

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

***Industrial Membrane Research Institute, Department of Chemical & Biological Engineering,
University of Ottawa, Ottawa, Ont., Canada K1N 6N5

(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 H₂S 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 CO₂ from CH₄, the permeation behavior of H₂S 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 H₂S from CH₄, notably the studies reported by Stern [2-7], Baker [8,9], and Klass and Landahl [10], in which the H₂S/CH₄ selectivities have been reported. Most results presented in these researches

were related to cellulose acetate (CA) [3,8], polyimide [6], polyurethane [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 CO₂/N₂ separation by "Research Institute of Innovative Technology for the Earth" (RITE, Japan) proved to be good candidates for CO₂/CH₄ 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_g) 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 H₂S on the performance of CA membranes in removing acid gases from CH₄. They indicated that at concentrations greater than 1% H₂S in a tertiary mixture of CH₄-CO₂-H₂S, not only CO₂, but also H₂S 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 H₂S impurity on the performance of the CA membrane and observed that in the presence of water vapor the plasticization effect of H₂S is magnified mainly in terms of permeation velocity. They proposed that membrane treatment

†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

of gases containing both H₂S and water vapor should be avoided, especially at relatively high concentrations of H₂S.

Cooley and Coady [18] also reached a similar conclusion by suggesting that for an effective removal of H₂S 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 CO₂/CH₄ selectivity compared with CA membranes, their H₂S/CH₄ selectivity is relatively low. For this reason, these membranes are not capable of economically removing H₂S 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 CO₂ from a tertiary mixture of CH₄-CO₂-H₂S at high H₂S concentrations (2.8 to 8%). The group concluded that the selectivity of membranes improved in the presence of H₂S. 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 H₂S and CO₂ from CH₄ with membranes such as Nylon 6, Nylon 6.6 (polyamide), polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) and also rubbery membranes. Although they achieved H₂S/CH₄ 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 H₂S/CH₄ selectivity than PU.

Bhide and Stern [2,3] and Bhide et al. [4] showed that H₂S 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 H₂S 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 H₂S, and perhaps for the same reason the studies were mainly carried out without taking into account the separation of H₂S from CH₄ by membranes. At lower feed concentrations of H₂S where the concentration of H₂S in the product can be reduced easily by absorption, the concentration of H₂S 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 H₂S 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 H₂S and CO₂ in gas mixtures are the same. For example, Kaldis et al. [19] substituted CO₂ for H₂S 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% H₂S. For example, Bhide et al. [4] reported a selectivity of 19 for H₂S/CH₄ and 21 for CO₂/CH₄.

Lokhandwala and Baker [20] studied H₂S and CO₂ separation from CH₄ by membrane. They proposed a two-step membrane pro-

cess in which the first step contains an H₂S selective module and the other a CO₂-selective one. For instance, if the natural gas contains water vapor, it is better to feed it first to the H₂S-selective module because such membrane would not be damaged by water vapor and the moisture would be transported along with H₂S to the permeate side. After examining a number of different membrane materials for CO₂ 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 H₂S 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 CO₂/CH₄ selectivity of 20 and H₂S/CH₄ selectivity of 25. A research group (Lokhandwala and Baker [20]) examined three membrane configurations in the study: single-membrane system with high H₂S/CH₄ selectivity, single-membrane system with high CO₂/CH₄ 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 H₂S 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 H₂S at low pressures, even when it is for N₂, H₂ and CO₂.

Lin et al. [23] studied plasticization-enhanced H₂ 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 CO₂ induced plasticization on the gas transport properties of glassy polyimide membranes. They investigated the time dependence of CO₂ 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 CO₂ permeability in the as-cast 6FDA-TeMPD membranes prepared from tetrahydrofuran and dichloromethane showed typical CO₂-induced plasticization at pressures over 10 atm. The critical plasticization pressure at which CO₂-induced plasticization begins to affect the gas permeability shifted from nearly 10 atm to 30 atm after heat treatment. The increase in CO₂ permeability upon plasticization is mostly caused by an increase in CO₂ diffusivity. Furthermore, they found that regardless of the membrane preparation protocol, there is a critical CO₂ diffusivity of $73 \pm 5 \times 10^8$ cm²/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 CO₂-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 CO₂ 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_x, NO_x, CO, H₂S, NH₃, as well as condensable water and hydrocarbons in terms of their permeability through polymeric membranes relative to CO₂, as well as their plasticization and aging effects on membrane separation performance in both pre- and post-combustion for CO₂ 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 H₂S, CO and water on the performance of a PDMS membrane in CO₂/N₂ separation. The permeability of CO₂ through PDMS is reduced upon exposure to CO, H₂S 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 CO₂. They concluded that the plasticization potential of CO₂ increases with decreasing membrane thickness, correlating with the plasticization pressure behavior. Furthermore, the plasticization potential decreased with temperature, implying that CO₂ 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

CO₂/CH₄ 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 CO₂-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 CO₂ 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% CO₂ 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 CO₂ 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 CO₂ partial pressures. The cross-linked membrane material showed high intrinsic separation performance for CO₂ and CH₄ (selectivity ~49, CO₂ permeability ~161 barrer, with a feed at 65 psia, 35 °C, and 10% CO₂). Cross-linked asymmetric hollow-fiber membranes made from the material showed good resistance to CO₂-induced plasticization. These researchers performed the experiments in CO₂ 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 H₂S from methane was studied using commercial Cardo-type polyimide and PPO membranes under different experimental conditions.

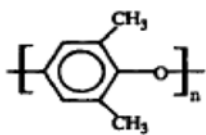
MATERIALS AND METHODS

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

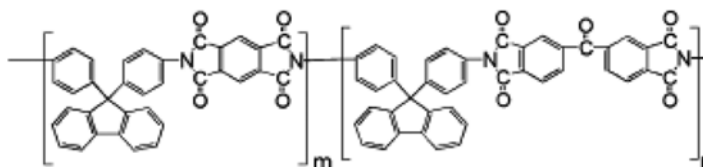
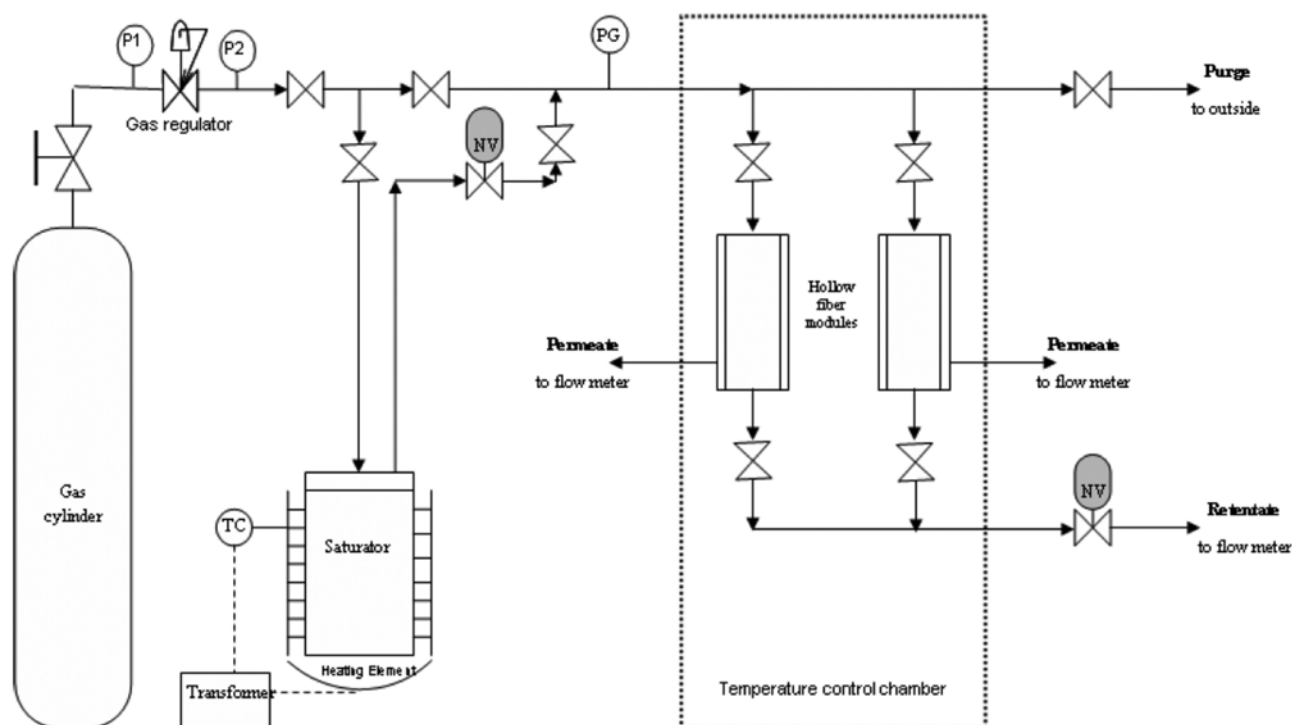


Fig. 1. Chemical structure of polyphenylene oxide (PPO) and Cardo-type polyimide membranes [11].

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

Module name	Membrane type	Hollow fiber parameters		Module specifications	
		Inside diameter (μm)	Outside diameters (μm)	Number of fibers	Permeation area (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 CH_4 and $\text{H}_2\text{S}/\text{CH}_4$ gas mixtures with 101, 198 and 401 ppm of H_2S in 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 ($23\text{ }^\circ\text{C}$) for each membrane. One set of experiments was also conducted at 100 psig and $40\text{ }^\circ\text{C}$ in order to understand the effect of temperature on the performance of the membranes.

The H_2S -rich permeate, was collected at atmospheric pressure and the 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 H_2S 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 CH_4 , $\text{CH}_4/\text{H}_2\text{S}$ mixtures at 101, 198, 401 ppm, H_2S contents and repeat of pure 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} cm^3 (STP)/ $\text{cm}^2\text{ s cmHg}$), Q_p permeation rate, cm^3 (STP)/s, A permeation area of the membrane, cm^2 , Δp pressure difference across the membrane, cmHg and F is permeation flux, cm^3 (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 , α_{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.

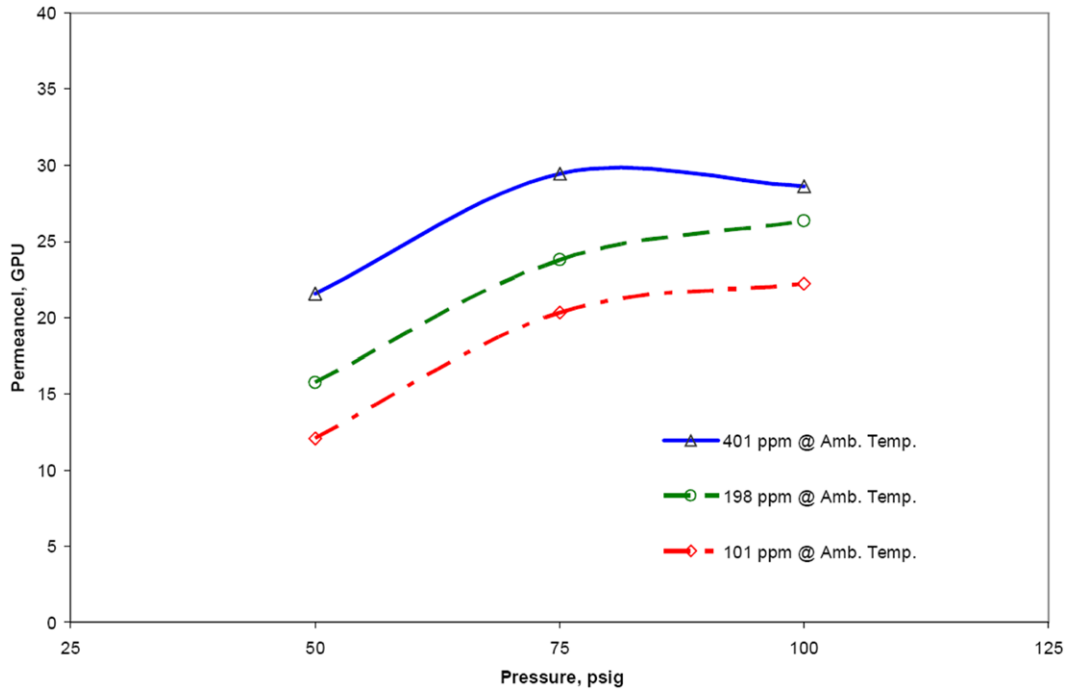


Fig. 3. H₂S permeance vs. feed pressure in separation of H₂S/CH₄ mixtures at room temperature for RITE-A module.

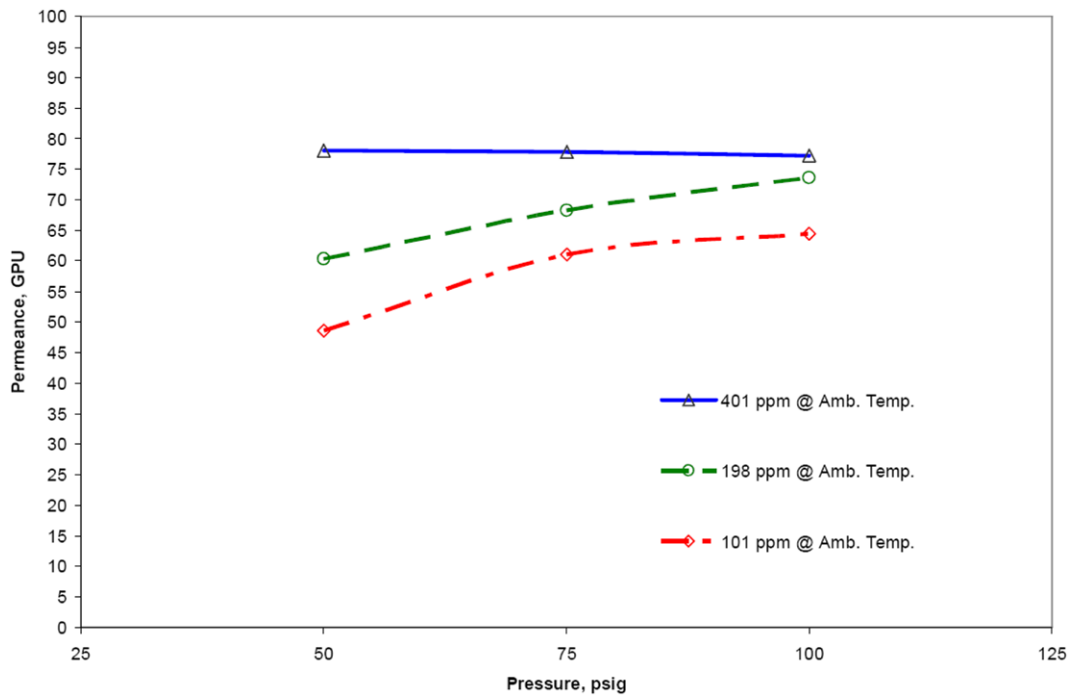


Fig. 4. H₂S permeance vs. feed pressure in separation of H₂S/CH₄ mixtures at room temperature for PPO module.

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 CH₄/H₂S 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 H₂S permeance at various pressures and different concentrations of H₂S for the RITE-A module (Cardo type PI). This figure shows that the permeance of H₂S increased as the feed pressure (except for H₂S concentration of 401 ppm) and the concentration of H₂S increased. This can be explained by the higher

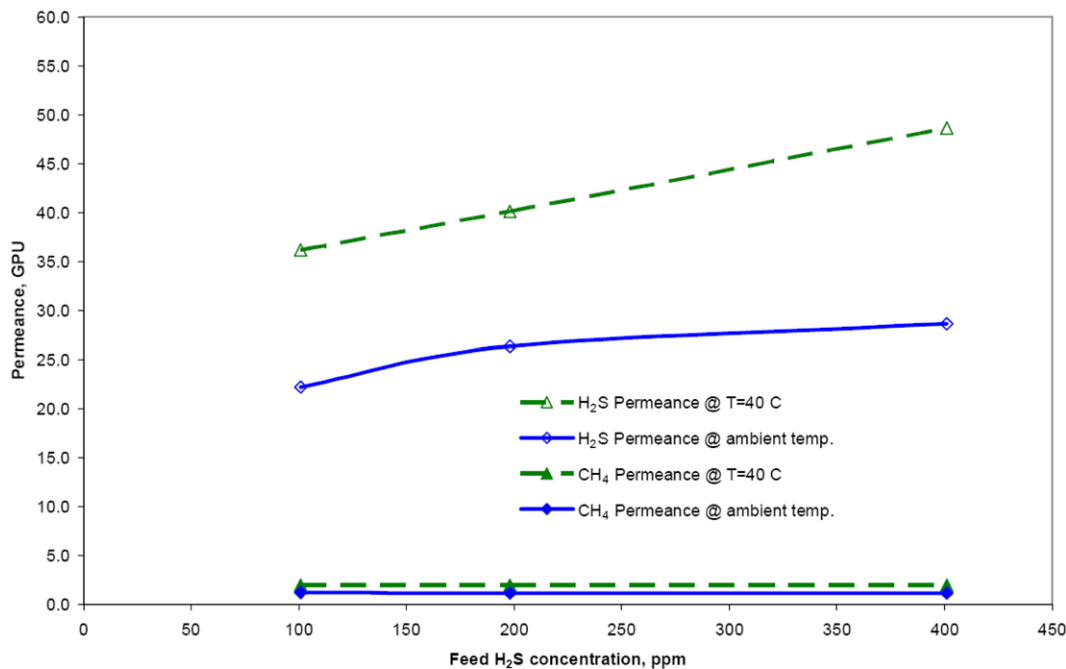


Fig. 5. CH₄ and H₂S permeabilities vs. H₂S feed concentration at different temperatures for RITE-A module.

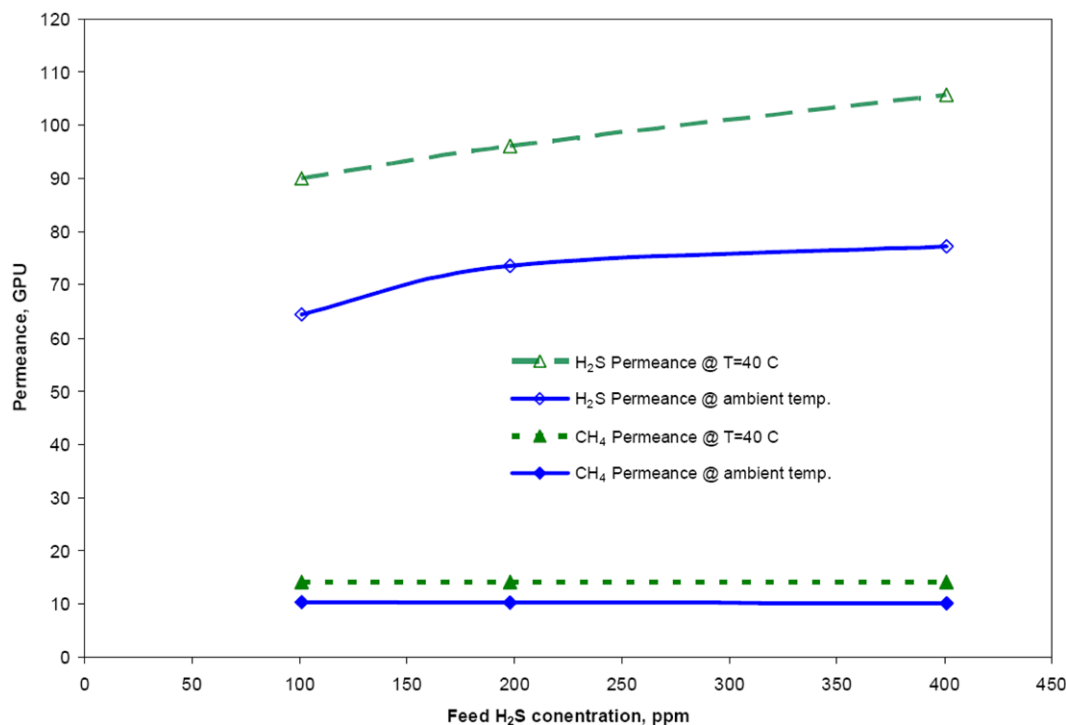


Fig. 6. CH₄ and H₂S permeabilities vs. H₂S feed concentration for PPO module.

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 CH₄ and H₂S 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 CH₄ and H₂S 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 H₂S plasticizes the membranes, which seems to be more pronounced at higher temperatures. To study the plasticization effect of H₂S, pure CH₄ permeation experiments

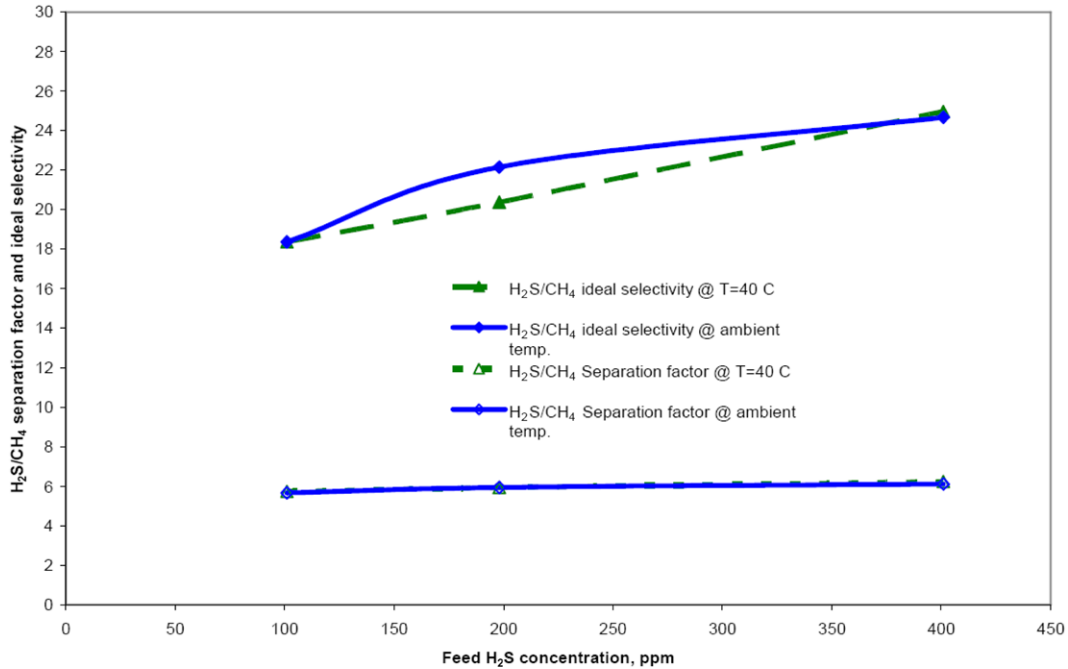


Fig. 7. The effect of temperature on the ideal selectivity and separation factor of RITE module for H₂S/CH₄ mixtures.

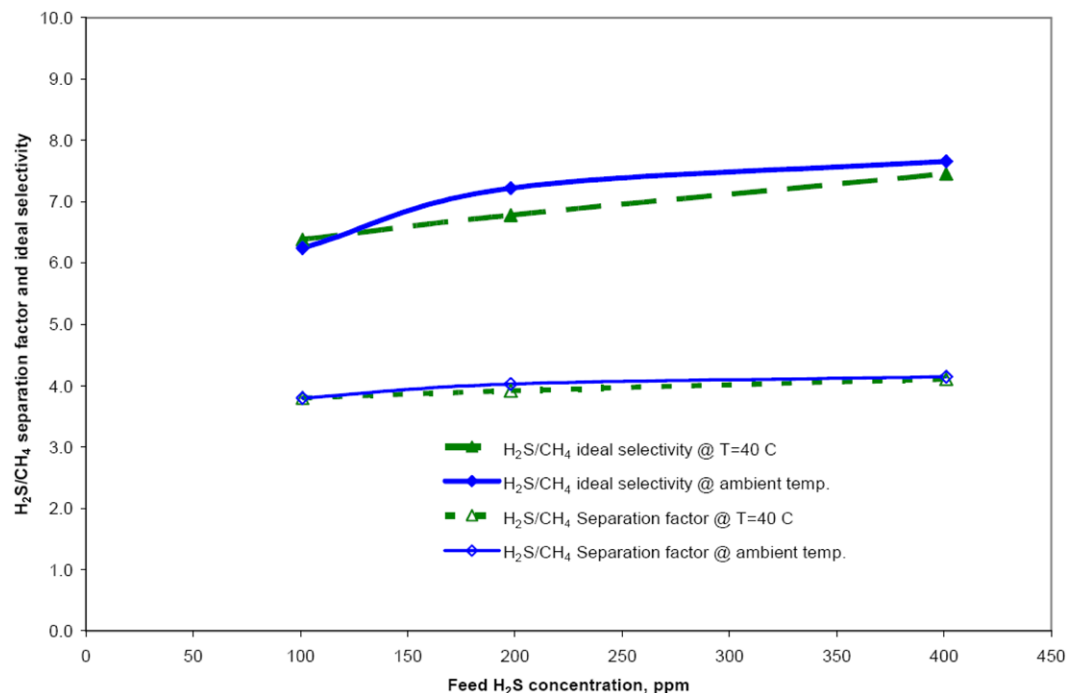


Fig. 8. The effect of temperature on the ideal selectivity and separation factor of PPO module for H₂S/CH₄ mixtures.

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.

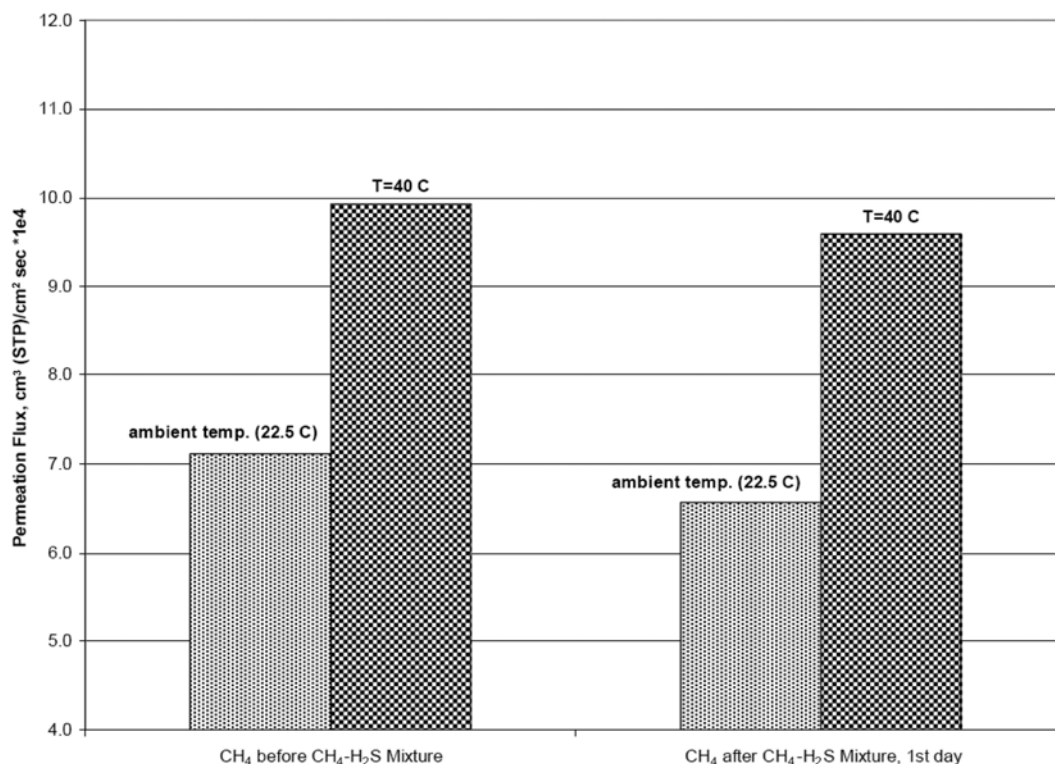


Fig. 9. The effect of temperature on permeation flux of CH₄ before and after experiments with H₂S mixtures for RITE module.

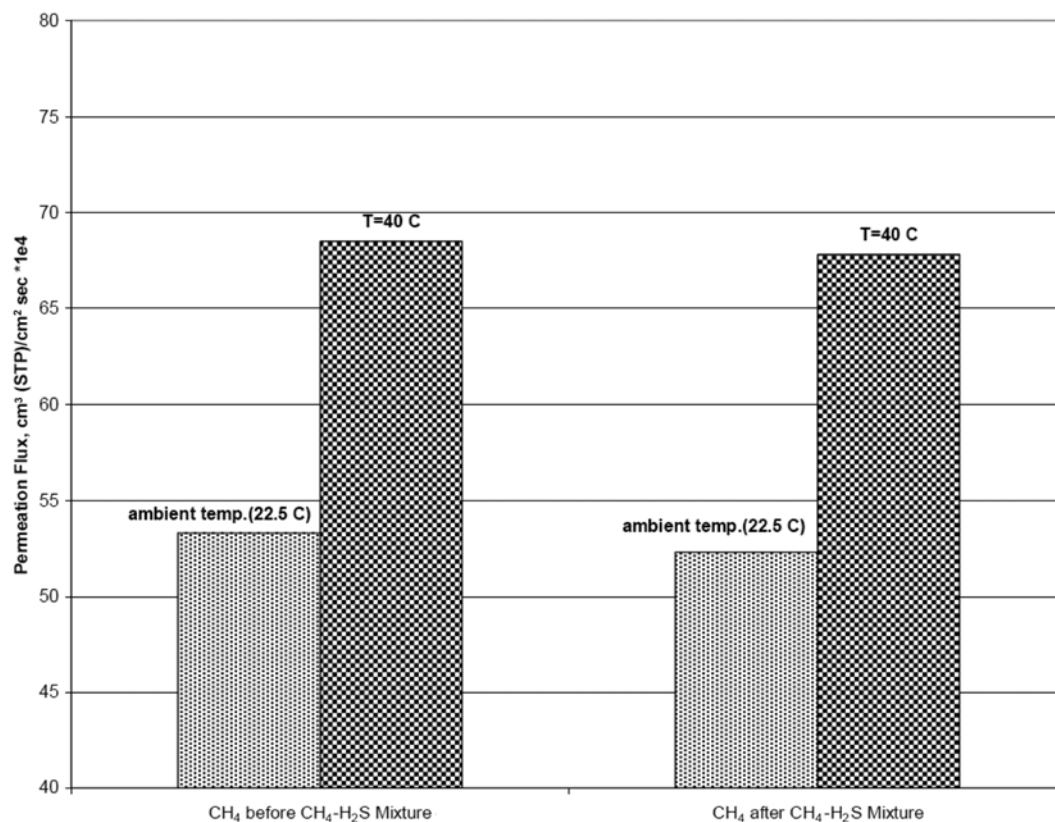


Fig. 10. The effect of temperature on permeation flux of CH₄ before and after experiments with H₂S mixtures for PPO module.

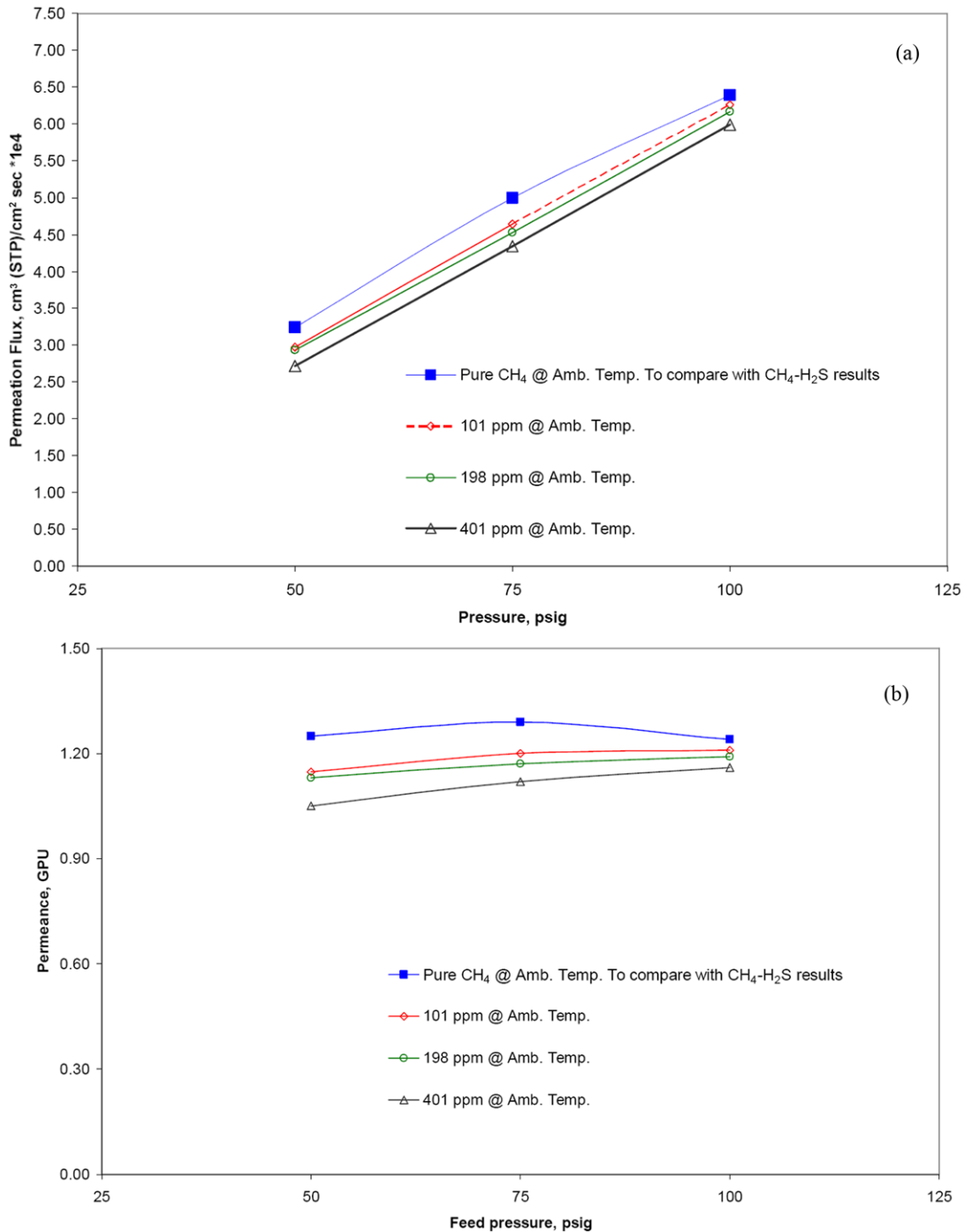


Fig. 11. (a) CH₄ permeation flux and (b) permeance of pure CH₄ and CH₄/H₂S mixtures for RITE module.

The effect of H₂S on CH₄ 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 H₂S through PI membrane. An obvious decreasing trend in the permeation flux and permeance of methane in the presence of H₂S 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 H₂S. The very low concentration of H₂S 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 H₂S, emphasizing that the concentration of H₂S is not large enough to plasticize the membrane and increase the methane permeation flux and permeance.

Table 2 shows the concentration of H₂S in feed, retentate and permeate along with the separation factors of H₂S/CH₄ at different feed

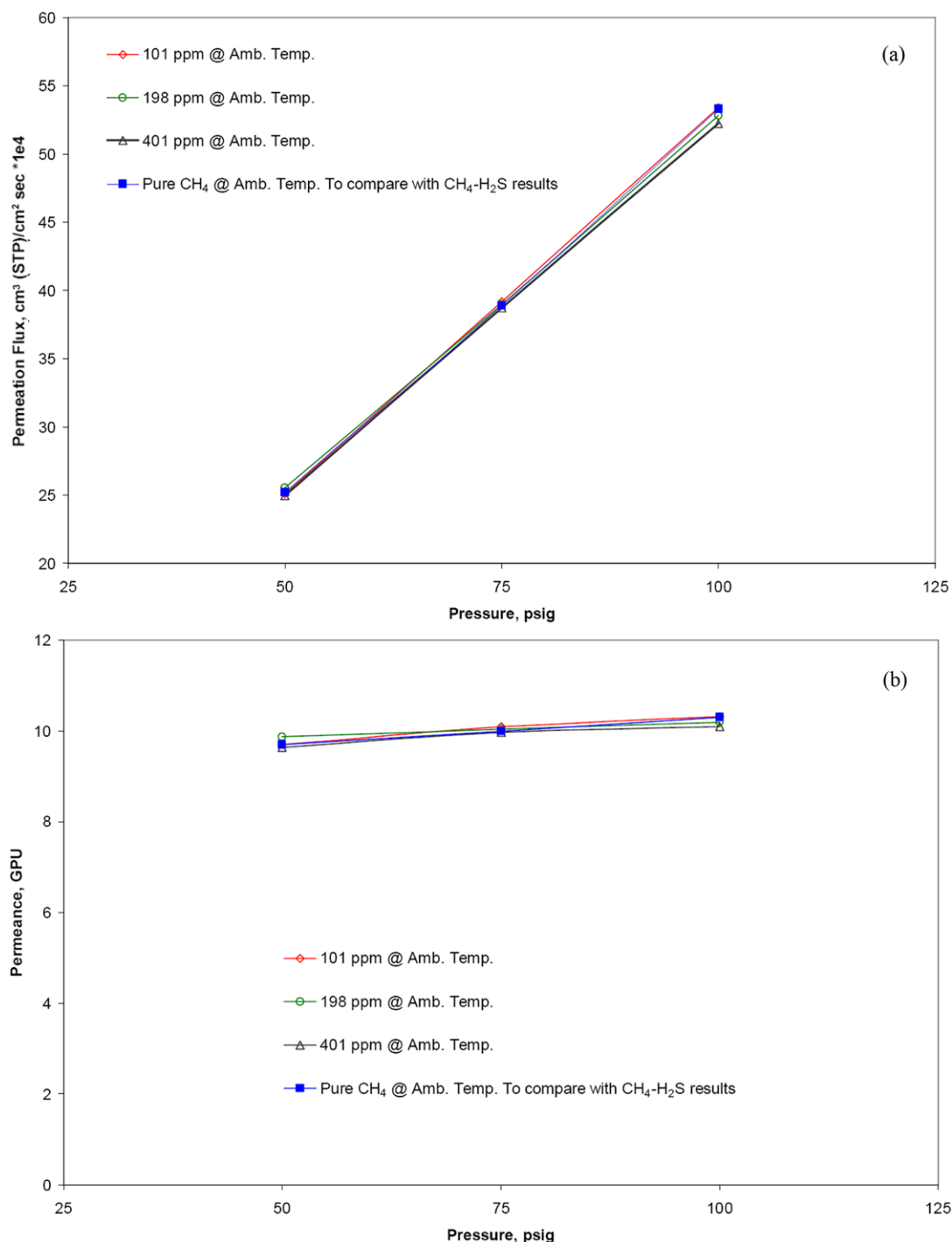


Fig. 12. (a) CH₄ permeability and (b) permence of pure CH₄ and CH₄/H₂S mixtures for PPO module.

pressures and three levels of feed concentrations of H₂S. These results indicate that the separation factors of the applied PPO and Cardo-type PI membranes are higher at high feed concentrations of H₂S and therefore it is expected that the performance of these membranes to be better at higher feed H₂S concentrations.

CONCLUSIONS

Separation of H₂S/CH₄ mixtures at various concentrations of H₂S

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 H₂S the permence of CH₄ declined for the Cardo-type polyimide membranes, whereas for the PPO membranes it remained relatively unchanged. The separation factors of H₂S/CH₄ 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 H₂S/CH₄ with RITE and PPO module

Feed pressure psig	101 ppm (vol%: 0.0101)			RITE-A Feed H ₂ S concentration 198 ppm (vol%: 0.0198)			401 ppm (vol%: 0.0401)		
	Retentate H ₂ S (vol%)	Permeate H ₂ S (vol%)	Separation factor (H ₂ S/CH ₄)	Retentate H ₂ S (vol%)	Permeate H ₂ S (vol%)	Separation factor (H ₂ S/CH ₄)			
	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 [cm²]
 p_F : feed pressure [cmHg]
 p_P : permeate pressure [cmHg]
 (p/l)_i : permeance of gas i [GPU]
 (p/l)_j : permeance of gas j [GPU]
 Q_F : feed flow rate [cm³ (STP)·s⁻¹]
 Q_P : permeate flow rate [cm³ (STP)·s⁻¹]
 Q_R : retentate flow rate [cm³ (STP)·s⁻¹]
 T : temperature, [°C]
 (x_i)_m : logarithmic average mole fraction of gas i in feed
 (x_j)_m : logarithmic average mole fraction of gas j in feed
 x_{i,F} : mole fraction of gas i in feed
 x_{j,F} : mole fraction of gas j in feed
 x_{i,R} : mole fraction of gas i in retentate
 x_{j,R} : mole fraction of gas j in retentate
 y_i : mole fraction of gas i in permeate
 y_j : mole fraction of gas j in permeate

Greek Letters

α_{ij} : separation factor of gas i over gas j, dimensionless
 α_{ij}^o : ideal selectivity of gas i over gas j, dimensionless

Subscripts

F : feed
 i : gas i (here is H₂S)

j : gas j (here is CH₄)
 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).