

Permeation of H₂, N₂, CH₄, C₂H₆, and C₃H₈ Through Asymmetric Polyetherimide Hollow-Fiber Membranes

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ABSTRACT: Permeation properties of pure H₂, N₂, CH₄, C₂H₆, and C₃H₈ through asymmetric polyetherimide (PEI) hollow-fiber membranes were studied as a function of pressure and temperature. The PEI asymmetric hollow-fiber membrane was spun from a *N*-methyl-2-pyrrolidone/ethanol solvent system via a dry-wet phase-inversion method, with water as the external coagulant and 50 wt % ethanol in water as the internal coagulant. The prepared asymmetric membrane exhibited sufficiently high selectivity (H₂/N₂ selectivity >50 at 25°C). H₂ permeation through the PEI hollow fiber was dominated by the solution-diffusion mechanism in the nonporous part. For CH₄ and N₂, the transport mechanism for gas permeation was a combination of Knudsen flow and viscous flow in the porous part and solution

diffusion in the nonporous part. In our analysis, operating pressure had little effect on the permeation of H₂, CH₄, and N₂. For C₂H₆ and C₃H₈, however, capillary condensation may have occurred at higher pressures, resulting in an increase in gas permeability. As far as the effect of operating temperature was concerned, H₂ permeability increased greatly with increasing temperature. Meanwhile, a slight permeability increment with increasing temperature was noted for N₂ and CH₄, whereas the permeability of C₂H₆ and C₃H₈ decreased with increasing temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 698–702, 2002

Key words: membranes; vapor; separation

INTRODUCTION

Off-gas streams from petrochemical processes contain mainly hydrogen (H₂), methane (CH₄), ethane (C₂H₆), propane (C₃H₈), and other higher hydrocarbons. In the application of polymeric membranes for hydrogen separation, the major concern is the effect of these hydrocarbons on the polymeric membranes. It is, therefore, of interest to study the permeation properties of these hydrocarbons through polymeric membranes.

In general, the removal of H₂ from the feed stream results in a quick increase in the retentate hydrocarbon concentration, which may have an adverse effect on the polymeric membranes. This is especially true for membranes coated with silicon material, as this can cause the silicone coating to swell and, hence, jeopardize its overall separation performance. In this regard, it is, therefore, ideal to use defect-free asymmetric membranes with good hydrocarbon resistances. However, the preparation of a completely defect-free asymmetric membrane, especially an asymmetric hollow-fiber membrane, has still not been well mastered.^{1,2}

Normally, a small fraction of defects exists on the outer surface of asymmetric membranes. For a relatively small amount of defects, the membrane selectivity is often much larger than that of Knudsen flow but is lower than that of the dense membrane. Theoretical analysis has demonstrated that membrane selectivity depends strongly on the selectivity of the membrane material chosen, the amount of defect, and its operating pressure and temperature.³ In brief, for some gases, membrane selectivity increases with increasing temperature and with the decrement of defects. For a negligible amount of defects, membrane materials with a higher selectivity will inevitably result in a much higher final membrane selectivity.

A study conducted by Barbari et al.⁴ showed that polyetherimide (PEI) exhibits much higher selectivity (>250) for H₂/N₂ and H₂/CH₄ than polysulfone and polyethersulfone (60–80). Additionally, this polymer also demonstrated good hydrocarbon and temperature resistances. Asymmetric PEI hollow-fiber membranes with sufficiently high selectivity (H₂/N₂ selectivity = 20–100 at 25°C) were prepared in our laboratory, which was believed to be suitable for the application of H₂ recovery from off-gas streams, particularly for petrochemical and refinery processes. It was, therefore, of interest to us to study the permeation behaviors of H₂, N₂, and C₁–C₃ hydrocarbons through this membrane. The objective of this study was to provide fundamental information on the per-

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meation properties of the aforementioned five gases through the asymmetric PEI hollow-fiber membranes prepared and to provide an explanation on their permeation behavior based on the combination of pore flow and nonporous flow mechanisms.

Theory

The permeation of noncondensable gases such as H₂, N₂, and CH₄ through asymmetric membrane involves the following flow mechanisms: Knudsen flow and viscous flow in the porous part and solution-diffusion flow in the nonporous part. Meanwhile, for C₂H₆ and C₃H₈, which are considered condensable gases due to their high boiling points, capillary condensation or surface diffusion may occur in the porous part of the asymmetric membrane. Theoretical analysis of the permeation of a simple gas through an asymmetric membrane with a small fraction of surface defects was made,³ and was found to be a combination of Knudsen flow and viscous flow in the porous part and solution-diffusion flow in the nonporous part as follows:³

$$\left(\frac{P}{L}\right)_i = P_k^o \frac{1}{\sqrt{M_i T}} \frac{\varepsilon r}{L_p} + P_v^o \frac{1}{\mu_i T} \frac{\varepsilon r^2}{L_p} \bar{p} + P_s^o \exp\left(-\frac{E_i}{RT}\right) \frac{1}{L} \quad (1)$$

where $P_k^o = 4/3(R)^{-1} (2R/\pi)^{0.5}$ and $P_v^o = 1/8R$ are constants; R is a gas constant; T is absolute temperature; μ and M are the viscosity and molecular weight of the gas, respectively; P_s^o is the preexponential factor and E is the activation energy of permeation in the polymer material; r is the mean pore size; ε is the surface porosity; L_p is the pore length and L is the skin-layer thickness; and \bar{p} is average gas pressure. Equation (1) is based on the following assumptions: (1) the porous part of the membrane is constructed by cylindrical pores with a mean pore size r and pore length of L_p , and (2) the nonporous part has a uniform skin with a thickness of L . The relative contribution of the each flow to the total gas permeability will depend on the gas permeability in the dense membrane, the membrane pore size, porosity of the membrane, and operating pressure and temperature.

It should be noted that the accuracy of eq. (1) is dependent on the slope of the equation. Error may be introduced if the slope is too steep.

EXPERIMENTAL

The PEI asymmetric hollow-fiber membranes were prepared from 30 wt % polymer dope with *N*-methyl-2-pyrrolidone as the solvent, ethanol as an additive, and 50 wt % ethanol in the balance of water as an internal coagulant at an air gap of 10 cm. The detailed preparation procedure was described elsewhere.³ The

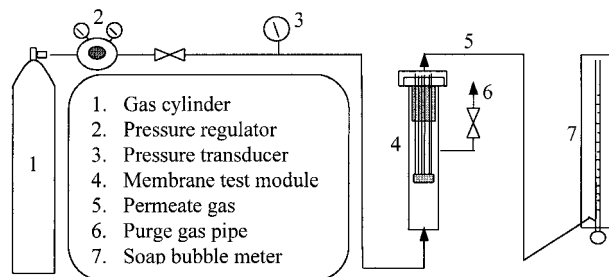


Figure 1 Schematic diagram of the gas-permeation apparatus.

resulting hollow fibers were dried at ambient conditions ($25 \pm 1^\circ\text{C}$, relative humidity = 60–65%), and were found to have an outer diameter of 696 μm and an inner diameter of 409 μm . These asymmetric hollow fibers were then arranged into bundle with a length of 120 cm and were housed in a stainless steel tube (inner diameter = 9 mm) with two equal Ts at both ends. These Ts were then connected to a reducer, where the fibers were sealed with epoxy resin. A normal shell-tube type hollow-fiber module, containing 98 fibers with an effective length of 86 cm and effective permeation area of 1841.9 cm^2 was prepared.

Figure 1 shows a schematic diagram of the experimental apparatus employed for the permeation measurement, with the hollow-fiber test module placed in the thermostat. A purified gas/vapor stream of H₂, N₂, CH₄, C₂H₆, or C₃H₈ was introduced to the shell side of the test module at regulated pressures ranging from 1 to 7 bars. The total gas permeation rate was measured at the lumen side at atmospheric pressure and room temperature with a soap flow meter. The outlet of the measuring tube was connected to a soft tube that was immersed in water to prevent the back diffusion of air. The gas permeability was calculated with the following equation:

$$\left(\frac{P}{L}\right)_i = \frac{N_{t,i}}{n \pi OD \delta \Delta P} \quad (2)$$

where $N_{t,i}$ is the total permeation rate, n is the number of hollow fibers used, OD is the outside diameter of the fiber, δ is the hollow-fiber length, and ΔP is the pressure difference. The ideal selectivity of H₂ relative to the other four gases was defined as the ratio of gas permeabilities of two pure gases as follows:

$$\alpha_{i/j} = \frac{\left(\frac{P}{L}\right)_i}{\left(\frac{P}{L}\right)_j} \quad (3)$$

RESULTS AND DISCUSSION

Pressure dependence

Figures 2 and 3 show the permeation flux of H₂, N₂, CH₄, C₂H₆, and C₃H₈ through the PEI hollow-fiber

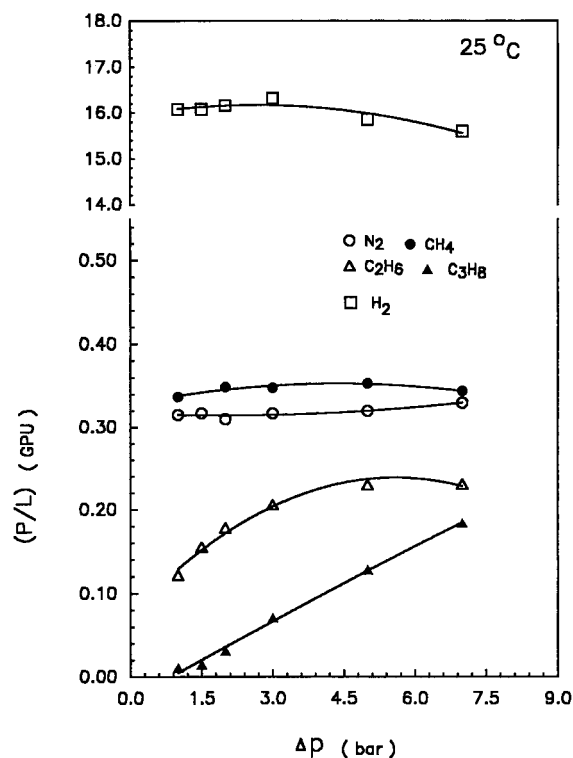


Figure 2 Permeation fluxes of H₂, N₂, CH₄, C₂H₆, and C₃H₈ versus the pressure difference at 25°C.

membranes measured at different pressures (1–7 bar) at 25°C and 70°C, respectively. Evidently, H₂ permeability in the PEI membrane was much higher than those of N₂ and CH₄. Characteristics of the H₂ permeabilities measured at the pressure range of 1–7 bars suggest that H₂ permeation was dominantly controlled by a solution-diffusion mechanism in the non-porous part. Permeabilities of N₂ and CH₄ measured at 25°C increased slightly with pressure. In this case, the contribution of pore flows, via both viscous flow and Knudsen flow, to the total gas flow were relatively significant due to the low permeability of N₂ and CH₄ in the PEI material.

As for C₂H₆ and C₃H₈, they may have caused membrane swelling due to their high boiling points, resulting in an increased permeation rate with increasing pressure. However, due to the fact that they could be easily condensed in the membrane pores, pore blockage then caused an undesirable reduction in the gas-phase transport according to pore flow. The condensed liquid then transferred from the high-gas-pressure side to the opposite low-pressure side, was driven by a capillary pressure difference.⁵ The condensing flux through the pores was normally quite small due to low surface porosity. When the gas pressure was greater than that of capillary pressure, the gas began to vacate the condensed liquid in the big pores, and gas started penetrating the pores again, therefore resulting in increased gas permeability with increasing operating pressure.

An increase in temperature increased the capillary pressure and hydrocarbon condensation in the big pores, which could be more easily vacated at higher pressure. As such, the scale of permeability increment was very much flattened at higher pressures for both C₂H₆ and C₃H₈, as shown in Figure 3. This could be further verified by examination of the selectivity of H₂/C₂H₆ and H₂/C₃H₈ at both 25 and 70°C (Figs. 4 and 5), which clearly demonstrated the same tendency.

Experimental results revealed that the selectivities of H₂/C₂H₆ and H₂/C₃H₈ were much higher than those of H₂/N₂, and H₂/CH₄. The selectivity of H₂/C₂H₆ and H₂/C₃H₈ decreased dramatically after the increase in pressure from 1 to 4 bars and from 1 to 3.5 bars at temperatures of 25 and 70°C, respectively. A further increment in operating pressure, however, had very little effect on the selectivity decrement. As for the selectivity of H₂/CH₄ and H₂/N₂, a very minor decrement was detected, as shown in Figures 4 and 5, which suggested a contribution of pore flow, which caused the reduction of membrane selectivity, which was still negligible.

Temperature dependence

Permeabilities of the five gases through the PEI hollow-fiber membranes were also examined at different temperatures and at a pressure difference of 5 bars, as shown in Figure 6. As indicated in eq. (1), gas perme-

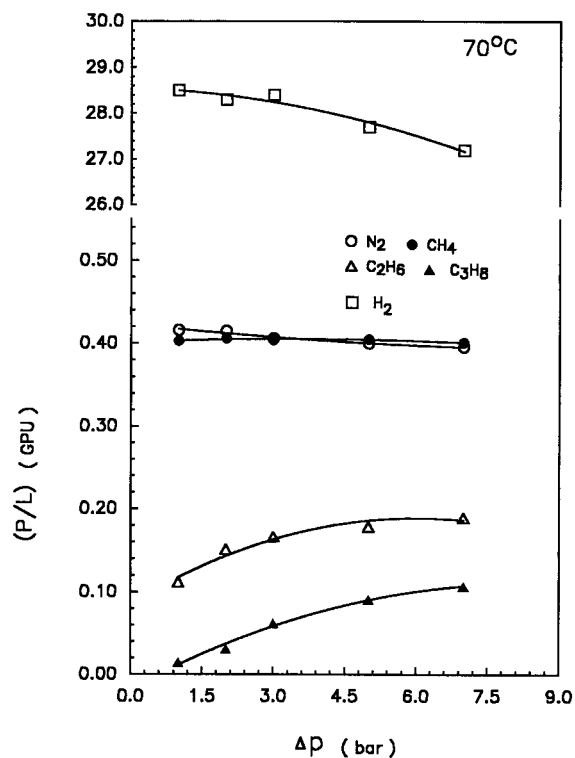


Figure 3 Permeation fluxes of H₂, N₂, CH₄, C₂H₆, and C₃H₈ versus the pressure difference at 70°C.

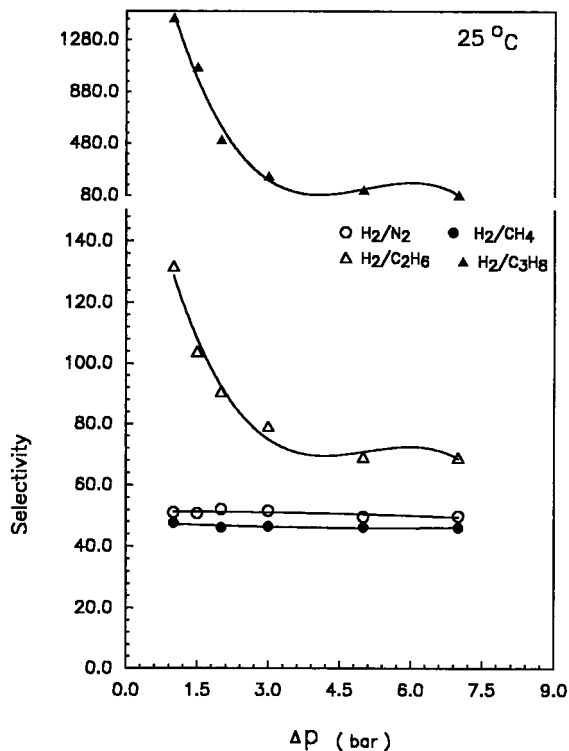


Figure 4 Effect of operating pressures on the selectivities of various gas pairs at 25°C.

ability increases exponentially with operating temperature. In Figure 6, a drastic increase in H₂ permeability with temperature is shown, with a 100% permeability

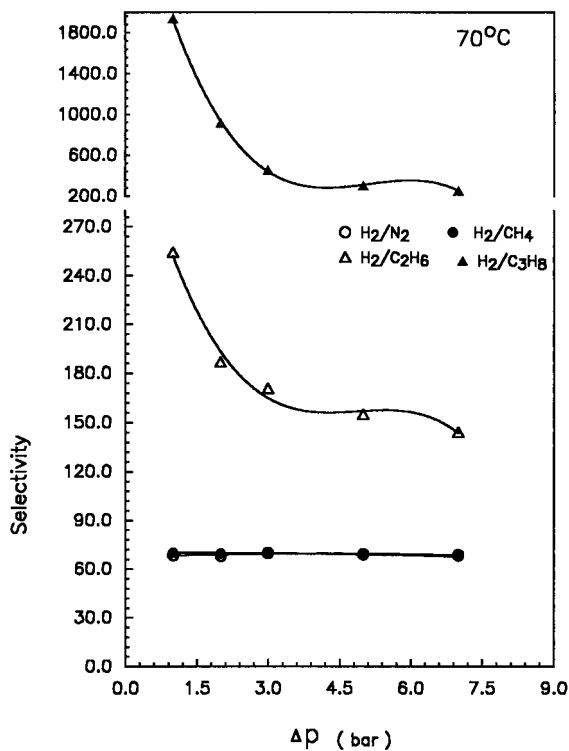


Figure 5 Effect of operating pressures on the selectivities of various gas pairs at 70°C.

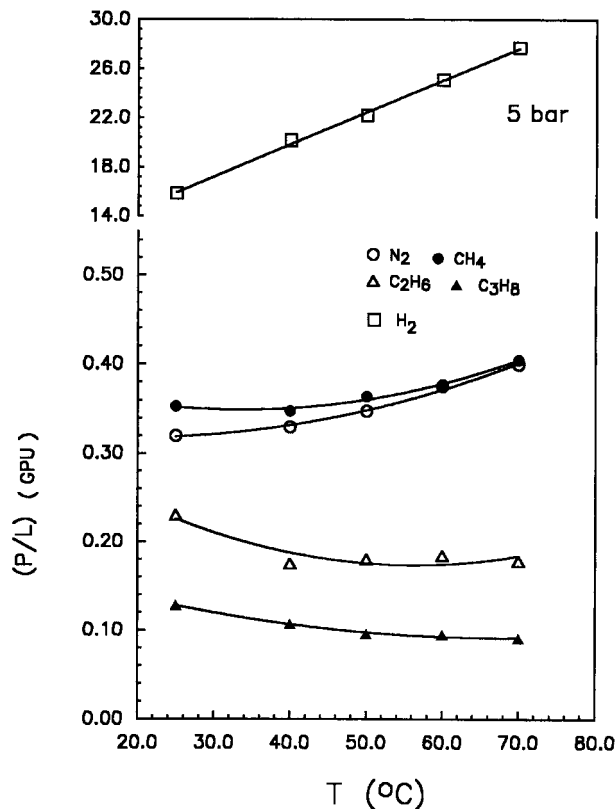


Figure 6 Effect of operating temperatures on the membrane permeation flux.

increase from 25 to 70°C. It is, thus, suggested that H₂ permeation through the membrane was essentially dominated by a solution-diffusion mechanism of the nonporous part.

For N₂ and CH₄, the permeability increment with operating temperature was relatively small, about 15–25% over the temperature range of 25–70°C. In this case, the pore flow gave a significant contribution to the total gas permeation due to low permeability in PEI material. Also, gas permeability decreased with increasing temperature by the pore flow mechanism.³ As a result, the selectivity of H₂/N₂ and H₂/CH₄ increased with temperature, as shown in Figure 7. Although the PEI hollow-fiber membranes contained some defects, the selectivity of H₂/N₂ and H₂/CH₄ was calculated to be about 50 at 25°C and 70 at 70°C, which was higher than those of silicone-coated polysulfone and polyethersulfone hollow-fiber membranes. For C₂H₆ and C₃H₈, their permeabilities decreased with increasing temperature, another indication of the pore flow through the PEI membrane. As a result of this, the selectivity of H₂/C₂H₆ and H₂/C₃H₈ was much higher than that of H₂/CH₄, and it increased far more quickly with increasing temperature. These results show that the increase in temperature could increase selectivity while preventing hydrocarbon condensation.

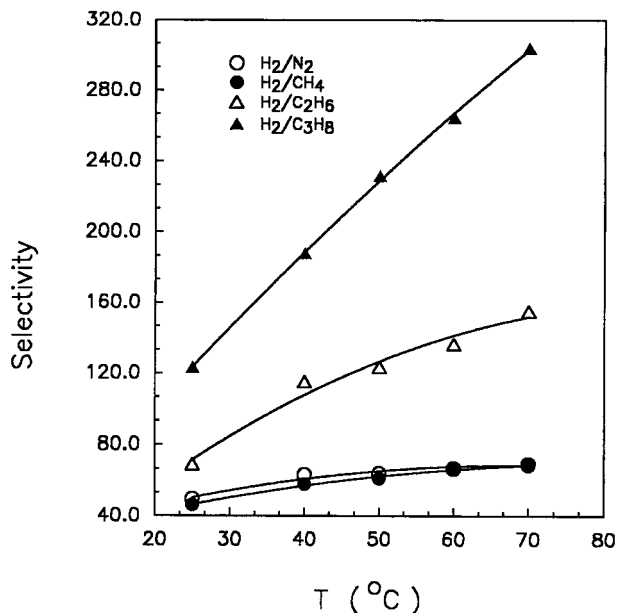


Figure 7 Effect of operating temperature on the selectivities of various gas pairs.

CONCLUSIONS

In this study, the gas-permeation properties of H₂, N₂, CH₄, C₂H₆, and C₃H₈ through asymmetric PEI hollow-fiber membranes with a small fraction of surface de-

fects were studied. The H₂ permeation was dominantly controlled by the solution-diffusion mechanism in the nonporous medium. The gas permeation of N₂ and CH₄ was a combination of Knudsen flow and viscous flow in the porous part and solution-diffusion flow in the nonporous part. For C₂H₆ and C₃H₈, the capillary condensation could take place in the porous part. The permeabilities of C₂H₆ and C₃H₈ increased quickly with increasing pressure over the low-pressure range. At higher operating temperatures, H₂ permeability increased far more rapidly than those of N₂ and CH₄, whereas the permeabilities of C₂H₆ and C₃H₈ decreased with operating temperature. As a result of this, the selectivity of H₂/N₂ and H₂/C₁-C₃ increased with increasing temperature. In conclusion, noncoated PEI hollow-fiber membranes exhibited a higher selectivity and permeability and, therefore, could be employed for H₂ recovery if the permeation behavior of the H₂/vapor mixture is not much different from those of pure gases.

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