied by RITE, Japan. The inside and outside diameters of fibers were 370 and 500 μm, respectively. The PPO hollow fibers were generously supplied by Aquilo Gas Separation B.V., the Netherlands (Parker Filtration and Separation B.V., The Netherlands). The inside and outside diameters of hollow fibers were 370 and 520 μm, respectively. The chemical structures of the polymers and the specifications of the membrane modules are shown in Fig. 1 and Table 1, respectively.

The PPO module was assembled by loading a bundle of 10 fibers in a shell and tube structure. Although the dense selective layer of

**Poly (2,6-dimethyl-1,4-phenylene oxide)**



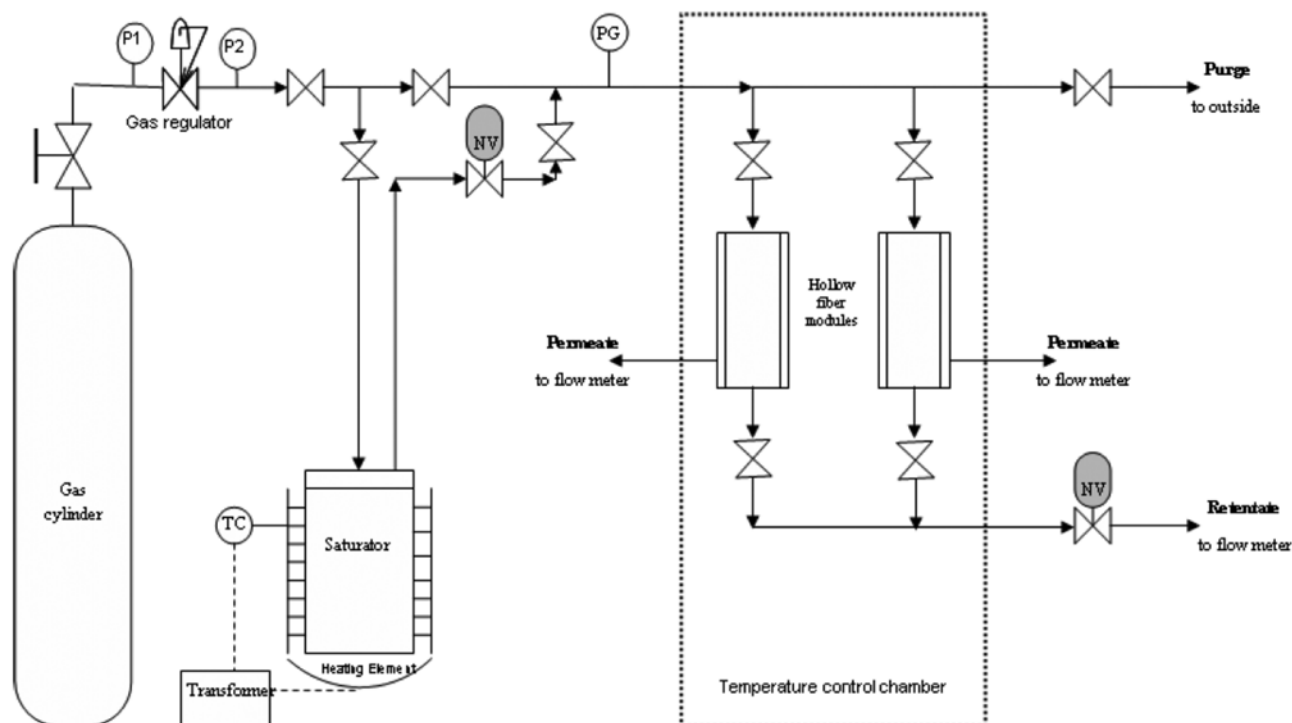
**Cardo-type polyimide**



**Fig. 1. Chemical structure of polyphenylene oxide (PPO) and Cardo-type polyimide membranes [11].**

**Table 1. Cardo-type polyimide and PPO modules and hollow fibers specifications**

Module name	Membrane type	Hollow fiber parameters		Module specifications	
		Inside diameter ( $\mu\text{m}$ )	Outside diameters ( $\mu\text{m}$ )	Number of fibers	Permeation area ( $\text{cm}^2$ )
RITE-A	Cardo-type PI (PI-BT)	370	500	135	416
PPO#1	PPO	370	520	10	49

**Fig. 2. Schematic diagram of the constant pressure membrane testing system.**

PPO hollow fibers was on the shell side, in this study, the feed gas was introduced inside the fibers and permeate was collected from the shell. The permeance was calculated based on the outer surface area of the hollow fibers. Ultrahigh purity  $\text{CH}_4$  and  $\text{H}_2\text{S}/\text{CH}_4$  gas mixtures with 101, 198 and 401 ppm of  $\text{H}_2\text{S}$  in  $\text{CH}_4$  were purchased from Praxair Distribution Inc., Canada.

## 2. Gas Permeation Experiments

The experimental gas separation system is illustrated schematically in Fig. 2. The separation experiments were carried out at 50, 75 and 100 psig and room temperature ( $23^\circ\text{C}$ ) for each membrane. One set of experiments was also conducted at 100 psig and  $40^\circ\text{C}$  in order to understand the effect of temperature on the performance of the membranes.

The  $\text{H}_2\text{S}$ -rich permeate, was collected at atmospheric pressure and the  $\text{CH}_4$ -rich retentate was collected at a pressure approximately equal to that of the feed. Pure methane or  $\text{H}_2\text{S}/\text{CH}_4$  gas mixture was supplied from a cylinder to the bore side of the hollow fibers. The entire system was placed in a temperature-controlled chamber with air circulation.

The permeation rate was measured by a bubble-flow-meter, and the retentate flow rate was measured by a wet-test-meter. The stage-cut was controlled by a metering valve installed at the retentate side. The compositions of the retentate and permeate streams were determined by a gas chromatograph (Varian 3400) equipped with a

thermal conductivity detector (TCD) and a ‘‘HayeSep T’’ column. The compositions were corrected using thermal response factors, TRFs. The TRF values were carefully calculated for each gas following Dietz’s method [32].

The effects of  $\text{H}_2\text{S}$  concentration, pressure, temperature and stage cut on the performance of the membranes were studied. At each operating conditions the experiments were conducted in the following order: pure  $\text{CH}_4$ ,  $\text{CH}_4/\text{H}_2\text{S}$  mixtures at 101, 198, 401 ppm,  $\text{H}_2\text{S}$  contents and repeat of pure  $\text{CH}_4$ . Each experiment was repeated three times to ensure the reproducibility of the results.

## THEORY

The permeance ( $P/l$ ) defined as pressure-normalized flux, is calculated as:

$$\left(\frac{P}{l}\right) = \frac{Q_p}{A\Delta p} \times 10^6 = \frac{F}{\Delta p} \times 10^6 \quad (1)$$

Where ( $P/l$ ) is permeance, GPU (gas permeation unit= $10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \text{ s cmHg}$ ),  $Q_p$  permeation rate,  $\text{cm}^3 (\text{STP})/\text{s}$ ,  $A$  permeation area of the membrane,  $\text{cm}^2$ ,  $\Delta p$  pressure difference across the membrane,  $\text{cmHg}$  and  $F$  is permeation flux,  $\text{cm}^3 (\text{STP})/\text{cm}^2 \text{ s}$ .

The ideal selectivity of gas A over gas B ( $\alpha'_{A/B}$ ) is calculated as follows:

$$\alpha_{AB}^o = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

The permeance of gas  $i$  ( $(P/l)_i$ ), and the separation factor of gas  $i$  over gas  $j$ ,  $\alpha_{ij}$ , in a mixture, are estimated by:

$$\left(\frac{P}{l}\right)_i = \frac{Q_p y_i}{(p_F \bar{x}_i - p_p y_i) A} \times 10^6 \quad (3)$$

Where  $(P/l)_i$  is permeance of gas  $i$ , GPU,  $y_i$  component mole fraction of gas  $i$  at permeate outlet,  $p$  pressure, cmHg and  $\bar{x}_i, \bar{x}_j$  are logarithmic average mole fractions of gases  $i$  and  $j$  in the feed side and are calculated as in Eq. (5).

$$(\bar{x}_i)_{ln} = \frac{x_{i,F} - x_{i,R}}{\ln(x_{i,F}/x_{i,R})} \quad (5)$$

Where  $x_i$  is the component mole fraction of gas  $i$  in the feed side.

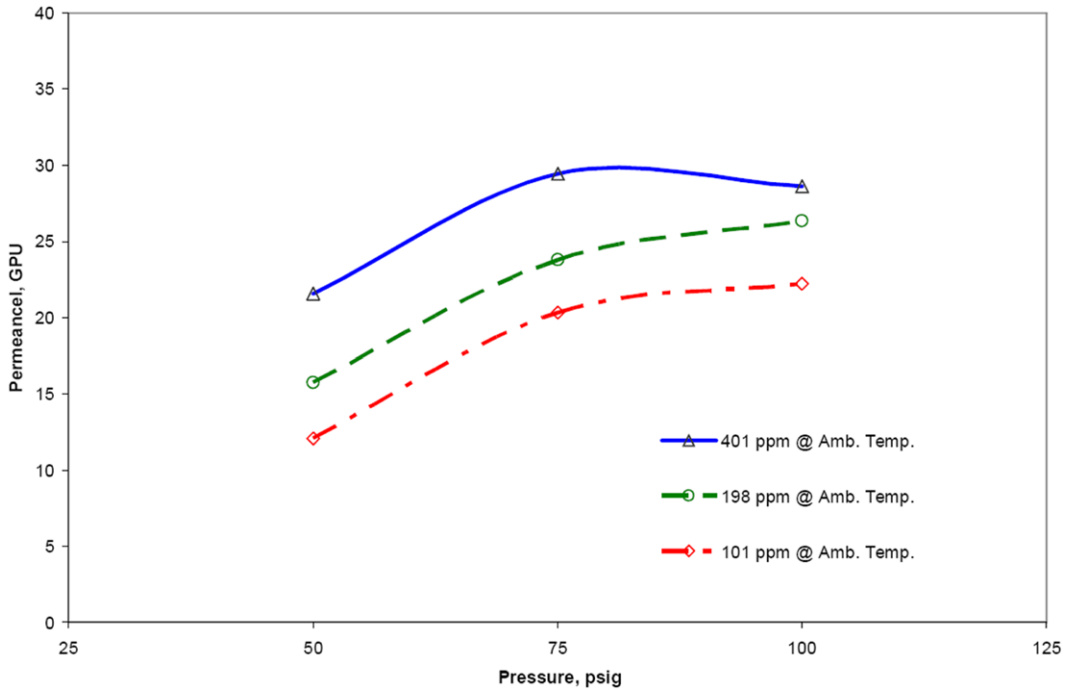


Fig. 3. H<sub>2</sub>S permeance vs. feed pressure in separation of H<sub>2</sub>S/CH<sub>4</sub> mixtures at room temperature for RITE-A module.

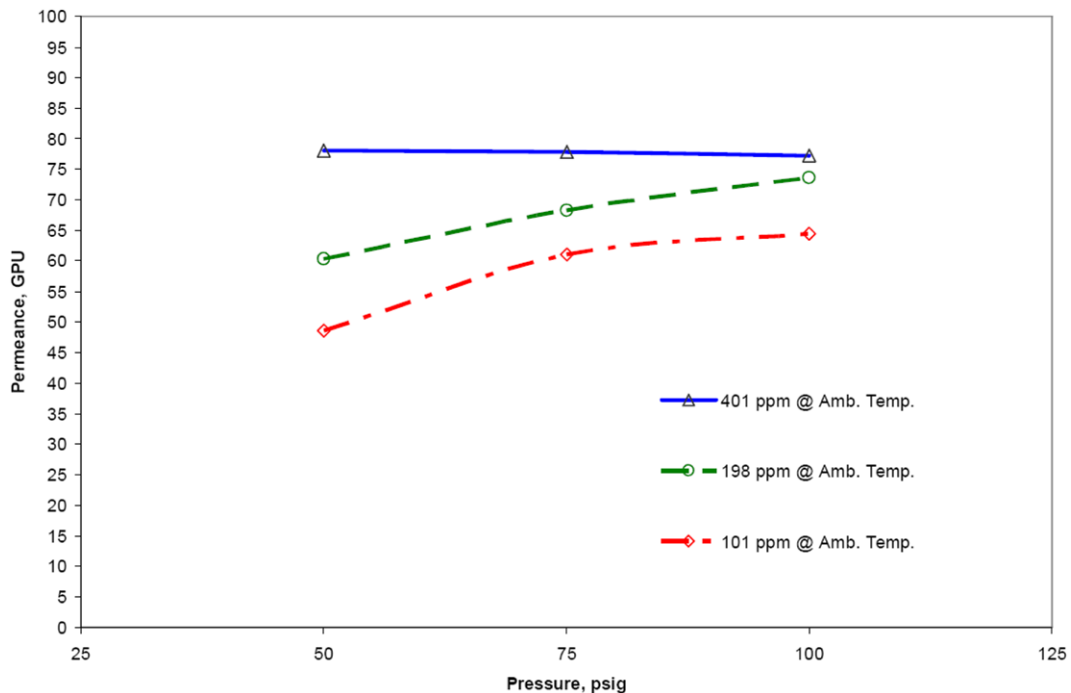


Fig. 4. H<sub>2</sub>S permeance vs. feed pressure in separation of H<sub>2</sub>S/CH<sub>4</sub> mixtures at room temperature for PPO module.

Subscripts F and R denote feed and retentate, respectively.

It should be noted that the separation factors for gas mixtures were calculated using Eq. (4), whereas the ideal selectivity data were estimated by inserting the values from Eq. (3) into Eq. (2).

## RESULTS AND DISCUSSION

The results of permeability experiments with CH<sub>4</sub>/H<sub>2</sub>S mixtures

at room temperature and different pressures of 50, 75 and 100 psig are shown in Figs. 3 and 4. The results for the same set of operating pressures but at 40 °C are shown in Figs. 5 to 8.

Fig. 3 shows the H<sub>2</sub>S permeance at various pressures and different concentrations of H<sub>2</sub>S for the RITE-A module (Cardo type PI). This figure shows that the permeance of H<sub>2</sub>S increased as the feed pressure (except for H<sub>2</sub>S concentration of 401 ppm) and the concentration of H<sub>2</sub>S increased. This can be explained by the higher

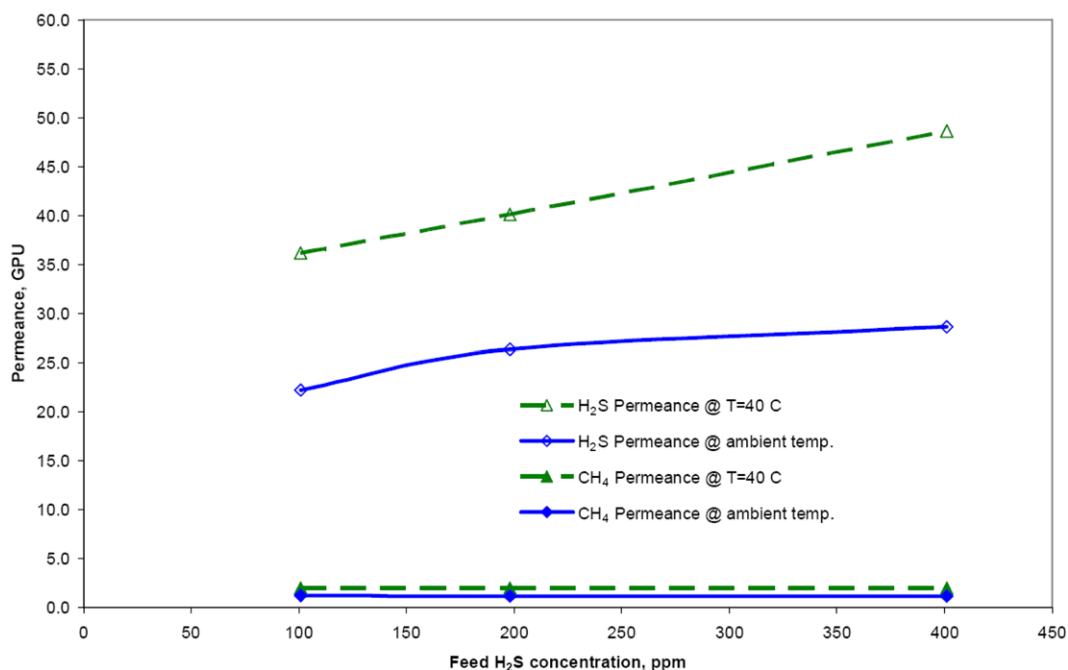


Fig. 5. CH<sub>4</sub> and H<sub>2</sub>S permeabilities vs. H<sub>2</sub>S feed concentration at different temperatures for RITE-A module.

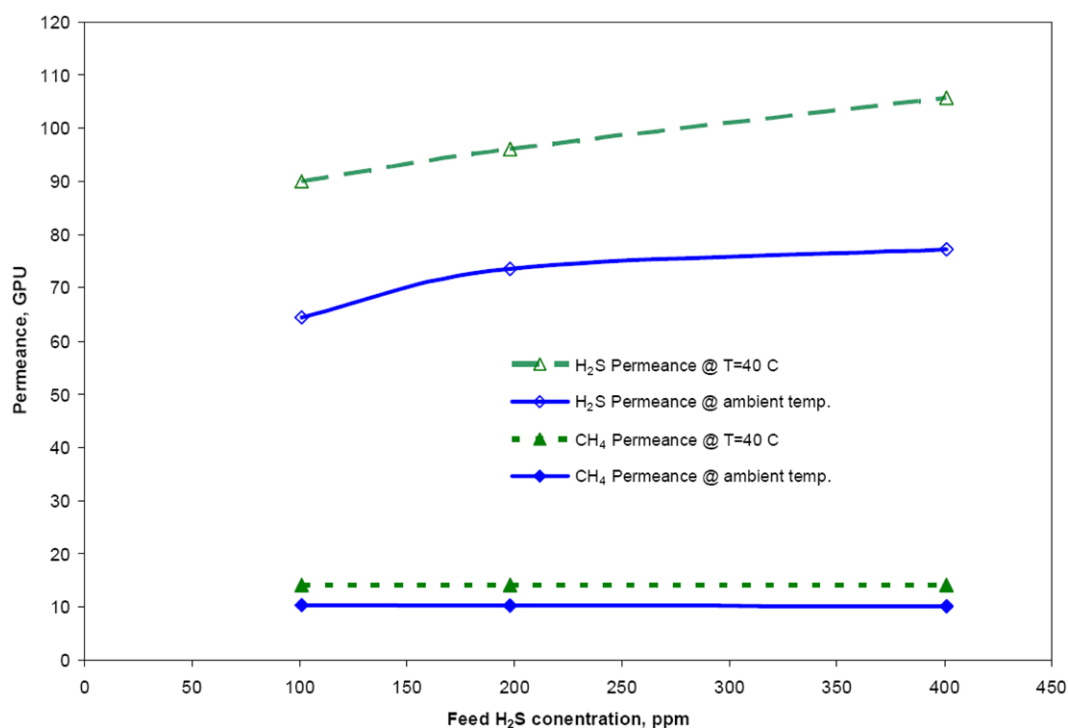


Fig. 6. CH<sub>4</sub> and H<sub>2</sub>S permeabilities vs. H<sub>2</sub>S feed concentration for PPO module.

driving force for the higher partial pressure difference across the membrane. These results were obtained at a stage cut of 5%. Fig. 4 shows a similar observation for PPO membrane.

The effect of temperature on the permeability of CH<sub>4</sub> and H<sub>2</sub>S is shown in Figs. 5 and 6. An increase in the temperature from 23 °C to 40 °C results in 60-70% increase in permeabilities of both CH<sub>4</sub> and H<sub>2</sub>S for RITE-A module and 35-40% for PPO module at the feed concentrations of 101 to 401 ppm. Because the permeability

of both components increased at the same rate with increasing temperature, the ideal selectivity and the separation factor for both modules remained constant (Figs. 7 and 8). The selectivities of membranes at lower temperature were slightly higher than those at high temperature.

It has been mentioned before that H<sub>2</sub>S plasticizes the membranes, which seems to be more pronounced at higher temperatures. To study the plasticization effect of H<sub>2</sub>S, pure CH<sub>4</sub> permeation experiments

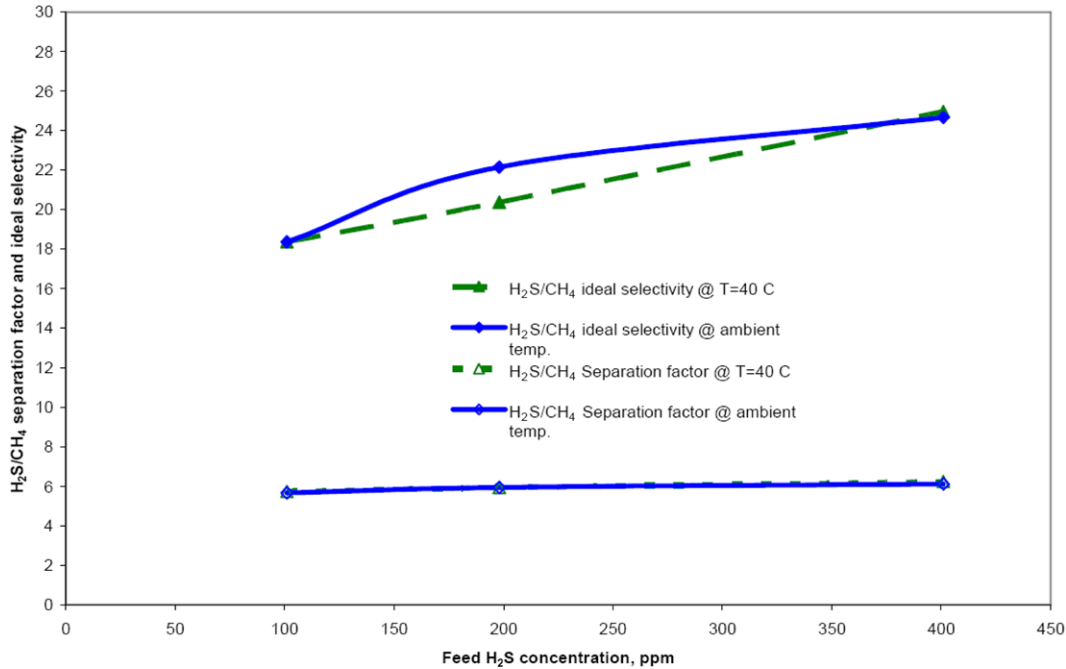


Fig. 7. The effect of temperature on the ideal selectivity and separation factor of RITE module for H<sub>2</sub>S/CH<sub>4</sub> mixtures.

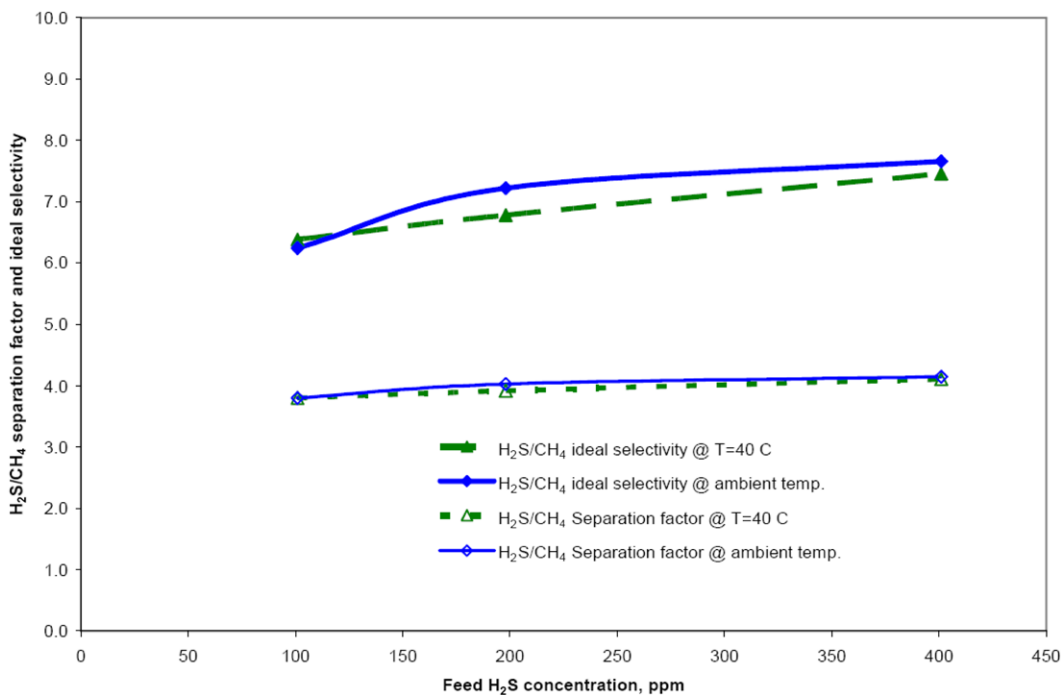


Fig. 8. The effect of temperature on the ideal selectivity and separation factor of PPO module for H<sub>2</sub>S/CH<sub>4</sub> mixtures.

were performed before and after each series of gas mixture tests. The results, as presented in Figs. 9 and 10, indicated that the perme-

ation rate of pure methane slightly declined in the tests done after the gas mixture experiments compared with that before.

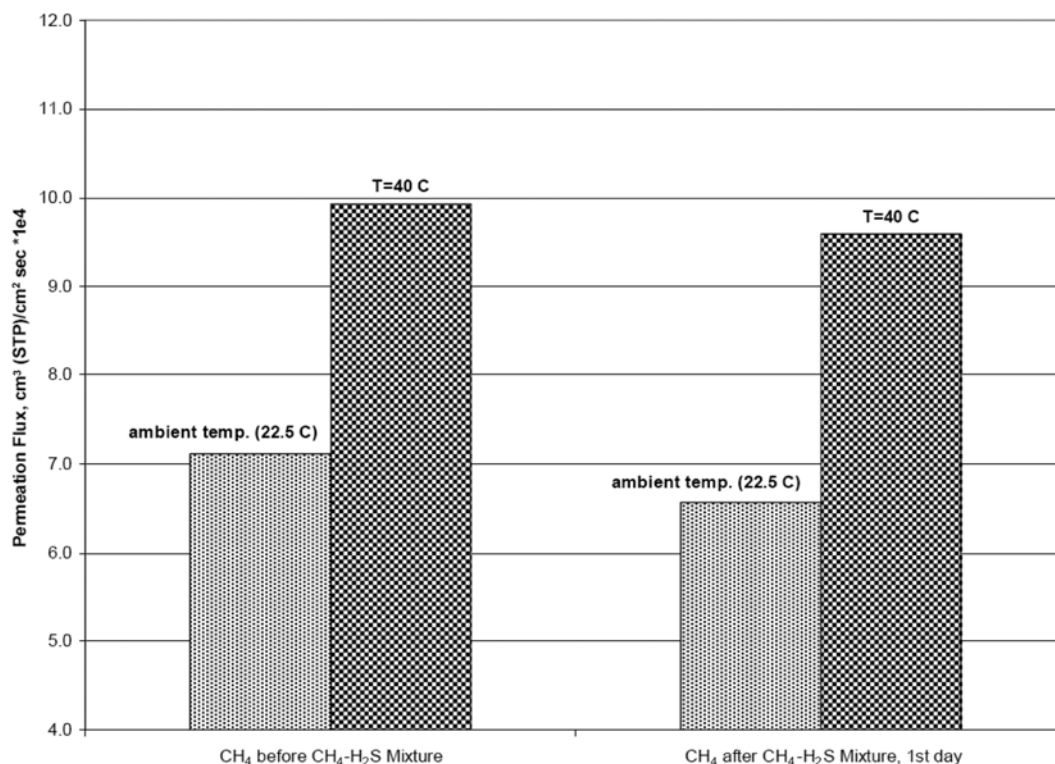


Fig. 9. The effect of temperature on permeation flux of CH<sub>4</sub> before and after experiments with H<sub>2</sub>S mixtures for RITE module.

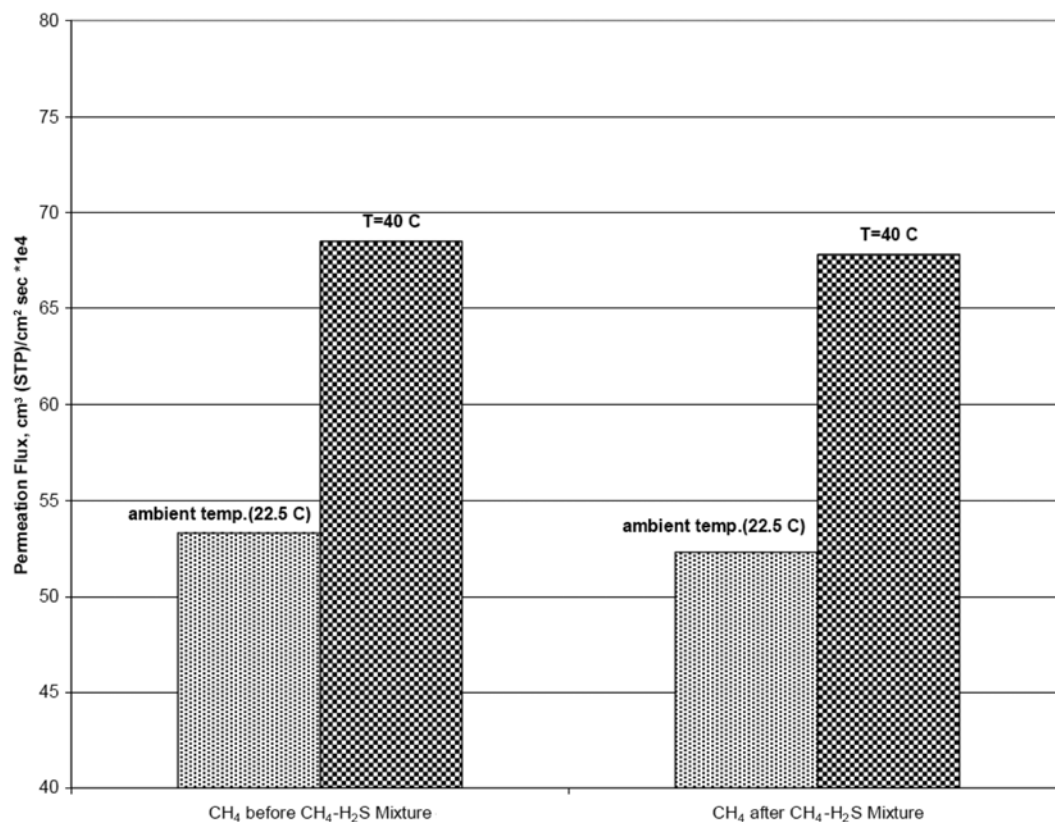


Fig. 10. The effect of temperature on permeation flux of CH<sub>4</sub> before and after experiments with H<sub>2</sub>S mixtures for PPO module.



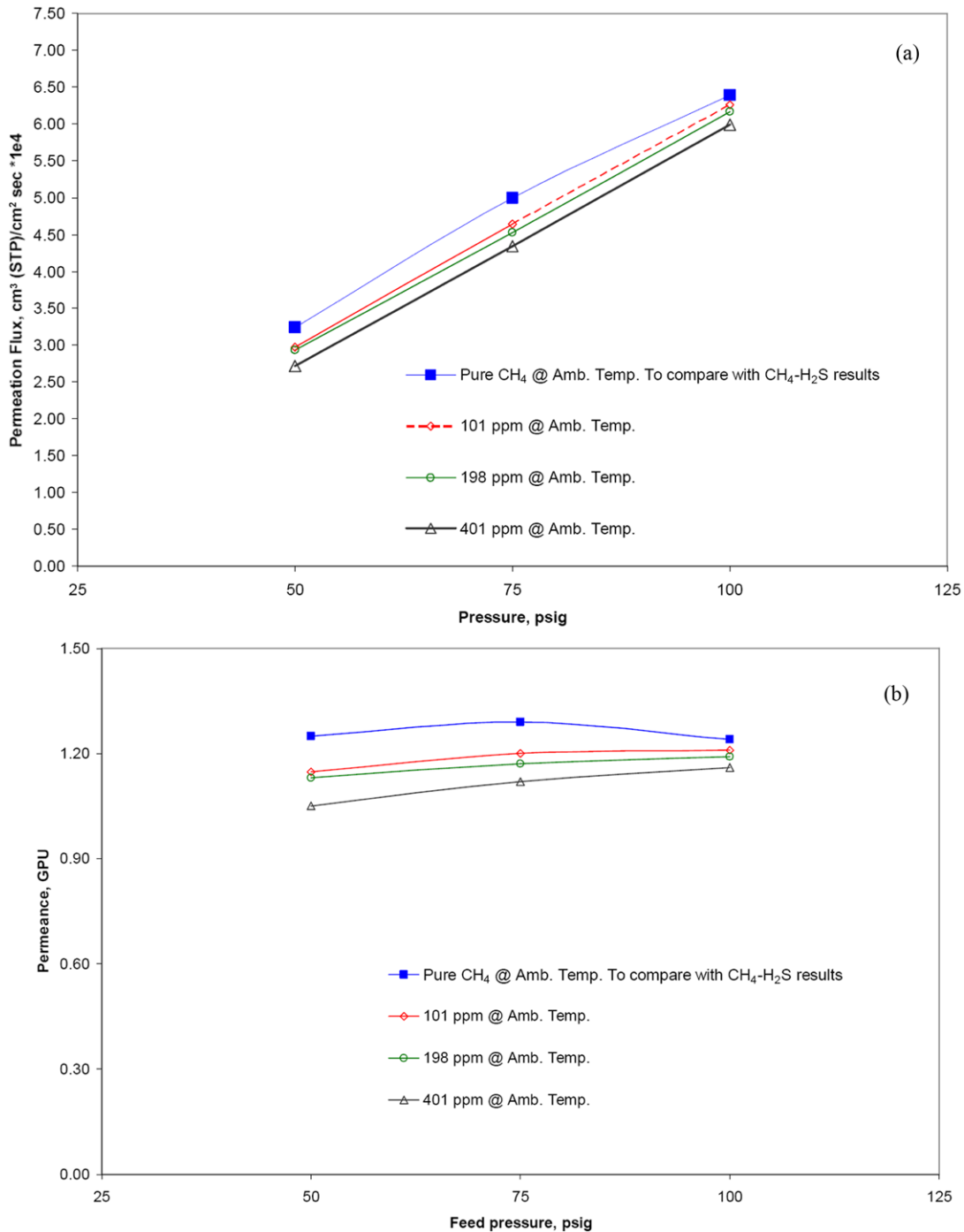


Fig. 11. (a) CH<sub>4</sub> permeation flux and (b) permeance of pure CH<sub>4</sub> and CH<sub>4</sub>/H<sub>2</sub>S mixtures for RITE module.

The effect of H<sub>2</sub>S on CH<sub>4</sub> permeation flux and permeance is shown graphically in Figs. 11 and 12. Fig. 11 compares the permeability and permeance of pure methane with the permeation flux and permeance of methane in the presence of H<sub>2</sub>S through PI membrane. An obvious decreasing trend in the permeation flux and permeance of methane in the presence of H<sub>2</sub>S can be observed from this figure. This observation is contrary to the expectation of higher methane permeation flux and permeance due to the plasticization effect of H<sub>2</sub>S. The very low concentration of H<sub>2</sub>S might play a role in this observation as it might not be enough for an effective plasticization

of the membrane. In such case, the decline in methane permeation flux and permeance should only be considered as a random process. This explanation is supported by the trend observed from PPO membrane, as shown in Fig. 12. The latter figure indicates a consistent permeation flux and permeance of methane gas in the presence or absence of H<sub>2</sub>S, emphasizing that the concentration of H<sub>2</sub>S is not large enough to plasticize the membrane and increase the methane permeation flux and permeance.

Table 2 shows the concentration of H<sub>2</sub>S in feed, retentate and permeate along with the separation factors of H<sub>2</sub>S/CH<sub>4</sub> at different feed

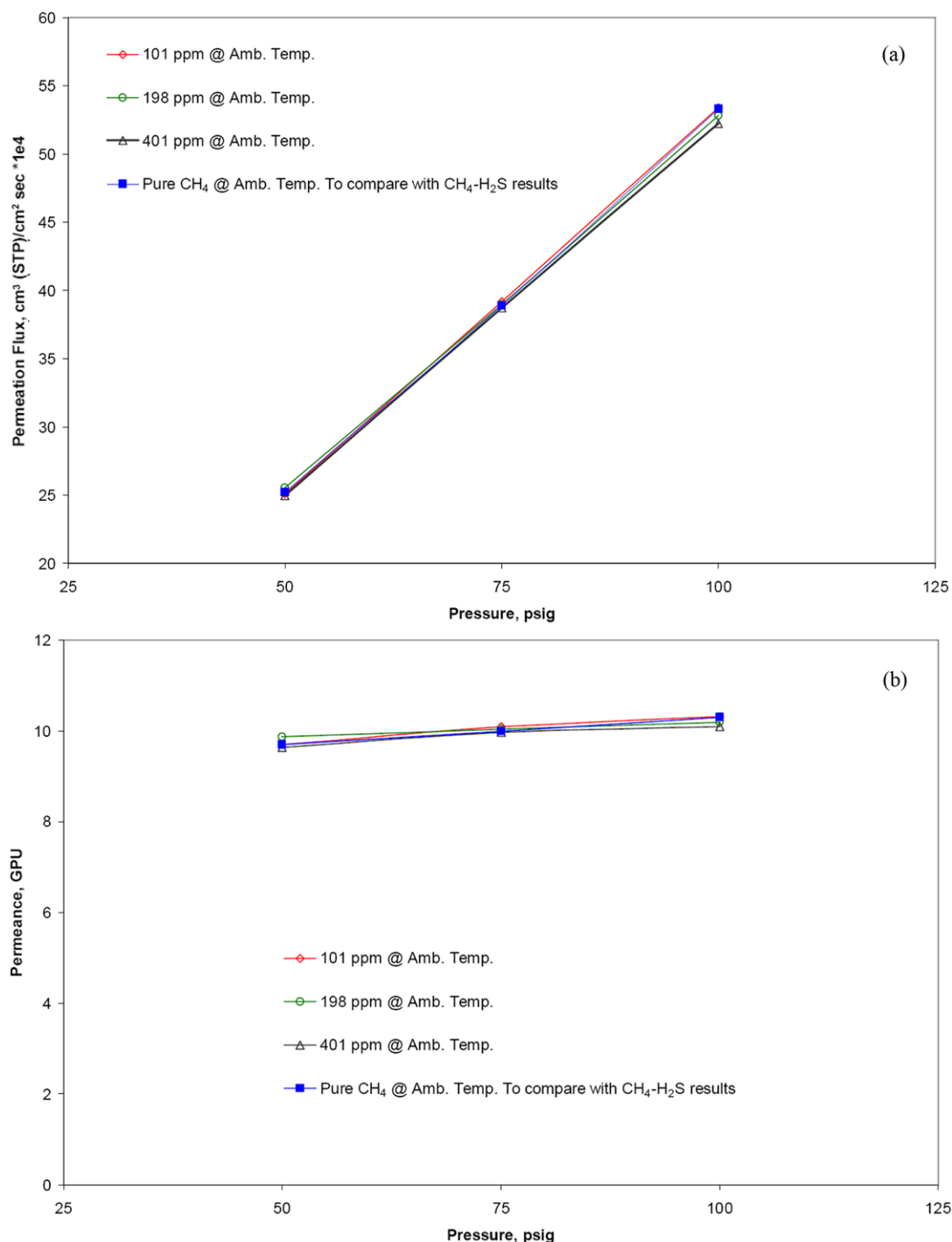


Fig. 12. (a) CH<sub>4</sub> permeability and (b) permence of pure CH<sub>4</sub> and CH<sub>4</sub>/H<sub>2</sub>S mixtures for PPO module.

pressures and three levels of feed concentrations of H<sub>2</sub>S. These results indicate that the separation factors of the applied PPO and Cardo-type PI membranes are higher at high feed concentrations of H<sub>2</sub>S and therefore it is expected that the performance of these membranes to be better at higher feed H<sub>2</sub>S concentrations.

### CONCLUSIONS

Separation of H<sub>2</sub>S/CH<sub>4</sub> mixtures at various concentrations of H<sub>2</sub>S

was investigated for two commercially available hollow fiber membranes, including Cardo-type polyimide and polyphenylene oxide (PPO) membranes, at different operating pressures and temperatures. In the presence of H<sub>2</sub>S the permeance of CH<sub>4</sub> declined for the Cardo-type polyimide membranes, whereas for the PPO membranes it remained relatively unchanged. The separation factors of H<sub>2</sub>S/CH<sub>4</sub> were 6 and 4 for Cardo-type polyimide and PPO membranes, respectively. It was also observed that the component permeabilities increased with temperature, but separation factor remained the same.

**Table 2. Composition of feed, permeate and retentate at different feed pressures. Separation of H<sub>2</sub>S/CH<sub>4</sub> with RITE and PPO module**

Feed pressure psig	101 ppm (vol%: 0.0101)			RITE-A Feed H <sub>2</sub> S concentration 198 ppm (vol%: 0.0198)			401 ppm (vol%: 0.0401)		
	Retentate H <sub>2</sub> S (vol%)	Permeate H <sub>2</sub> S (vol%)	Separation factor (H <sub>2</sub> S/CH <sub>4</sub> )	Retentate H <sub>2</sub> S (vol%)	Permeate H <sub>2</sub> S (vol%)	Separation factor (H <sub>2</sub> S/CH <sub>4</sub> )			
	50	0.0090	0.0315	3.3	0.0174	0.065	3.5	0.0349	0.141
75	0.0084	0.043	4.7	0.0162	0.087	4.9	0.0324	0.184	5.1
100	0.0080	0.051	5.7	0.0153	0.104	5.9	0.0309	0.216	6.1
100*	0.0079	0.051	5.7	0.0153	0.104	5.9	0.0306	0.219	6.2
PPO#1									
50	0.0093	0.0255	2.6	0.0180	0.053	2.8	0.0359	0.118	3.1
75	0.0090	0.0317	3.3	0.0174	0.065	3.5	0.0350	0.139	3.7
100	0.0088	0.0353	3.8	0.0168	0.074	4.0	0.0342	0.154	4.1
100*	0.0088	0.0358	3.8	0.0171	0.072	3.9	0.0342	0.152	4.1

### ACKNOWLEDGEMENTS

The authors are grateful to C. Y. Feng, K. C. Khulbe, Louis Trembley and Franco Ziroldo of the Department of Chemical & Biological Engineering of the University of Ottawa for their kind assistance in setting up the experimental apparatus. The courtesy of Parker Filtration and Separation B.V. of the Netherlands and the Research Institute of Innovative Technology for the Earth (RITE) of Japan for providing the membrane samples is highly appreciated. The financial support provided by the National Iranian Gas Company (NIGC) is greatly appreciated.

### NOMENCLATURE

- A : permeation area of membrane [cm<sup>2</sup>]  
 p<sub>F</sub> : feed pressure [cmHg]  
 p<sub>P</sub> : permeate pressure [cmHg]  
 (p/l)<sub>i</sub> : permeance of gas i [GPU]  
 (p/l)<sub>j</sub> : permeance of gas j [GPU]  
 Q<sub>F</sub> : feed flow rate [cm<sup>3</sup> (STP)·s<sup>-1</sup>]  
 Q<sub>P</sub> : permeate flow rate [cm<sup>3</sup> (STP)·s<sup>-1</sup>]  
 Q<sub>R</sub> : retentate flow rate [cm<sup>3</sup> (STP)·s<sup>-1</sup>]  
 T : temperature, [°C]  
 (x<sub>i</sub>)<sub>m</sub> : logarithmic average mole fraction of gas i in feed  
 (x<sub>j</sub>)<sub>m</sub> : logarithmic average mole fraction of gas j in feed  
 x<sub>i,F</sub> : mole fraction of gas i in feed  
 x<sub>j,F</sub> : mole fraction of gas j in feed  
 x<sub>i,R</sub> : mole fraction of gas i in retentate  
 x<sub>j,R</sub> : mole fraction of gas j in retentate  
 y<sub>i</sub> : mole fraction of gas i in permeate  
 y<sub>j</sub> : mole fraction of gas j in permeate

### Greek Letters

- α<sub>ij</sub> : separation factor of gas i over gas j, dimensionless  
 α<sub>ij</sub><sup>o</sup> : ideal selectivity of gas i over gas j, dimensionless

### Subscripts

- F : feed  
 i : gas i (here is H<sub>2</sub>S)

j : gas j (here is CH<sub>4</sub>)

P : permeate

R : retentate

### REFERENCES

1. R. W. Baker, *Membrane technology and applications*, 2nd Ed., John Wiley & Sons, Ltd. (2004).
2. B. D. Bhide and S. A. Stern, *J. Membr. Sci.*, **81**, 209 (1993).
3. B. D. Bhide and S. A. Stern, *J. Membr. Sci.*, **81**, 239 (1993).
4. B. D. Bhide, A. Voskericyan and S. A. Stern, *J. Membr. Sci.*, **140**, 27 (1998).
5. J. Hao, P. A. Rice and S. A. Stern, *J. Membr. Sci.*, **209**, 177 (2002).
6. S. A. Stern, H. Kawakami, A. Y. Houde and G. Zhou, US Patent, 5,591,250 (1997).
7. G. Chatterjee, A. A. Houde and S. A. Stern, *J. Membr. Sci.*, **135**, 99 (1997).
8. K. A. Lokhandwala and R. W. Baker, US Patent, 5,407,467 (1995).
9. R. W. Baker and K. A. Lokhandwala, US Patent, 5,558,698 (1996).
10. D. L. Klass and C. D. Landahl, US Patent, 4,561,864 (1985).
11. M. Pourafshari Chenar, M. Soltanieh, T. Matsuura, A. Tabe-Mohammadi and C. Feng, *Sep. Purif. Technol.*, **51**, 359 (2006).
12. B. J. Story and W. J. Koros, *J. Membr. Sci.*, **67**, 191 (1992).
13. S. Mortazavi, PhD Thesis, University of Ottawa (2004).
14. M. Aguilar-Vega and D. R. Paul, *J. Polym. Sci. B: Polym. Phys.*, **31**, 1577 (1993).
15. G. Chowdhury, B. Kruczek and T. Matsuura (Eds.), "Gas, Vapour and Liquid Separation," Kluwer Academic Publishers (2001).
16. N. A. Plate and Y. Yampolskii, "High free volume polymers," in: D. R. Paul, Y. Yampolskii (Eds.), *Polymer Gas Separation Membranes*, CRC Press, London (1994).
17. A. L. Lee, H. L. Feldkirchner, S. A. Stern, A. Y. Houde, J. P. Gamez and H. S. Meyer, *Gas Sep. Purif.*, **9**, 35 (1995).
18. T. E. Cooley and A. B. Coady, US Patent 4,130,403 (1978).
19. S. P. Kaldis, G. C. Kapantaidakis and G. P. Sakellaropoulos, *J. Membr. Sci.*, **173**, 61 (2000).
20. K. A. Lokhandwala and R. W. Baker, US Patent, 5,407,466 (1995).
21. A. F. Ismail and W. Lorna, *Sep. Purif. Technol.*, **27**, 173 (2002).
22. T. C. Merkel and L. G. Toy, *Macromolecules*, **39**, 7591 (2006).

23. H. Lin, E. V. Wagner, B. D. Freeman, L. G. Toy and R. P. Gupta, *Science*, **311**, 639 (2006).
24. S. Kanehashi, T. Nakagawa, K. Nagai, X. Duthie, S. Kentish and G. Stevens, *J. Membr. Sci.*, **298**, 147 (2007).
25. T. Visser, N. Masetto and M. Wessling, *J. Membr. Sci.*, **306**, 16 (2007).
26. Y. Xiao, B. T. Low, S. S. Hosseini, T. S. Chung and D. R. Paul, *Prog. Polym. Sci.*, **34**, 561 (2009).
27. C. A. Scholes, S. E. Kentish and G. W. Stevens, *Sep. Purif. Technol. Rev.*, **38**, 1 (2009).
28. C. A. Scholes, G. W. Stevens and S. E. Kentish, *J. Membr. Sci.*, **350**, 189 (2010).
29. C. A. Scholes, G. Q. Chen, G. W. Stevens and S. E. Kentish, *J. Membr. Sci.*, **346**, 208 (2010).
30. S. Basu, A. Cano-Odena and I. F. J. Vankelecom, *Sep. Purif. Technol.*, **75**, 15 (2010).
31. I. C. Omole, R. T. Adams, S. J. Miller and W. J. Koros, *Ind. Eng. Chem. Res.*, **49**, 4887 (2010).
32. W. A. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1967).