Nitrogen Removal from Natural Gas by Membrane Separation

by

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AUTHOR's DECLARATION

I hereby declare that I am the sole author of this thesis. This is the true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Canada is globally the third largest natural gas producer with a total production of 13.9 billion ft^3/day. Natural gas is a naturally occurring mixture consisting of mainly CH_4 and varying amounts of other gases such as nitrogen. N_2 is difficult to remove from natural gas. Cryogenic distillation is energy intensive and costly, while pressure swing adsorption only applies to very limited cases. Membrane separation is expected to offer a promising alternative process for nitrogen removal from natural gas.

In this research, a series of Poly(ether block amide) (PEBA) and Poly(dimethyl siloxane) (PDMS) membranes were employed to separate nitrogen from methane under different pressures and temperatures. These rubbery polymers have a higher methane permeability than nitrogen, and the selectivity is presented as the permeability ratio of methane over nitrogen. The study involved pure gas permeation tests by using different PEBA membranes (PEBA 2533, PEBA 1074, PEBA 1657 and PEBA 3000) and PDMS. Based on the gas permeability data, PEBA 2533 and PEBA 1074 were chosen for further studies. Polymer blending was employed to combine the beneficial properties of the two materials. A series of blend polymers of PEBA 2533/1074 were used to prepare the membranes for gas permeability tests with pure and mixture gas at different operating conditions. At 0.813 MPa and -20^0C, a blend membrane with the blend ratio of PEBA 2533/1074 (50/50) showed a CH_4/N_2 permeability ratio greater than 6, which is better than the conventional membrane reported in the literature.

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Chapter 1 Introduction

1.1 Background

Traditional gas separation processes often involve in a large energy input to maintain a certain operating conditions, such as extreme high or low temperatures. With industry's demand for lowering operating costs and increasing separation efficiency, more and more researches are being focused on process improvements. Over the past two decades, gas separation using polymeric membranes has drawn a great interest since membrane separation processes offer a number of advantages in terms of low energy use and capital cost. This is especially true for the purification of natural gas.

Canada is globally the third largest natural gas producer. When natural gas is extravted, a high reservoir pressure is introduced to ensure the flowing of the gases to the production wells and then gush to the surface. This procedure often involves increasing the pressure in the natural gas reservoirs, which can be done by injecting N_2 into a gas pocket. Depending on the geological conditions, some of the injected N_2 can mix over time with the natural gas during recovery. If the N_2 content is too high, the natural gas is no longer viable for industrial use. The pipeline specification for natural gas requires the total inert content, predominantly N_2, to be less than 4 mol% (Tannehill and Galvin 1993). However, many natural gas reserves contain more than 4 mol% N_2, which do not meet the pipeline specification. Many of these sub-quality high-nitrogen gas streams can be diluted with some other high quality gas streams containing little nitrogen to fulfill the specifications. However, when the dilution is not available, a N_2 removal unit must be installed. Cryogenic distillation is the most widely accepted operation to remove N_2. Distillation is often used in chemical industry to separate a mixture of components, which involves in supplying heat at the bottom of the column to evaporate the mixture and withdrawing heat at the top of the column to condense the volatile components (Roffel et al., 2000). Cryogenic distillation is similar to the normal distillation, except that an extremely low temperature is used, which makes this process energy-intensive, costly. Moreover, this separation technology is only suitable for large gas fields (Lokhandwala et al., 2010). As a matter of fact, many current natural gas productions are from small, remote or offshore fields, which need a technology that is suitable to treat small gas streams (Lokhandwala et al., 1999). One of the separation technologies that has been tried with some success is pressure-swing adsorption (PSA), which uses molecular sieves to preferentially adsorb N_2 (Fatehi et al., 1995). This separation process can be operated at ambient temperature. However, the commercialisation of PSA processes for N_2 removal is slow since it is difficult to find satisfactory sorbents, that possess a reasonable high N_2/CH_4 selectivity (Jayaraman et al., 2004). Another promising technology is the membrane separation.

The first large commercialisation of gas separation membrane was launched in 1980 by Permea (now a division of air products) using Prism® membrane. It is used for separation and recovery of H_2 from the purge gas streams of ammonia plants (Baker 2002). These days, with the development of polymer materials and membrane fabricating technology, membrane gas separation has become one of the most promising separation processes, especially in the natural gas industries. Cellulose acetate membranes has been used to separate CO_2 from natural gas, and silicone rubber membranes can be used to deal with the removal of C_{3+} hydrocarbons from natural gas stream (Baker and Lokhandwala 2008). However, when dealing with N_2 removal from natural gas, the low selectivities of N_2/CH_4 (with glassy membranes) and CH_4/N_2 (with rubbery membranes) hinder the development. According to Lokhandwala et al. (2010), the best selectivity of N_2/CH_4 with glassy membranes was around 2.5, and with rubbery membranes, the best selectivity of CH_4/N_2 was around 3.7. With a single-stage permeation process, a N_2-permeable membrane must have a N_2/CH_4 selectivity of 17 and a CH_4-permeable membrane must have a CH_4/N_2 selectivity of 6 to achieve the target separation (Baker and Lokhandwala 2008). As a result, both glassy and rubbery membranes currently available cannot achieve the goal of N_2 removal. However, rubbery membranes are often studied for this application.

Poly(dimethyl siloxane) (PDMS) is a silicon rubber, which has received lots of attention because of its high intrinsic permeability to gases (Stern 1994). The high permeability of PDMS is probably due to its large free volume, which is caused by the flexibility of the siloxane linkages (-SiO-) of this polymer. In gas separation, there are two important parameters, permeability and selectivity. PDMS is a highly permeable membrane material with a low selectivity (Stern 1994). Merkel et al. (2000) reported that the permeability of CH_4 and N_2 at 35^0C are 1200 and 400 Barrer, respectively. The gas permeability is remarkably high, but the CH_4/N_2 selectivity is only around 3.

Poly(ether block amide) copolymers (PEBA) is a relatively new thermoplastic elastomers produced by Arkema Inc. under the trade name of Pebax®. The polymer consists of soft polyether (PE) and hard polyamide (PA) blocks. Many different grades of the copolymers have been developed by changing the types and the contents of the PE and PA components. These copolymers are commercially used in a wide variety of applications such as textile, construction, agriculture, and medical. Bondar et al. (1999) studied gas sorption in five different grades of PEBA. They found that gas solubility increases an increase in PE content. Later on, they also found that the gas permeability depends strongly on the amount of the PE component and the polarity of the PE element (Bondar et al., 2000). However, all the PEBA materials showed a

CH_4/N_2 selectivity of less than 5, which does not meet the target selectivity required for N_2 removal from natural gas using a single stage membrane separation process. One factor that arose my interest was that for rubbery membranes, the gas permeability usually decreases with decreasing temperatures, but the permeability ratio of a pair of gases often increases. That is, by decreasing the operating temperatures, one may be able to obtain a higher permeability ratio that may be adequate for N_2 removal from natural gas, though the permeability may be compromised.

Polymer blending is a unique way to combine the advantages of each polymer into a new material. Polymer blending of PEBA with other polymers has been studied. For example, PEG/PEBA 1657 blend membranes were prepared for gas transport of H_2, N_2, CH_4, and CO_2(Car et al., 2008). The permeabilities of CO_2, CH_4, and N_2 were increased, but there were no significant changes in CO_2/CH_4 and CO_2/N_2 selectivities, while a slight improvement in CO_2/H_2 selectivity was observed. Reijerkerk et al. (2010) studied PEBA/PEG-PDMS blend membranes, and the permeabilities of gases studied significantly increased, while the selectivity remained almost the same. In spite of these studies trying to combine the advantages of PEBA and other polymer materials, very few data can be found for blend membranes using different grades of PEBA.

1.2 Objectives

The main purpose of this research is to evaluate the permeability of N_2 and CH_4 in PEBA and PDMS membranes at different temperatures and pressures. Several different rubbery membranes were first tested with pure gas permeation under different pressures and temperatures. Then membranes with the best performance were further studied for separation of binary N_2/CH_4

mixtures, which can simulate the real natural gas stream. By changing the operating conditions (e.g., composition, feed pressure and temperature), the membrane performance for CH_4/N_2 separation was studied.

1.3 Outline of the Thesis

This thesis is divided into 5 chapters. To start with, a fundamental understanding of gas permeation through membranes, including mass transport mechanism and the polymers, is presented in Chapter 2. Mass transport models are described, and the physical properties of polymer materials are introduced. Polymer blending, a popular method of combining the advantages of two materials into one is also presented. Some operating conditions affecting gas permeation are discussed as well.

Chapter 3 presents the preparation of single component PEBA membranes. The gas permeability in PEBA membranes as well as a PDMS membrane was determined under different gas pressures and temperatures. The best performed membranes were employed for further studies with permeation of binary CH_4/N_2 gas mixtures, and the gas permeability in the membrane was evaluated under various operating conditions (e.g., feed pressure and composition, temperatures).

Chapter 4 describes how polymer blending would improve the membranes performance. Several blended membranes were produced with different blending ratios. These membranes were evaluated with pure gas permeation at different pressures and temperatures, and the effects of blend ratio on the membrane permselectivity was also discussed. The best blended membrane was further studied in binary gas separation. The experimental data was fitted to semi-empirical model of polymer blending.

Finally, the conclusions drawn from this study are presented in Chapter 5, some recommendations for further studies are provided as well.

Chapter 2 Literature Review

Membrane separation technology is rapidly growing in recent years. Several books have been published to describe the fundamental principles and applications of membrane technology in details (Koros et al., 1988, Mulder 1991, Baker 2012), and some articles have provided reviews to membrane structure and formation (Ghosal and Freeman 1994, Pinnau and Freeman 1999)

2.1 Overview of Membrane Separation

J. K. Mitchell observed that different gases had different permeation rates when they transported through a rubber balloon in 1831 (Paul and Yampol'skii 1993). This was considered the first scientific observation related to membrane gas separation. At almost the same time, Fick studied gas transport through nitrocellulose membranes and developed his famous law of diffusion, which is known today as the Fick’s first law (Paul and Yampol'skii 1993). Later on, Graham made the first quantitative measurements of gas permeation rates and proposed the solution-diffusion model in 1866, and it is now known as Graham’s law of diffusion (Baker 2012). In the 1940s to 1950s, modern theories of gas permeation in membranes was established by Barrer, Van Amerongen, Stern and other researchers (Paul and Yampol'skii 1993).

One of the biggest problems with those early membranes was that the membrane selectivity was insufficient and the fluxes were too low for practical applications. Loeb and Sourirajan brought the first breakthrough with the introduction of asymmetric membranes in 1960s (Baker 2012). A membrane with a very thin dense layer supported on a thick porous sub-layer was produced by the so-called phase inversion process. The thin dense layer was the selective layer, which had the ability to achieve the separation, while the thick porous sub-layer provided mechanical support to the thin dense layer with negligible resistance to mass permeation. Such a membrane structure significantly improved permeation flux, and it was successfully used in water desalination. However, it was not suitable for gas separation as the membrane would lose its separation functions after drying. Vos and Burris found a solution to such a problem, by adding a surfactant to water to reduce the interfacial tension between the walls of the membrane and water molecules during membrane formation and drying (Tabe-Mohammadi 1999).

During the past two decades, membrane separation technology has been rapidly growing, and many different processes have been developed and new processes are constantly emerging. Processing of natural gas is one of the largest industrial gas separation applications. The total consumption of natural gas is around 95 trillion scf/yr globally, the market for new natural gas separation equipment is around 5 billion dollar/yr. However, less than 5% of the market is occupied by membrane processes, and almost all of which is for the removal of CO_2 from natural gas (Baker and Lokhandwala 2008). Grace Membrane Systems, Separex, and Cynara were the first companies that commercialized gas separation membrane for CO_2 removal from natural gas using anisotropic cellulose acetate membranes (Baker and Lokhandwala 2008). As a matter of fact, natural gas also contains many other undesirable impurities (e.g., water, hydrogen sulfide and nitrogen), which need to be treated in order to meet pipeline specifications. Thus, there are still many opportunities for membranes in processing natural gas.

2.1.1 Types of Gas Separation Membranes

There are two types of membranes, as shown in Figure 2.1, which are widely used in the gas separation process: isotropic membranes and anisotropic membranes. Isotropic membranes have a uniform composition structure, and they can be either porous or non-porous (dense). The resistance to mass transfer in these membranes are determined by the total membrane thickness. Anisotropic membranes usually consist of a number of layers, each with different structures and permeability. A typical anisotropic membrane has a relatively dense, extremely thin surface layer supported on an open, much thicker porous substructure. The resistance to mass transfer is determined largely by the thin surface layer (Pinnau and Freeman 1999).

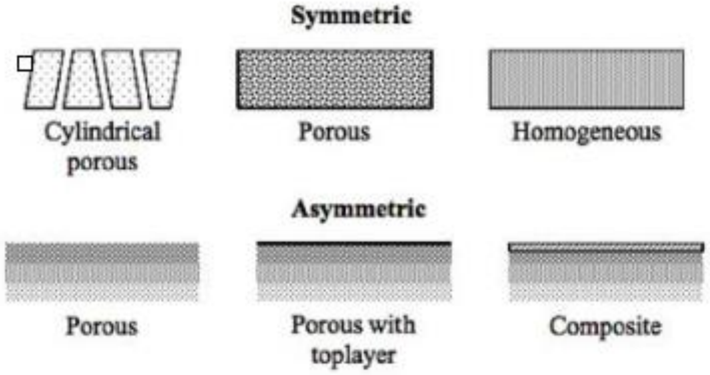


Figure 2.1 Cross section of membrane structures (Mulder 1991)

Different raw materials have been used to fabricate membranes, and gas separation membranes can be divided into glassy membranes and rubbery membranes. If the operating temperature is below the glass transition temperature of the materials, the polymer chains are rigid and segmental motion is limited. These tough and rigid membranes are called glassy membranes. The effect of differences in molecular sizes of the permeating gases on their relative mobility in the membrane is large (Baker and Lokhandwala 2008). On the contrary, if the operating temperature is above the glass transition temperature of the material, the polymer chains have sufficient thermal energy to allow limited rotation around the chain backbone, and these materials are rubbery polymers and they are soft and flexible. The difference in permeability of different gases mainly depend on the difference of gas condensabilities (Baker and Lokhandwala 2008).

The molecular size and condensability of the principal components in natural gas, relative to methane, are shown in Figure 2.2 (Baker and Lokhandwala 2008).

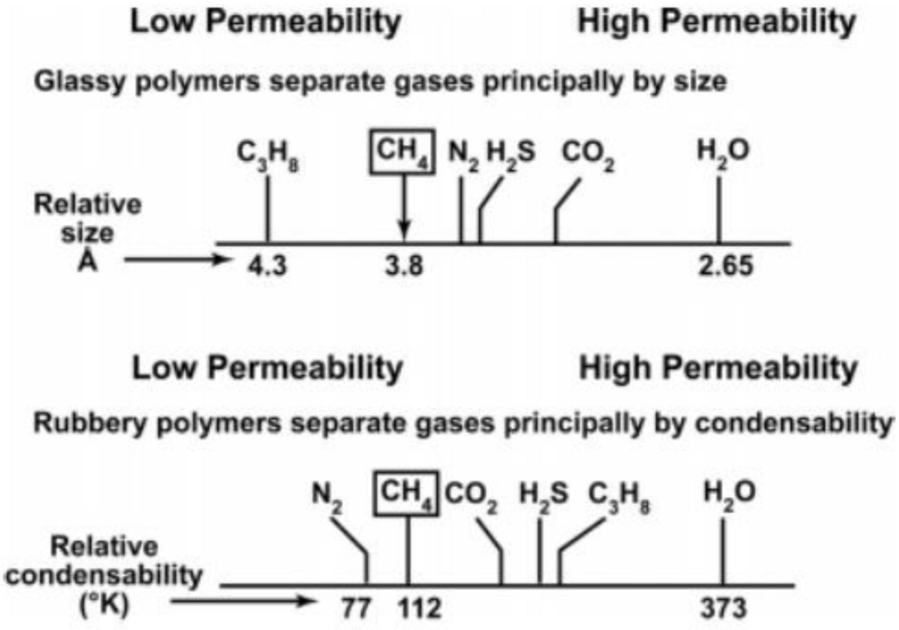


Figure 2.2 Relative size (kinetic diameter) and condensability (boiling point) of the main components of natural gas (Baker and Lokhandwala 2008).

From Figure 2.2 we know that CO_2 is better separated by glassy polymer membranes due to the large differences in molecular sizes, whereas N_2 is better separated by rubbery polymers because the difference in molecular sizes is smaller than the difference in the gas condensabilities, as shown in Table 2.1. However, the selectivity of CH_4/N_2 is pretty low compared with other gas pairs (Lokhandwala et al., 1999). Therefore, new membrane materials for better gas separations are needed to achieve N_2 removal from natural gas.

Table 2.1 Some physical properties of N_2 and CH_4

Gas	Size		Condensability	
	Critical volume (cm^3/mol)[a]	Kinetic diameter (Å)[b]	Normal boiling point (K)[a]	Critical temperature (K)[a]
N_2	89.8	3.64	77.4	126.2
CH_4	98.6	3.82	111.66	190.56

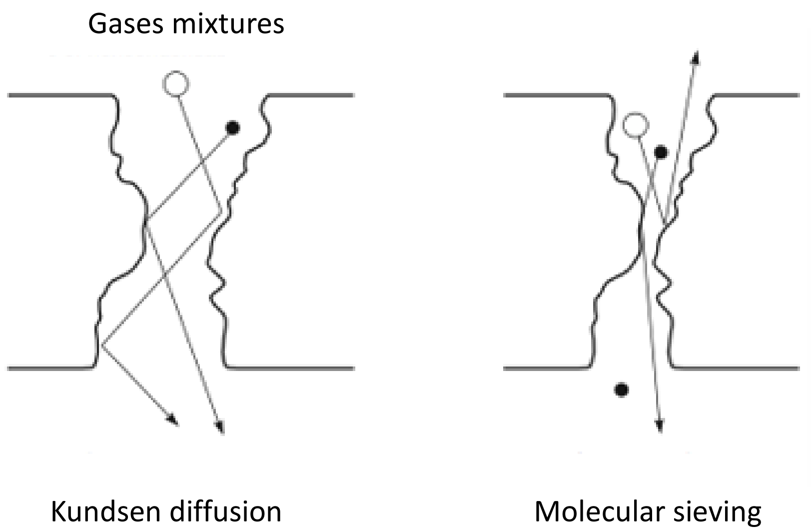
[a] Poling et al., (2001)

[b] Breck (1974)

2.1.2 Gas Transport in Membranes

The mechanism of gas transport in membranes depends on the pore size of the membranes. For porous membranes, the gas flow can be described by three models: convective flow, Knudsen diffusion and molecular sieving.

When the pore size is relatively large (0.1-10 um), gas transport though the membrane can be seen as a convective flow and no separation can be achieved. Knudsen diffusion happens when the membrane pore radius are much smaller than the mean free path of the permeating gas. Since the mean free path of gases at the atmospheric pressure is in the range of 500-2000 Å, the pore radius of the membrane must be typically less than 500 Å for Kundsen diffusion to occur. This is illustrated schematically in Figure 2.3. When this occurs, the diffusing gas molecules have more chances to collide with the pore walls than among the gas molecules. At every collision with the pore wall, the gas molecules are momentarily adsorbed and reflected in a random direction, and the gas molecules move independently of others. Hence, a separation is achieved for gas molecules with different average velocities. When the pore size decreases to 5-10 Å, the pores begin to separate gases by a molecular sieving effect. Molecules small enough to pass through the pores are adsorbed while larger molecules are retained (Baker 2012).



Kundsen diffusion

Molecular sieving

Figure 2.3 Mass transport in porous membranes (Baker 2012)

For non-porous membranes, the mass transport can be described by the solution-diffusion model, which is based on both the solubility and diffusivity factors. The details of this model are discussed in more details in the following section.

Solution-diffusion model

The solution-diffusion model is the most widely accepted mass transport model to describe gas permeation within non-porous membranes. According to this model, permeant gas first dissolves onto the membrane and then diffuses through the membrane down a concentration gradient as shown in Figure 2.4. The separation is achieved by the different amount of penetrant dissolved in the membrane and the rate difference of penetrant diffusion through the membrane (Wijmans and Baker 1995). The permeation process can be described as:

1. Adsorption and dissolution of gas molecules at the polymer membrane interface.

2. Diffusion of the gas molecules through the bulk polymer.
3. Desorption of the gas molecules at the downstream interface of the polymer membrane.

In order to define the solution-diffusion model, some assumptions are often made (Wijmans and Baker 1995). Firstly, the fluids on either side of the membrane are in equilibrium with the membrane at the interface, which means that a continuous chemical potential gradient is achieved from one side of the membrane to the other. This means that the sorption and desorption rates are much higher than the rate of diffusion through the membrane, and thus the rate of diffusion within the membrane is the rate-determining step. Secondly, the pressure within a membrane is uniform and the chemical potential gradient of a penetrant across the membrane may be represented in the form of a concentration gradient (Wijmans and Baker 1995). The relationship between the permeation flux (J) and concentration gradient can be described by the Fick's law:

$$J = -D\frac{dC}{dx} \tag{2.1}$$

where D is the diffusion coefficient of the penetrant in the membrane, dC/dx is the concentration gradient across the membrane.

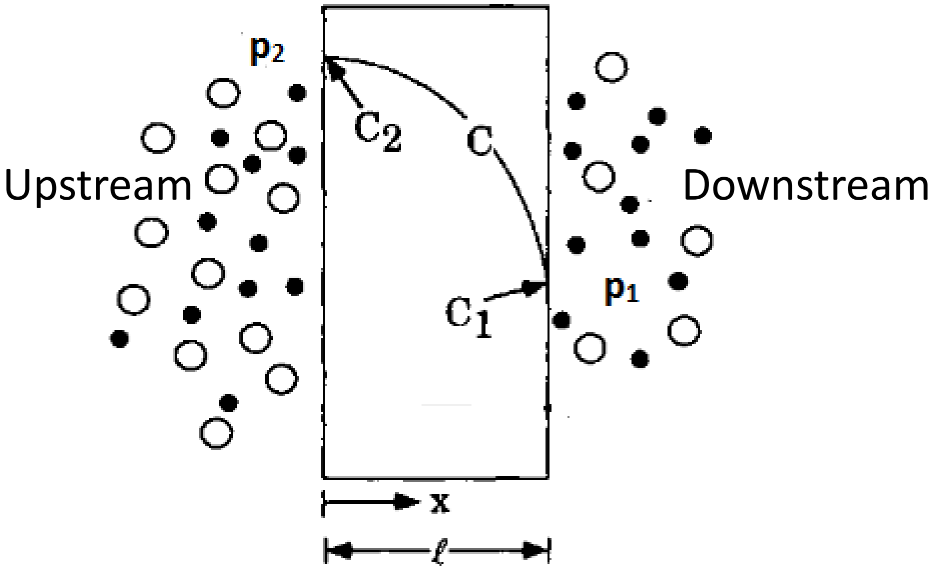


Figure 2.4 Schematic description of solution-diffusion mechanism

The permeability coefficient (P) can be defined by the following equation (Ghosal and Freeman 1994):

$$P = \frac{J}{(p_2 - p_1)/l} \tag{2.2}$$

where p_2 is the upstream pressure and p_1 is the downstream pressure, and l is the thickness of the membrane. The permeability coefficient is commonly expressed in Barrer unit (Ghosal and Freeman 1994), named after Richard Barrer who developed the first scientific method for measuring gas permeation rate:

$$1\ Barrer = 1 \times 10^{-10}\ \frac{cm^3(STP) \cdot cm}{cm^2 \cdot sec \cdot cmHg} \tag{2.3}$$

Applying equation 2.1 into equation 2.2 we have:

$$P = -\frac{D}{(p_2 - p_1)} \cdot l \frac{dC}{dx} \tag{2.4}$$

Integrating the equation with boundary conditions $C = C_2$ at $x = 0$ and $C = C_1$ at $x = l$.

$$P = \int_{C_1}^{C_2} \frac{D}{(p_2 - p_1)} dC = D \frac{(C_2 - C_1)}{(p_2 - p_1)} \tag{2.5}$$

When the downstream pressure is much lower than the upstream pressure, and the downstream gas concentration in the membrane is much lower than the upstream concentration in the membrane, the permeability can be viewed as the product of diffusivity (D) and solubility (S) (Ghosal and Freeman 1994):

$$P = D \times S \tag{2.6}$$

The diffusion coefficient D describes molecular mobility and is mainly governed by the molecular size when it travels through the permanent and transient voids afforded by the free volume of the membrane (Zou et al., 2008). The solubility coefficient S is a thermodynamic parameter which provides a measurement of the quantity of penetrant molecules taken up by the membrane (Zou et al., 2008).

The ability of a membrane to separate a mixture is measured by its selectivity. For a binary gas mixtures consisting of components i and j with the component i as the fast permeating species, the selectivity can be expressed as (Koros et al., 1988):

$$\alpha_{ij} = \frac{P_i}{P_j} = (\frac{D_i}{D_j}) \times (\frac{S_i}{S_j}) \tag{2.7}$$

The selectivity depends on both the diffusivity selectivity (D_i/D_j) and the solubility selectivity (S_i/S_j). At given operating conditions (e.g., pressure, temperature and feed composition), the diffusivity selectivity is governed by the free volume of the membrane as well as the sizes of the penetrants (Merkel et al., 2000). It always favors the permeation of smaller molecules through the membrane. The solubility selectivity is affected by the penetrant condensability, and it increases with an increase in the difference in condensability between two penetrants in the binary mixtures (Merkel et al., 2000).

2.2 Polymers

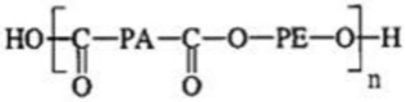
As mentioned before, polymers used to fabricate membranes can be divided into two groups, glassy polymers and rubbery polymers. Typically, rubbery polymers contain a large free volume because of gaps created by the highly mobile polymer chains (Ghosal and Freeman 1994). Free volume is the portion of volume in a polymer not occupied by the electronic clouds of the polymer, which affects penetrant diffusivity (Bernardo et al., 2009).

Glassy polymers are rigid and the polymer chains have limited motion, which results in a lower free volume fraction. Thus the size difference of the permeating molecules has a significant effect on the relative mobility. For rubbery polymers, the polymer chains can move more freely, and the diffusivity selectivity decreases. Typically the diffusivity selectivity of D_{N_2}/D_{CH_4} is between 1.2 and 2.0 for rubbery polymers, and between 3 and 6 for glassy polymers. Meanwhile, the solubility selectivity S_{N_2}/S_{CH_4} usually lies between 0.2 and 0.4 for both rubbery and glassy polymers (Merkel et al., 2006). As discussed before, glassy polymers tend to permeate nitrogen preferentially, and the expected permeation selectivity of α_{N_2/CH_4} is around 2.5. Similarly, rubbery polymers tend to permeate methane preferentially, and the expected selectivity of α_{CH_4/N_2} is around 3 (Baker and Lokhandwala 2008).

Most polymers are semi-crystalline, which contains both amorphous and crystalline regions. Crystalline regions are considered to be impermeable, which increase the tortuosity of penetration paths (Ghosal and Freeman 1994). Therefore, diffusion mainly occurs in the amorphous regions. As a result, the size and distribution of crystalline regions, degree of crosslinking, and the nature of substituents in the polymer affect segmental mobility of the polymer chains, and they are important to membrane permeability (Mulder 1991, George and Thomas 2001).

2.2.1 Poly(ether block amide) (PEBA)

PEBA resins were developed in 1972, but only in 1981 did they begin to be used commercially under the trade name Pebax®. PEBA is a group of thermoplastic elastomers with a general chemical structure



$$\mathrm{HO}\left[\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{PA}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{PE}-\mathrm{O}\right]_n\mathrm{H}$$

where PA is an aliphatic polyamide “hard” block (e.g., nylon-6, nylon-12) and PE is a polyether “soft” block (e.g., poly(ethylene oxide) [PEO], poly(tetramethylene oxide) [PTMEO]) (Bondar et al., 1999). The “hard” polyamide blocks provide the mechanical strength, whereas the polyether “soft” blocks provide elastic properties. PEBA 2533, PEBA 1074, PEBA 1657 and PEBA 3000 were used in this work. Some of their properties are listed in Table 2.2.

Only in recent years have the PEBA membranes been studied for separation applications. Rezac et al. (1997) investigated the sorption and diffusion properties of water and methanol in four different grades of PEBA (2533, 3533, 5533, and 6333), in order to recover methanol from water wet air stream, which is relevant to controlling the hazardous air pollutant emissions in the pulp and paper industry. They found that PEBA materials can selectively separate methanol vapor form air, but not from water vapor, and PEBA 2533 was the most promising grade among the four due to its high permeation rates.

Bondar et al. (2000) studied the removal of CO_2 from mixtures with hydrogen in synthesis gas by four different grades of PEBA (2533, 4033, 1074, and 4011). PEBA was found to have very high selectivity on acid or polar/nonpolar gas mixtures with very good permeability. They also found that the PE content in the membrane and CO_2 permeability are highly correlated. As the amount of PE increases, CO_2 permeability increases. Marcq et al. (2005) also found that PEBA membranes exhibited a high intrinsic permeability due to their elastomer nature, and the CO_2/N_2 selectivity is sufficiently high to separate CO_2 from flue gas. Among the four different grades of PEBA (1074, 6100, 1657, and 3000) tested, PEBA 1657 had the highest permeability to CO_2, which is almost four times as PEBA 1074 did. PEBA 3000 had the largest permeability to N_2, which is almost five times larger than PEBA 1074. PEBA 1074, PEBA 6100, and PEBA 1657 had almost the same CO_2/N_2 selectivity (about 45), and PEBA 3000 had a lower selectivity of 16 due to its higher permeability to N_2.

Although PEBA copolymers have a good gas selectivity for CO_2 separation from nonpolar gases, they are not very effective for the separation of CH_4 from N_2 due to the similar physical properties of this gas pair.

Table 2.2 shows the physical properties of different grades of PEBA. The type and the molecular weight of the polyamide segment affect its melting point T_m and chemical resistance of the copolymer, while the type of polyether segment influences the glass transition temperature T_g. The relative amount of polyamide and polyether segments determines the hardness of the polymer (Flesher 1986).

Table 2.2 Physical properties of PEBA polymers

Polymer	Commercial Grade	PE Content (wt%)	Density (g/cm^3)	T_g (^{0}C)	T_m (PE) (^{0}C)	T_m (PA) (^{0}C)	Crystallinity in PA Block (wt%)	Hardness (D)	Reference
PTMEO/PA12	2533	80	1.01	-77	9	126	14	25	(Marcq et al., 2005)
PEO/PA12	1074	55	1.09	-55	11	156	40	40	
PEO/PA12	3000	50	1.02	-60	5	158	36	35	(Bondar et al., 1999)
PEO/PA6	1657	60	1.14	-55	49	204	25	40	

PEBA has good chemical resistance to acid, basic and organic solvents as well as thermal and mechanical stability (Liu et al., 2004). Table 2.3 is the solubility of PEBA in some commonly used solvents.

Table 2.3 Solubility of PEBA in common solvents (Bondar et al., 1999)

Solvent	Solubility
Methanol	Non-soluble
Ethanol	Non-soluble
Chloroform	Non-soluble
ɣ-butylolactone	Non-soluble
N,N-Dimethyl formamide (NMF)	Partially soluble
N,N-Dimethyl acetamide (DMAc)	Partially soluble
N-methyl-2 pyrrolidone (NMP)	Partially soluble
Trichloroethane	Soluble
Formic acid/sulfuric acid	Soluble
Mixture (3:1) of 1-propanol/1-butanol (80^0C)	Soluble

The available gas permeation data for the series of PEBA used in this work are shown in Table 2.4

Table 2.4 Previous experimental data for PEBA membranes

	Test Conditions		Permeability (Barrer)			Selectivity
PEBA	T (℃)	p (MPa)	N_2	CO_2	CH_4	CH_4/N_2
1074[a]	25	0.30	0.58	25.5		
1074[b]	35	3.04	2.33	120		
1657[a]	25	0.30	2.04	97.9		
1657[c]	25	0.30	1.29	89.0		
1657[d]	35	0.40	1.84	98.0	6.09	3.31
1657[e]	30	0.30	1.62	73.0	4.68	2.89
1657[f]	25	0.30	1.71	122		
2533[g]	25	0.35	7.75	254		
2533[h]	35	0.30	6.40	121		
2533[i]	30	0.30	4.80		20.0	4.20
2533[c]	35	0.30	9.44	221		
3000[a]	25	0.30	2.86	45.8		

[a] Marcq et al., (2005); [b] Bondar et al., (2000); [c] Ren et al., (2012); [d] Reijerkerk et al., (2010); [e] Car et al., (2008); [f] Kim et al., (2001); [g] Liu et al., (2009); [h] Scholes et al., (2012); [i] Blume and Pinnau (1990);

With an increase in the percentage of the “soft” PE block, the membrane permeability to both nitrogen and methane increases. This indicates that the “soft” polyether blocks are the locus of most of the gas transport while the “hard” nylon blocks provide mechanical strength (Bondar et al., 1999).

2.2.2 Poly(dimethyl siloxane) (PDMS)

Kammermeyer (1957) first reported that poly(dimethyl siloxane) (PDMS) had a much higher gas permeability than other rubbery polymers known at that time. Even now, PDMS is still one of the most permeable rubbery polymers. The high permeability of PDMS is attributed to its larger free volume, which may be due to the flexibility of the siloxane linkages in the polymer (Stern 1994). PDMS also has the lowest glass-transition temperature (-120^{0}C) among the current rubbery polymers. It has a very flexible polymer backbone with long-range segmental motion active even at very low temperature (Freeman and Pinnau 1997). PDMS can be used to separate VOCs from waste gas streams in industrial processes. Yeom et al. (2002) studied the separation of VOC/N_2 by PDMS membranes. They found that the selectivity of VOC/N_2 is very good, and that the VOC permeability increases and the N_2 permeability decreases with a decrease in temperature, which results in an increase in selectivity at lower temperatures.

PDMS has also been considered for the removal of higher hydrocarbons from natural gas. Raharjo et al. (2007) studied pure and mixed gas permeabilities of n-C_4H_{10} and CH_4 in PDMS membranes at different temperatures and pressures. They discovered that the presence of n-C_4H_{10} in PDMS enhanced the permeability of both CH_4 and n-C_4H_{10}, while the presence of CH_4 did not affect the permeability of n-C_4H_{10}. Therefore, due to the higher permeability of CH_4, the selectivity of n-C_4H_{10}/CH_4 is lower than that estimated from pure gas measurements.

2.2.3 Polymer Blending

Polymer blending is a versatile tool to combine the beneficial properties of two or more components. This method offers an effective way to combine polymers with different separation and physicochemical properties to obtain the desired superior properties which are not found in individual polymers (Mannan et al., 2013). Polymer blends can be categorised as miscible and phase-separated blends (immiscible and partially miscible blends) (Robeson 2010). In the miscible blends, polymers can dissolve in each other and form a homogeneous solution, while in phase-separated blends, heterogeneous solution occurs (Mannan et al., 2013).

The permeability of miscible blends can be described by:

$$lnP_b = \emptyset_1 lnP_1 + \emptyset_2 lnP_2 \qquad \text{Homogeneous model (2.8)}$$

where P_b, P_1, and P_2 are the permeability coefficients of the blend and components 1 and 2, respectively, and $\emptyset_1$ and $\emptyset_2$ are the respective volume fractions of components 1 and 2 in the blend. This relationship predict random copolymer permeability as a function of the blend composition (Paul 1984).

For phase-separated polymer blends, the permeability-composition relationships are more complex since both components 1 and 2 can be the continuous phase. At the extremes of composition, the parallel and series models may be employed as the upper and lower bounds of the permeability in the blend (Paul 1984).

$$P_b = \emptyset_1 P_1 + \emptyset_2 P_2 \qquad \text{Parallel model (2.9)}$$

$$P_b = P_1 P_2 / (\emptyset_1 P_2 + \emptyset_2 P_1) \qquad \text{Series model (2.10)}$$

Polymer blends are often used in gas separation membranes because of the potential advantages of the blended membranes. By blending a less plasticizable polymer, the plasticizing behavior of the original membrane will be reduced. Blends can also improve the mechanical and thermal properties of the resulting membrane. Moreover, facilitated transport of a certain gas can be reached by polymer blending (Mannan et al., 2013).

Car et al. (2008) studied the modification of PEBA by adding a low-molecular-weight PEG. A simple binary solvent of ethanol/water was used to prepare the membrane, and gas transport was determined for four gases (H_2, N_2, CH_4, and CO_2). They found that the permeability of CO_2 was significantly increased in the membrane with 50 wt.% of PEG. Although the CO_2/N_2 and CO_2/CH_4 selectivities remained unchanged, an increase in CO_2/H_2 selectivity was observed. Such a polymer blending increased the membrane permeability to gases, but very little improvement in selectivity was achieved.

Reijerkerk et al. (2010) prepared PEBA/PEG/PDMS blend membranes to take advantages of the high selectivity of PEG for CO_2 and the high permeability of PDMS. 80 wt.% of PEG and 20 wt.% of PDMS was used as the PDMS-PEG additive, and four gases (H_2, N_2, CH_4, and CO_2) were tested in both pure and mixed gas permeation tests. Similar to the research results of Car et al. (2008),the gas permeability increased, and the CO_2/H_2 selectivity slightly increased while the CO_2/N_2 and CO_2/CH_4 selectivities decreased.

Very little work is done on N_2 removal from natural gas by blend membranes. Nonetheless, the above work appeared to suggest that using proper polymer blending, both CH_4 and N_2 permeabilities may increase, and the CH_4/N_2 selectivity may also be enhanced if the increase in N_2 permeability is less significant than the increases in CH_4 permeability

2.3 Factors Affecting Gas Permeation

Permeability coefficient is one of the most important parameter in gas separation, which depends on the solubility and diffusivity coefficients. Factors affecting the solubility and diffusivity include: operating conditions (temperature, pressure, and feed composition), polymer structure, and the properties of permeating species (molecule size, condensability). Some of the factors are discussed below.

2.3.1 Feed Gas Pressure

The effect of feed pressure on the permeability coefficient is due to the competing effects of hydrostatic pressure and plasticization (Bondar et al., 2000). Generally speaking, non-condensable gases are mainly influent by the hydrostatic pressure, while high soluble (condensable) gases influences permeability through plasticization (Bondar et al., 2000).

Two typical isotherm patterns are often observed for the relationship between permeability and pressure in rubbery membranes (Chen et al., 2005): the diffusivity and solubility of low sorbing penetrants like N_2 and He are independent with the pressure. On the other hand, the permeability of an organic vapor may increase linearly or exponentially with an increase in the gas pressure.

2.3.2 Temperature

The effects of temperature on the permeability, diffusivity and solubility often follow Arrhenius type of relationship (Ghosal and Freeman 1994):

$$D = D_0 \cdot e^{\frac{-E_d}{RT}} \tag{2.11}$$

$$S = S_0 \cdot e^{\frac{-\Delta H_S}{RT}} \tag{2.12}$$

$$P = P_0 \cdot e^{\frac{-E_p}{RT}} \tag{2.13}$$

where E_d and E_p are the activation energies of diffusion and permeation, respectively. ΔH_s is the enthalpy change of sorption. The activation energy for permeation E_p can be calculated from the $lnP\ vs. 1/T$ plot. As an approximation, $P = D \cdot S$, and thus E_p is related to E_d and ΔH_s by:

$$E_p = E_d + \Delta H_s \tag{2.14}$$

Gas diffusion coefficient increases with increasing temperature when the polymer does not undergo thermal change such as glass transition. Less permeable gases often have a higher activation energy than more permeable gases, because the former needs more energy to permeate through the membrane. Also increasing temperature can elevate the diffusivity of less permeable gases more significantly than the more permeable gases. As a result, the higher the temperature is, the lower the diffusivity selectivity will be (Ghosal and Freeman 1994).

The dissolution of a penetrant molecule into a polymer matrix can be viewed as a two-step thermodynamic process: the condensation and the creating of molecular space to accommodate the penetrant molecule. Thus, the enthalpy of sorption can be written as (Ghosal and Freeman 1994):

$$\Delta H_s = \Delta H_{condensation} + \Delta H_{mixing} \tag{2.15}$$

where $\Delta H_{condensation}$ and ΔH_{mixing} are the enthalpy changes associated with the two-step process, respectively. For non-condensable penetrants, ΔH_s is governed by ΔH_{mixing} since $\Delta H_{condensation}$ is very small. Since ΔH_{mixing} is normally positive, the solubility increases with an increase in temperature. For condensable gases, ΔH_s is dominated by $\Delta H_{condensation}$ which is negative. In this cases, the gas solubility decreases with an increase in temperature. Since $P = D \cdot S$, and diffusivity is generally a stronger function of temperature than the solubility coefficient (i.e.,$E_p > |\Delta H_s|$), the gas permeability usually increases with temperature (Ghosal and Freeman 1994).

2.3.3 Feed Gas Composition

Unlike pure gas permeation test, the binary or multi-component gas mixture, where one of the permeants has higher permeation flux than the other ones, is more complicated.

Liu et al. (2006) discussed interaction of different penetrants in propylene/nitrogen binary gases permeation with PEBA/PSf composite membrane. They stated that due to the presence of nitrogen, the permeability of propylene is lower compared with the pure propylene permeability, meanwhile, the presence of propylene in the binary mixture enhanced the permeation of nitrogen(Liu et al., 2006). The decrease in propylene permeability is due to the competitive sorption and coupling transport between the two permeants. Therefore, the selectivity for propylene/nitrogen is lower than that based on pure gas permeation(Liu et al., 2006).

Different tendency occurs when facing the multi-component gases permeation of VOC/N_2 with PEBA 2533 membrane (Liu et al., 2009). The presence of VOCs not only improves the permeance of N_2 due to membrane swelling caused by the VOCs, which increases the free volume and chain mobility in the polymers, but also enhanced VOC permeability. And the increase in VOC permeability was more significantly than the increase in N_2 permeability (Liu et al., 2009). Therefore, the selectivity of VOC/N_2 was increased with an increase in VOC concentration in the feed (Liu et al., 2009).

Chapter 3 CH_4/N_2 Separation by PEBA and PDMS Membranes

3.1 Introduction

N_2 is a common contaminant in natural gas, which is quite hard to remove. N_2 lowers the BTU value of the gas and makes it unsaleable. BTU value is a traditional unit of energy; it is the amount of energy needed to cool or heat one pound of water by one degree Fahrenheit. The lower the BTU value is, the less efficient the natural gas will be. Therefore, the removal of N_2 is necessary. Current technologies for N_2 removal, as discussed before, are energy-intensive and costly. A more efficient method is needed to remove N_2 from natural gas with a low energy consumption as well as low operating cost.

Membrane process for gas separation has the potential to solve the problem. The “heart” of a membrane process is the membrane itself. High selectivity and permeability are always desirable since a low driving force and a smaller membrane area will be needed to achieve a given separation. Unlike CO_2/CH_4 separation membranes, where CO_2 permeates faster than CH_4, CH_4 molecules permeate faster than N_2 through the membrane. In a single-stage process, CH_4-permeable membrane with a CH_4/N_2 selectivity of 6 can achieve the target of N_2 removal, while for N_2-selective membrane, the N_2/CH_4 selectivity should be 17 (Baker and Lokhandwala 2008). However, current studies showed the CH_4/N_2 selectivity of 3-4 obtained with rubbery membranes and the N_2/CH_4 selectivity of 2.5 with glassy membranes are far below the value required. Therefore, it is essential to explore alternative rubbery membrane materials with a better ability to separate CH_4 and N_2.

3.2 Experimental

3.2.1 Materials

Samples of Pebax® MV 1074 SA 01, Pebax® 2533 SA 01, Pebax® MV 3000 SP 01 and Pebax® MH 1657 were supplied by Arkema Inc. (Philadelphia, PA) in the form of melt processed pellets (2-3 mm in diameter). Reagent grade 1-methly-2-pyrrolidinone (NMP) (99%) and dimethylacetyamide (DMAc) (99%) from Sigma Aldrich (Oakville, ON) were used as solvents for preparing membrane casting solutions. Nitrogen (N_2) and methane (CH_4) were provided by Praxair Canada Inc. (Mississauga, ON). All materials were used without further purification.

3.2.2 Membrane Preparation

The membranes were prepared by the solution-casting method, which involved three major steps: formulating the polymer solution, casting the polymer solution to films and drying the cast films to produce the final membrane (Siemann 2005).

All PEBA pellets were first dissolved completely in a proper solvent with vigorous stirring. DMAc was used to dissolve PEBA 2533, and the solution was maintained at 60^0C with agitation for 24 hours yielding a homogenous solution. However, DMAc cannot uniformly dissolve other grades of PEBA even at higher temperature for a longer period of time. PEBA 2533 has a higher PE content than other PEBA polymers, and the PE segments have good solubility in most organic solvents. This may explain that PEBA 2533 can be dissolved in DMAc even at a lower temperature and less agitating time, while the other PEBA polymers cannot. NMP was employed to dissolve PEBA 1074, PEBA 3000, and PEBA 1657 pellets, and the solutions were maintained at 90^0C with agitation for 34 hours to ensure homogenous solutions were produced. All polymeric solutions were kept at their respective temperatures for 12 hours to degas any bubbles formed during the agitation.

Flat films of PEBA 2533 and the other PEBA grades were prepared by casting the polymer solutions on a heated glass plate at temperatures of 40^0C and 80^0C, respectively. The casting was performed using a casting knife which was in the form of a glass rod with wires rounded at both ends to control the membrane thickness. Then the plates were kept in the oven at 50^0C for PEBA 2533 and 80^0C for the rest PEBA polymers for 24 hours in order to evaporate the solvent. After that, membranes were removed from the glass plates by immersing the plates into a deionized water bath for 5 minutes. Finally the membranes were dried again in the oven at 50^0C for 24 hours. The thicknesses of these membranes ranged from 30 to 70 μm since different wires with different diameters were used. The thicknesses reported were the average of measurements taken from four quadrants and the center of a membrane sample when it was produced. The membranes were stored at room temperature until use.

A commercial PDMS membrane (Speciality Silicone Products Inc., Ballston Spa, NY) was used without any further modifications, the thickness of which is 63.5 μm.

3.2.3 Gas Permeation Measurements

Pure gas permeability tests were performed using the dense PEBA films prepared in the lab and the commercial PDMS film. Gas permeability coefficient was measured at pressures varying from 0.3013 to 0.8013 MPa absolute, and temperatures varying from 25 to -20^0C. A membrane cell with an effective area of 13.88 cm^2 was used. A piece of membrane and Whatman grade 1 qualitative filter paper was cut and placed inside the cell between the O-rings and a porous metal plate (support screen).

The experimental setup for pure gas permeation test was shown in Figure 3.1, which consisted of an upstream gas, a membrane cell, a cooling bath and a downstream gas bubble flow meter. The gas bubble flow meter used to measure the permeation rate was a Mohr pipette filled with a drop of Swagelok Snoop leak detector fluid. The membrane cell was immersed into a cooling bath (Polystat® temperature controller from Cole-Parmer, model 12101-31) containing ethylene glycol anti-freeze to control and maintain its temperature. The retenate valve was opened prior to each run to purge the feed gas remaining in the cell, and during the tests, it remained closed.

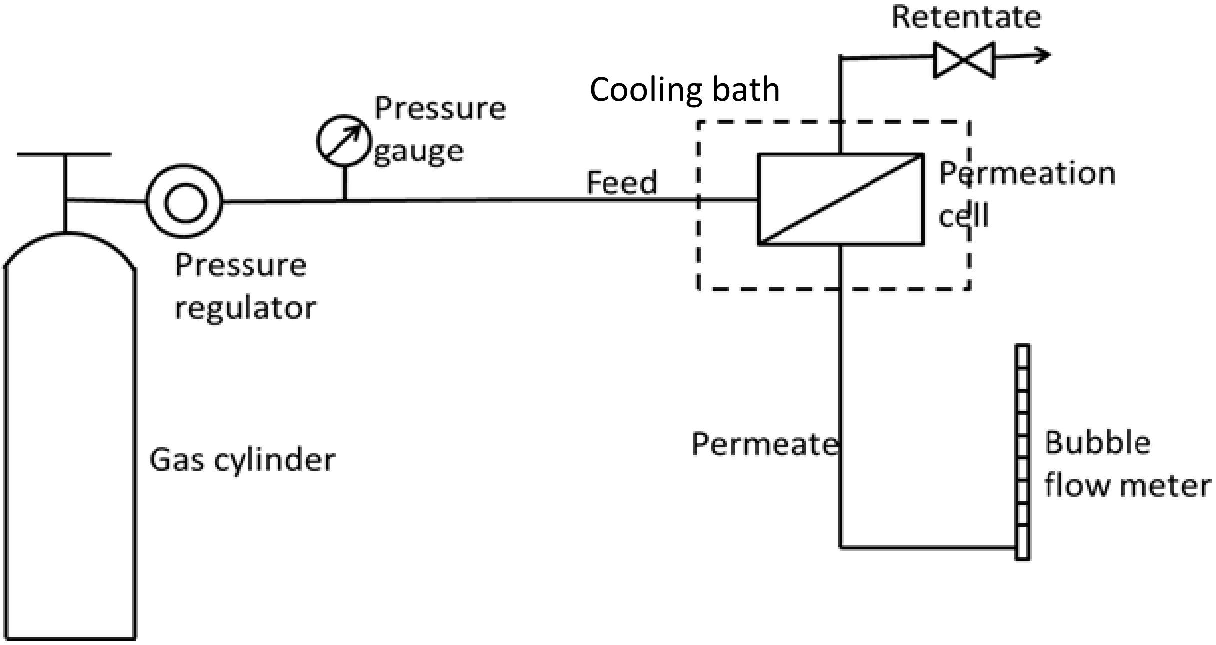


Figure 3.1 Schematic diagram of experimental setup for pure gas permeation

The permeability (P) of the gas is calculated by:

$$P = \frac{Vl}{At\Delta p} \tag{3.1}$$

where V is the volume of the permeate over a period of time t, l is the thickness of the membrane, A is the effective membrane area. Δp is the pressure difference between the upstream feed gas and the downstream permeate gas. The permeability ratio of faster gas i over the slower gas j was used to measure the membrane selectivity (permeability ratio):

$$\alpha_{ij} = \frac{P_i}{P_j} \tag{3.2}$$

The permeability ratio indicates the ability of the membrane to separate these two spices. It is sometimes called ideal selectivity.

The experimental setup for binary gas mixture permeation tests is shown in Figure 3.2. PEBA 2533 and PEBA 1074 membranes were mounted in the same membrane cell as used in the pure gas permeation tests. The operating pressure was 0.7013 MPa absolute, while the temperature varied from 25 to -20^{0}C. The feed gas mixture was prepared by using a dynamic gas blending system comprised of two Matheson mass flow controllers (Model 8270). The flow rates of the permeate and the residue streams were measured by bubble flow meters. A very small stage cut (<0.05) was used so that the composition of residue stream was the same as that of the feed. The composition of residue (or feed) and permeate streams were analyzed by an online Agilent gas chromatograph (Model 6890N) equipped with a Supelco packed column (60/80 mesh Carboxen-1000, 15’×1/8’) and a thermal conductivity detector. The permeability (P_i) of an individual component in the gas mixture through the membrane was calculated by:

$$P_i = \frac{Vly_i}{At\Delta p_i} = \frac{Vly_i}{At(p_f x_i - p_p y_i)} \tag{3.3}$$

where x_i and y_i are the mole fractions of gas i in the feed and the permeate, respectively, p_f is the feed pressure, and p_p is the permeate pressure. The membrane selectivity was measured in terms of the CH_4/N_2 permeability ratio.

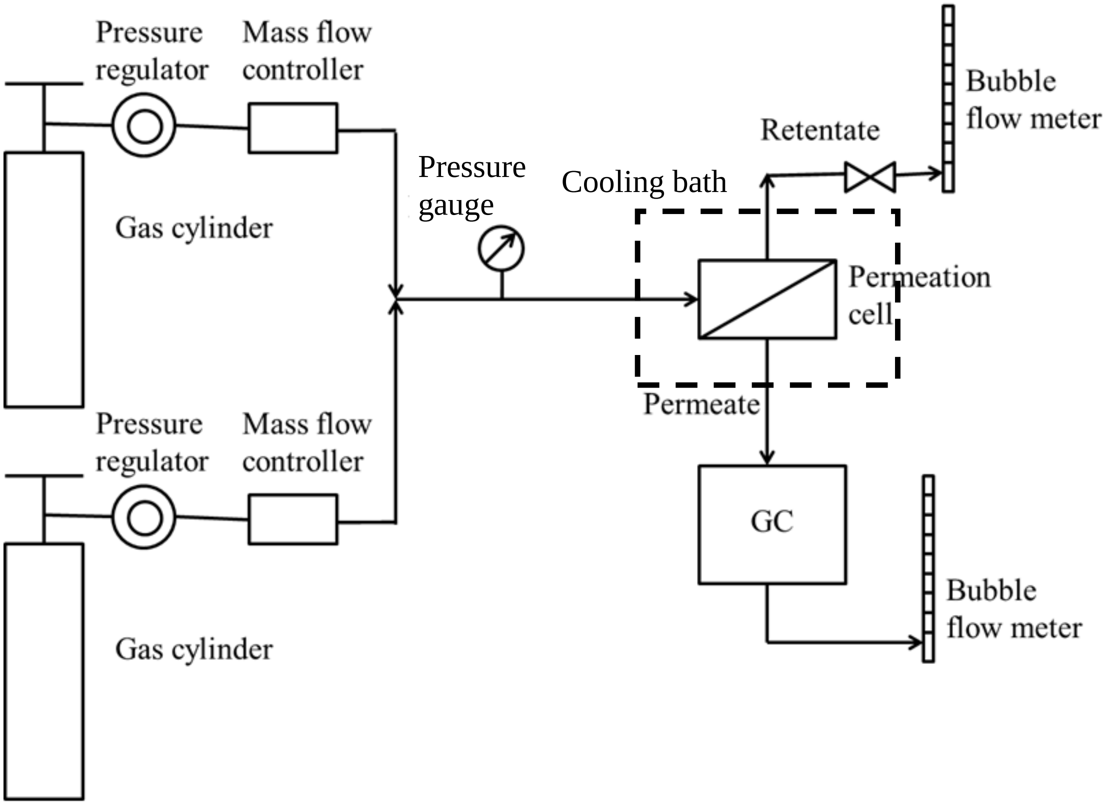


Figure 3.2 Schematic diagram of experimental setup for binary gas permeation

3.3 Results and Discussion

3.3.1 Pure Gas Permeation Tests

Pure gas permeation tests were conducted with N_2 and CH_4 under different pressures and temperatures using membranes fabricated from PEBA 1074, PEBA 2533, PEBA 1657, PEBA 3000, and a commercial PDMS membrane. PEBA membranes were fabricated in the laboratory using the solution casting method, and a commercial PDMS membrane was used without any further modification. Three permeability measurements were made at each test condition to ensure repeatability.

Effect of temperature

Gas permeability through the polymer matrix strongly depends on temperature. In order to analyze the temperature influence on gas permeation, the membrane cell was immersed into a temperature-controlled oil bath with the temperatures ranging from 25 to -20^{0}C. During the tests, the permeation flux was measured at different pressures at a given temperature.

As discussed in Chapter 2, the effect of temperature on permeability can normally be represented by the Arrhenius relationship. Figure 3.3 illustrates a linear relationship between the log permeability vs. 1000/T, which agreed with equation (2.13). Clearly, the temperature dependence of permeability can be described by the Arrhenius relationship. Generally, the permeability decreases with a decrease in temperature. This is because the gas diffusion coefficient decreases at a lower temperature, if the polymer does not undergo any morphologically change within the range of operating temperatures (Ghosal and Freeman 1994). At a lower temperature, the motion of polymer chains is restricted, resulting in less diffusive jumps conducted by the penetrant molecules. Therefore, it is getting harder for the molecules to transport across the membrane, and consequently the permeability coefficient is reduced. However, in terms of solubility, the solubility of condensable gases increases with a decrease in temperature, while the solubility of non-condensable gases decreases with a decrease in temperature (Ghosal and Freeman 1994). Unlike CO_2, which is considered to be a condensable gas, CH_4 and N_2 are considered to be non-condensable gases, and the insolubilities are expected to decrease with a decrease in temperature. The sorption of gases into a membrane is consisting of two thermodynamic processes: the first one is the condensation of the molecules, the second one is the integration of the molecules into the polymer matrix. The enthalpy change of the integration step is the domination step of the non-condensable gases due to the weak interaction with the polymer. Therefore, the solubility decreases with a decrease in temperature. Meanwhile, for condensable gases like CO_2, the dominating step is the condensation step, which will cause an increase in its solubility as the temperature decreases. Therefore, both diffusivity and solubility of CH_4 and N_2 decrease with a decrease in temperature, which leads to a decrease in permeabilities.

Figure 3.4 illustrates an increase in permeability ratio of CH_4/N_2 with a decrease in temperature. Compared with N_2, CH_4 is more condensable due to its higher normal boiling point and the critical temperature. As a result, CH_4 will behave more like a condensable gas here, which means the solubility of CH_4 will decrease less significantly than N_2. Although the diffusivity is a stronger function of temperature than solubility, the less significant decrease in CH_4 solubility still plays an important role, and hence the CH_4 permeability decreases less significantly than that of N_2 when temperature decreases. As a result, the CH_4/N_2 permeability ratio increased.

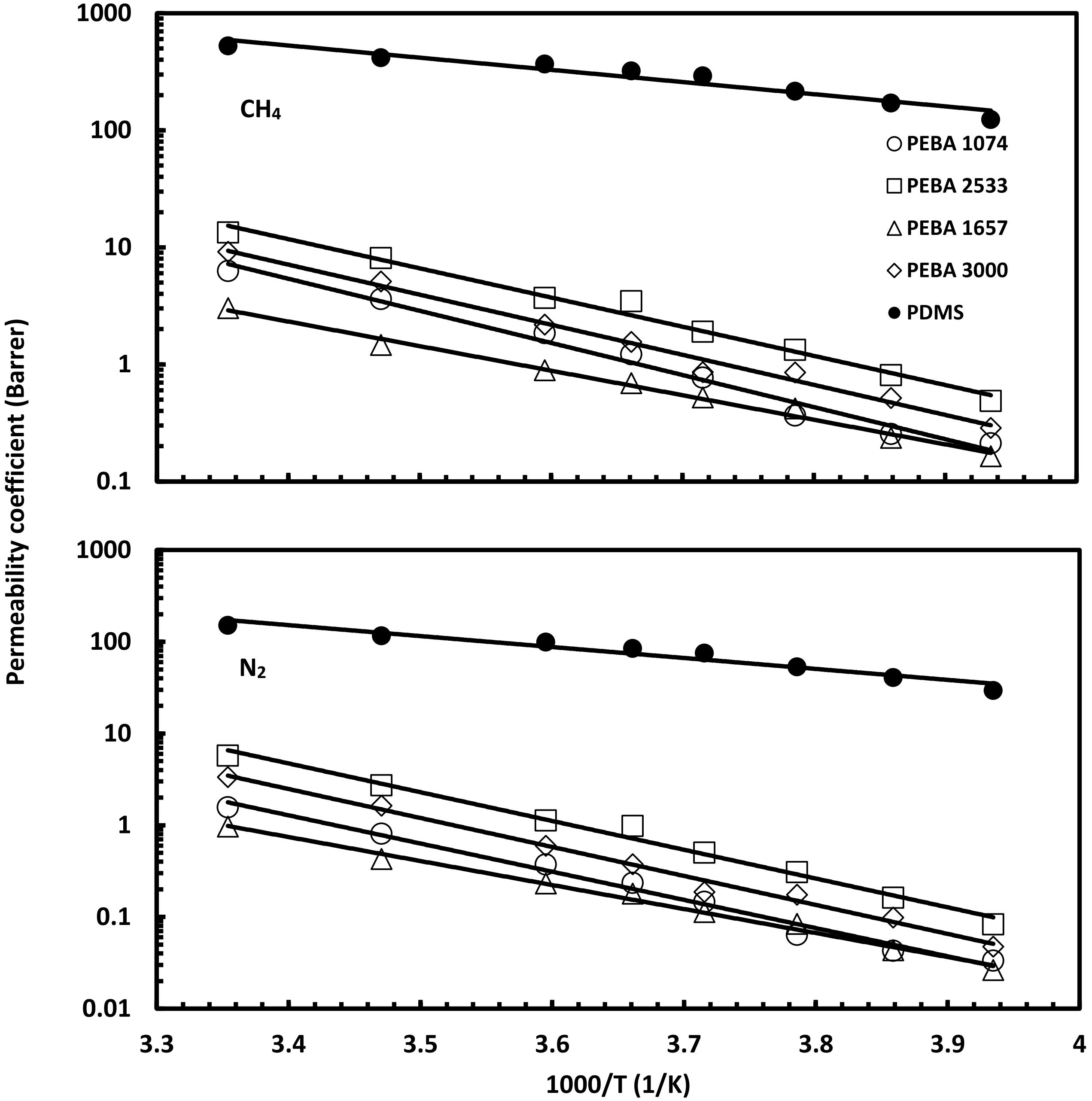


Figure 3.3 Effect of temperature on the permeability coefficients of CH_4 and N_2 for pure gas permeation through membranes. Feed pressure is 0.8013MPa absolute.

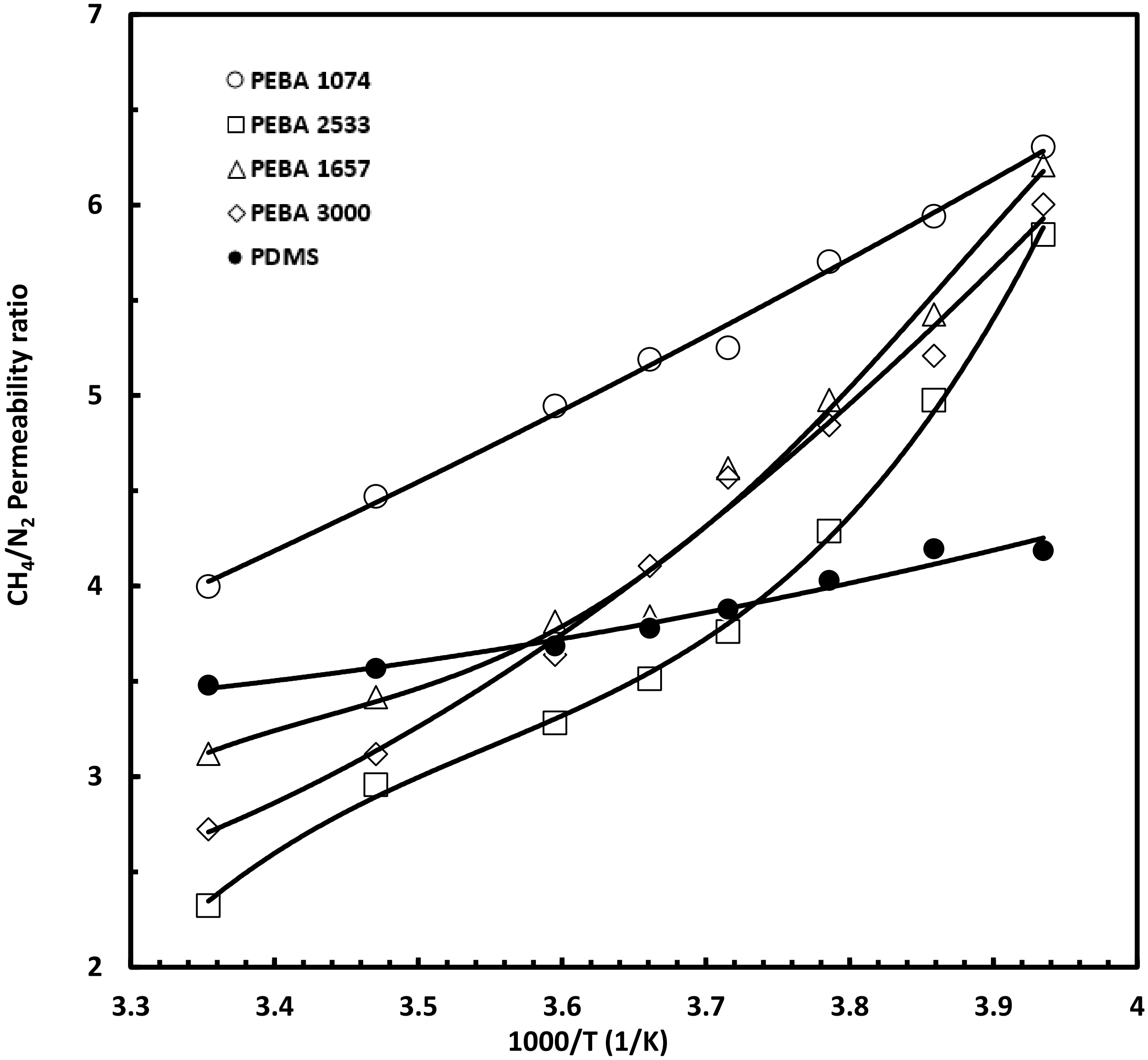


Figure 3.4 Effect of temperature on CH_4/N_2 permeability ratio based on pure gas permeation. Feed pressure is 0.8013 MPa absolute.

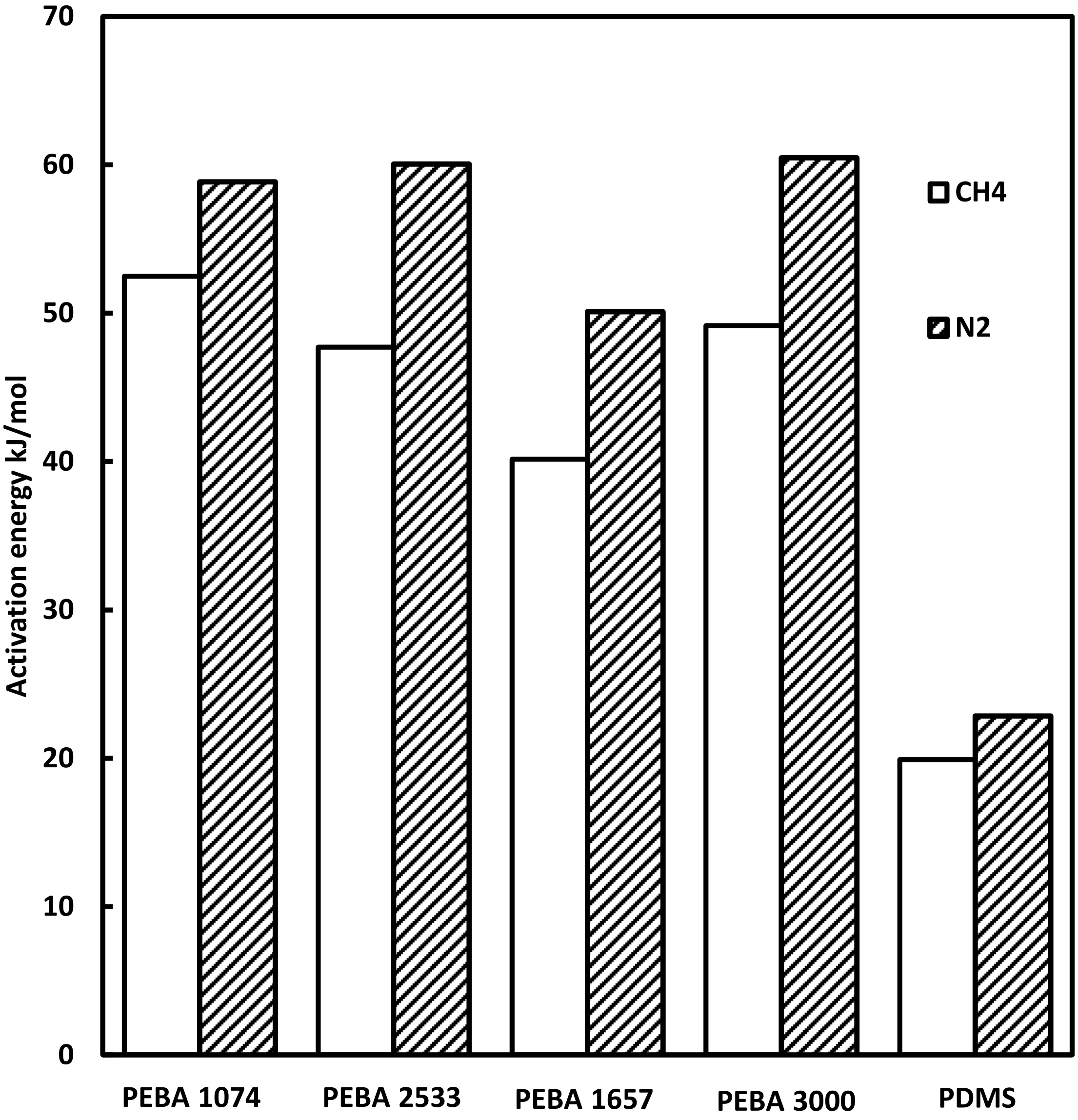


Figure 3.5 Activation energies for permeation of CH_4 and N_2. Feed pressure is 0.8013 MPa absolute

Figure 3.5 presents the activation energy of CH_4 and N_2 permeation in the membranes. The activation energy represents the overall energy needed for penetrants to overcome in order to permeate through the membrane matrix as well as the extent of temperature influence on the permeability coefficient. N_2 has a higher activation energy than CH_4, which means N_2 needs more energy to permeate through the membrane than CH_4, and it also means the change of N_2 permeability with the temperature is more significantly than the change of CH_4 permeability with the temperature. PDMS has the lowest activation energy for CH_4 and N_2 permeation among the membranes tested, which means both CH_4 and N_2 can permeate through PDMS membrane with the minimum energy needed, and the gas permeability in PDMS is not easily affected by temperature. The calculation of the activation energy can be found in Appendix A.

Effect of polymer structure

Figures 3.3 and 3.4 show that PDMS has the highest permeability among all the membranes studied here. It also has a relatively good permeability ratio at room temperature. However the CH_4/N_2 permeability ratio slightly increases with a decrease in temperature. PDMS is a rubbery material and is unable to sieve penetrant molecules based on their sizes. However, CH_4 is slightly larger than N_2, which makes the CH_4/N_2 diffusivity selectivity less than one. CH_4 is more soluble than N_2, which leads to a CH_4/N_2 solubility selectivity higher than one, which appears to be large enough to overcome the effect of diffusivity selectivity. As a result, the CH_4/N_2 permselectivity becomes greater than one (Bondar et al., 2000).

Among the PEBA membranes tested, PEBA 2533 shows the best permeability to both N_2 and CH_4 at 0.8013 MPa absolute and -20^0C with the value of 0.083 and 0,487 Barrer, respectively. While PEBA 1074 has the best CH_4/N_2 selectivity of 6.30. The semi-crystalline nylons hard blocks are considered as barriers, which provide mechanical support of the membrane, and the PE component is the key to the gas permeation. It is not surprising to see gas permeability decreasing with a decrease in PE content, as shown in Table 2.2. PEBA 2533 has the highest PE content of 80 wt.%, while PEBA 1657, PEBA 1074, and PEBA 3000 have a PE content of 60 wt.%, 55 wt.% and 50 wt.%, respectively. PEBA 2533 has the best gas permeability due to its highest PE content, whereas PEBA 1074 contains a smaller amount of PE segment but has a higher permeability than PEBA 1657. This is because of another important factor that influences gas permeation. There is an important difference between PEBA 1074 and PEBA 1657 in their PA segments. PEBA 1074 has PA12 as its PA segment, while PEBA 1657 has PA6. PA12 is a less polar backbone element, and PA6 is a more polar one. As the content of polar groups in the polymer matrix increases, the cohesive energy density increases of the polymer (Bondar et al., 2000). Cohesive energy density is the energy needed to remove a given molecule from its nearest neighbors. An increase in the cohesive energy density means a higher energy is needed for a gas molecule to permeate through the membrane, which typically leads to reductions in gas diffusion coefficients, resulting in a decrease in the permeability. No specific trend for the permeability ratio with respective to the polymer structure can be found from the experimental data. Similar observations have been reported by Bondar et al., (2000).

Effect of pressure

Gas separation processes are often operated under a wide range of feed pressures, which may lead to different behaviors of gas permeation Therefore, it is important to determine the effects of feed pressure on CH_4 and N_2 permeations. Pure gas permeation tests were conducted with those gases at different temperatures (25 to -20^{0}C) with increasing feed pressure from 0.3013 to 0.8013

MPa absolute. During the tests, the permeation fluxes were measured at different feed pressures at given temperatures. At least three permeability measurements were made at each pressure to ensure the repeatability.

As shown in Figure 3.6, the permeability for both N_2 and CH_4 slightly increased with an increase in feed pressures. This is typical of pressure dependence of gas permeabilities in rubbery or glassy polymers (Ghosal and Freeman 1994), which can be explained by the combined effects of hydrostatic pressure and plasticization. When a large number of penetrant molecules are dissolved in a polymer matrix, plasticization of the polymer occurs, which increases both the free volume of the polymer matrix and segmental motion of the polymer chains, and thus the permeation of penetrants is enhanced. With an increase in feed pressure, more and more CH_4 molecules dissolved into the membrane matrix, thereby, the membrane matrix was swollen, which can cause an increase in permeability.

On the other hand, as the pressure increases, the free volume within the polymer matrix decreases, thereby reducing the diffusivity of a gas. N_2 is a less condensable gas, so N_2 molecules are not able to dissolve into the membrane matrix as CH_4 molecules, the effect of hydrostatic pressure is dominating over membrane plasticization. Therefore, because of the duel effect, the N_2 permeability almost remains the same with an increase in feed pressure.

Figure 3.7 shows the relationship between the CH_4/N_2 permeability ratio and the feed pressure. The CH_4/N_2 permeability ratio slightly increases with an increase in the feed pressure for all the membranes used in this study. As discussed above, CH_4 is more condensable than N_2. Thus, the permeability of CH_4 increased with an increase in feed pressure, while the permeability of N_2 was almost the same. Thereby, a small increase in CH_4/N_2 permeability ratio was found with an increase in feed pressure. Although the permeability for both N_2 and CH_4 and the permeability ratio increase with an increase in the feed pressure, the difference was not so significant. The same behavior can be observed for the in PDMS membrane in the Appendix B.

The highest CH_4/N_2 permeability ratio with PDMS membrane is 4.19, which is far below the target CH_4/N_2 permeability ratio. However the highest CH_4/N_2 permeability ratio with PEBA membrane is 6.30, which can reach the goal of N_2 removal from natural gas. Thus, PDMS is less effective in terms of N_2 removal from CH_4, so the PDMS membrane will no longer be discussed in the following sections. The operating condition for the highest permeability ratio is the same, where the feed pressure is 0.8013 MPa absolute and the temperature is -20^0C. Among the four grades of PEBA polymer membranes, PEBA 2533 has the best permeability, while PEBA 1074 has the best CH_4/N_2 permeability ratio. Therefore, PEBA 1074 and PEBA 2533 were chosen to be further studied.

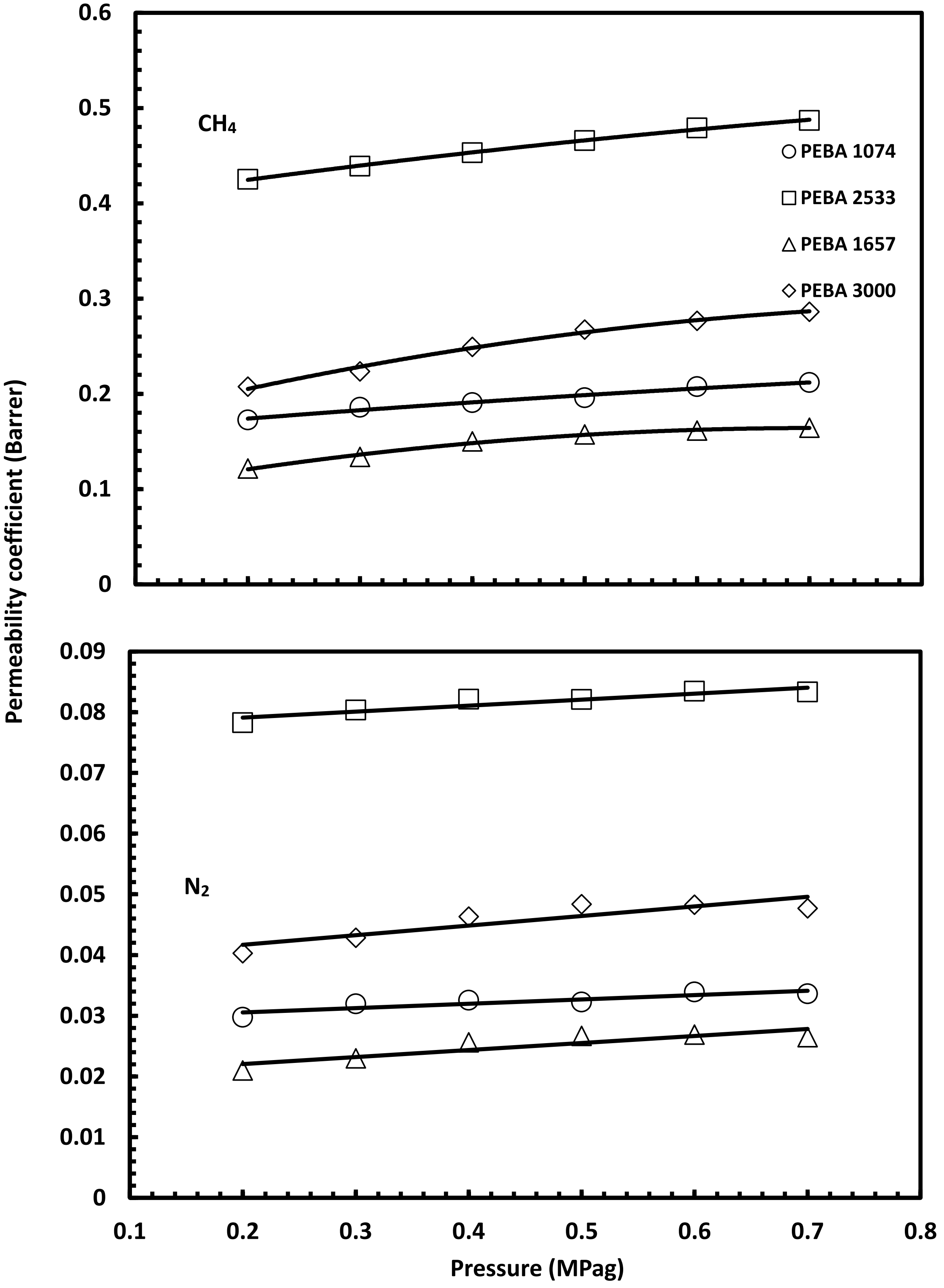


Figure 3.6 Effects of pressure on CH_4 and N_2 permeability for pure gas permeation. The operating temperature is -20^{0}C

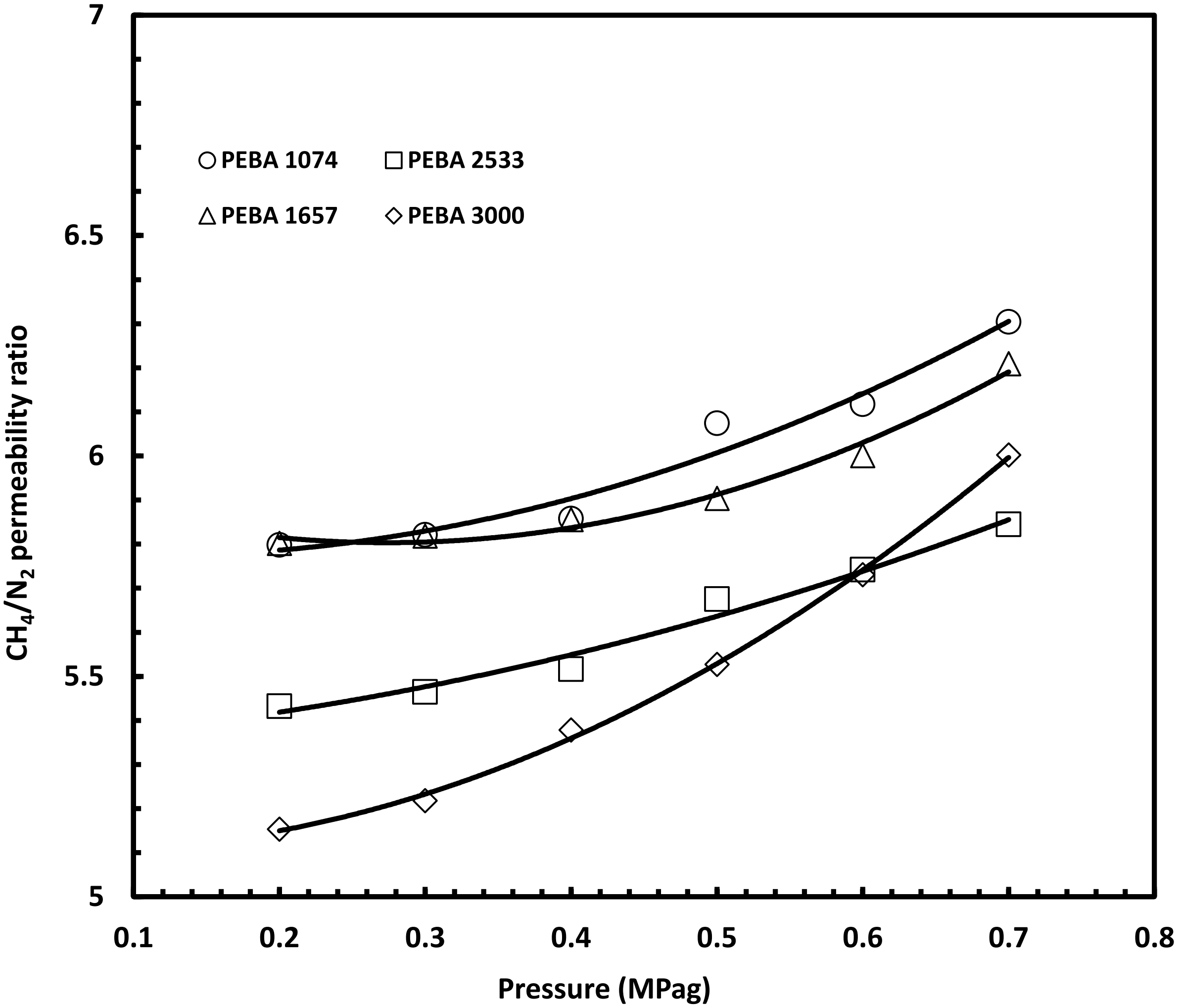


Figure 3.7 Effects of pressure on CH_4/N_2 permeability ratio for pure gas permeation. The operating temperature is -20^{0}C

3.3.2 CH_4/N_2 Binary Gas Permeation Tests

As stated before, PEBA 1074 and PEBA 2533 showed good performance in CH_4 and N_2 pure gas permeation tests. PEBA 2533 had the best permeability to both gases, and PEBA 1074 has the best CH_4/N_2 permeability ratio at a feed pressure of 0.8013 MPa absolute and an operating temperature of -20^0C. Although the gas permeability coefficient is not very high, the CH_4/N_2 permeability ratio is fairly good. When it comes to the real world scenario, the separation performance may be affected by other factors like the feed gas composition, which generally decreases the permeability ratio (Liu et al., 2006). Therefore, the permeability and selectivity of the PEBA 1074 and PEBA 2533 membranes to binary CH_4/N_2 gases mixtures needed to be determined. A sample calculation of gas permeability for binary gas permeation can be found in the Appendix A.

At a feed pressure of 0.7013 MPa, the CH_4 permeate concentration as a function of the feed CH_4 concentration for both PEBA 1074 and PEBA 2533 is shown in Figure 3.8. The mole fraction of CH_4 in permeate is always greater than that in the feed, which indicates the membranes can block N_2, and separation of CH_4 from N_2 was achieved. Moreover, the mole fraction of CH_4 in the permeate increases with an increase in feed CH_4 content. However, when the mole fraction of CH_4 in feed is sufficiently high, the increase in the permeate CH_4 concentration becomes less significant. For example, when PEBA 2533 was operated at 25^0C, the mole fraction of CH_4 in the permeate increased from 0.55 to 0.85 when the CH_4 concentration in feed increased from 0.4 to 0.8. However, a further increases in feed CH_4 concentration to 0.95 led to a moderate increase in mole fraction of CH_4 in permeate. This is due to the fact that CH_4 is more permeable than N_2 and a high concentration of CH_4 in permeate will reduce the driving force for CH_4 permeation through the membrane, which affects the permeate concentration negatively. Figure 3.8 also shows that lowering the operating temperature will increase the concentration of CH_4 in the permeate side, and the influence of temperature becomes less significant as the concentration of CH_4 in the feed side increases. At a feed CH_4 mole fraction of 0.9, the change in permeate CH_4 concentration caused by lowering temperature was not significant, especially for PEBA 1074 membrane. Additionally, under the same operating conditions, for example, at 25^0C with 70 mole% of CH_4 in feed, the permeate CH_4 mole fraction using PEBA 1074 was over 0.82, which is slightly higher than permeate CH_4 concentration obtained using PEBA 2533.This indicates that PEBA 1074 is more permselective to CH_4 than PEBA 2533 membrane, which is in agreement with the permeability observed in pure gas permeation tests.

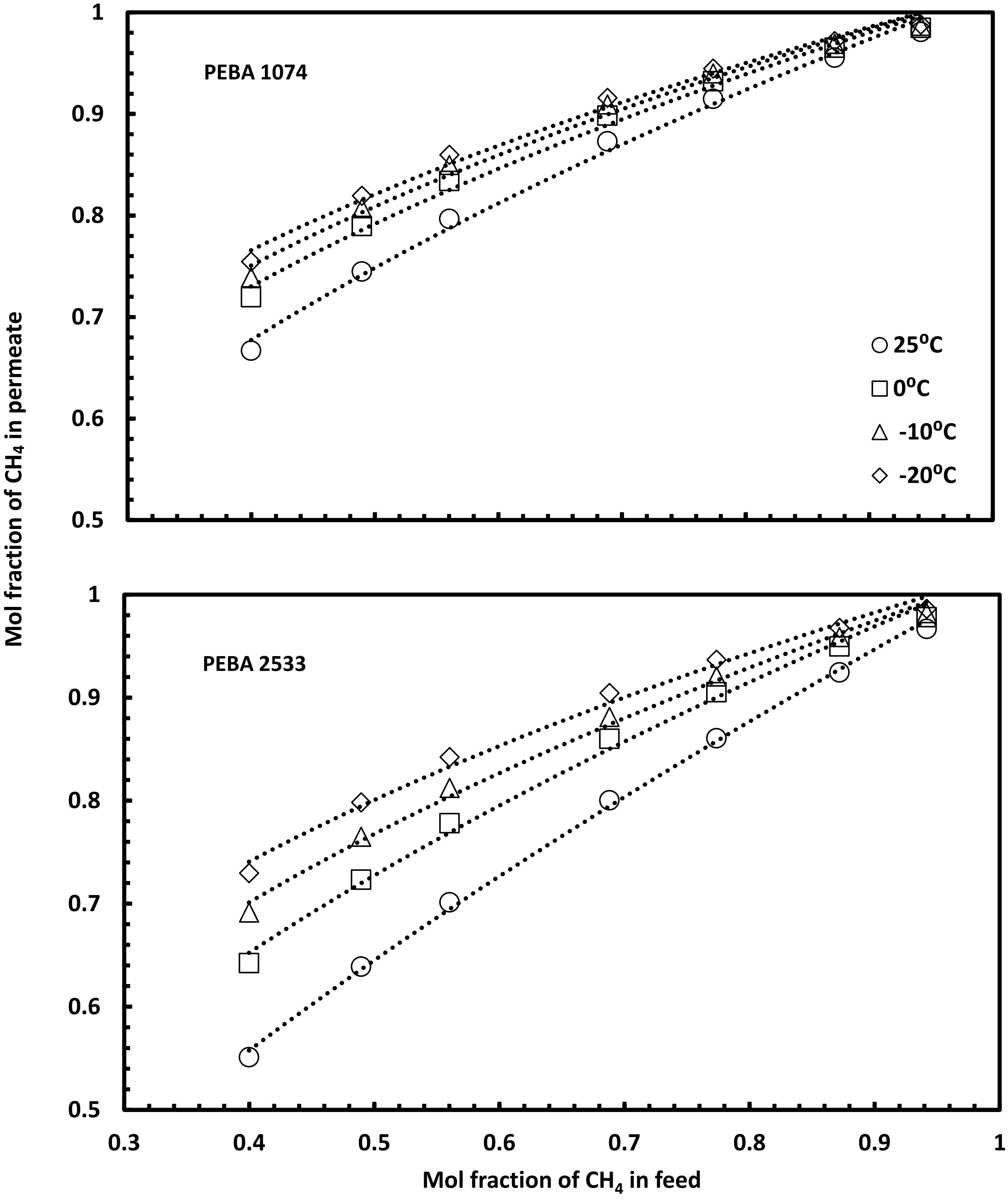


Figure 3.8 Effect of CH_4 feed concentration on permeate concentration. Feed pressure: 0.7013 MPa absolute

The permeability and the permeability ratio for gas mixture permeation at different feed compositions are presented in Figure 3.9. In general, PEBA 2533 is more permeable to CH_4 and N_2 than PEBA 1074, whereas the selectivity of PEBA 2533 is lower than PEBA 1074. The same as observed in the pure gas permeation tests. When the feed N_2 concentration increases, the permeabilities of both CH_4 and N_2 decreases slightly. An increase of N_2 concentration in feed means a decrease of CH_4 concentration in feed. CH_4 can dissolve into the membrane more easily than N_2 and cause the membrane swell. The membrane swelling can facilitate the permeation of both gases, therefore with the decrease of CH_4 in feed, the membrane swelling was decreased, so the permeability of both gases decreased. The CH_4/N_2 selectivity slightly increases with an increase in the feed N_2 concentration but the change was so small that can be negligible. This indicated that for the permeation of gas mixtures, the membrane swelling caused by CH_4 increases the permeability of both permeating gases to a similar extent. Compared with pure gas permeation tests, the CH_4/N_2 permeability ratio with either PEBA membrane was higher than the CH_4/N_2 selectivity obtained from the binary gas permeation tests. This indicates that the separation ability of the membrane was reduced in the binary gas permeation tests.

Figure 3.9 also shows that the permeabilities of CH_4 and N_2 decrease in the binary gas permeation tests than in the pure gas permeation tests. As discussed in previous section, the permeabilities of both gases in pure gas permeation tests were independent of feed pressure, so the values of the permeabilities from the pure gas permeation tests in the figure were the average values under different pressures at the temperature of -20^0C. For pure gas permeation tests (CH_4), the membrane permeability was determined by the interaction between the membrane material and CH_4 molecules. When N_2 was presented in the feed gas, the permeation was complicated by competitive sorption and coupling transport between the two permeating spices.

N_2 is a slower gas compared with CH_4, so the CH_4 permeability was reduced by the presence of N_2. The N_2 permeability was slightly higher in binary gas permeation tests than pure N_2 permeation tests. This is because with the presence of CH_4, the membrane was swollen by the dissolving of CH_4, which facilitated the permeation of smeller molecules. Molecules of N_2 are smaller than the molecules of CH_4, so the permeation of N_2 was enhanced by the presence of CH_4 in feed. Consequently, the membrane selectivity for CH_4/N_2 mixture permeation was lower than the membrane selectivity based on the pure gas permeation.

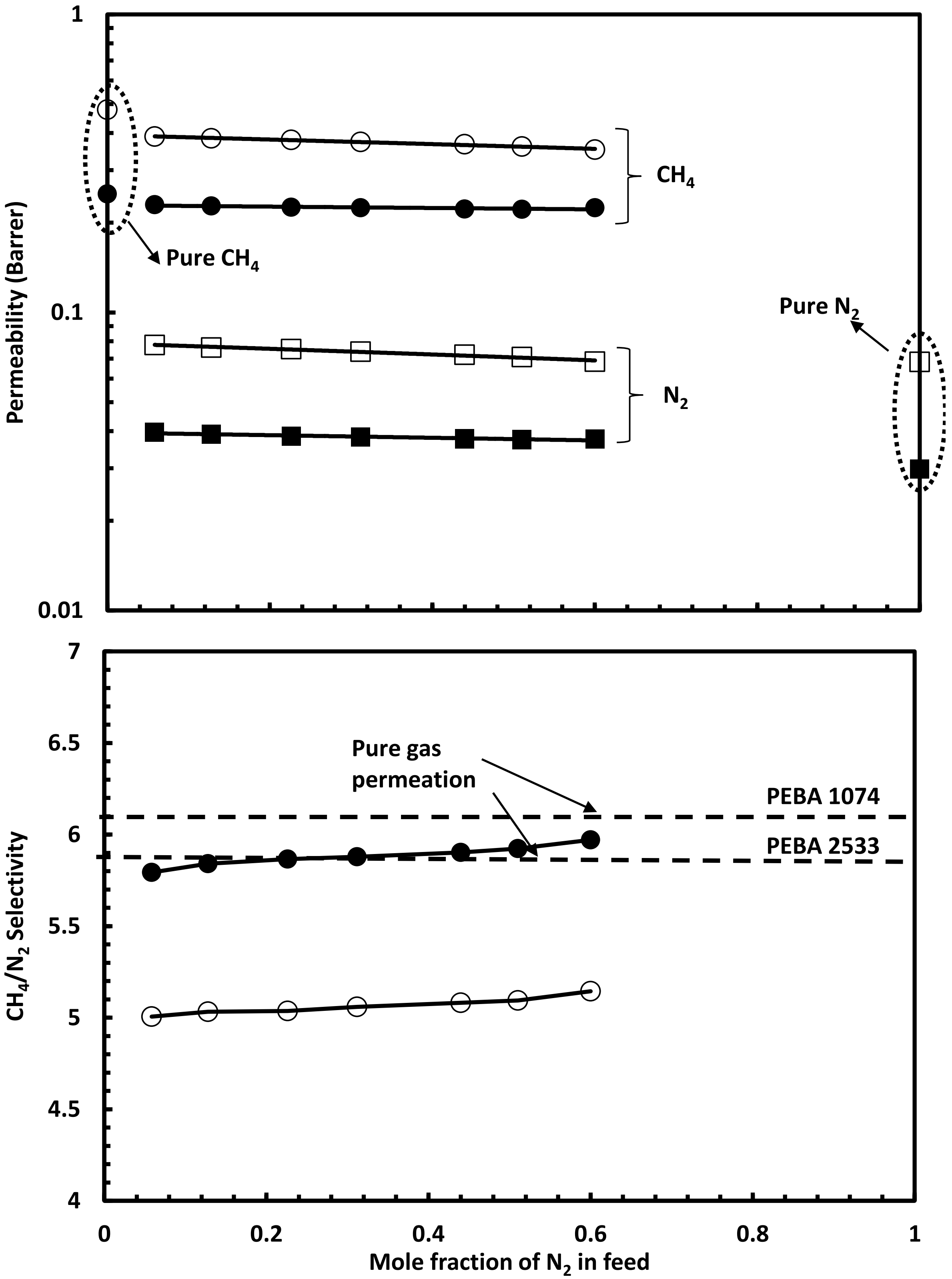


Figure 3.9 Effect feed N_2 concentration on permeability and selectivity. Feed pressure: 0.7013 MPa absolute, temperature: -20^0C.Note: closed marks represent PEBA 1074, open marks represent PEBA 2533

Figure 3.10 shows the effect of temperature on the membrane permeability to CH_4/N_2 and CH_4/N_2 selectivity. The permeabilities of both gases decrease with a decrease in temperature, and the relationship between the gas permeability and temperature follows an Arrhenius relationship. The CH_4/N_2 selectivity is found to increase with a decrease in temperature, and the selectivity of PEBA 1074 membrane is higher than the selectivity of PEBA 2533 membrane. However, the selectivity obtained with the gas mixtures is lower than that obtained from the pure gas permeation. This means that the presence of N_2 in the feed decreases the permeability ratio of CH_4/N_2. Figure 3.11 shows the activation energy for CH_4 and N_2. N_2 has a higher activation energy than CH_4, which indicates that it will be more difficult for N_2 to permeate through the membrane than CH_4. The activation energy of N_2 slightly decreases with an increase in N_2 content in feed, and the activation energy of CH_4 is essentially independent of the feed N_2 content.

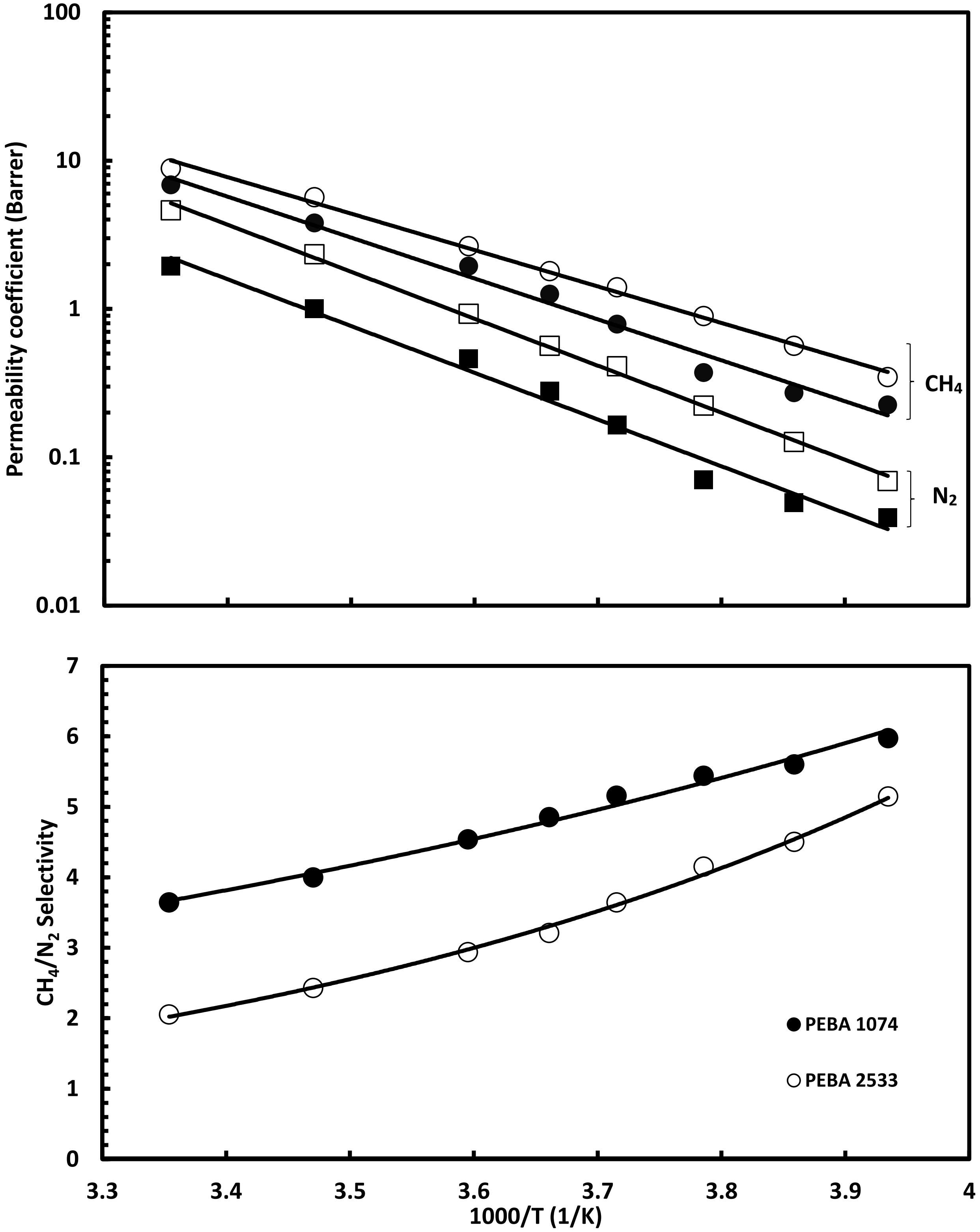


Figure 3.10 Effects of temperature on permeability and selectivity. Feed pressure: 0.7013 MPa absolute, feed contains 60% of N_2.Note: closed marks represent PEBA 1074, open marks represent PEBA 2533

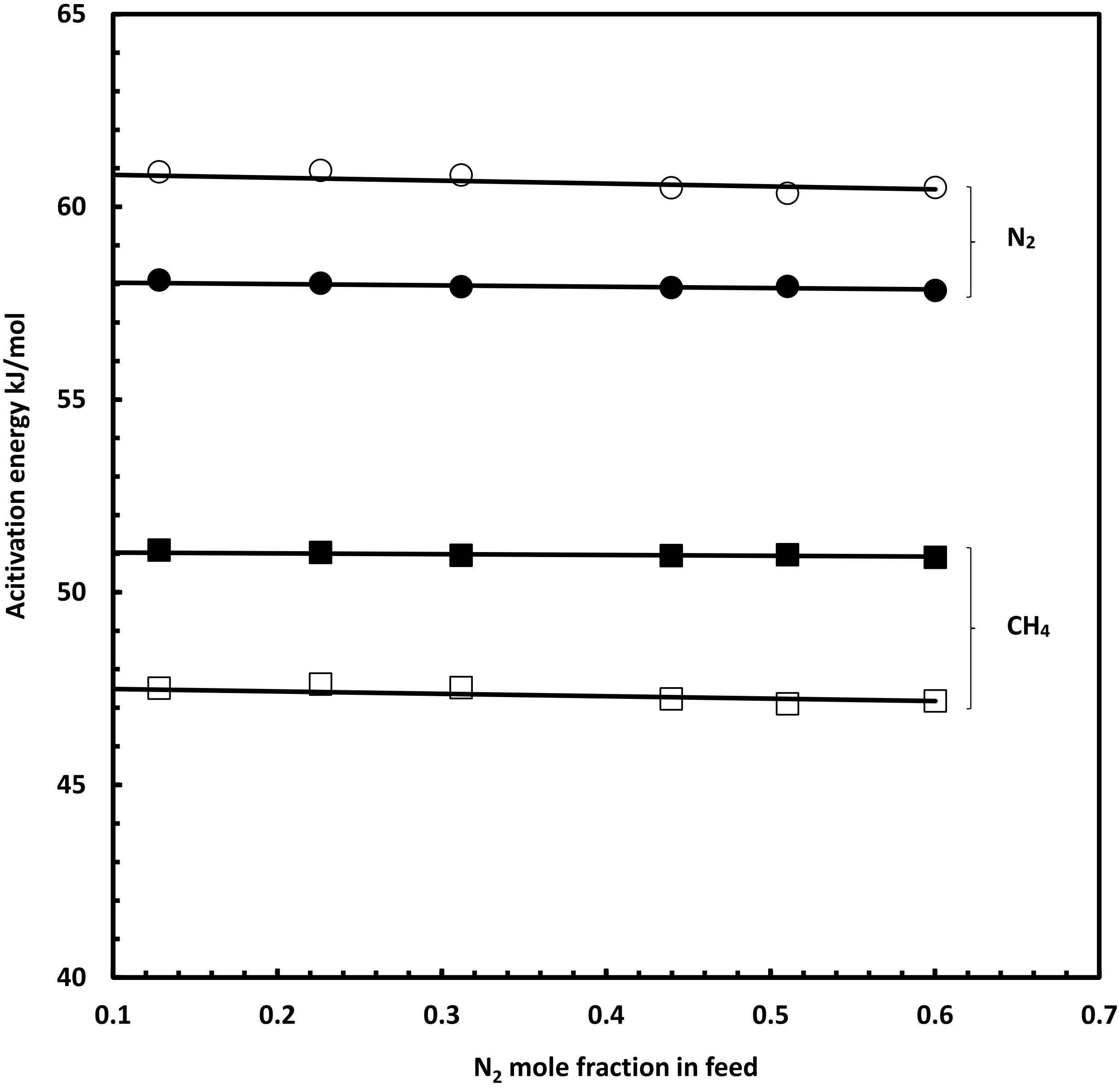


Figure 3.11 Activation energy vs. N_2 mole fraction in feed. Feed pressure: 0.7013 MPa absolute. Note: closed marks represent PEBA 1074, open marks represent PEBA 2533

3.4 Conclusions

Membranes were prepared from PEBA 1074, PEBA 2533, PEBA 1657, and PEBA 3000 by the solution casting method. The gas permeabilities in these membranes and a commercial PDMS membrane were studied. Pure gas permeation tests with CH_4 and N_2 were conducted at pressures ranging from 0.3013 to 0.8013 MPa absolute and temperatures ranging from 25 to -20^{0}C. The following conclusions can be drawn:

(1) PDMS had the highest permeability among all the membranes studied used in this work for CH_4 and N_2, but its CH_4/N_2 permeability ratio was low.

(2) Among the PEBA materials used, PEBA 2533 had the highest permeability, and PEBA 1074 had the highest CH_4/N_2 permeability ratio. At -20^{0}C, a CH_4/N_2 permeability ratio of 6.3 was obtained.

(3) The gas permeability through the membranes decreased with a decrease in temperature, and temperature dependence of the membrane permeability followed an Arrhenius relation. Pressure affected the membrane permeability slightly.

(4) The CH_4/N_2 permeability ratio increased with a decrease in temperature.

To evaluate the membrane performance for actual gas separation, PEBA 2533 and PEBA 1074 were studied for binary CH_4/N_2 gas mixture permeation under different operating temperatures and feed compositions. The following conclusions can be drawn:

(1) The permeability and selectivity (actual permeability ratio) showed the same trends with temperature as they did for pure gas permeation.

(2) The permeability of CH_4 in the CH_4/N_2 mixtures was lower than pure CH_4 permeability, while the permeability of N_2 in the feed mixture was slightly higher than pure N_2 permeability.

Chapter 4 CH_4/N_2 Separation by PEBA 2533/1074 Blend Membranes

4.1 Introduction

PEBA membranes showed very good performance in the pure gas permeation tests with a CH_4/N_2 permeability ratio over 6 at -20^{0}C. However, when the same membranes were operated for binary gas permeation, the permeability ratio decreased. Permeability is a property of a material that measures the ability to permeate a certain penetrant, and it is the material that determines the permeability. In order to fulfill the task of N_2 removal from natural gas by membrane separation, membranes with both a good permeability and CH_4/N_2 selectivity are desired.

Polymer blending is a widely-used approach to combine the advantages of two materials into one. This chapter focuses on gas separation with membranes formed from PEBA 2533/1074 blends. PEBA 2533 is more permeable but less selective to CH_4/N_2 than PEBA 1074, and their blends are expected to produce a balanced permeability and selectivity.

4.2 Experimental

Solution-casting method was also employed to fabricate the blend membranes. PEBA 2533 and PEBA 1074 pellets were dissolved in NMP at 90^{0}C for 72 hours. Agitation was necessary to ensure homogeneous solutions was produced. A series of polymer solutions were prepared with different blend ratios. They were kept at the same temperature for 24 hours to degas bubbles formed during the agitation. Flat films were prepared by casting the polymer solution on heated glass plates at 80^0C, and the plates were kept in the oven at 80^0C for 48 hours to evaporate the solvent. Then the plates were immersed into a deionized water bath for 5 minutes to remove the membranes. Finally, the membranes were dried in the oven at 50^0C for 24 hours. The thickness of these membranes ranged from 50 to 70 µm. The polymer concentration for all the blended solutions is 15 wt. %. All the chemicals used here were the same as those described in Chapter 3.

The experimental setup and procedure for pure gas permeation tests as well as binary gas mixture permeation experiments have been described in Chapter 3. The permeation tests were repeated several times with the same membrane samples, and the experimental error was found to be within 5%.

4.3 Results and Discussion

4.3.1 Pure Gas Permeation Tests

Several blend polymers were prepared with different PEBA 2533/1074 blend ratio. Pure gas permeation tests were conducted with CH_4 and N_2 under different pressures ranging from 0.3013 to 0.8013 MPa absolute and temperatures ranging from 25 to -20^0C. During the tests, the permeation flux was measured at different pressures for a given temperatures.

Effect of operating conditions

In pure gas permeation with PEBA constituent membranes, the permeabilities of both CH_4 and N_2 and the CH_4/N_2 permeability ratio slightly increased with an increase in the pressure, but the changes were not significant. Figure 4.1 shows that with the blend polymer membranes, same tendency can be found that the CH_4 and N_2 permeabilities slightly increases with an increase in the feed pressure. Membrane with a blend ratio of 93.75/6.25 (PEBA 2533/1074) has the highest permeability, while the membrane with a blend ratio of 25/75 has the lowest permeability. With an increase in the PEBA 2533 content, the gas permeabilities of both CH_4 and N_2 increased. The permeabilities of CH_4 and N_2 with PEBA 2533, PEBA 1074, and two PEBA 2533/1074 (93.75/6.25, 25/75) blend membranes at -20^{0}C are listed in Table 4.1:

Table 4.1 Permeabilities of CH_4 and N_2 with PEBA 2533, PEBA 1074, and PEBA 2533/1074 (93.75/6.25, 25/75) blend membranes at -20^{0}C

Membrane materials	CH_4 permeability (Barrer)			N_2 permeability (Barrer)		
	0.2 MPa	0.4 MPa	0.7 MPa	0.2 MPa	0.4 MPa	0.7 MPa
PEBA 2533	0.425	0.453	0.487	0.078	0.082	0.083
PEBA 2533/1074 (93.75/6.25)	0.343	0.408	0.440	0.059	0.068	0.070
PEBA 2533/1074 (25/75)	0.202	0.230	0.258	0.033	0.036	0.039
PEBA 1074	0.172	0.191	0.211	0.030	0.032	0.033

The permeabilities of CH_4 and N_2 with PEBA 2533 membrane are always higher than the blend membranes while the permeabilities with PEBA 1074 are always lower than the blend membranes at the same temperature. A sharp increase occurred when the PEBA 2533 content was over 50%. This can be explained that below the blend ratio of 50/50, PEBA 1074 was the continuous phase in the blend, which leads the system to perform more like PEBA 1074 that has relatively lower permeability. When the blend ratio was above 50/50, PEBA 2533 will dominate the permeation performance of the blend system, resulting in a sharp increase in the permeability coefficient.

Figure 4.2 shows the CH_4/N_2 permeability ratio of the blend membranes. Generally speaking, the permeability ratio increased with an increase in the feed pressure, which follows the same trends as observed in the previous chapter. However the change in permeability ratio did not show a clear tendency as the change in permeability with respect to the blend composition. Ideally, the CH_4/N_2 permeability ratio will decrease with an increase in the PEBA 2533 content, since the blend membranes will perform more like PEBA 2533, exhibiting a good permeability and a lower permeability ratio. When the blend ratio was over 75/25, this tendency can be found where the CH_4/N_2 permeability ratio with PEBA 2533/1074 (75/25) membrane was higher than the other two blend membranes (87.5/12.5, 93.75/6.25). However, when the blend ratio was below 75/25, this trend was no longer available. The same phenomenon was also observed by Bondar et al., (1999), and they suggested that permeability ratio of PEBA membranes for CH_4/N_2 is irrelevant with the PEBA structures. Figure 4.2 also shows a blend ratio of 50/50 had the best permeability ratio throughout the pressure range studied, while the blend ratio of 93.75/6.25 had the lowest permeability ratio. Compared with PEBA 2533 and 1074 membranes, the blend membranes showed a better CH_4/N_2 permeability ratio at the same operating temperature.

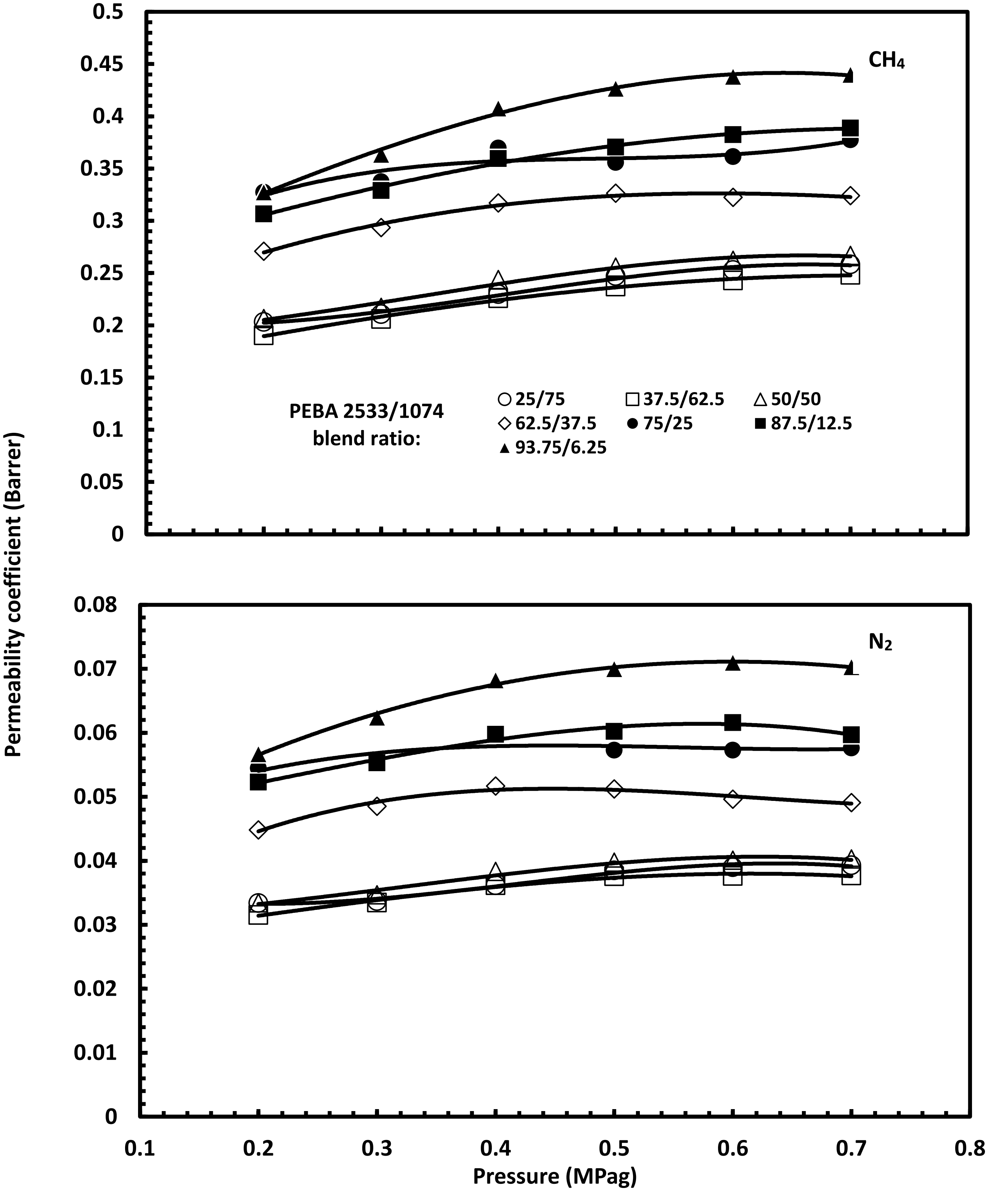


Figure 4.1 Effects of pressure on the permeability coefficient of CH_4 and N_2 for pure gas permeation through PEBA 2533/1074 blend membranes at different PEBA 2533 content. Temperature: -20^0C

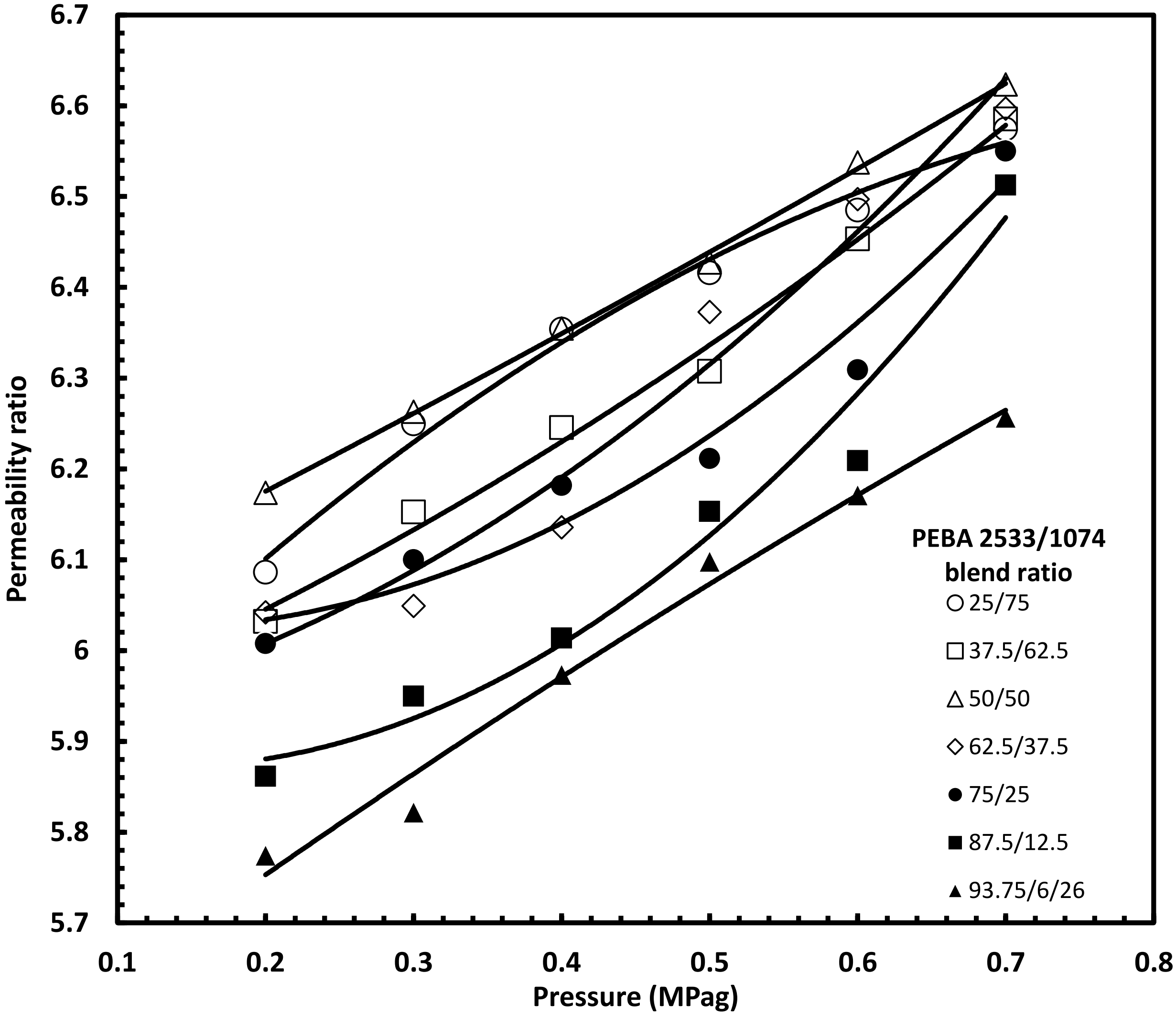


Figure 4.2 Effects of pressure on permeability ratio of CH_4 to N_2 for pure gas permeation through PEBA 2533/1074 blend membranes at different PEBA 2533 content. Temperature: -20^0C

Figure 4.3 illustrates the effects of temperature on the permeability coefficients. The permeability coefficient decreased with a decrease in temperature, and it followed an Arrhenius relationship. Compared with the constituent PEBA membrane, at the same feed pressure, the blend membranes showed higher gas permeabilities than PEBA 1074 but lower permeabilities than PEBA 2533. More supporting figures can be found in the Appendix B. Therefore, the CH_4 and N_2 permeabilities with the blend membranes are always higher than PEBA 1074, but lower than PEBA 2533 at the same operating condition (feed pressure and temperature), which means by blending PEBA 1074 with PEBA 2533, the permeabilities for both gases with the blend membranes were significantly improved. This is in agreement with results of polymer blending to fabricate polymeric membranes reported elsewhere (Car et al., 2008) suggesting that, by blending a less permeable material with a more permeable one, the permeability of the blend material often laid between the permeabilities of the two constituent polymers. A sharp change was also found when the blend ratio changed from 50/50 to 62.5/37.5 suggesting the change of the continuous phase from PEBA 1074 to PEBA 2533.

Figure 4.4 shows the permeability ratio dramatically increased with a decrease in temperature. At room temperature (25^0C) the membrane with a blend ratio of 25/75 has the best CH_4/N_2 permeability ratio, and membrane with a blend ratio of 93.75/6.25 has the lowest selectivity. However, the changes in the permeability ratio with temperature are different for different polymer blends. At -20^0C, the blend membrane with a PEBA 2533/1074 ratio of 93.75/6.25 still has the selectivity, but the membrane with a blend ratio of 25/75 is not the best one under this operating condition. Although the difference of the permeability ratios among these membranes is not dramatic, the best permeability ratio is over 6.6 when membrane with a blend ratio of 50/50 was used. This value is about 5% higher than the best permeability ratio that had achieved by the constituent membranes. Therefore, by blending PEBA 2533 with PEBA 1074, the separation ability of PEBA 2533 is significantly improved.

Figure 4.5 shows the activation energy of blend polymer membranes as well as the constituent PEBA 2533 and PEBA 1074 membranes at a pressure of 0.8013 MPa absolute. The higher the activation energy is, the harder for the gas to permeate through the membrane. Apparently, the activation energy of the gas in blend polymers is not a linear function of the blend composition.

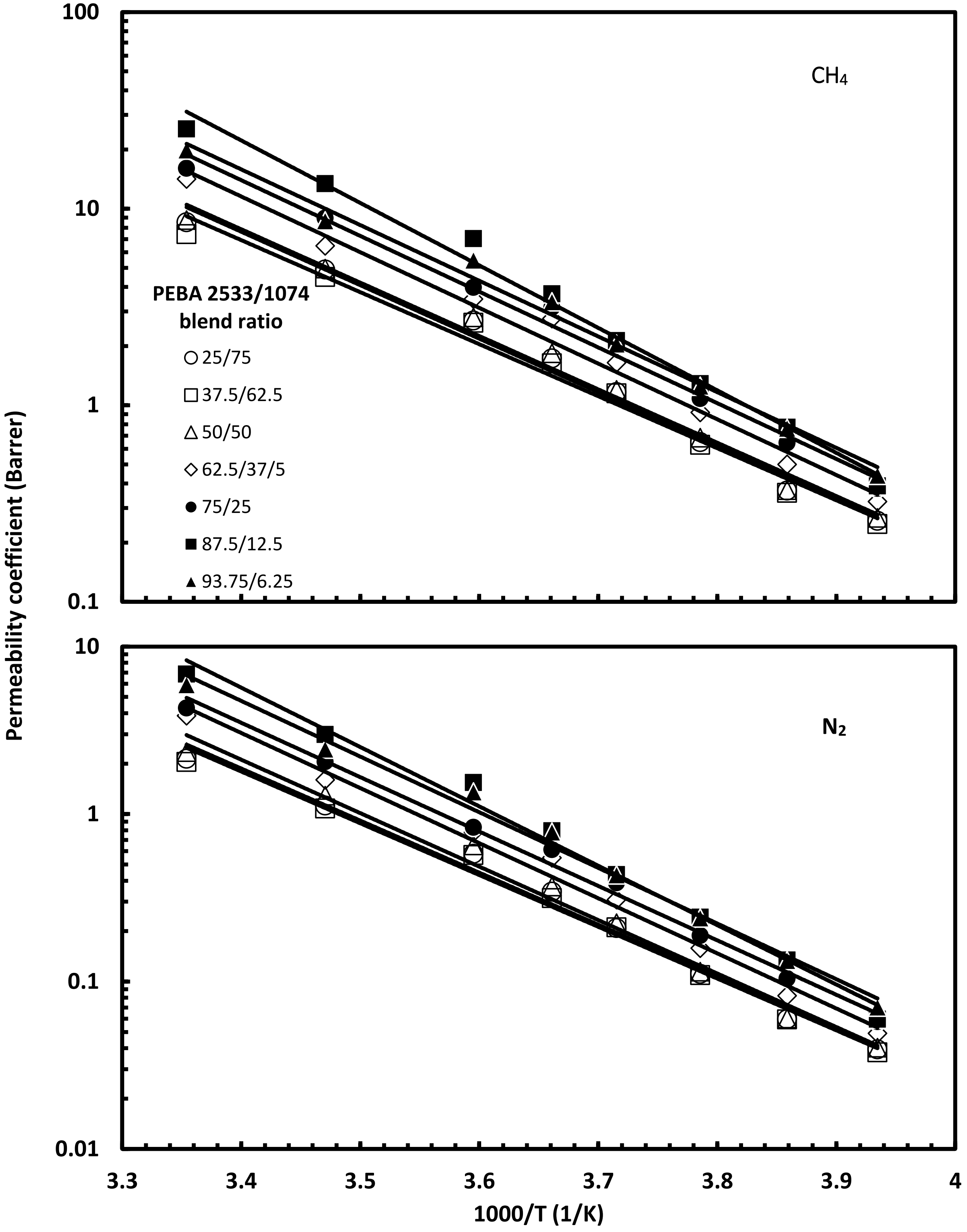


Figure 4.3 Effects of temperature on the permeability coefficient of CH_4 and N_2 for pure gas permeation through PEBA 2533/1074 blend membranes at different PEBA 2533 content. Pressure: 0.8013 MPa absolute

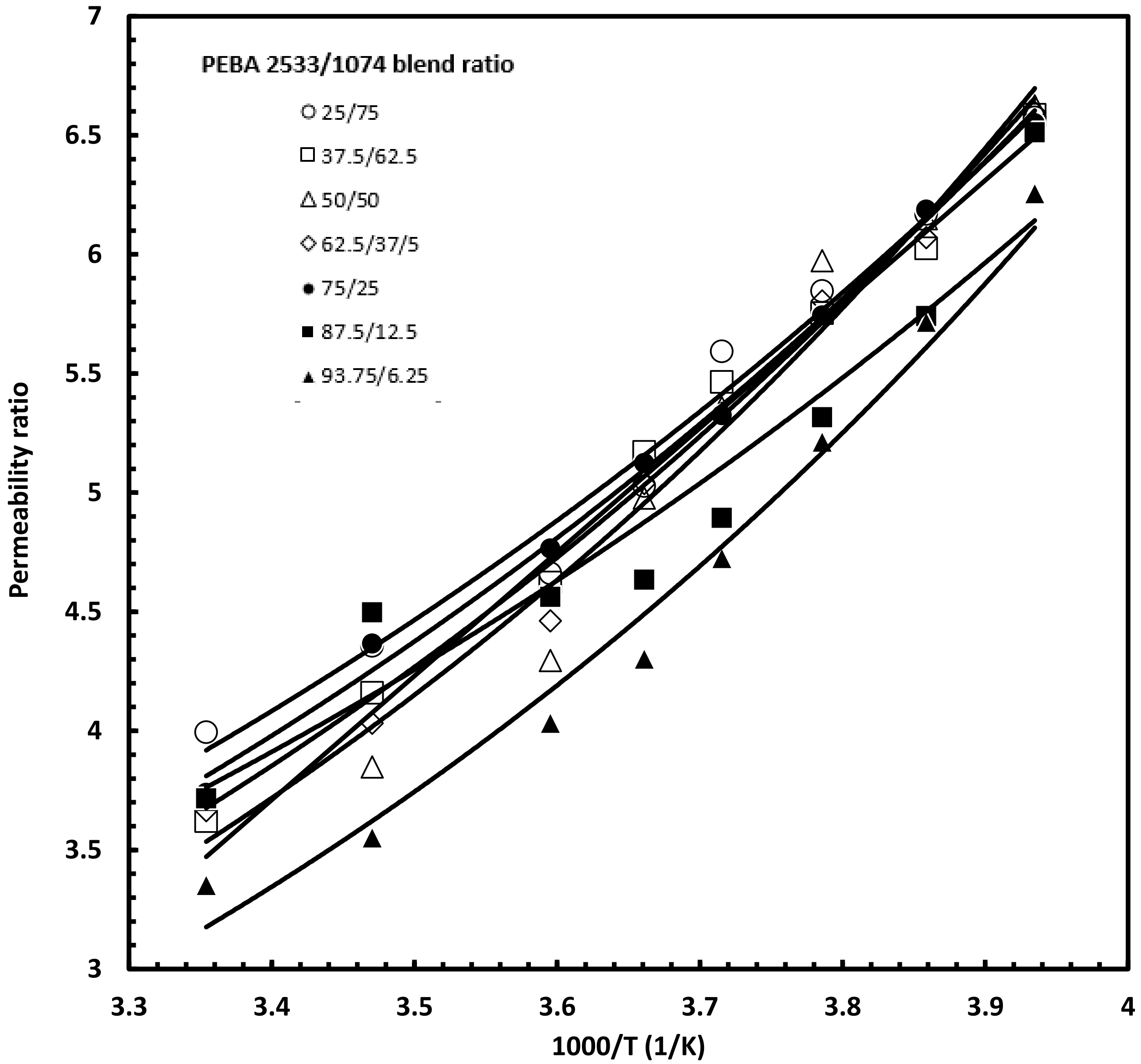


Figure 4.4 Effects of temperature on permeability ratio of CH_4 to N_2 for pure gas permeation through PEBA 2533/1074 blend membranes at different PEBA 2533 content. Pressure: 0.8013 MPa absolute

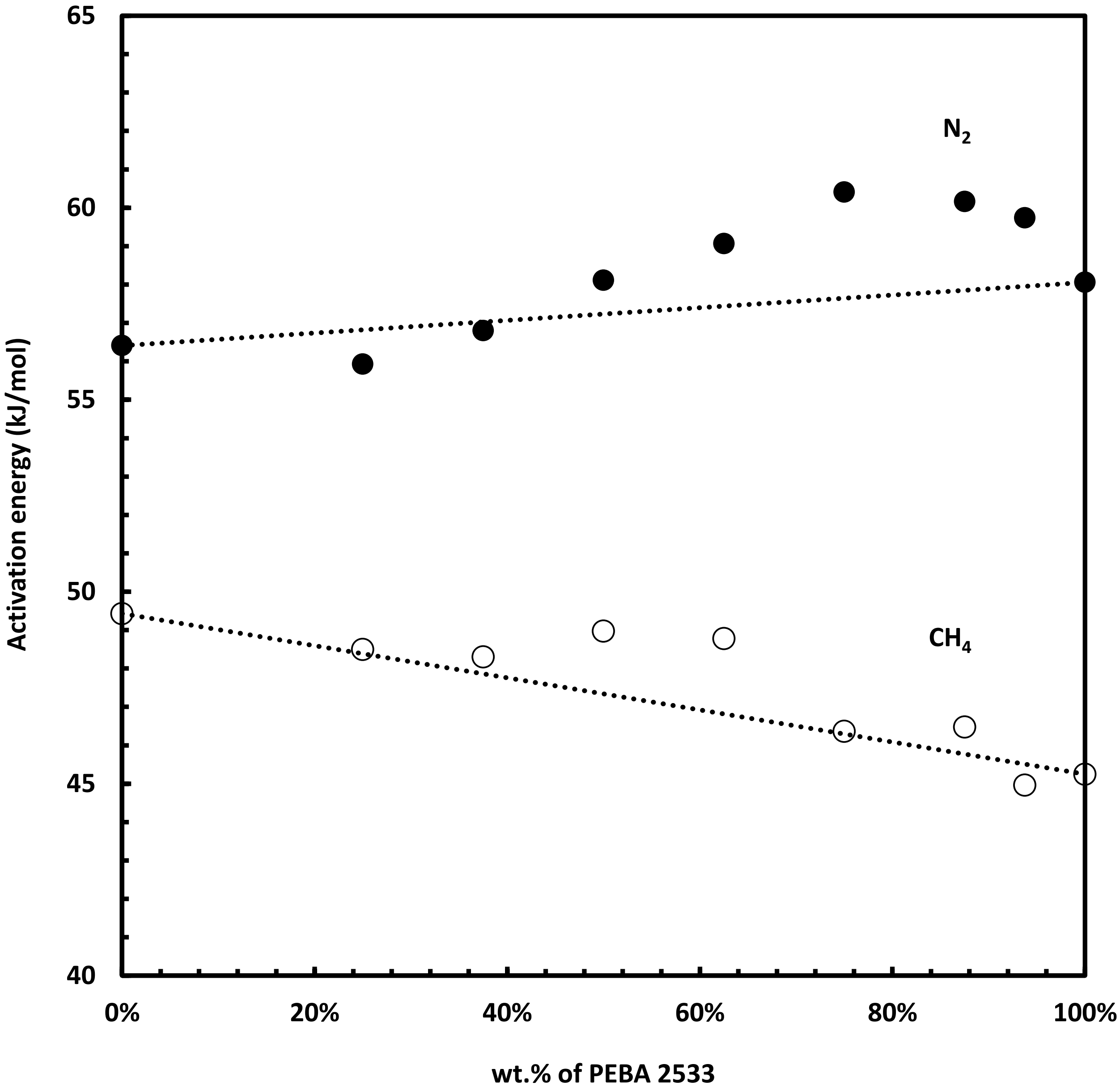


Figure 4.5 Activation energy for CH_4 and N_2 for pure gas permeation through PEBA 2533/1074 blend membranes at different PEBA 2533 content. Pressure: 0.8013 MPa absolute

Effect of blending ratio

Figure 4.6 shows the permeabilities of CH_4 and N_2 and their permeability ratio in membranes with different PEBA 2533/1074 blend ratios at 0.8013 MPa, -20^0C. Compared with single component PEBA 2533 and PEBA 1074 membranes, the blend membranes tend to have a moderate permeability for CH_4 and N_2. The permeability of both gases increased with an increase in the PEBA 2533 content. And the blend membranes yielded a higher CH_4/N_2 permeability ratio than either single component membrane. The maximum permeability ratio was observed at a blend ratio of 50/50.

PEBA 2533 contains more PE segment than PEBA 1074, and PE segment is important for gas molecules to permeate through the membrane (Bondar et al., 1999). Increasing PE content will make the polymer chain more flexible, which enhances the permeation of gas. Also, the PE segment in PEBA 2533 is PTMEO, which is less polar than PEO, the PE segment in PEBA 1074. Increasing the polar groups in the polymer matrix tends to decrease the permeability, and this will affect the less permeable gas more significantly(Bondar et al., 2000). Therefore, blend membranes with more PEBA 1074 content will tend to have a lower permeability, and the N_2 permeability will decrease more significantly than CH_4 permeability. The best permeability ratio was obtained at a blend ratio is 50/50. A sharp decrease in the permeability ratio was noticed when the blended polymer containing more than 70% of PEBA 2533. When the PEBA 2533 content in the blended solution is sufficiently high, the blended polymer will behave more like PEBA 2533, resulting in a higher permeability but a lower permeability ratio for CH_4 and N_2.

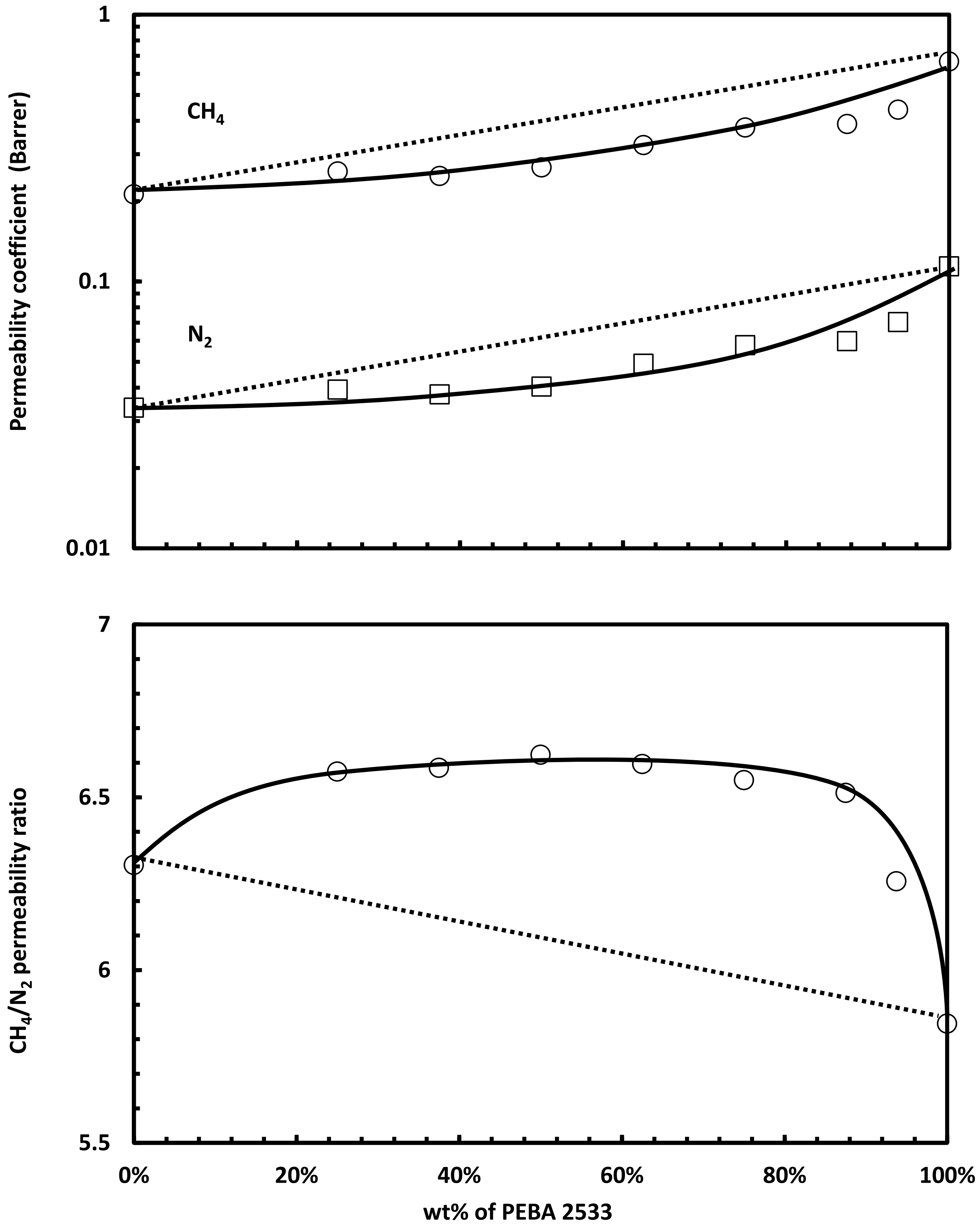


Figure 4.6 Performance of membranes with different blend ratios. Temperature: -20^{0}C, pressure: 0.8013 MPa absolute

As discussed in the Chapter 2, blend polymers can be classified into two groups: miscible polymer blends polymer and immiscible polymer blends. In order to see the behavior of PEBA 2533/1074 blend polymers, three permeability prediction models were used to fit the experimental data. They are the homogenous model, the parallel model and the series model. Since the polymer solutions were prepared by using the weight fraction of the two PEBA polymers, the volume fraction of PEBA 2533 was calculated by using the density of PEBA 2533 and PEBA 1074 from Table 2.2. Figure 4.7 shows the relationship between $ln(P)$ and volume fraction of PEBA 2533 at 25^{0}C. The experimental data is compared with the homogenous model:

$$lnP_b = \emptyset_1 lnP_1 + \emptyset_2 lnP_2 \qquad \text{Homogenous model (2.8)}$$

From the plot we can see that the homogenous model overestimated the permeability, and the experimental data did follow a strict straight line. Therefore, the homogenous model fails to predict the permeability of the blend membranes, which means the blend solutions were not homogenous. This agreed with the previous conclusion that the continuous phase changed from PEBA 1074 to PEBA 2533 with the increase in the PEBA 2533 content.

Figure 4.8 shows a comparison between the experimental data and predicted permeability based on the parallel model:

$$P_b = \emptyset_1 P_1 + \emptyset_2 P_2 \qquad \text{Parallel model (2.9)}$$

Again, the model predictions overestimated the gas permeability in the blend membranes.

Figure 4.9 shows that permeability predicted by the series model,

$$P_b = P_1 P_2 / (\emptyset_1 P_2 + \emptyset_2 P_1) \qquad \text{Series model (2.10)}$$

agreed very well with the experimental data. Among the 3 models tested, the series model worked the best to describe the gas permeability in the PEBA 2533/1074 blend membranes.

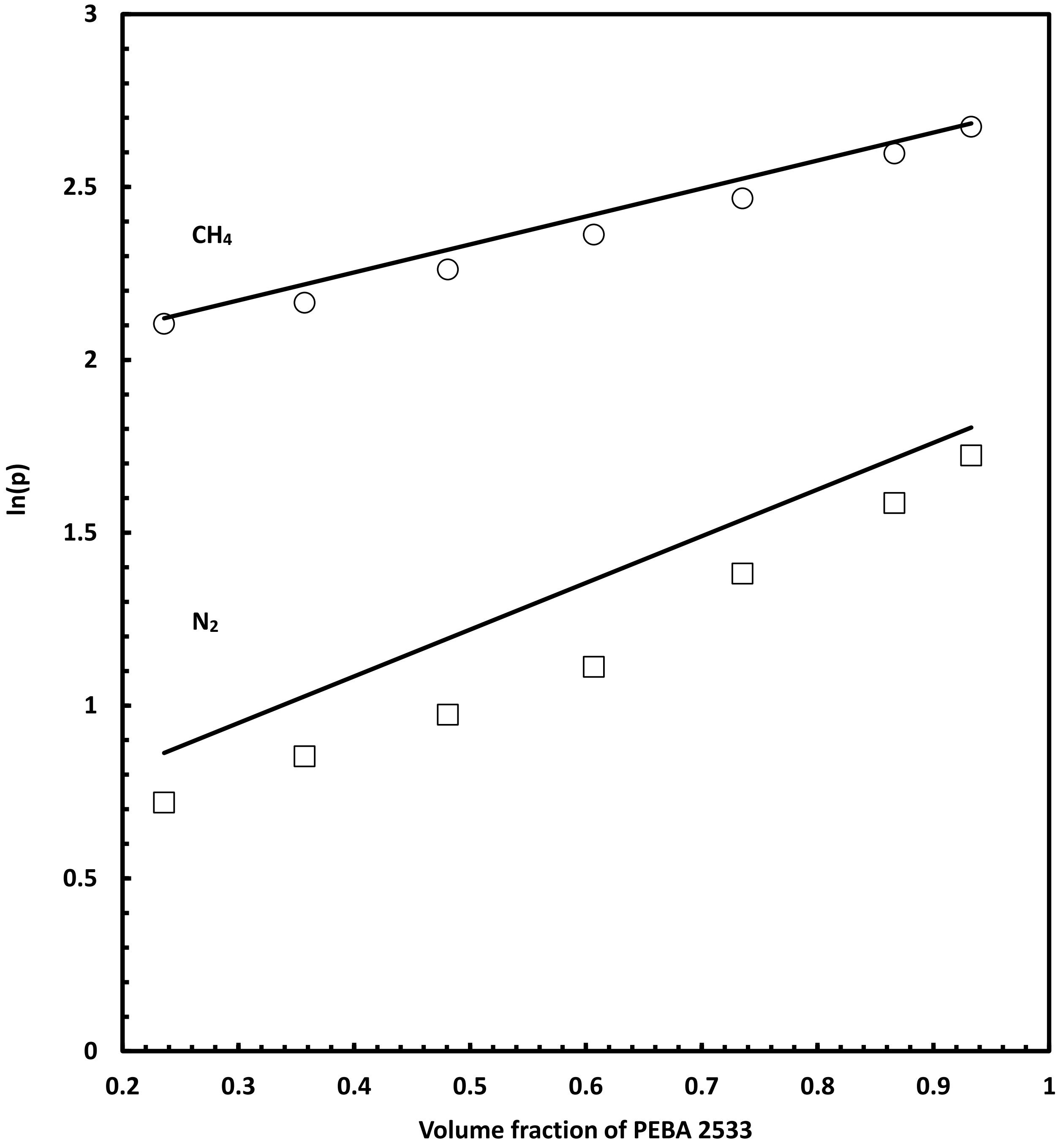


Figure 4.7 $ln(P)$ vs. volume fraction of PEBA 2533. Pressure: 0.8013 MPa absolute, temperature: 25^0C. Note: open marks indicate experimental data, solid lines indicate the homogenous model predictions

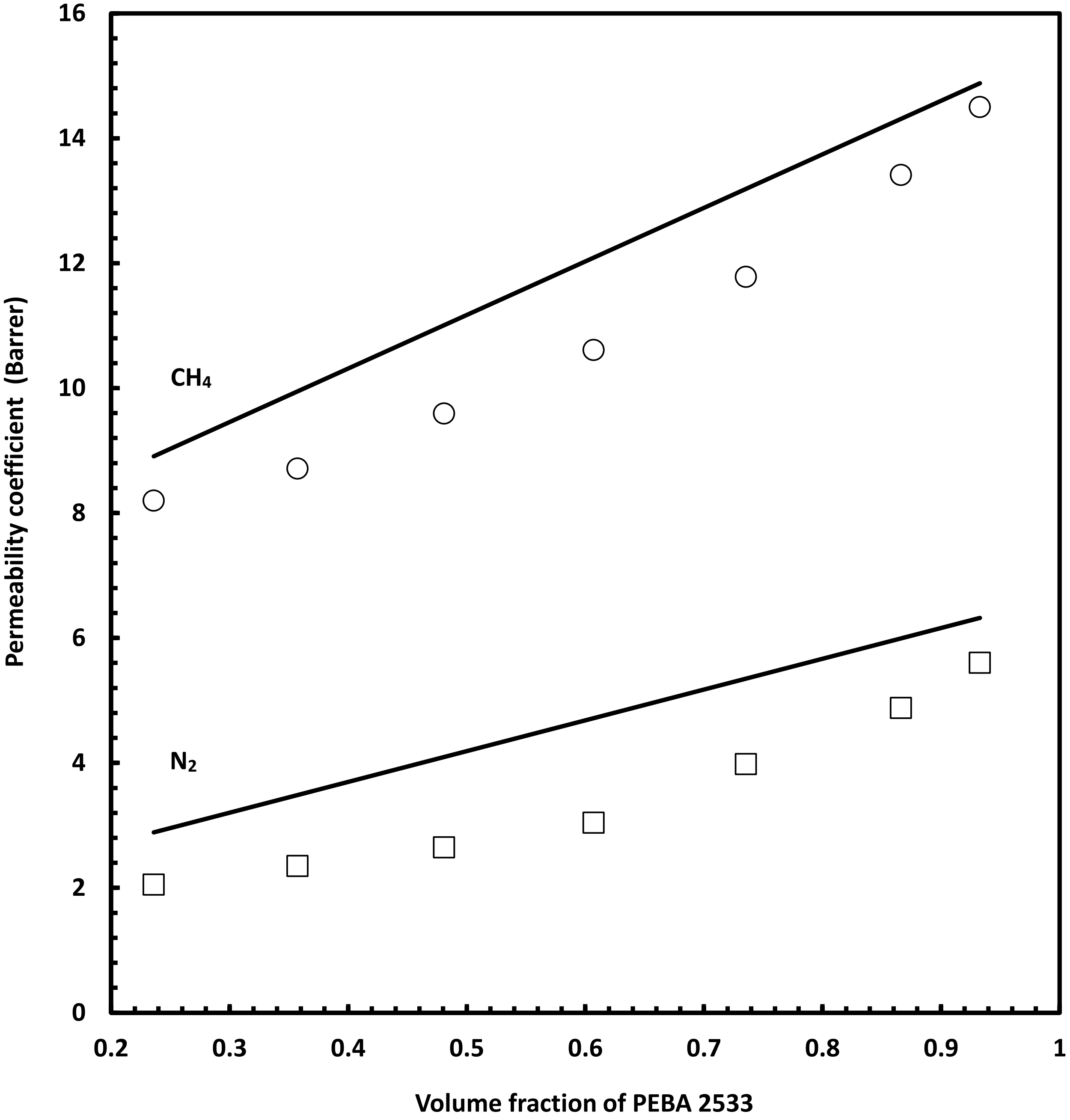


Figure 4.8 Permeability coefficient vs. volume fraction of PEBA 2533. Pressure: 0.8013 MPa absolute, temperature: 25^0C. Note: open marks indicate experimental data, solid lines indicate the parallel model predictions

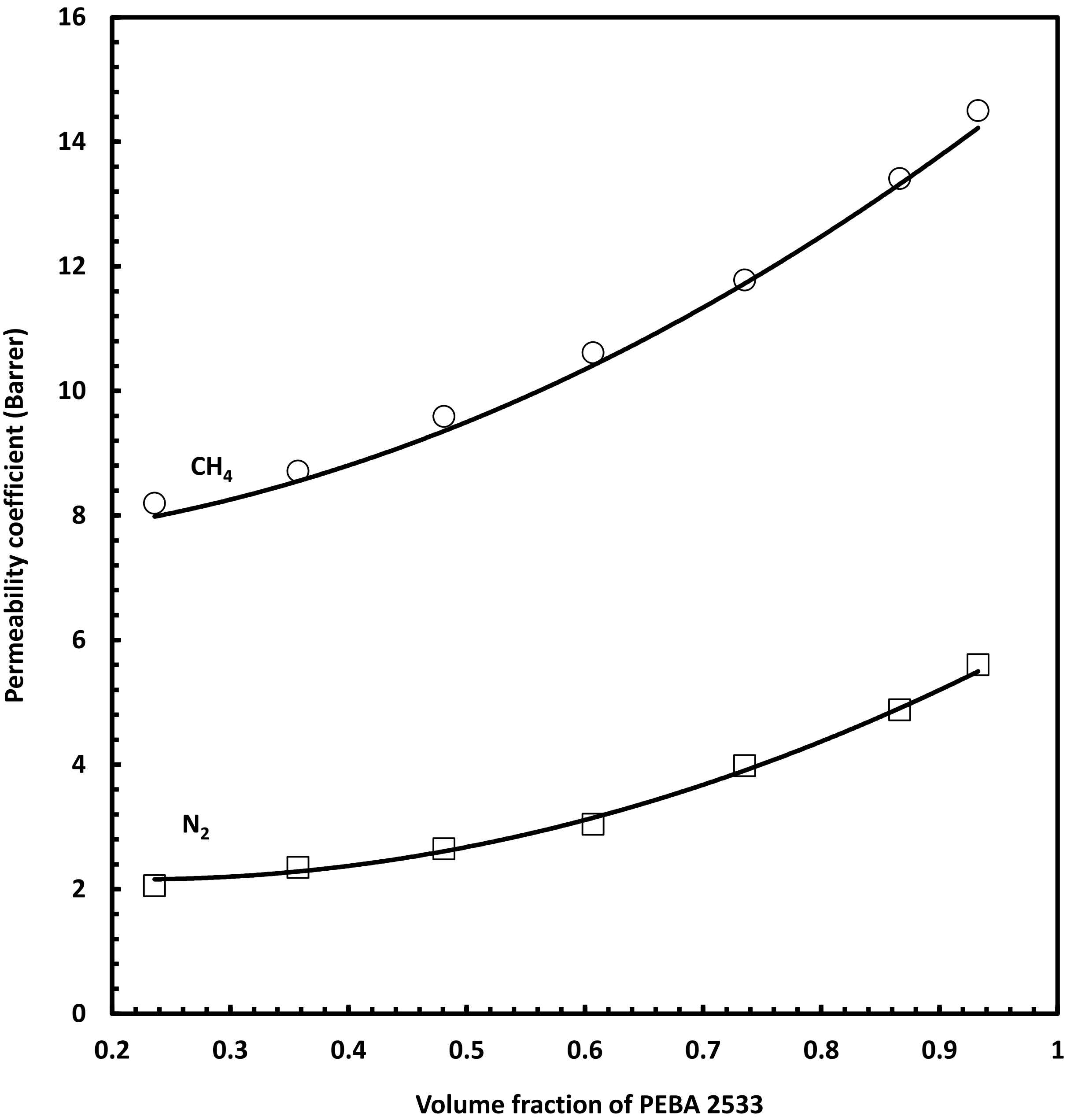


Figure 4.9 Permeability coefficient vs. volume fraction of PEBA 2533. Pressure: 0.8013 MPa absolute, temperature: 25^0C. Note: open marks indicate experimental data solid lines indicate the series model predictions

The above results were for an operating temperature of 25^0C. The density of PEBA polymers at different temperatures are unknown. Therefore, it was decided to determine if there is any significant changes in density of PEBA polymers in the temperature range studied here. Rearranging Equation 2.10 gives:

$$\emptyset_1 = \frac{P_1(P_2 - P_b)}{P_b(P_2 - P_1)} \tag{4.1}$$

where $\emptyset_1 = 1 - \emptyset_2$, $\emptyset_1$ and $\emptyset_2$ are the volume fractions of PEBA 1074 and PEBA 2533, respectively, P_1 and P_2 are the gas permeability coefficient in PEBA 1074 and PEBA 2533, respectively, $P_b$is the gas permeability coefficient in blend membrane. Both CH_4 and N_2 permeabilities were used for all the calculations. The volume fraction of PEBA 1074 at 25^0C can also be calculated by the weight of each polymer and their densities:

$$\emptyset_1' = \frac{V_1}{V_1 + V_2} = \frac{\frac{m_1}{\rho_1}}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}} = \frac{m_1}{m_1 + m_2\frac{\rho_1}{\rho_2}} \tag{4.2}$$

where m_1 and m_2 are the weight of PEBA 1074 and PEBA 2533, respectively; ρ_1 and ρ_2 are the densities of PEBA 1074 and PEBA 2533 at 25^0C. The weight of each polymer was set when preparing the membranes. If $\emptyset_1 = \emptyset_1'$, no significant changes in PEBA 2533/1074 density ratio (ρ_1/ρ_2) occur in the temperature ranging from 20 to -20^0C; if $\emptyset_1 \neq \emptyset_1'$, it means the PEBA 2533/1074 density ratio is dependent with temperature. Figure 4.10 showed the calculation results for the PEBA 2533/1074 membranes with blend ratios of 25/75, 37.5/62.5, 50/50, and 62.5/37.5. And Figure 4.11 showed the calculation results for the PEBA 2533/1074 membranes with blend ratios of 75/25, 87.5/12.5, and 93.75/6.25. To make it more clear, instead of a single label, $\emptyset_1'$ was presented as a solid line in the following figures. Labels represented $\emptyset_1$, which were obtained from Equation 4.1. As we can see, all the volume fractions of PEBA 1074 calculated by Equation 4.1 were fluctuating around the $\emptyset_1'$, which means the volume fractions of PEBA 1074 calculated by Equation 4.1 were almost the same with the values calculated by weights and densities of the polymers. Therefore, at the temperature ranging from 25 to -20^{0}C, the PEBA 2533/1074 density ratio (ρ_1/ρ_2) can be considered as a constant. The densities of PEBA 2533 and 1074 were either constants, or at the same changing rate with respect to the change of temperatures.

The calculated gas permeabilities and the actual permeabilities were shown in Figure 4.12. The plot showed that the actual CH_4 permeabilities were fluctuating around the calculated permeabilities, while the actual N_2 permeabilities were slightly lower than the calculated ones, especially at lower temperature. The N_2 permeabilities were almost the same as the predicted ones at -10^{0}C. When the temperature dropped to -15 and -20^{0}C, the series model tended to overestimate the N_2 permeability, while the CH_4 permeability still followed the series model. As a result, the CH_4/N_2 permeability ratios calculated by the series model were lower than the CH_4/N_2 permeability ratios calculated by the experimental data, as shown in Figure 4.13.

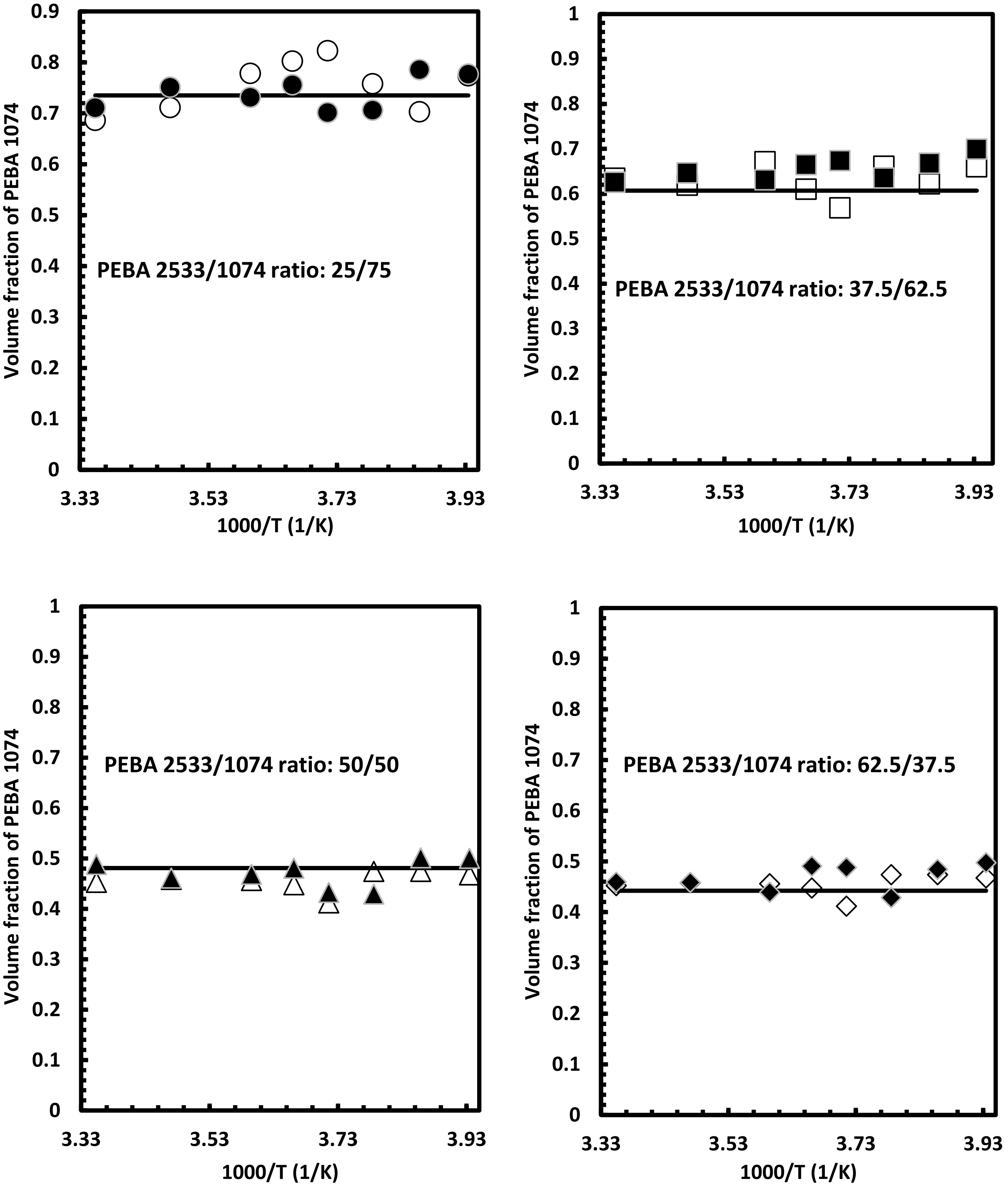


Figure 4.10 Volume fraction of PEBA 1074 vs. temperature. PEBA 2533/1074 ratio: 25/75, 37.5/62.5, 50/50, and 62.5/37.5. Note: labels were the results calculated by Equation 4.1, open marks were using CH_4, close marks were using N_2; solid line was the result calculated by Equation 4.2

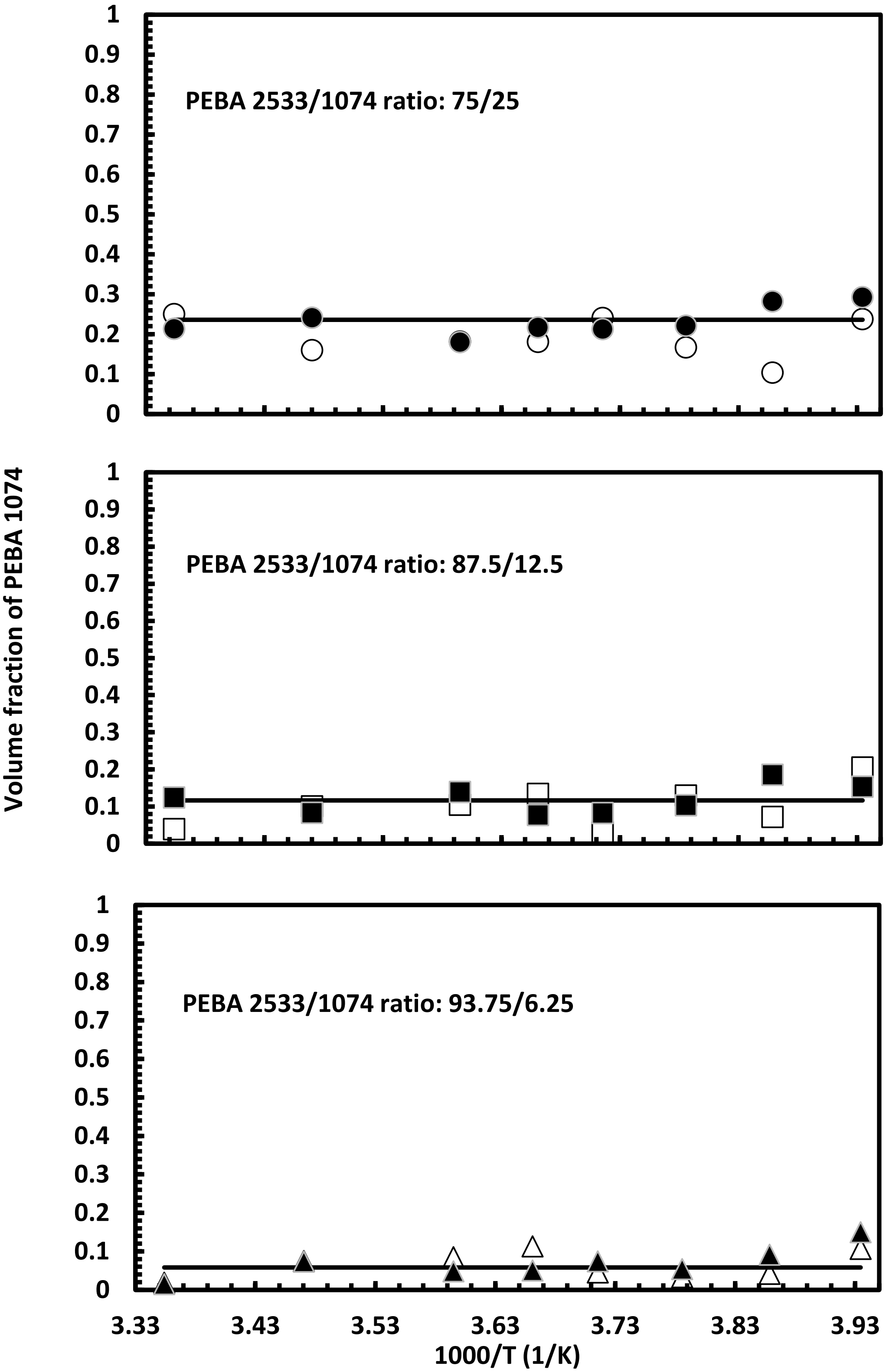


Figure 4.11 Volume fraction of PEBA 1074 vs. temperature. PEBA 2533/1074 ratio: 75/25, 87.5/12.5, and 93.75/6.25. Note: labels were the results calculated by Equation 4.1, open marks were using CH_4, close marks were using N_2; solid line was the result calculated by Equation 4.2

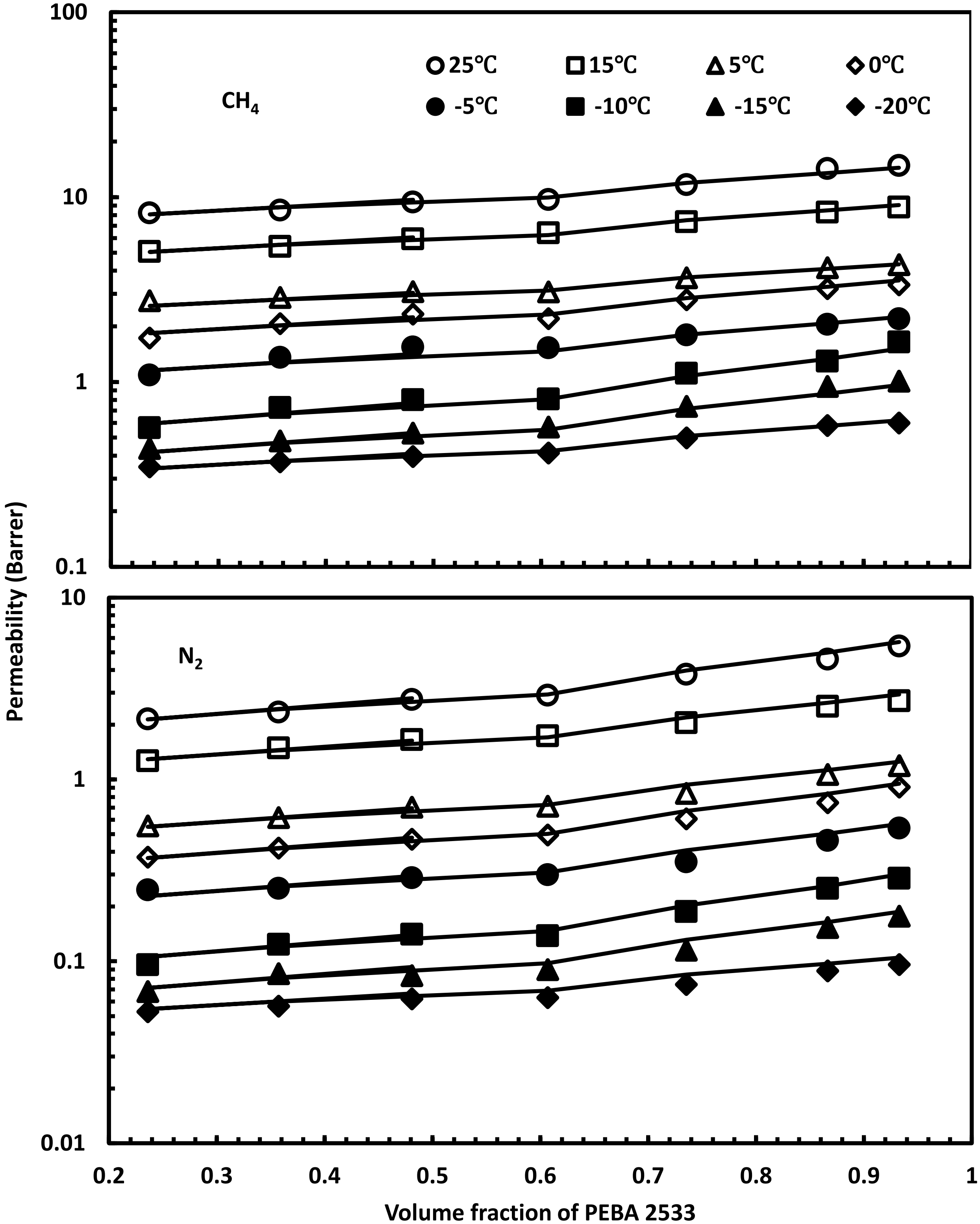


Figure 4.12 Permeability coefficient of CH_4 and N_2 vs. volume fraction of PEBA 2533. Pressure: 0.8013 MPa absolute. Note: labels indicate experimental data, solid lines indicate model predictions.

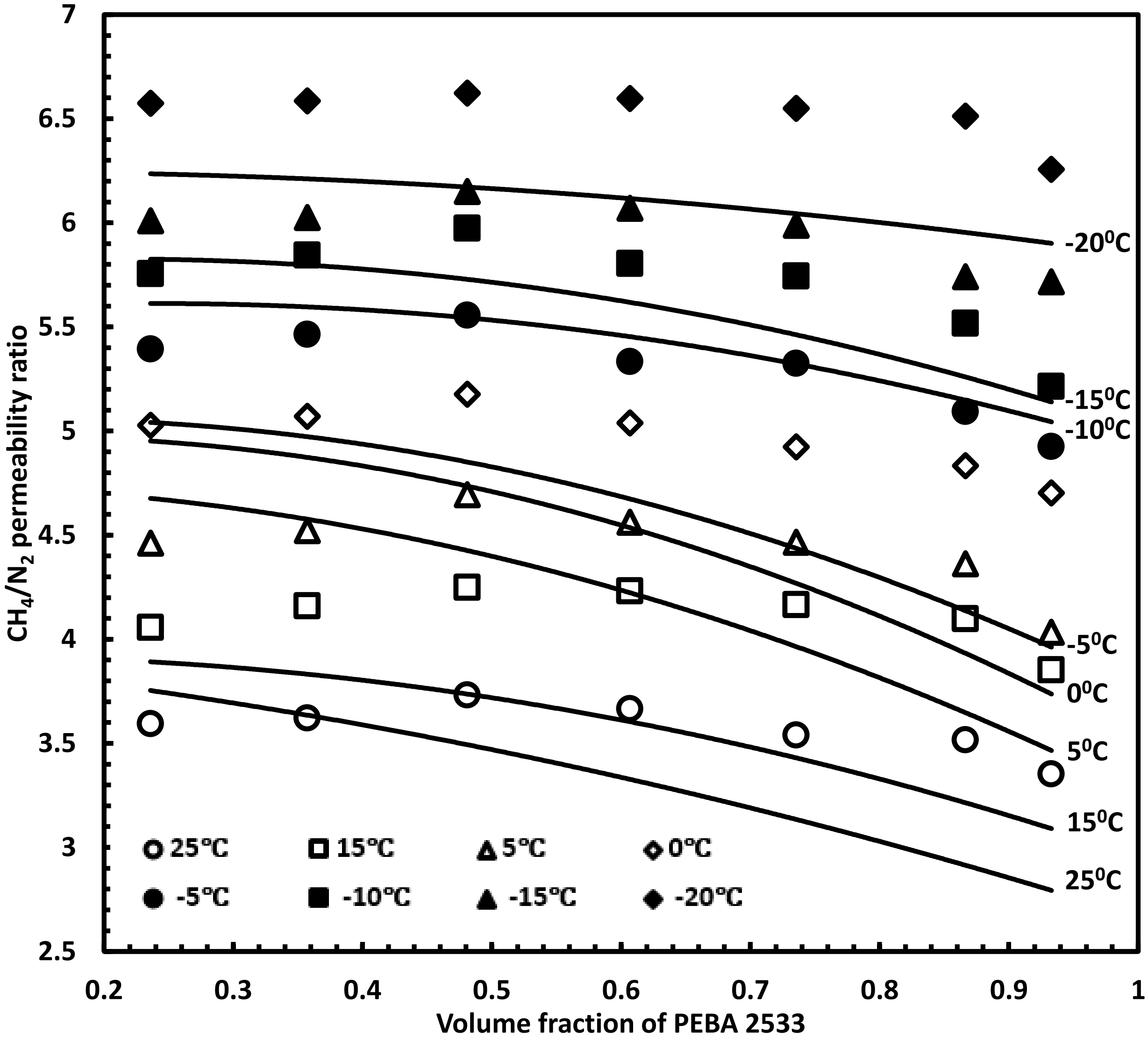


Figure 4.13 CH_4/N_2 permeability ratio vs. volume fraction of PEBA 2533. Pressure: 0.8013 MPa absolute. Note: labels indicate experimental data, solid lines indicate the Series model predictions.

4.3.2 CH_4/N_2 Binary Gas Permeation Tests

The blend polymers of PEBA 2533/1074 showed good performance in the pure gas permeation tests. When they are used for gas mixture permeation, it is unclear if they still perform well. Therefore, binary mixtures of CH_4 and N_2 were used to determine the gas permeability of CH_4 and N_2 at various pressures, temperatures and feed compositions using a membrane with a blend ratio of 50/50. For convenience of characterizing membrane performance, a small stage cut (less than 0.05) was used in all the experiments, which means the concentration of the feed gas on the feed side could be considered as a constant along the membrane surface.

The operating temperatures showed the similar effect on the gas permeability in the blend membrane as they did on PEBA 2533 or 1074 membrane, as shown in Figure 4.14. With a decrease in the temperature, the permeabilities of both CH_4 and N_2 decreased. Compared with PEBA 2533 and 1074 membranes, the blend membrane showed a permeability higher than PEBA 1074 and lower than that of PEBA 2533. Figure 4.15 shows that the membrane selectivity (actual CH_4/N_2 permeability ratio) has different trends. At a higher temperature (above -5^0C), the selectivity of the blend membrane is not as good as PEBA 1074; below -5^0C, the blend membrane became more selective than either PEBA 2533 or PEBA 1074. At -20^0C, the selectivity of the blend membrane reached over 6, which appears to be close to the target value for N_2 removal from natural gas.

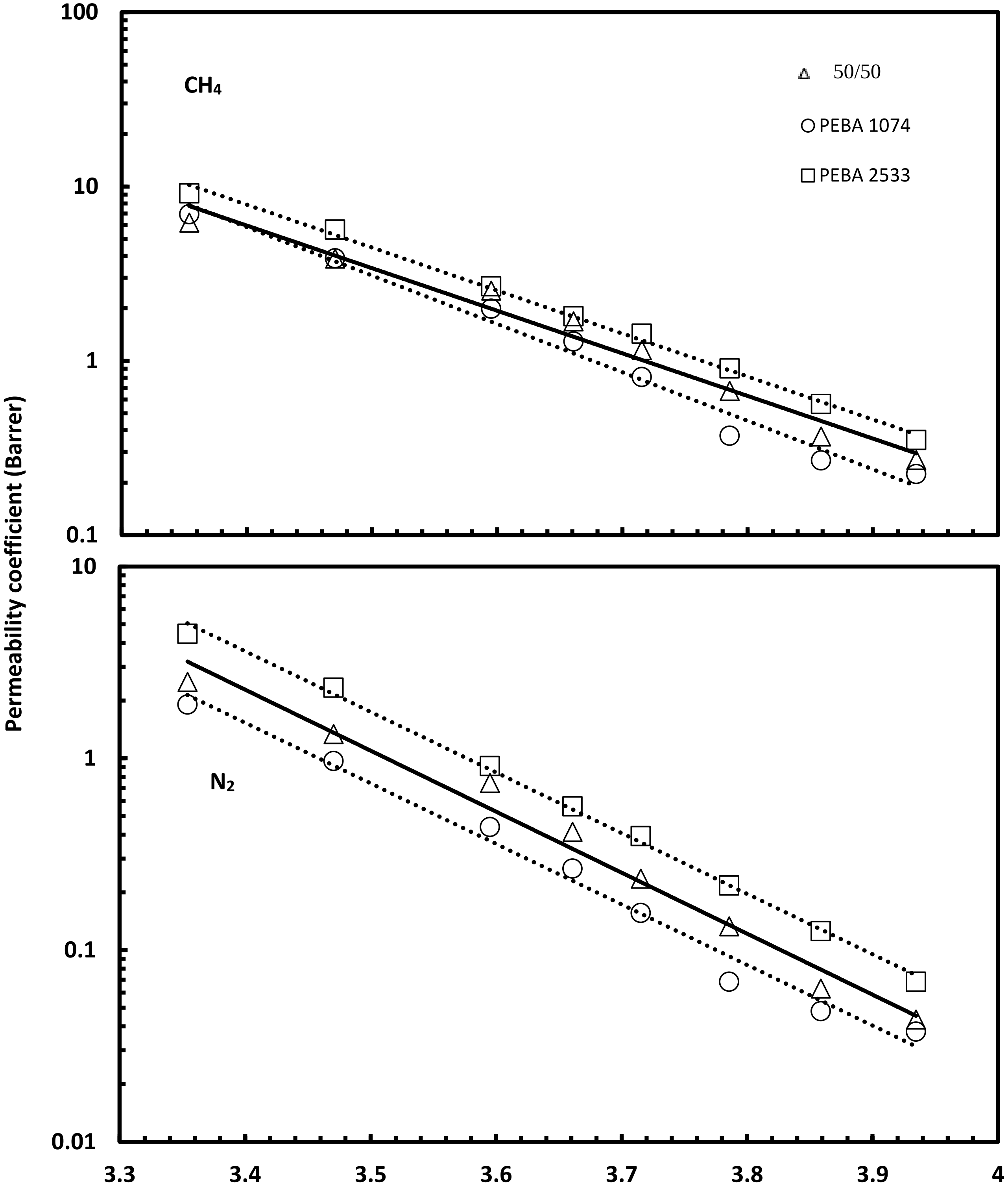


Figure 4.14 Effects of temperature on permeability coefficient of CH_4 and N_2 for binary gas permeation through PEBA 2533, PEBA 1074, and a PEBA 2533/1074 (50/50) blend membrane. Pressure: 0.7014 MPa absolute, feed composition: 60% N_2

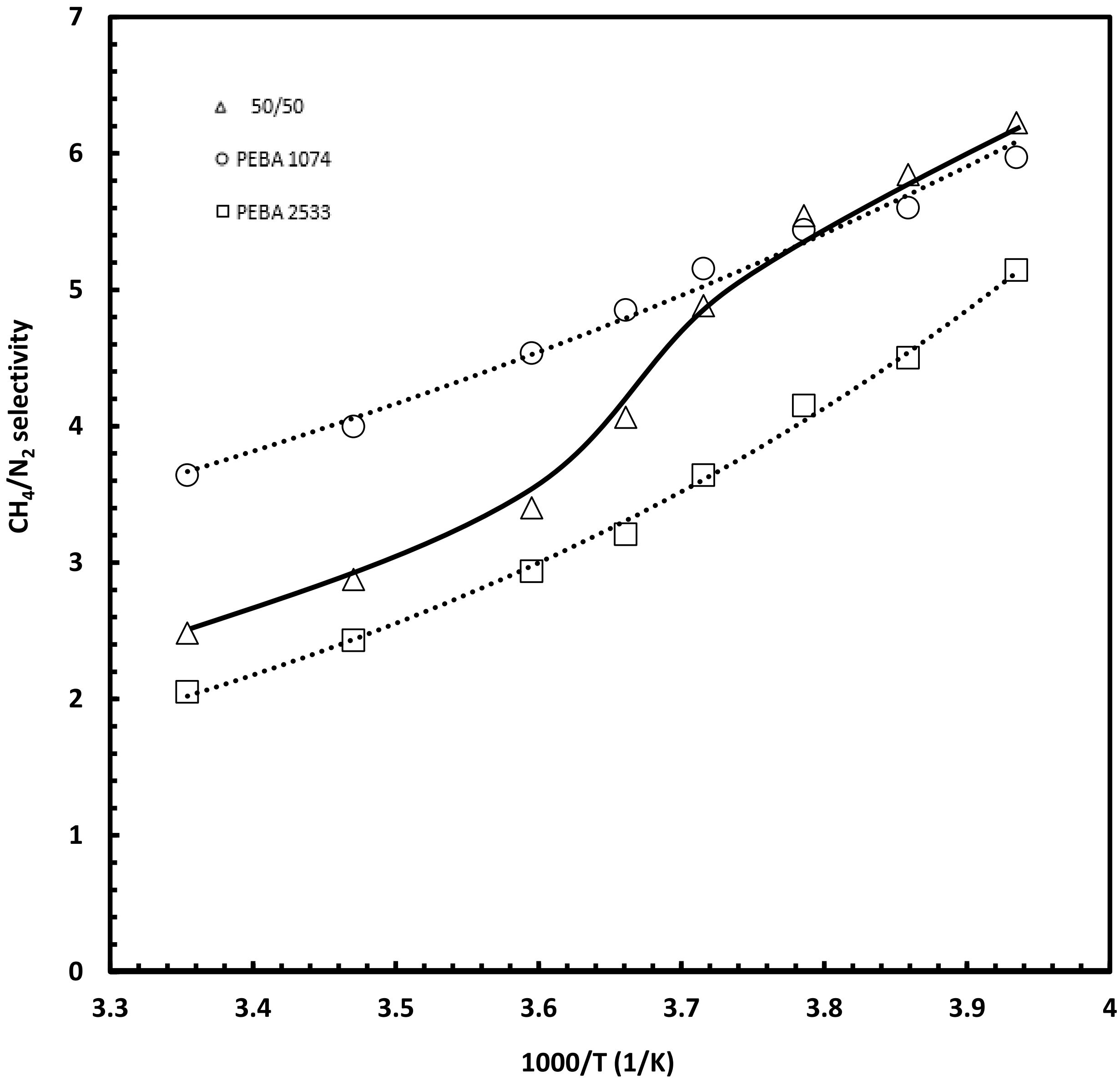


Figure 4.15 Effects of temperature on CH_4/N_2 selectivity for binary gas permeation through PEBA 2533, PEBA 1074, and a PEBA 2533/1074 (50/50) blend membrane. Pressure: 0.7013 MPa absolute, feed composition: 60% N_2

Figure 4.16 shows the effect of feed composition on the membrane performance. The blend membrane showed a moderate permeability to CH_4 and N_2 that is higher than PEBA 1074 but lower than PEBA 2533. This is similar to the results with pure gas permeation. One thing was different from the pure gas permeation was that the selectivity of the blend membrane was higher than either PEBA constituents alone, as shown in Figure 4.17. The selectivity of the blend membrane increased with an increase in feed N_2 concentration. This was because with the increase in the feed N_2 concentration, both CH_4 and N_2 permeabilities were reduced, and the reduction of N_2 permeability was more significantly than CH_4 permeability. The reason for that was the concentration of N_2 on the surface of the membrane would increase with an increase in the feed concentration of N_2, which would reduce the driving force for N_2 to permeate through the membrane. Therefore, the N_2 permeability decreased more significantly than the CH_4 permeability, which leaded to an increase in CH_4/N_2 selectivity.

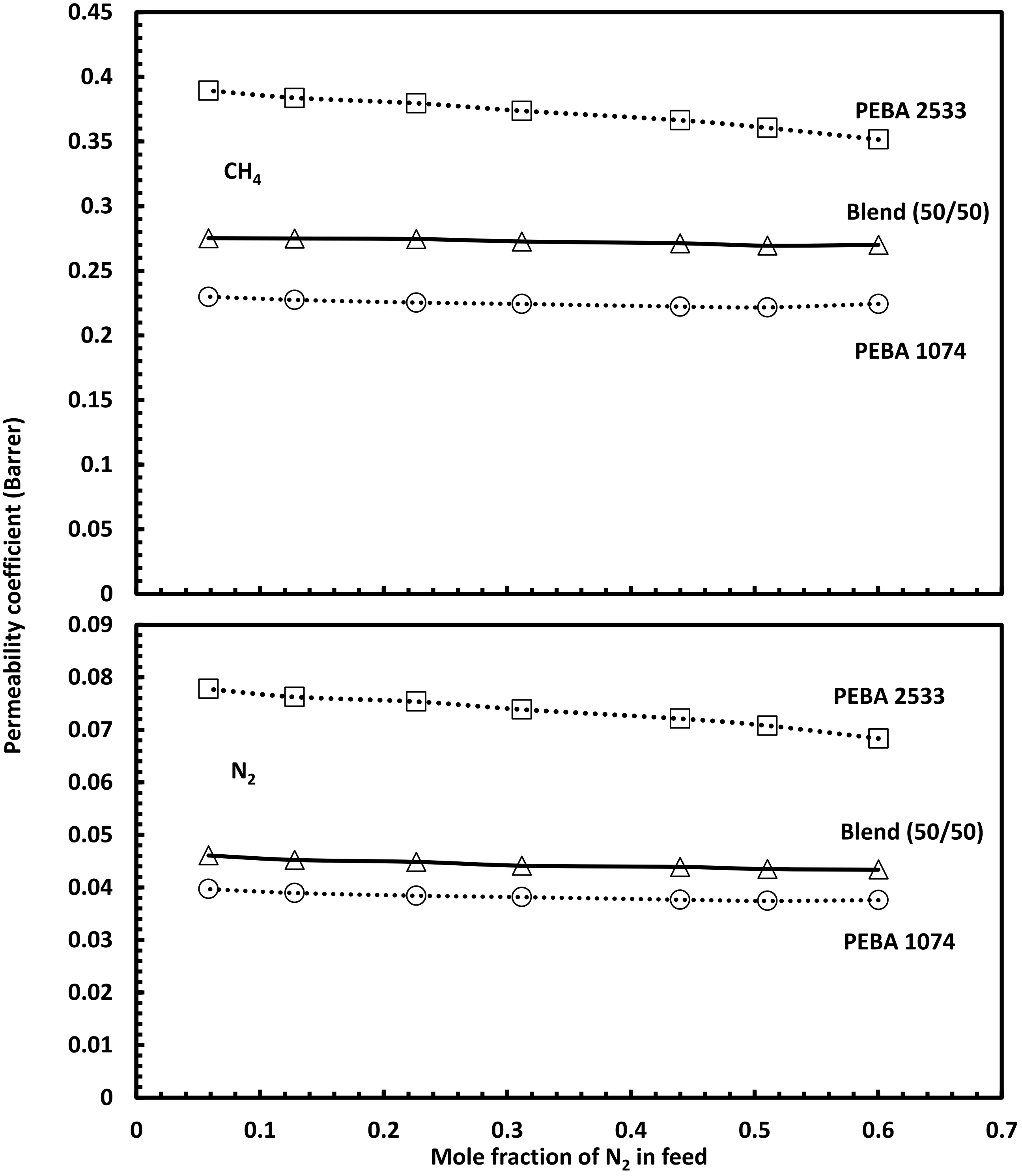


Figure 4.16 Effect of feed composition on permeabilities of CH_4 and N_2 for binary gas mixture permeation in PEBA 2533, PEBA 1074, and a PEBA 2533/1074 (50/50) blend membrane. Pressure: 0.7013 MPa absolute, temperature: -20^0C

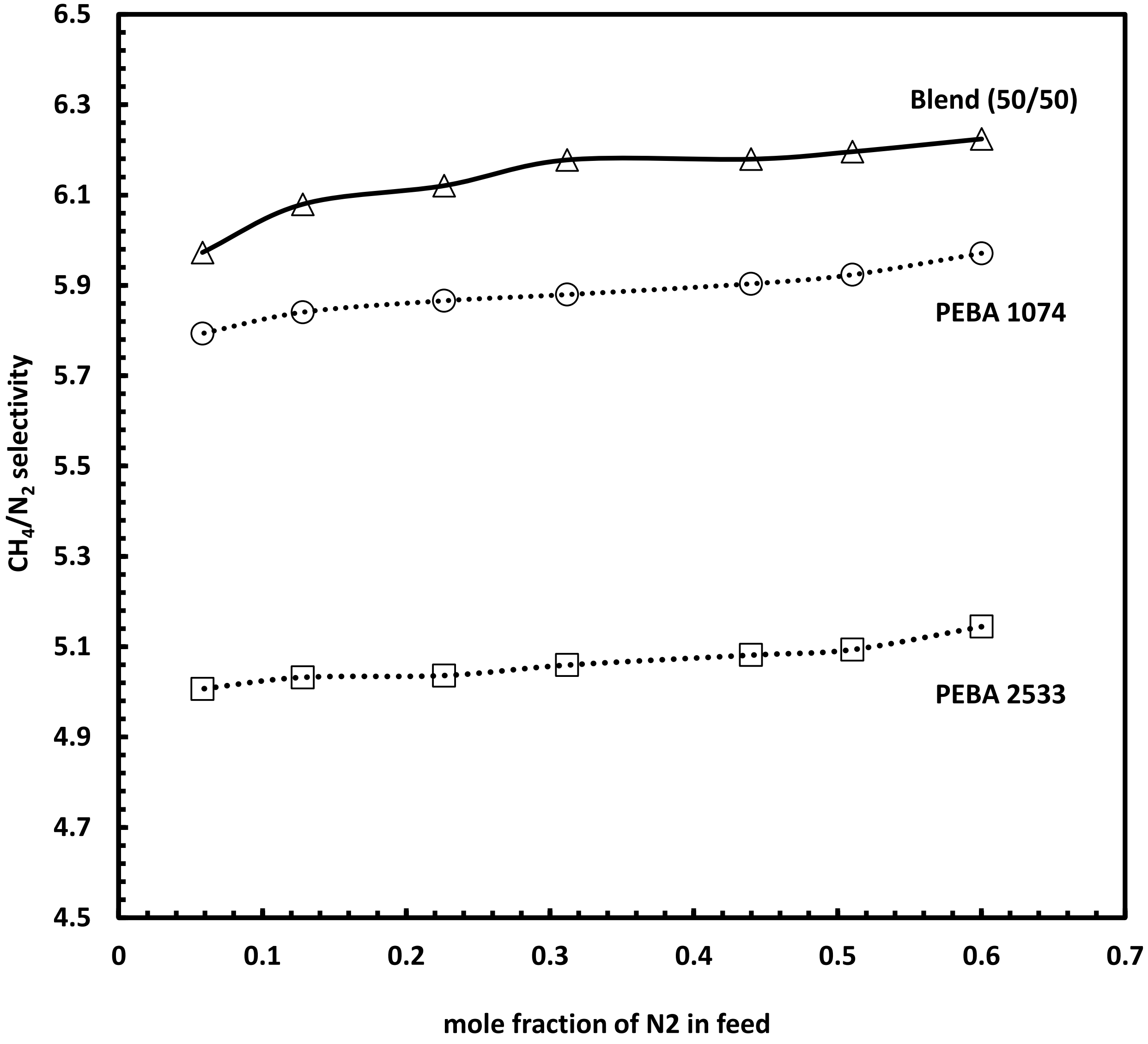


Figure 4.17 Effect of feed composition on CH_4/N_2 selectivity for binary gas permeation through PEBA 2533, PEBA 1074, and a PEBA 2533/1074 (50/50) blend membrane. Pressure: 0.7013 MPa absolute, temperature: -20^{0}C

As discussed before, density ratio of PEBA 2533 over PEBA 1074 was independent with the temperature within the range used in this study. Therefore, in order to see if gas permeability of the blend membrane still subjects to the series model, the operating condition was set to be 60% of N_2 in feed and feed pressure at 0.7013 MPa absolute, the operating temperature was varying from 25 to -20^{0}C. The volume fraction of PEBA 1074 for the blend membrane PEBA 2533/1074 (50/50) was calculated using Equation 4.2, and the volume fraction of PEBA 2533 was calculated by one minus the volume fraction of PEBA 1074. Gas permeabilities of the blend membrane obtained from the gas separation tests was compared with gas permeabilities calculated by Equation 2.10 at different operating temperature. CH_4/N_2 selectivity obtained from the binary gas permeation was also compared with the predicted selectivity, where the predicted selectivity was calculated by predicted CH_4 permeability divided by predicted N_2 permeability, as shown in Figure 4.18. Generally speaking, both CH_4 and N_2 permeabilities follows the series model. The experimental CH_4/N_2 selectivity was lower than the predicted selectivity at higher temperatures (25, 15, and 5^{0}C) but higher at lower temperatures (-5, -10, -15, and -20^{0}C). This agreed with the observation obtained from Figure 4.15, that only at lower temperature, the blend membrane would show a better CH_4/N_2 selectivity in the binary gas permeation tests.

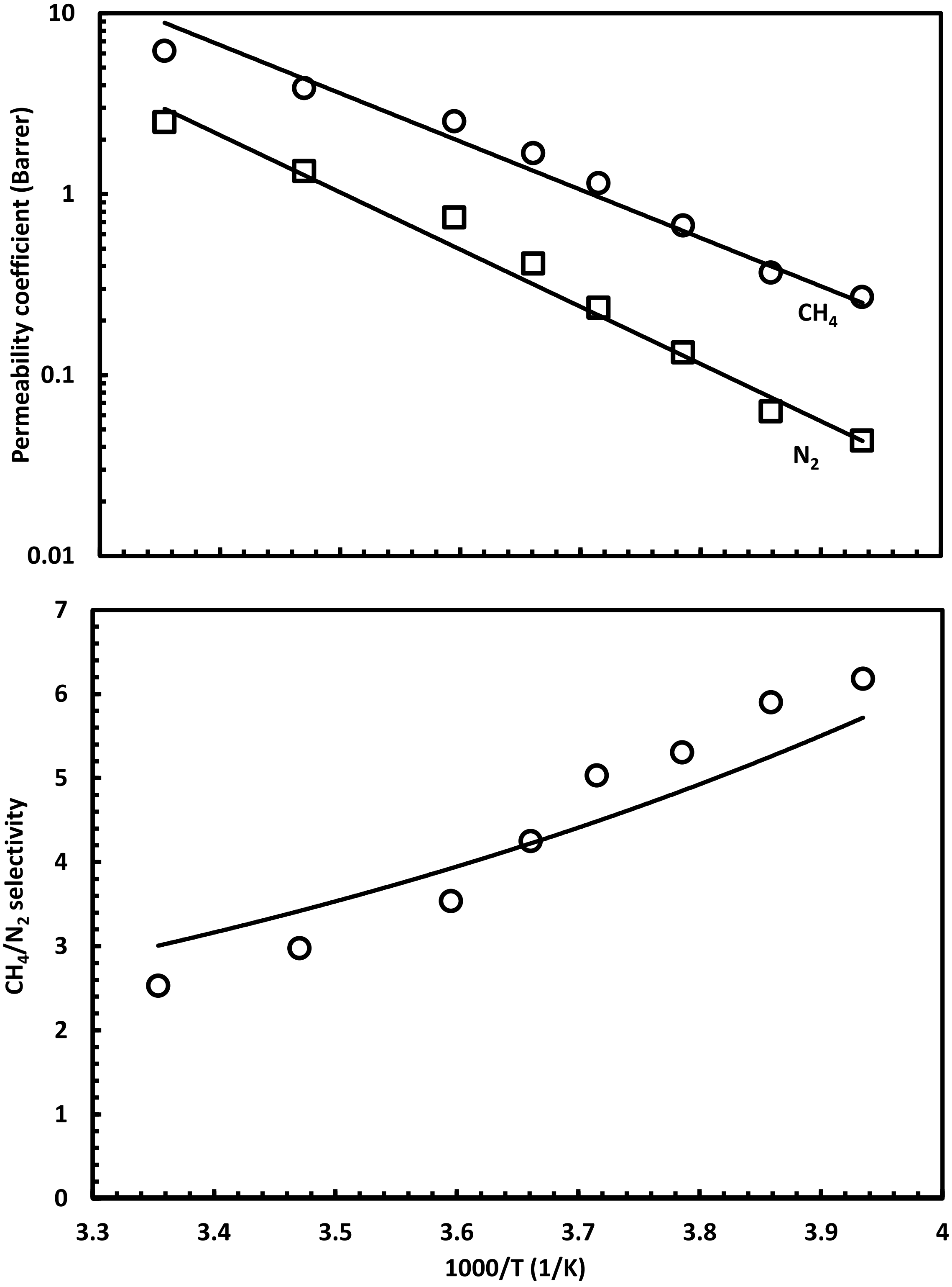


Figure 4.18 Permeability coefficient and CH_4/N_2 selectivity vs. temperature for binary gas mixture permeation. N_2 concentration in feed: 60%, pressure: 0.7013 MPa absolute. Note: open marks indicate experimental data, solid lines indicate the series model predictions

4.4 Conclusions

PEBA 2533 and PEBA 1074 were used to form polymer blend to fabricate blend membranes. In order to find the best blend ratio, a series of solutions were prepared with different blend ratios, and then they were used to form membranes. Pure gas permeation tests were conduct using these membranes at varying temperatures and pressures, and the gas permeability was compared with model predictions. Binary gas mixture permeation was carried out as well to evaluate the membrane performance for N_2 removal from natural gas. The following conclusions can be drawn:

(1) The operating conditions (pressure and temperature) showed the same effects on the permeation of CH_4 and N_2 gas mixtures through blend membranes as they did on permeation through constituent PEBA membranes.

(2) Blend membranes showed a gas permeability higher than PEBA 1074 and lower than PEBA 2533, resulting a CH_4/N_2 permeability ratio higher than either constituent membranes at low temperatures.

(3) A blend ratio of 50/50 appeared to be suitable to produce a membrane with good CH_4/N_2 selectivity.

(4) Both CH_4 and N_2 permeabilities of the blend membranes fit the series model very well. And the density ratio of PEBA 2533/1074 was independent with temperature within the temperature range used in this study.

Chapter 5 General Conclusions and Recommendations

5.1 General Conclusions

Permeation of CH_4 and N_2 through PEBA 1074, PEBA 2533, PEBA 1657, PEBA 3000, a series of PEBA 2533/1074 blend membranes, and a commercial PDMS membrane was investigated at different temperatures and pressures. Generally speaking, pressure has little effect on the gas permeation through these membranes, while the permeabilities of both gases were affected significantly by temperature. PDMS membrane showed the highest permeability but its selectivity to CH_4/N_2 was the lowest. Among the PEBA membranes, PEBA 2533 had the highest permeability, while PEBA 1074 had the best CH_4/N_2 selectivity. The blend membranes showed a permeability higher than PEBA 1074 and lower than PEBA 2533, and its CH_4/N_2 selectivity was better than either constituent PRBA membranes. At a blend ratio of 50/50, the CH_4/N_2 permeability ratio was over 6.6 at 0.8013 MPa and -20^0C. The permeability coefficient of the blend membranes can be predicted by using the series model, and the density ratio of PEBA 2533/1074 was independent with temperature within the temperature range used in this study.

Binary gas permeation through PEBA 1074, PEBA 2533 and a PEBA 2533/1074 blend membrane (blend ratio of 50/50) were investigated further at different temperatures and feed compositions. The presence of N_2 in the feed tended to reduce CH_4 permeability, therefore, causing the CH_4/N_2 selectivity lower than that in the pure gas permeation tests. The blend membrane exhibited a CH_4/N_2 selectivity of over 6 at -20^0C with 60% N_2 in feed, which appeared to very close to the target selectivity required for N_2 removal from natural gas.

5.2 Recommendations

1. This study showed that CH_4/N_2 selectivity increased with a decrease in temperature, and the temperature range studied was 25 to -20^{0}C. It would be of interest to use a lower temperature in order to improve the membrane selectivity. It is recommended to operate the membrane at temperatures lower than -20^{0}C to see how the membrane would perform.
2. Homogenous membrane was used in the study, which had a relatively large membrane thickness, resulting in low permeation flux. Composite membranes with a thin PEBA skin layer supported on a microporous substrate could be prepared to enhance the permeation flux without compromising the membrane selectivity.
3. Flat sheet PEBA 2533/1074 blend membranes were shown to be promising for N_2 removal from natural gas. Hollow fibers with a high packing density may be developed to increase the N_2 removal efficiency. Hollow fiber membranes may be prepared by dip-coating the PEBA 2533/1074 blend polymer solution onto a microporous hollow fiber substrate. The membrane performance at industrially relevant conditions (pressure, composition) for N_2 removal from natural gas needs to be determined.

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Appendix A – Sample Calculations

A.1 Sample Calculations for Pure Gas Permeation

Calculations of gas permeability

The permeability of pure gas was calculated from the following data

Membrane: PEBA 2533;

Gas: CH_4;

Room temperature: 23^0C (296.15 K);

Membrane area: 13.85 cm^3;

Membrane thickness: $4.826*10^{-3}$ cm;

Feed pressure: 0.8013 MPa absolute (601.043 cmHg);

Downstream pressure: 0.1013 MPa absolute (76 cmHg);

Permeate flow rate: $2.174*10^{-3}$ cm^3/s;

The permeability of CH_4 can be calculated as follows:

$$P = \frac{Vl}{At\Delta p}\frac{273.15}{T_0}\frac{p_0}{76} = \frac{2.174 \times 10^{-3} \times 4.826 \times 10^{-3}}{13.85 \times (601.043 - 76)}\frac{273.15}{296.15}\frac{76}{76}$$

$$= 1.3307 \times 10^{-9}\ cm^3(STP).\frac{cm}{cm^2.s.cmHg} = 13.307\ Barrer$$

For N_2, the calculated permeability at the same conditions is 5.729 Barrer.

Calculation of ideal selectivity

The ideal selectivity for CH_4 over N_2 can be calculated as the ratio of CH_4 permeability to N_2 permeability.

$$\alpha_{\frac{CH_4}{N_2}} = \frac{P_{CH_4}}{P_{N_2}} = \frac{13.307}{5.729} = 2.323$$

A.2 Sample Calculations for Gas Mixture Permeation

Calculation of gas permeability

The permeability of gas mixtures can be obtained from the calculation detailed below:

Membrane: PEBA 2533;

Gas mixture: CH_4/N_2;

Room temperature: 23^0C (296.15 K);

Membrane area: 13.85 cm^2;

Membrane thickness: $4.826*10^{-3}$ cm;

Total feed pressure: 0.7013 MPa absolute (526.037 cmHg);

Feed concentration of CH_4: 39.98 mol%;

Permeate concentration of CH_4: 55.10 mol%;

Permeate pressure: 0.1013 MPa absolute (76 cmHg);

Permeate flow rate: $8.7*10^{-4}$ cm^3/s

The permeability of CH_4 (P_{CH_4}) in the mixture can be calculated as follows:

$$P_{CH_4} = \frac{Vy_{CH_4}l}{At\left(p_f x_{CH_4} - p_p y_{CH_4}\right)}\frac{273.15}{T_0} = \frac{8.7 \times 10^{-4} \times 0.5567 \times 4.826 \times 10^{-3}}{13.85 \times (526.037 \times 0.3998 - 76 \times 0.5510)}\frac{273.15}{296.15}$$

$$= 0.9148 \times 10^{-9}\ cm^3(STP).\frac{cm}{cm^2.s.cmHg} = 9.148\ Barrer$$

The permeability of N_2 (P_{N_2}) in the mixture is:

$$P_{N_2} = \frac{Vy_{N_2}l}{At\left(p_f x_{N_2} - p_p y_{N_2}\right)}\frac{273.15}{T_0}$$

$$= \frac{8.7 \times 10^{-4} \times (1 - 0.5567) \times 4.826 \times 10^{-3}}{13.85 \times (526.037 \times (1 - 0.3998) - 76 \times (1 - 0.5567))}\frac{273.15}{296.15}$$

$$= 0.4458 \times 10^{-9}\ cm^3(STP).\frac{cm}{cm^2.s.cmHg} = 4.458\ Barrer$$

Calculation of selectivity

The selectivity for CH_4 over N_2 in the mixture can be calculated as the ratio of CH_4 permeability over N_2 permeability.

$$\alpha_{\frac{CH_4}{N_2}}=\frac{P_{CH_4}}{P_{N_2}}=\frac{9.148}{4.458}=2.052$$

A.3 Temperature Dependence on Permeability

The temperature dependence of permeability can be expressed by Arrhenius equation and the apparent activation energy can be obtained from lnP vs. $(1000/T)$ plot based on the following form of the equation:

$$lnP = lnP_0 + \frac{-E_a}{R}\frac{1000}{T}$$

$$Slope\ k = -Ea/R$$

Using the permeability of pure CH_4 permeation test with PEBA 2533 membrane at a feed pressure of 0.7013 MPa absolute,:

Temperature (^{0}C)	1000/T (1/K)	Permeability (Barrer)
25	3.354016	13.344
15	3.470415	7.822
5	3.595182	3.637
0	3.660992	3.364
-5	3.7154	1.860
-10	3.785728	1.292
-15	3.858769	0.781
-20	3.934684	0.479

$$E_a/R = 5.738 \times 10^3$$

$$E_a = 5.738 \times 10^3 \times 8.314\frac{J}{mol} = 47.706\ kJ/mol.$$

A.4 Sample Calculations for Polymer Blending Models

Miscible blending models

The permeability can be predicted by the calculations detailed below

Membrane: PEBA 1074/PEBA 2533=50/50;

Gas: CH_4;

Operating temperature: 25^0C (298.15 K);

Feed pressure: 0.8013 MPa absolute (601.043 cmHg);

Density: 1.09 g/cm^3 (PEBA 1074), 1.01 g/cm^3 (PEBA 2533);

Permeability of CH_4: 6.281 Barrer (PEBA 1074), 13.387 Barrer (PEBA 2533), 8.761 Barrer (PEBA 1074/PEBA 2533=50/50);

The permeability of the blend membrane can be predicted by the following calculations:

$$lnP_b = \emptyset_1 lnP_1 + \emptyset_2 lnP_2$$

$$\emptyset_1 = \frac{V_1}{V_1 + V_2} = \frac{\frac{m_1}{\rho_1}}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}} = \frac{m_1}{m_1 + m_2 \frac{\rho_1}{\rho_2}} = \frac{0.5}{0.5 + 0.5 \times \frac{1.09}{1.01}} = 0.481$$

$$\emptyset_2 = 1 - \emptyset_1 = 1 - 0.481 = 0.519$$

$$lnP_b = 0.481 \times ln6.281 + 0.519 \times ln13.387 = 2.230$$

$$P_b = e^{2.230} = 9.303\ Barrer \neq 8.761\ Barrer$$

Immiscible blending models

The predicted CH_4 permeability can be calculated by the series model and parallel model.

Membrane: PEBA 1074/PEBA 2533=50/50;

Gas: CH_4;

Operating temperature: 25^0C (298.15 K);

Feed pressure: 0.8013 MPa absolute (601.043 cmHg);

Density: 1.09 g/cm^3 (PEBA 1074), 1.01 g/cm^3 (PEBA 2533);

Permeability of CH_4: 6.281 Barrer (PEBA 1074), 13.383 Barrer (PEBA 2533), 8.761 Barrer (PEBA 1074/PEBA 2533=50/50);

Volume fraction of PEBA 1074: 0.481 (the same as above)

Calculation with the parallel model:

$$P_b = \emptyset_1 P_1 + \emptyset_2 P_2 = 6.281 \times 0.481 + 13.383 \times (1 - 0.481) = 9.967\ Barrer$$
$$\neq 8.761\ Barrer$$

Calculation with the series model:

$$P_b = \frac{P_1 P_2}{\emptyset_1 P_2 + \emptyset_2 P_1} = \frac{6.281 \times 13.383}{0.481 \times 13.383 + (1 - 0.481) \times 6.281} = 8.668\ Barrer$$
$$\approx 8.761\ Barrer$$

Calculation of PEBA 2533/1074 density ratio

As discussed in Chapter 4, the series model is the best one to predict the permeability of the PEBA blend membrane. So the volume fraction of PEBA 1074 can be calculated by both Equation 4.2 and Equation 2.3. If $\emptyset_1 = \emptyset_1'$, the density ratio of PEBA polymers is independent with temperature.

Membrane: PEBA 2533/1074=50/50;

Gas: CH_4;

Operating temperature: 0^0C (273.15 K);

Feed pressure: 0.8013 MPa absolute (601.043 cmHg);

Downstream pressure: 0.1013 MPa absolute (76 cmHg);

Permeability of CH_4: 1.220 Barrer (PEBA 1074), 3.452 Barrer (PEBA 2533), 1.839 Barrer (PEBA 1074/PEBA 2533=50/50);

Density of PEBA 1074: 1.09 g/cm^3 at 25^0C;

Density of PEBA 2533: 1.01 g/cm^3 at 25^0C;

$$\emptyset_1 = \frac{P_1(P_2 - P_b)}{P_b(P_2 - P_1)} = \frac{1.220 \times (3.452 - 1.839)}{1.839 \times (3.452 - 1.220)} = 0.479$$

$$\emptyset_1' = \frac{V_1}{V_1 + V_2} = \frac{\frac{m_1}{\rho_1}}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2}} = \frac{m_1}{m_1 + m_2 \frac{\rho_1}{\rho_2}} = \frac{0.5}{0.5 + 0.5 \times \frac{1.09}{1.01}} = 0.481$$

$$\emptyset_1 \approx \emptyset_1'$$

Appendix B – Supporting Figures

B.1 Pure Gas Permeation Tests with Constituent PEBA and PDMS Membranes

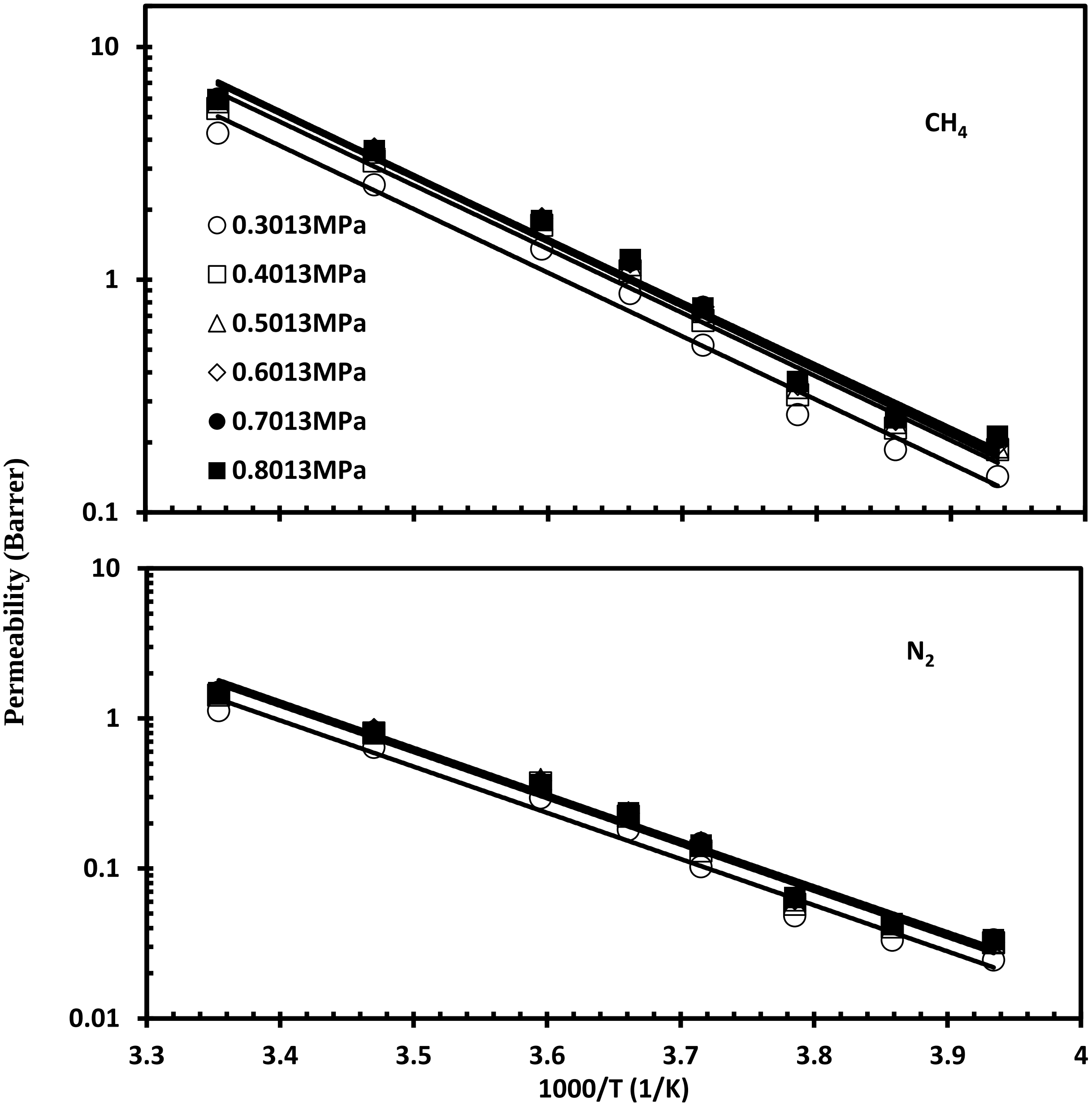

Figure B.1 Effect of temperature on the permeability of the gases permeate through PEBA 1074 membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

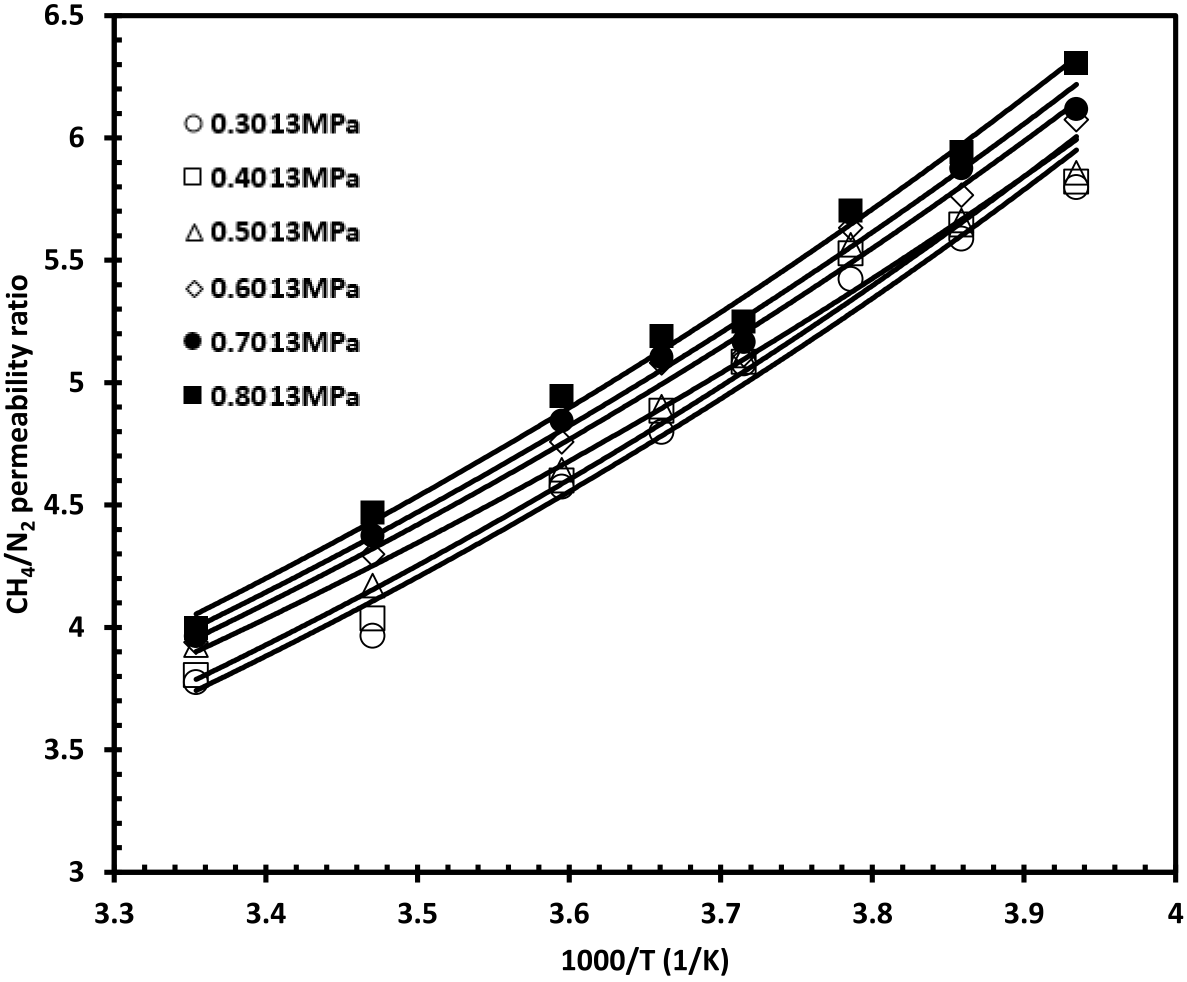

Figure B.2 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 1074 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

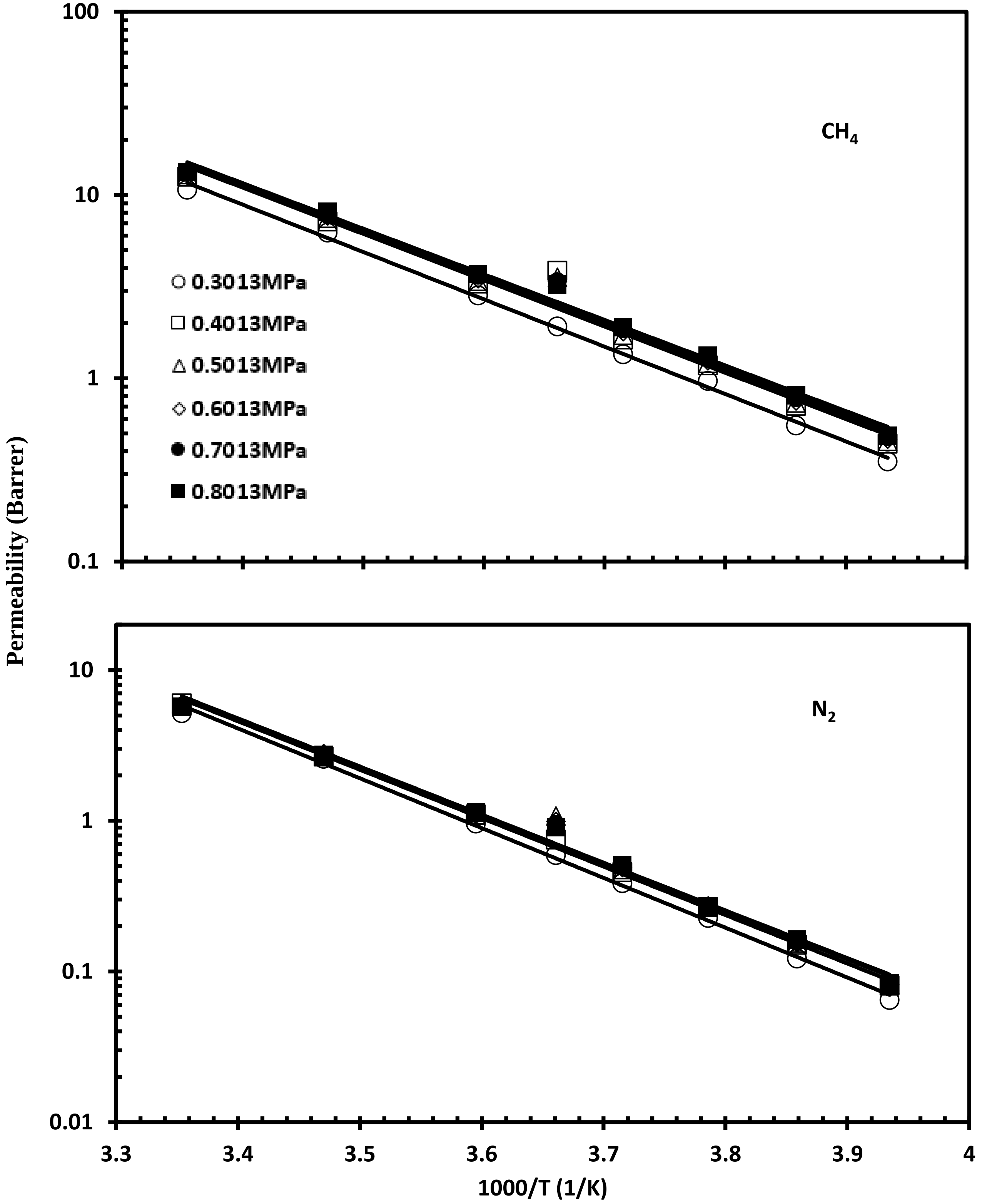

Figure B.3 Effect of temperature on the permeability of the gases permeate through PEBA 2533 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute

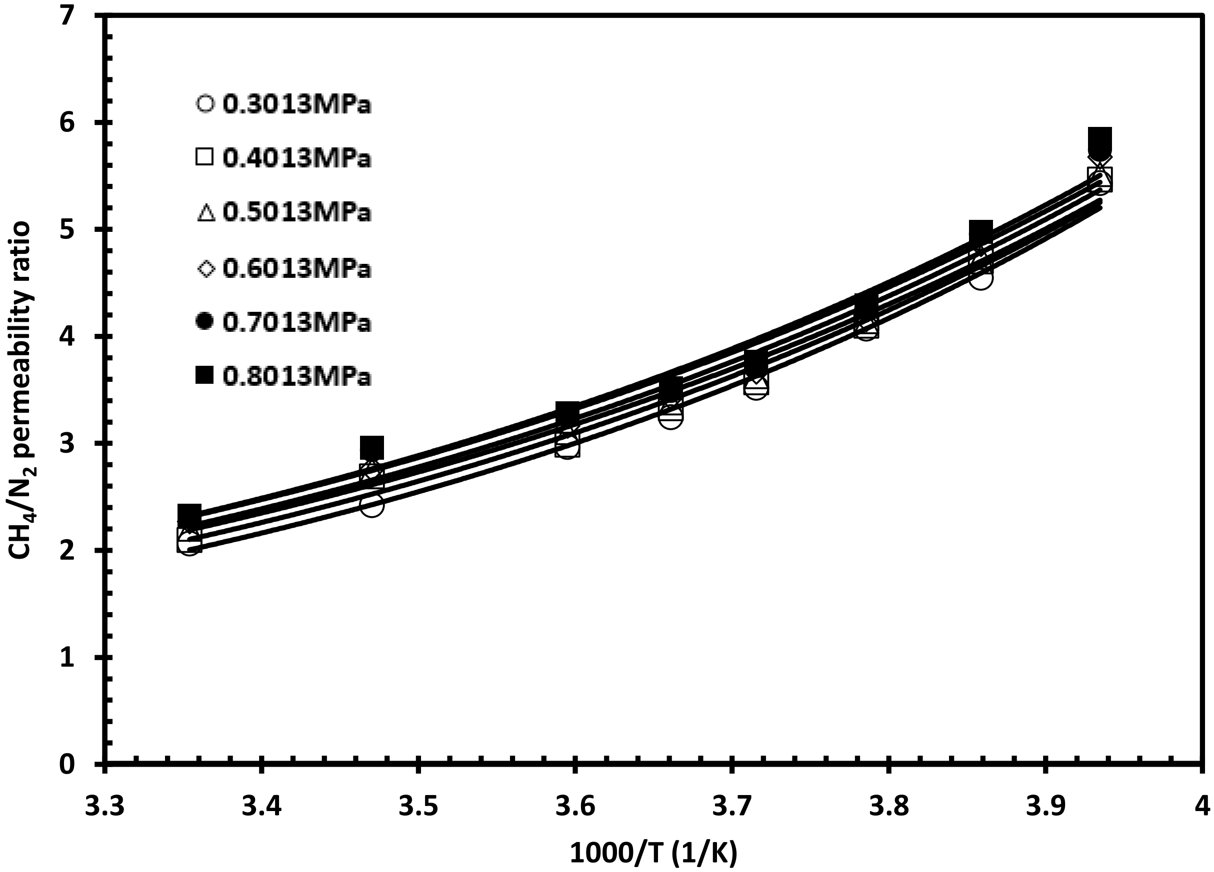

Figure B.4 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533 membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

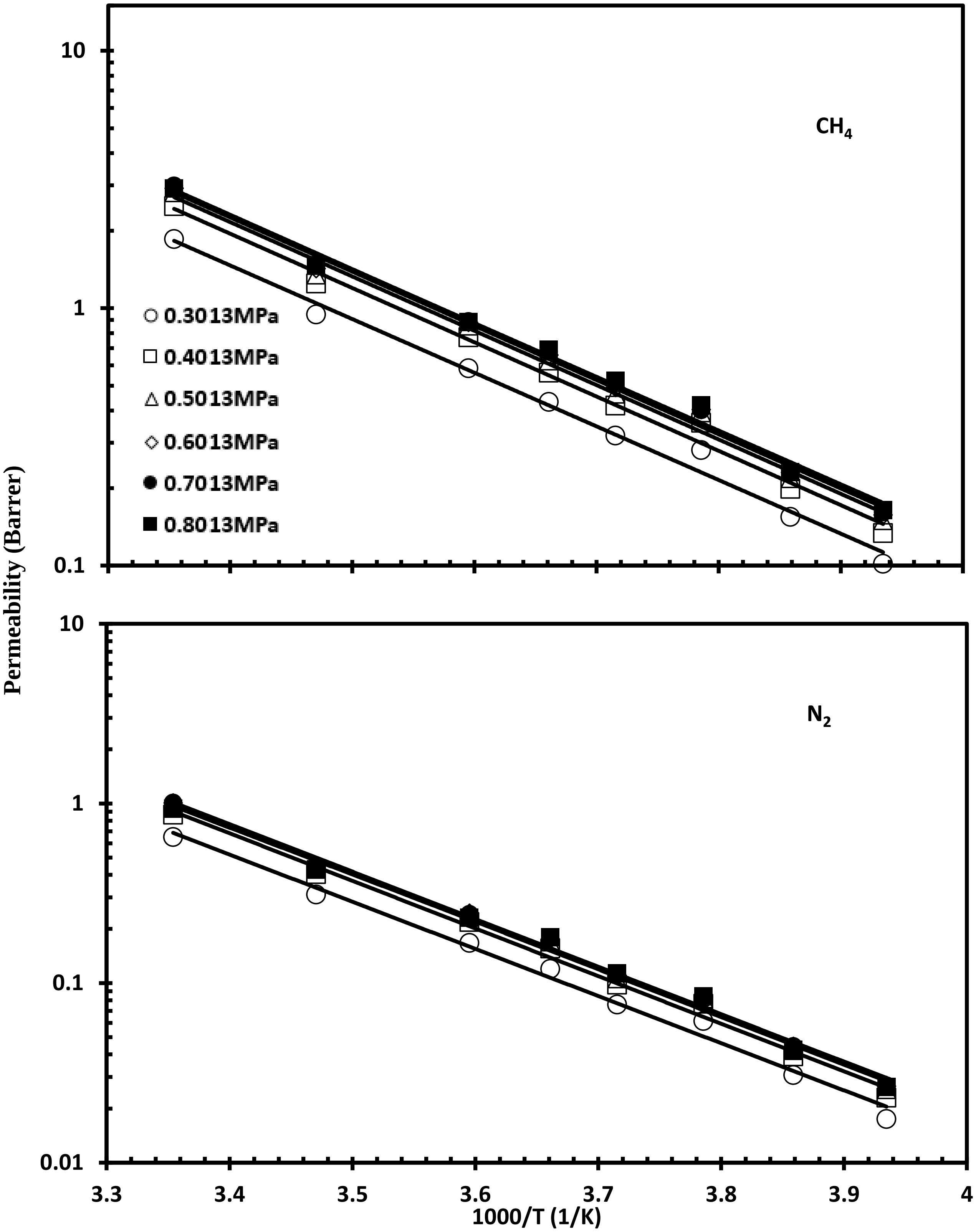

Figure B.5 Effect of temperature on the permeability of the gases permeate through PEBA 1657 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

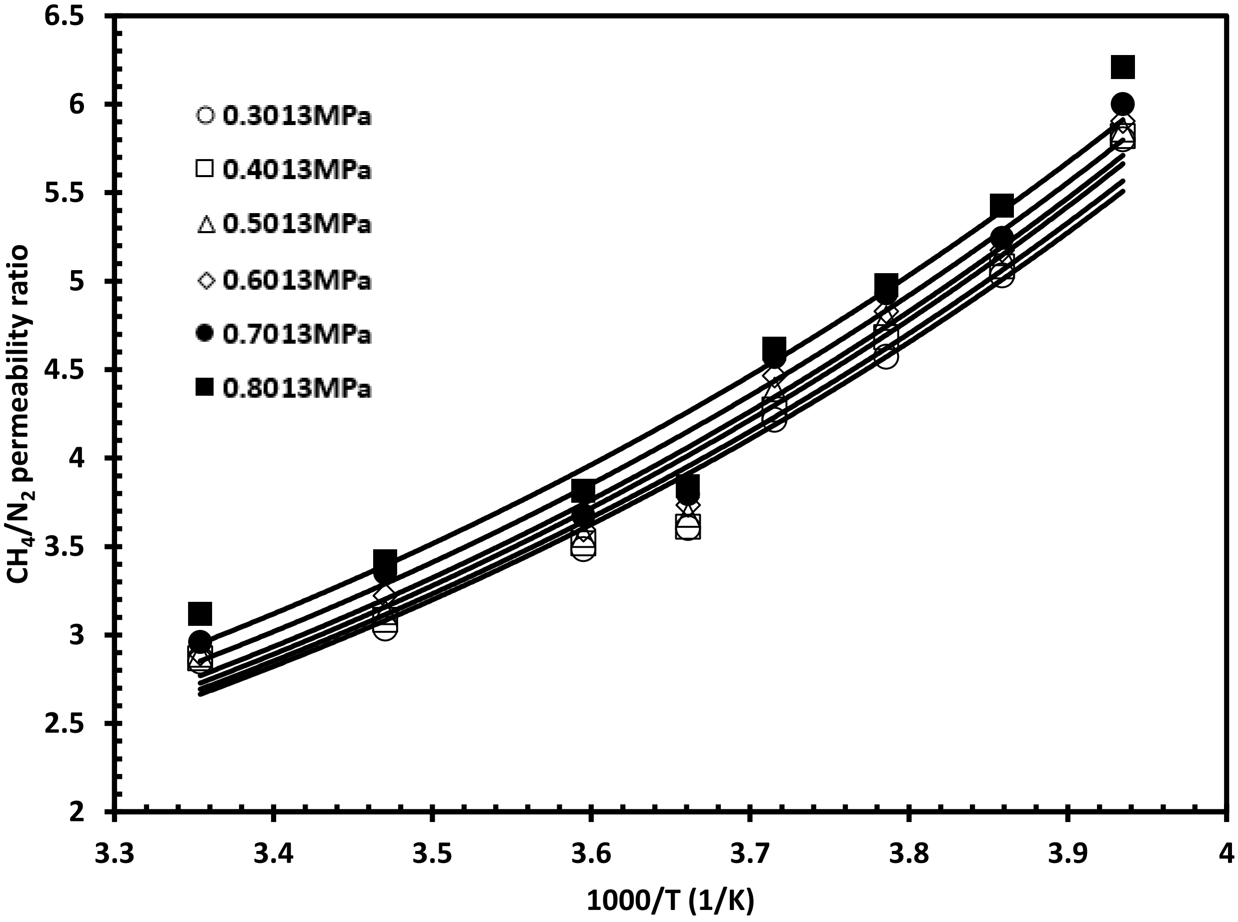

Figure B.6 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 1657 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

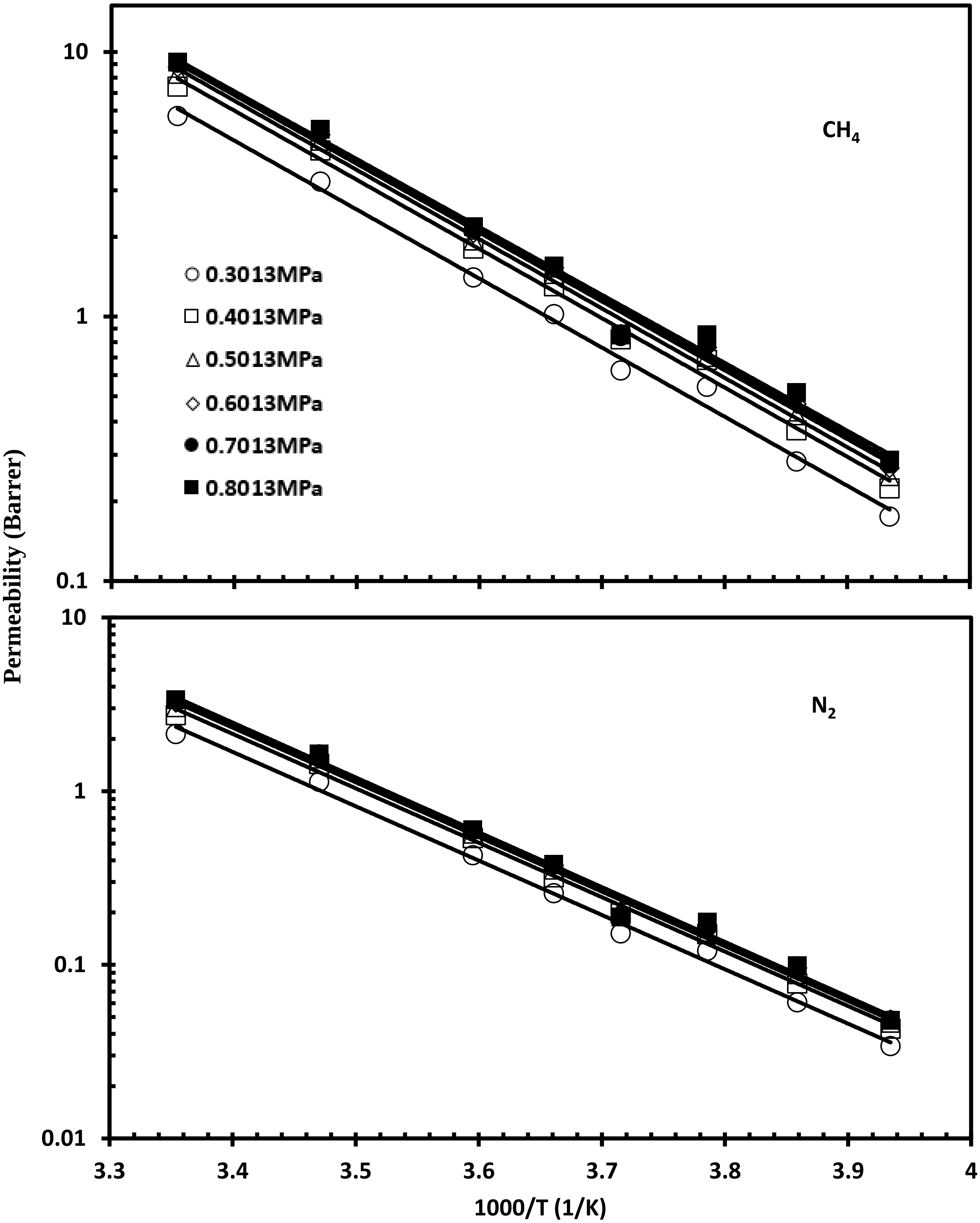

Figure B.7 Effect of temperature on the permeability of the gases permeate through PEBA 3000 membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

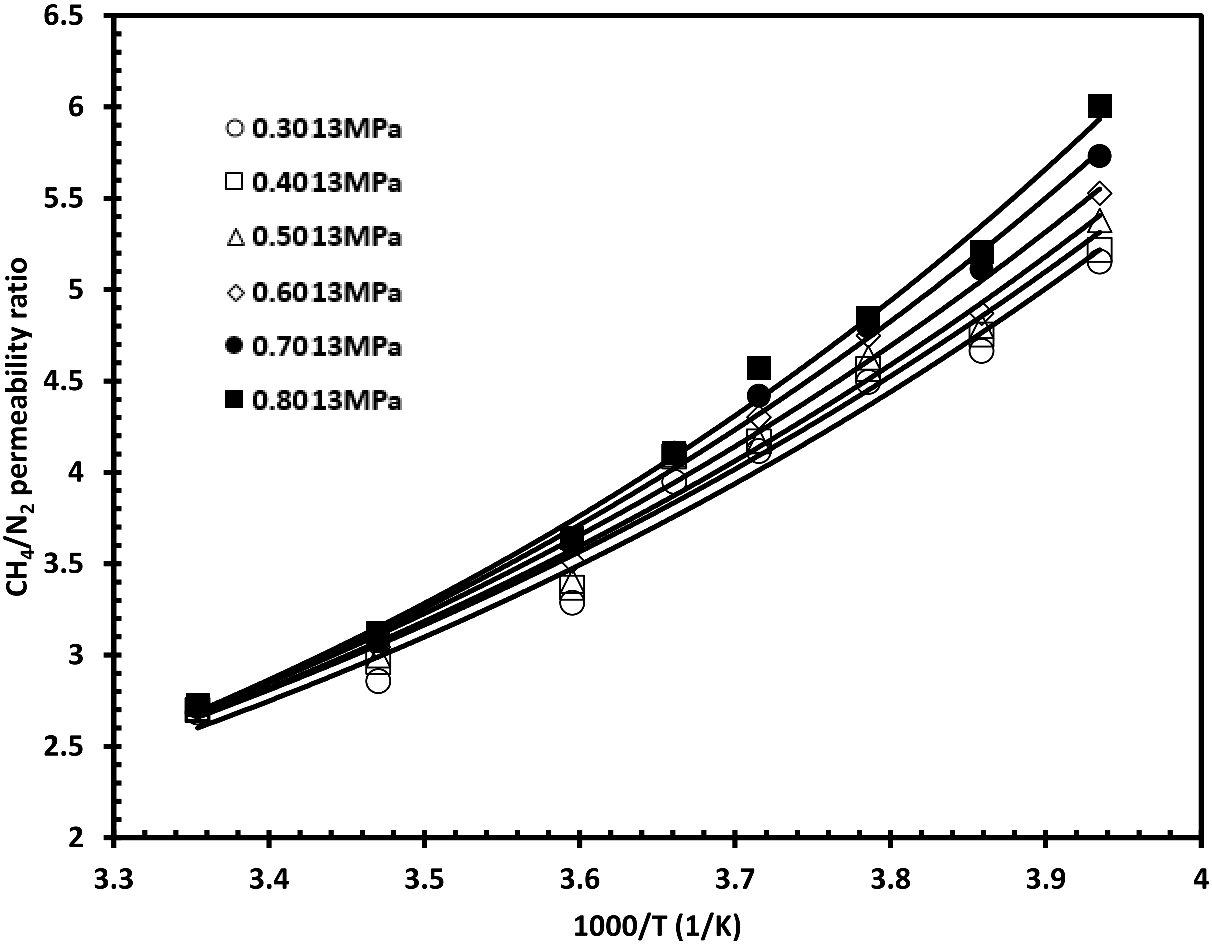

Figure B.8 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 3000 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute

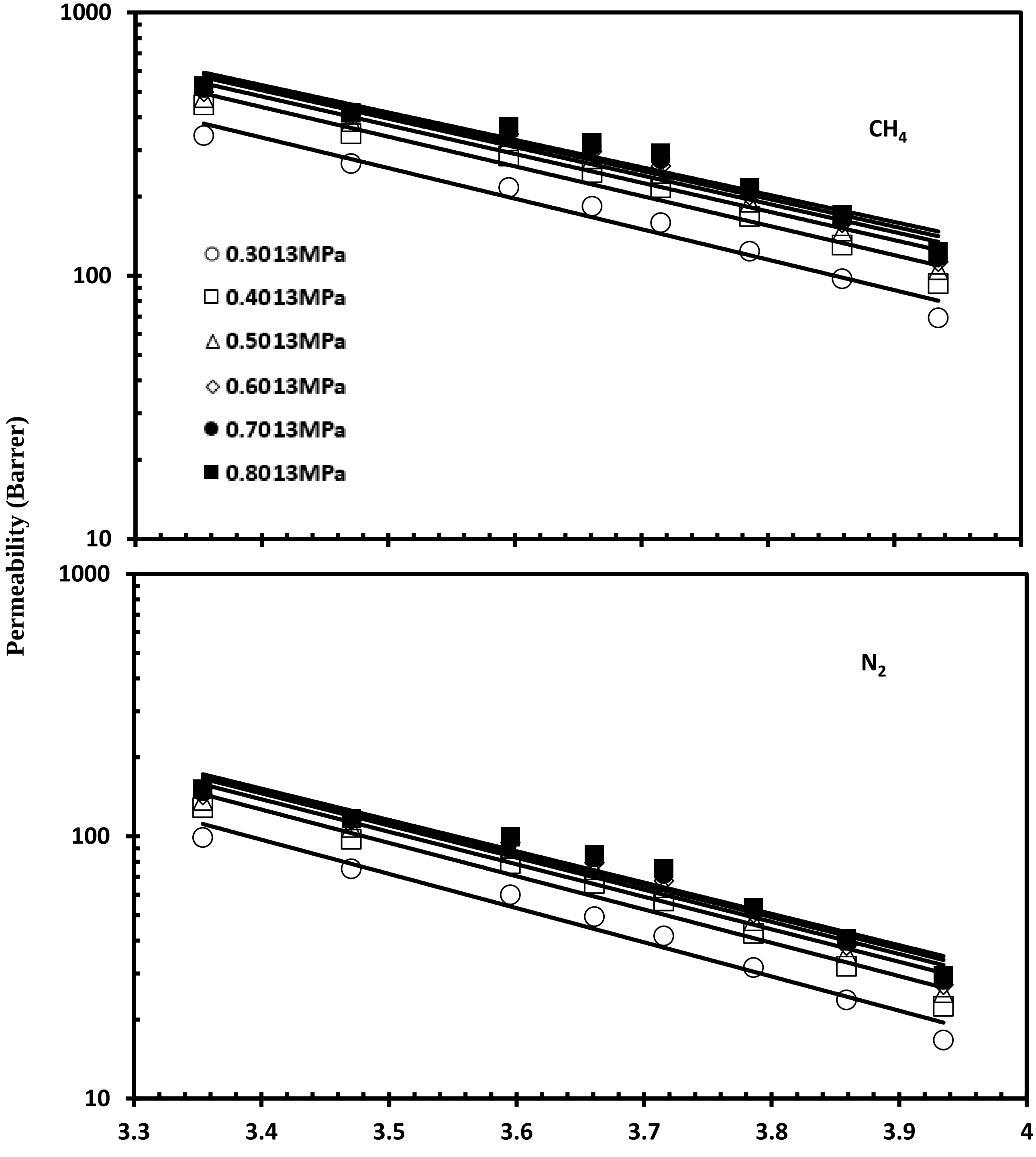

Figure B.9 Effect of temperature on the permeability of the gases permeate through PDMS membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute

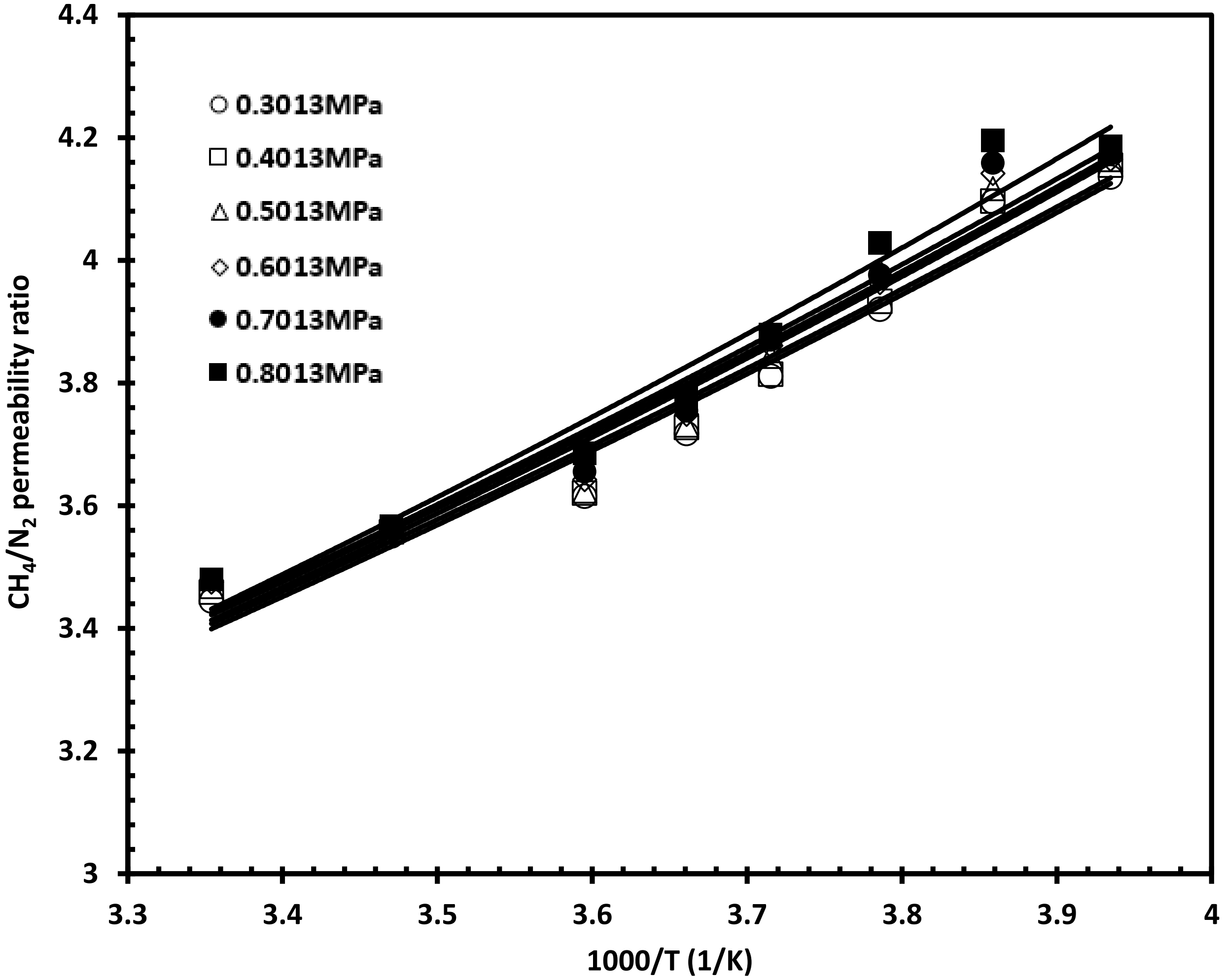

Figure B.10 Effect of temperature on the CH_4/N_2 permeability ratio for PDMS membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute

B.2 Binary Gas Permeation Tests with PEBA 1074 and PEBA 2533

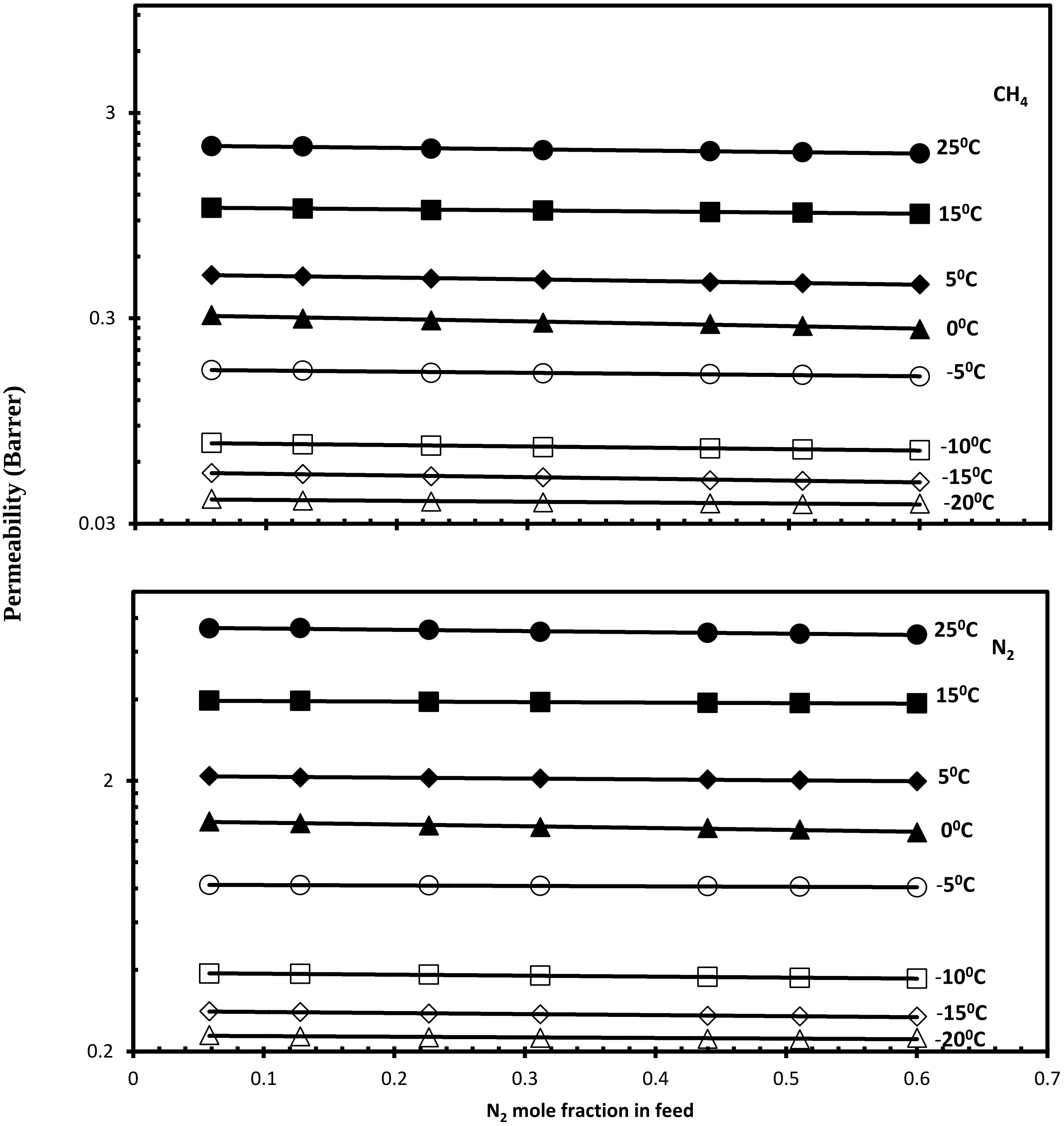

Figure B.11 Effect of N_2 mole fraction in feed on the permeability of the gases permeate through PEBA 1074 membrane in binary system. Note the applying pressure is 0.7013 MPa absolute, temperature varies from 25^0C to -20^0C.

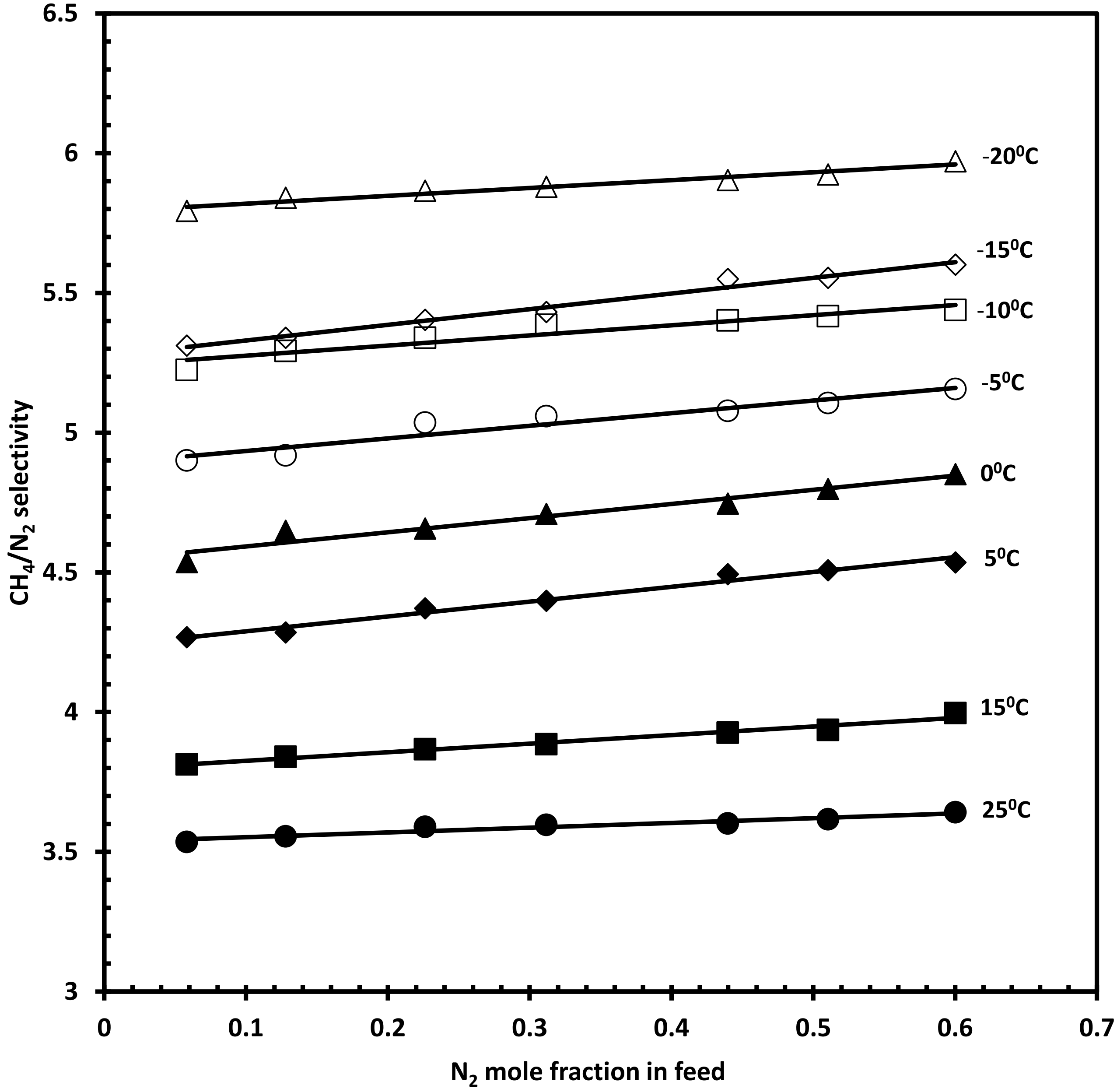

Figure B.12 Effect of N_2 mole fraction in feed on CH_4/N_2 selectivity of PEBA 1074 membrane in binary system. Note the applying pressure is 0.7013 MPa absolute, temperature varies from 25^0C to -20^0C.

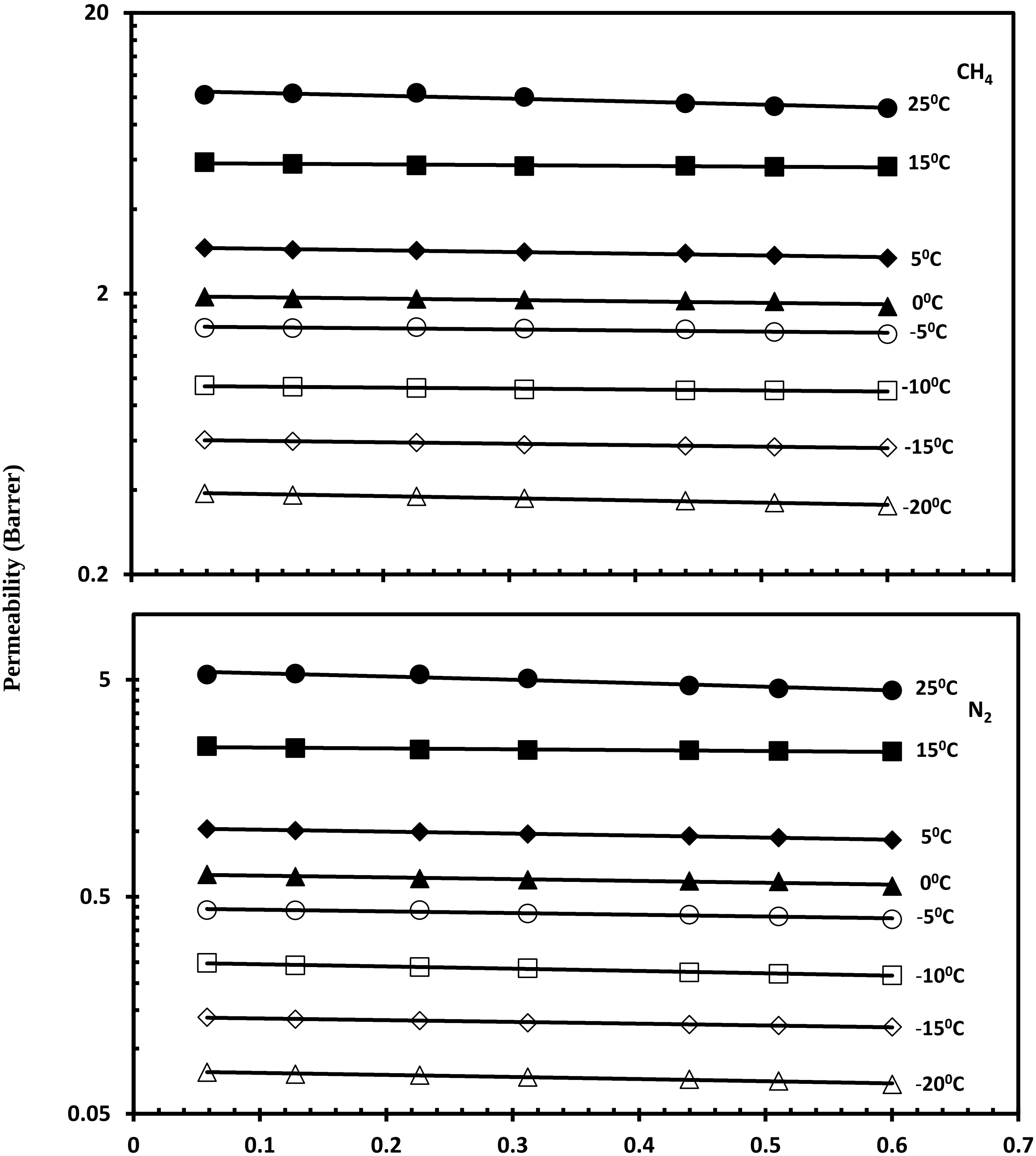

Figure B.13 Effect of N_2 mole fraction in feed on the permeability of the gases permeate through PEBA 2533 membrane in binary system. Note the applying pressure is 0.7013 MPa absolute, temperature varies from 25^{0}C to -20^{0}C.

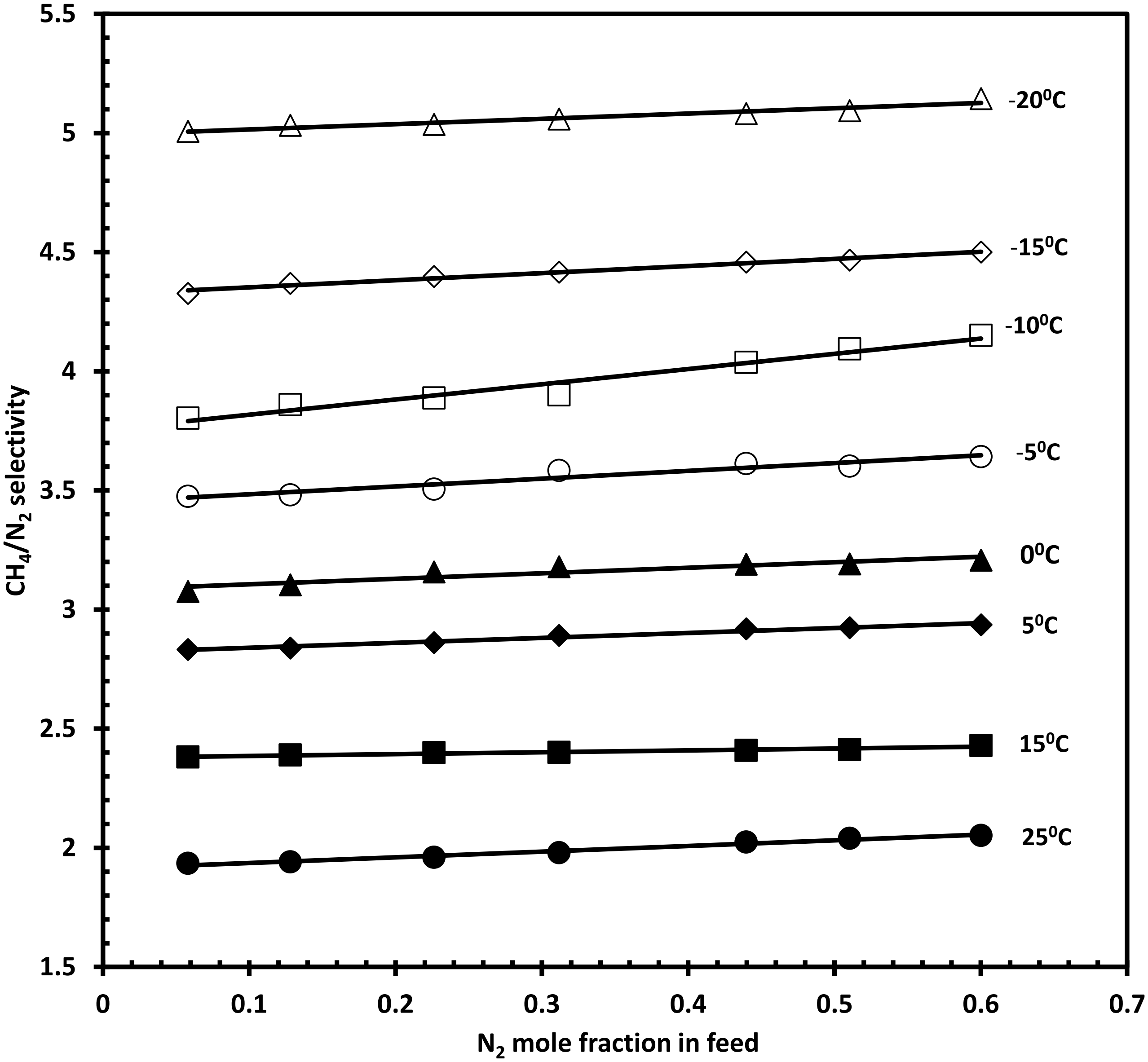

Figure B.14 Effect of N_2 mole fraction in feed on CH_4/N_2 selectivity of PEBA 2533 membrane in binary system. Note the applying pressure is 0.7013 MPa absolute, temperature varies from 25^0C to -20^0C.

B.3 Pure Gas Permeation Tests with PEBA 2533/1074 Blend Membranes

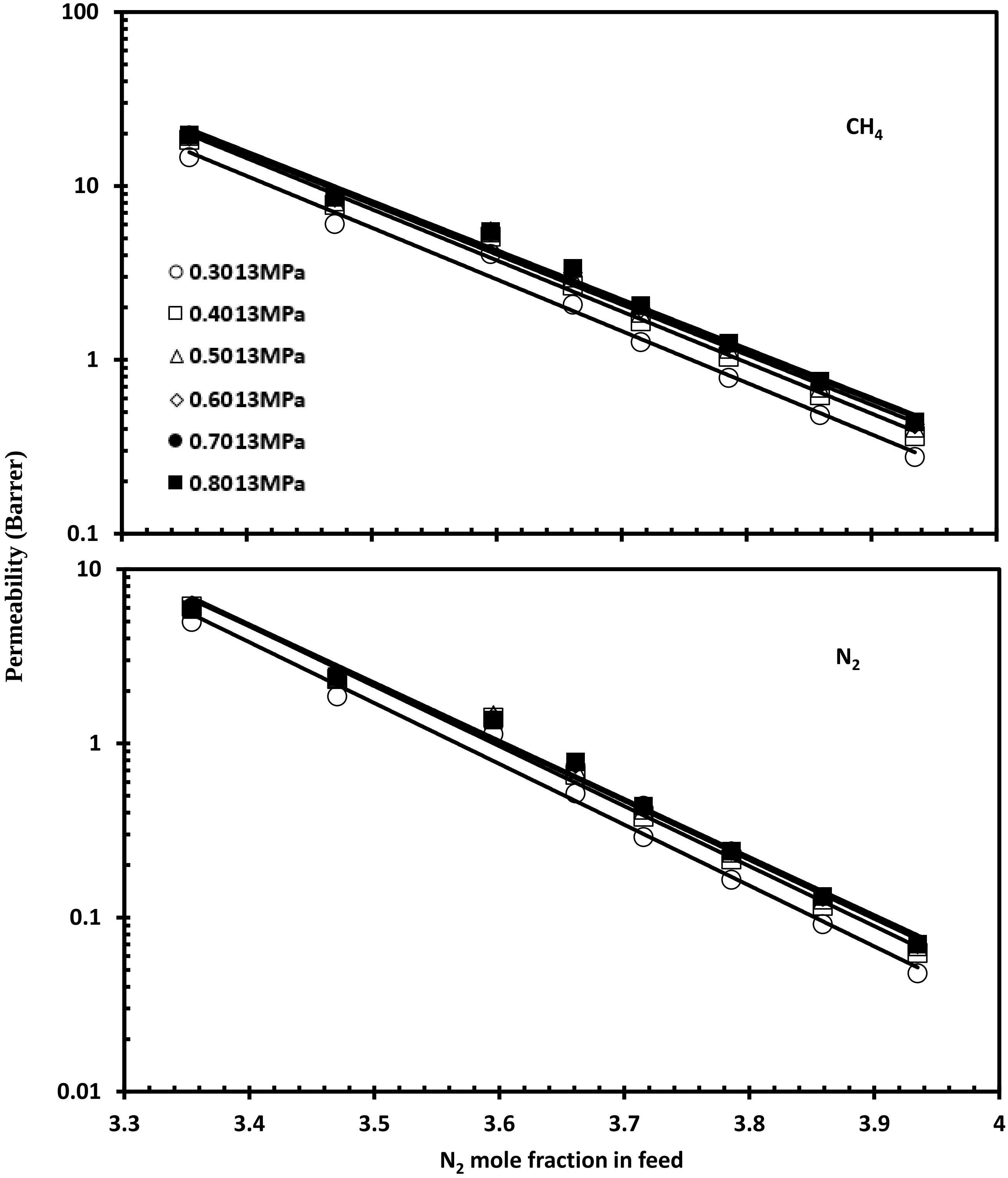

Figure B.15 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=93.75/6.25 membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

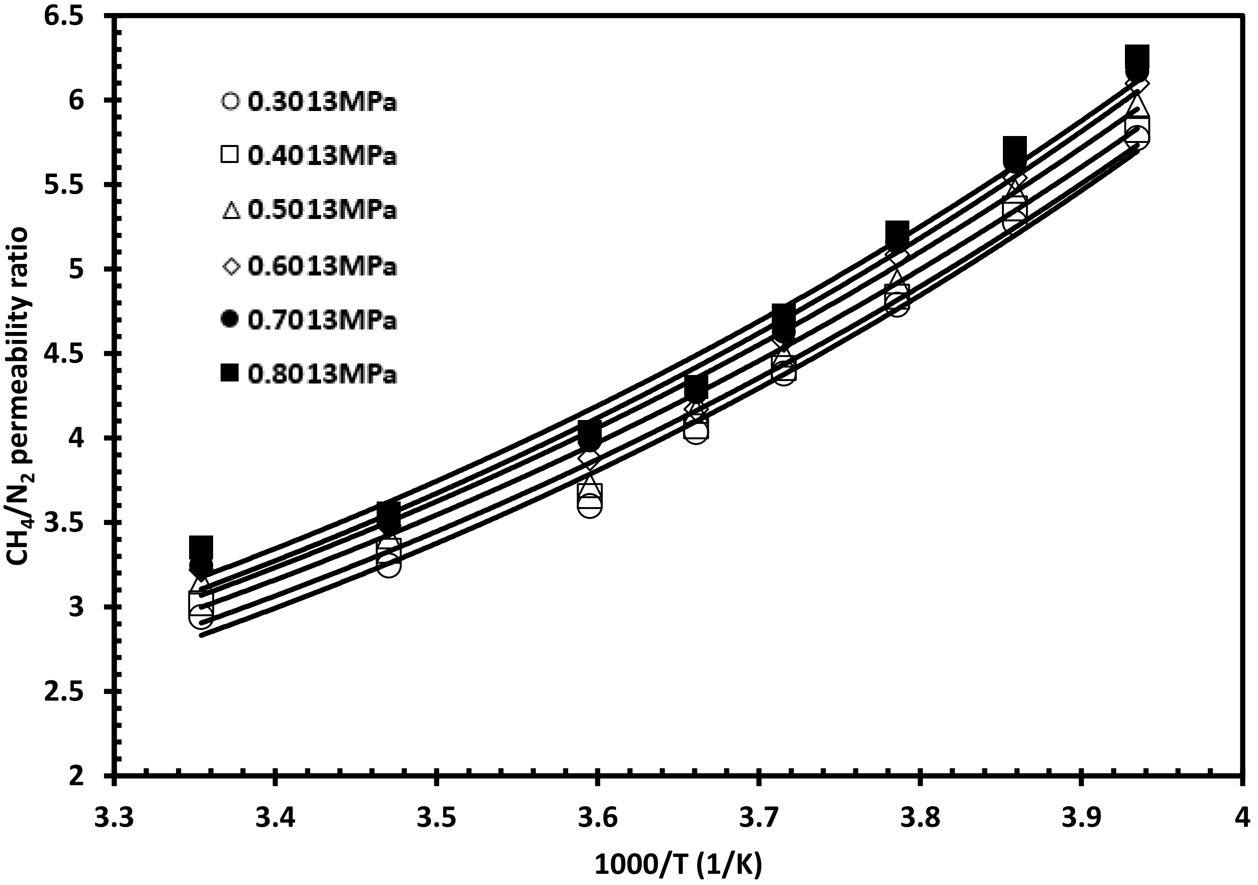

Figure B.16 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=93.75/6.25 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

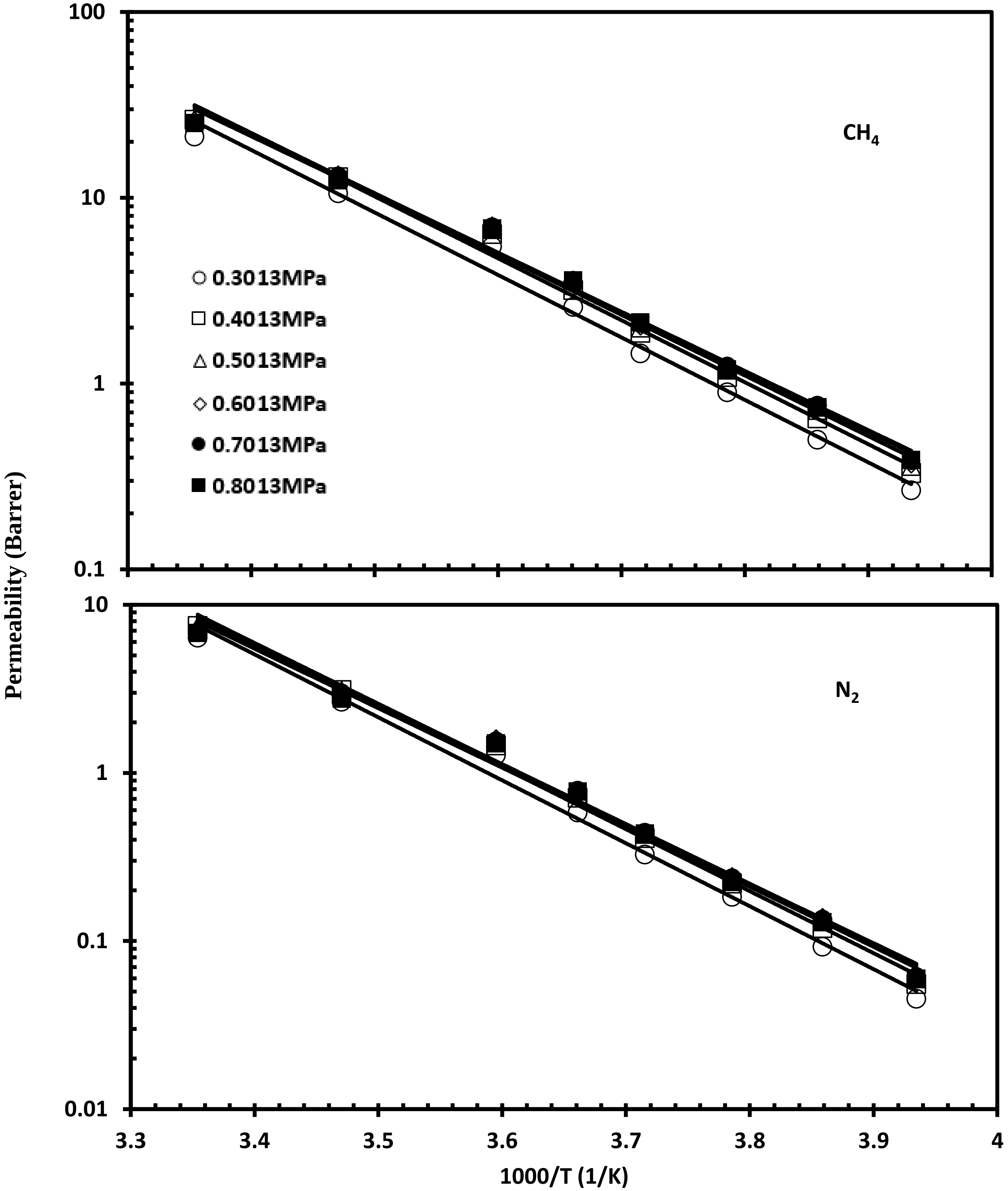

Figure B.17 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=87.5/12.5 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

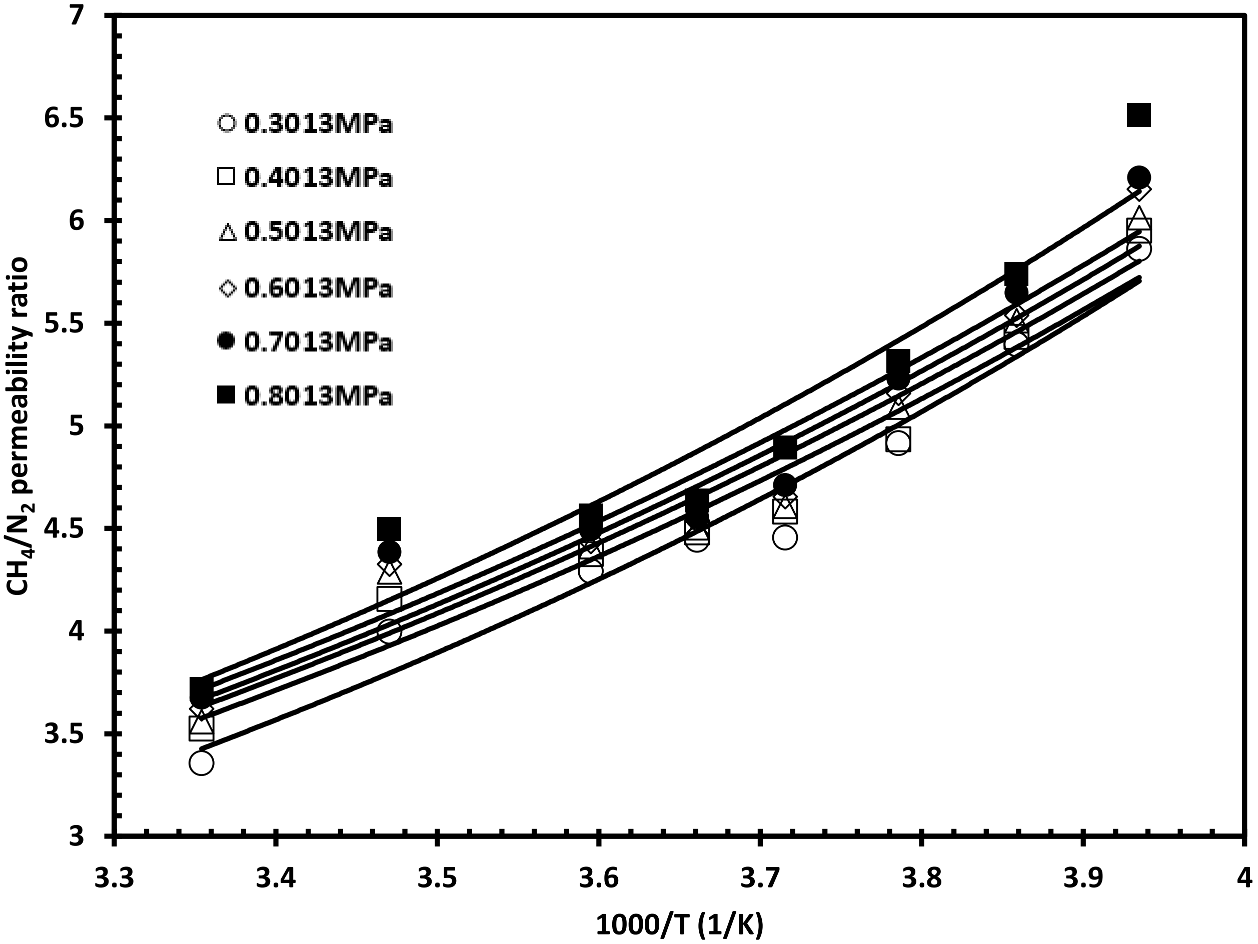

Figure B.18 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=87.5/12.5 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

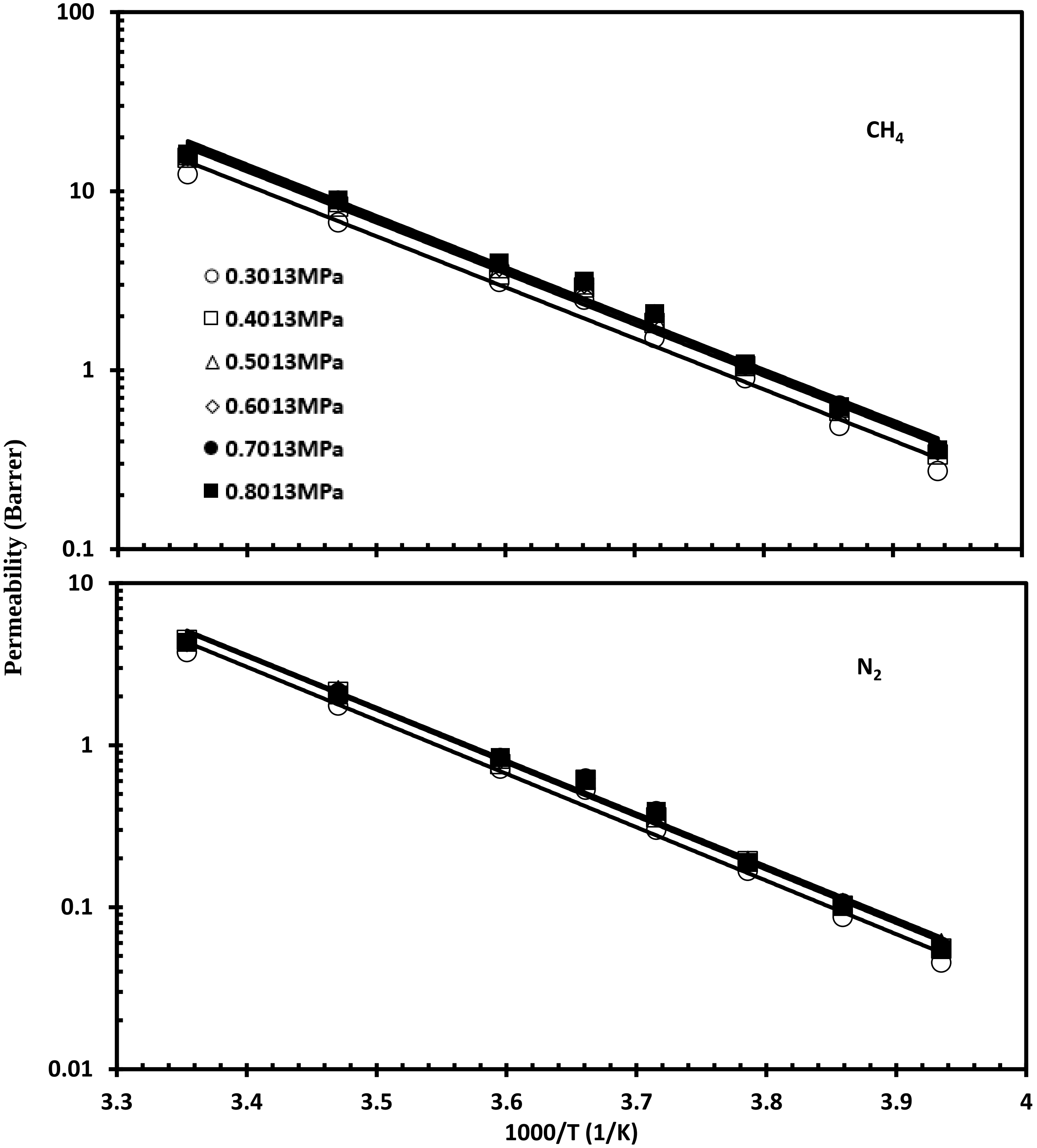

Figure B.19 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=75/25 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

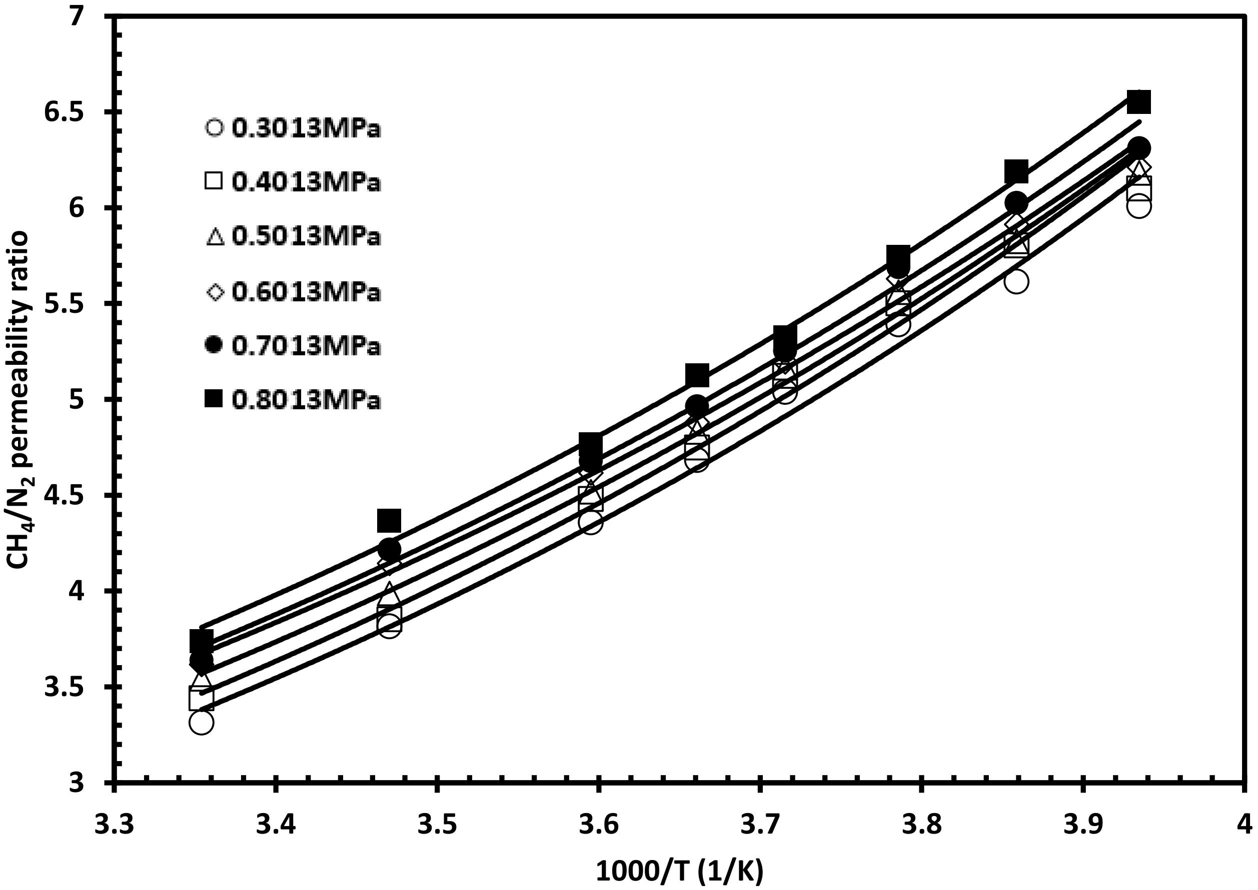

Figure B.20 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=75/25 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

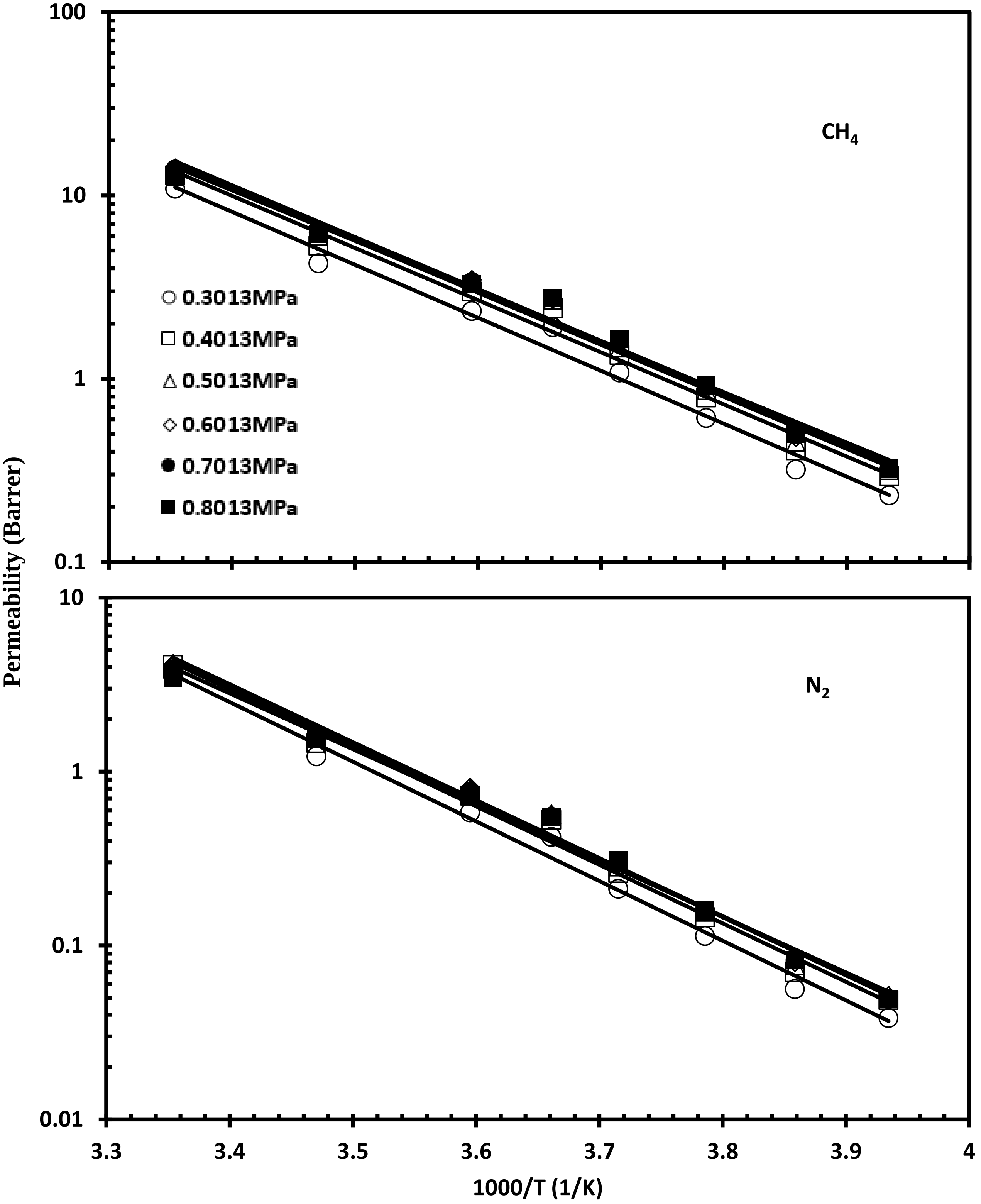

Figure B.21 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=62.5/37.5 membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

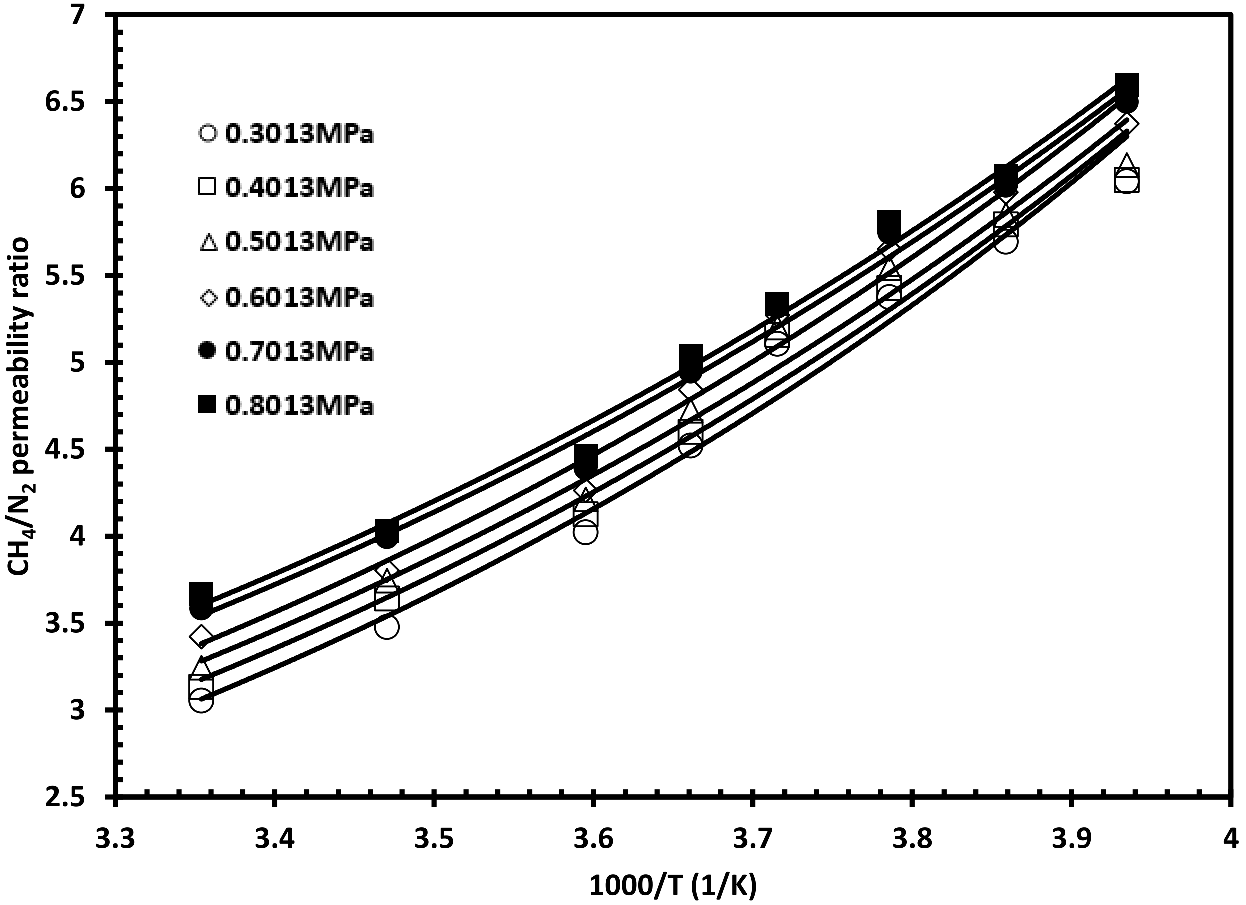

Figure B.22 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=62.5/37.5 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

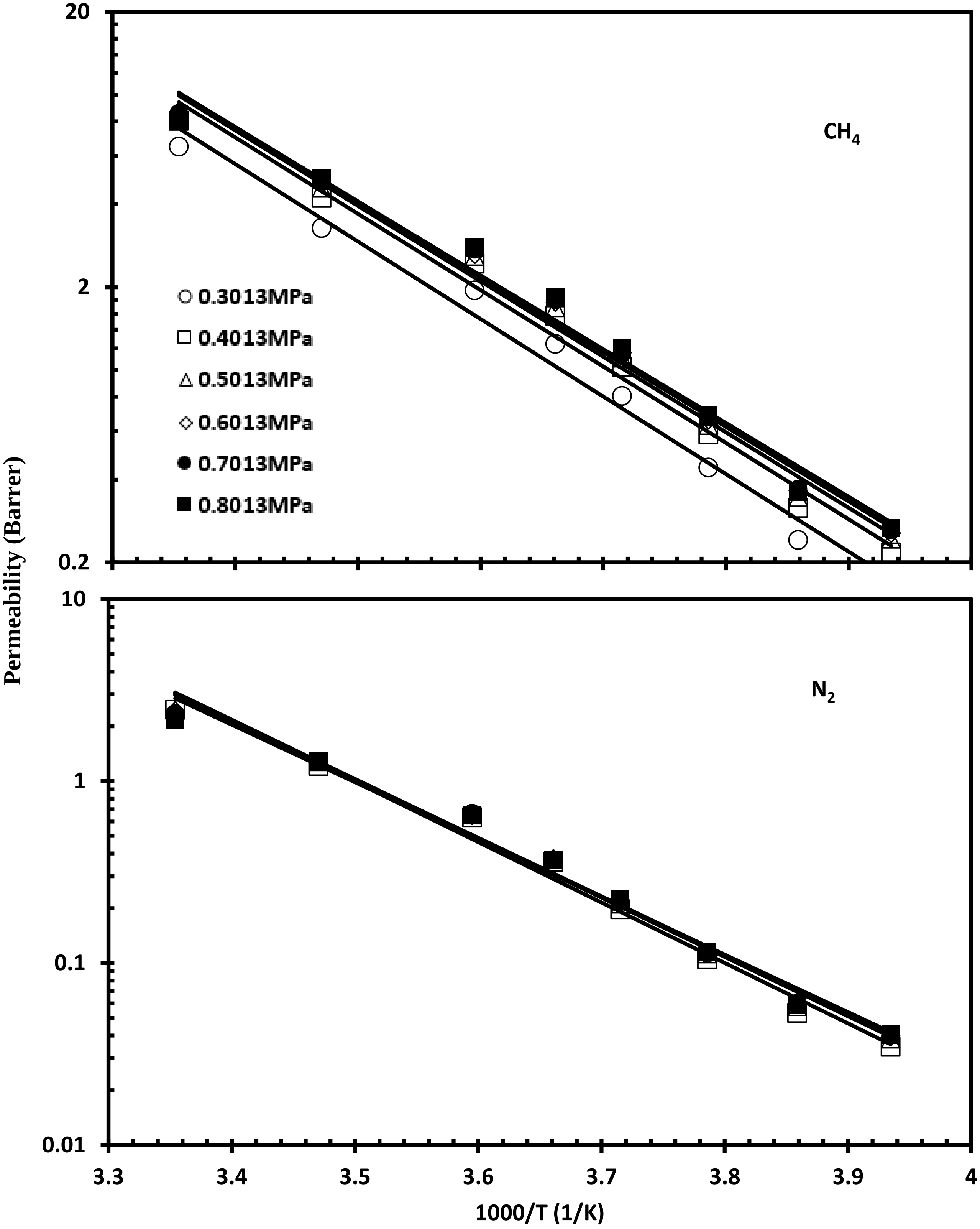

Figure B.23 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=50/50 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

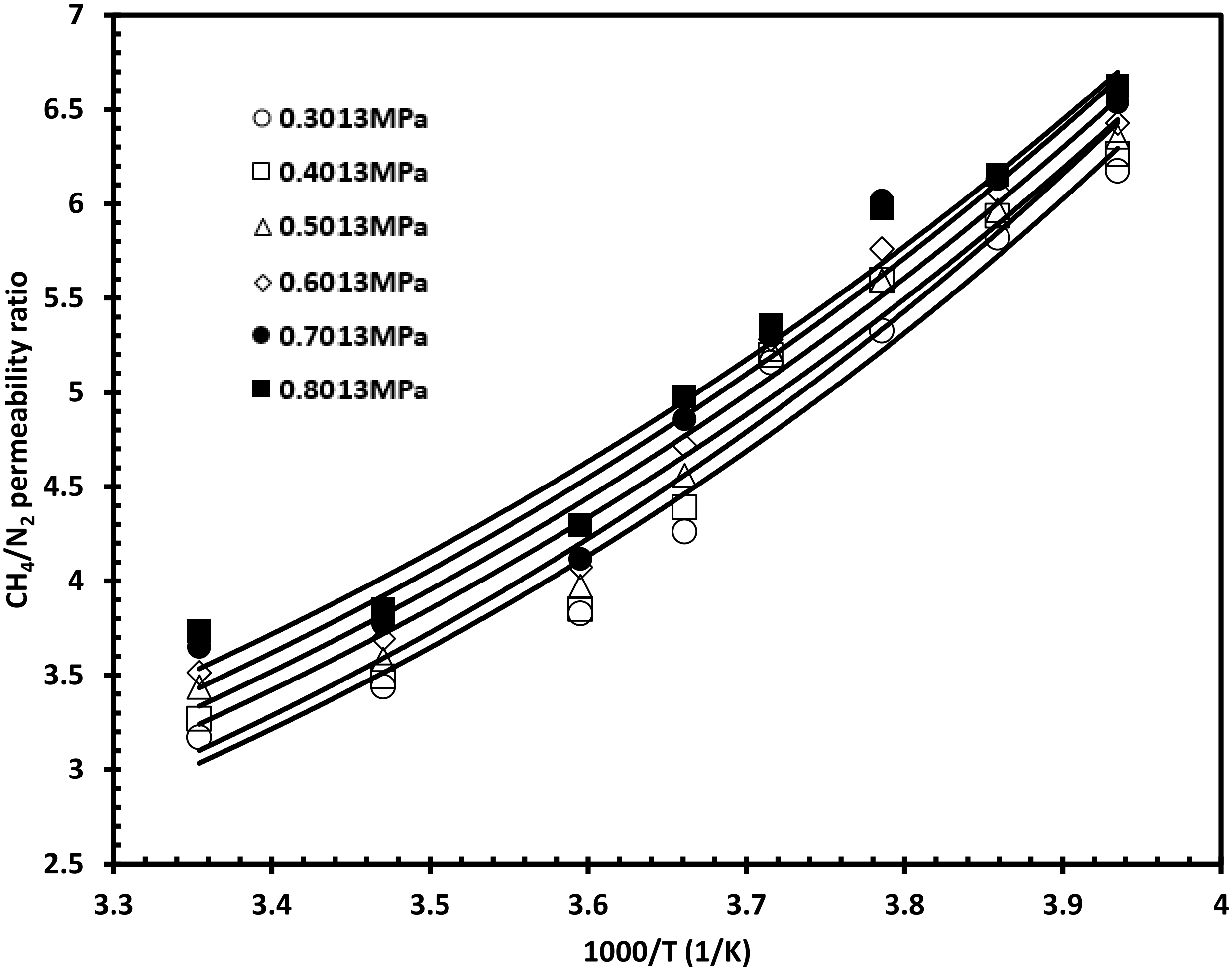

Figure B.24 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=50/50 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute

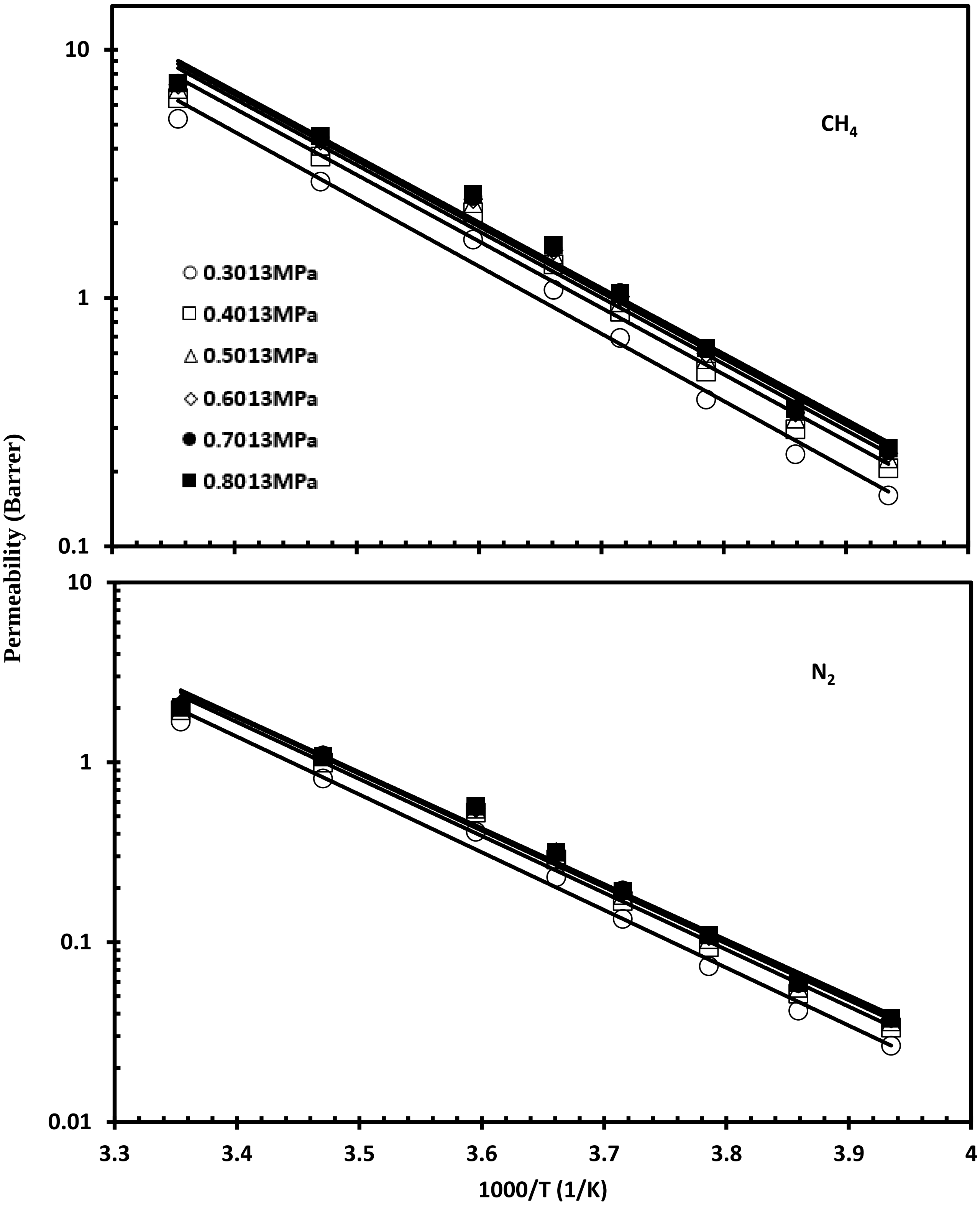

Figure B.25 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=37.5/62.5 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

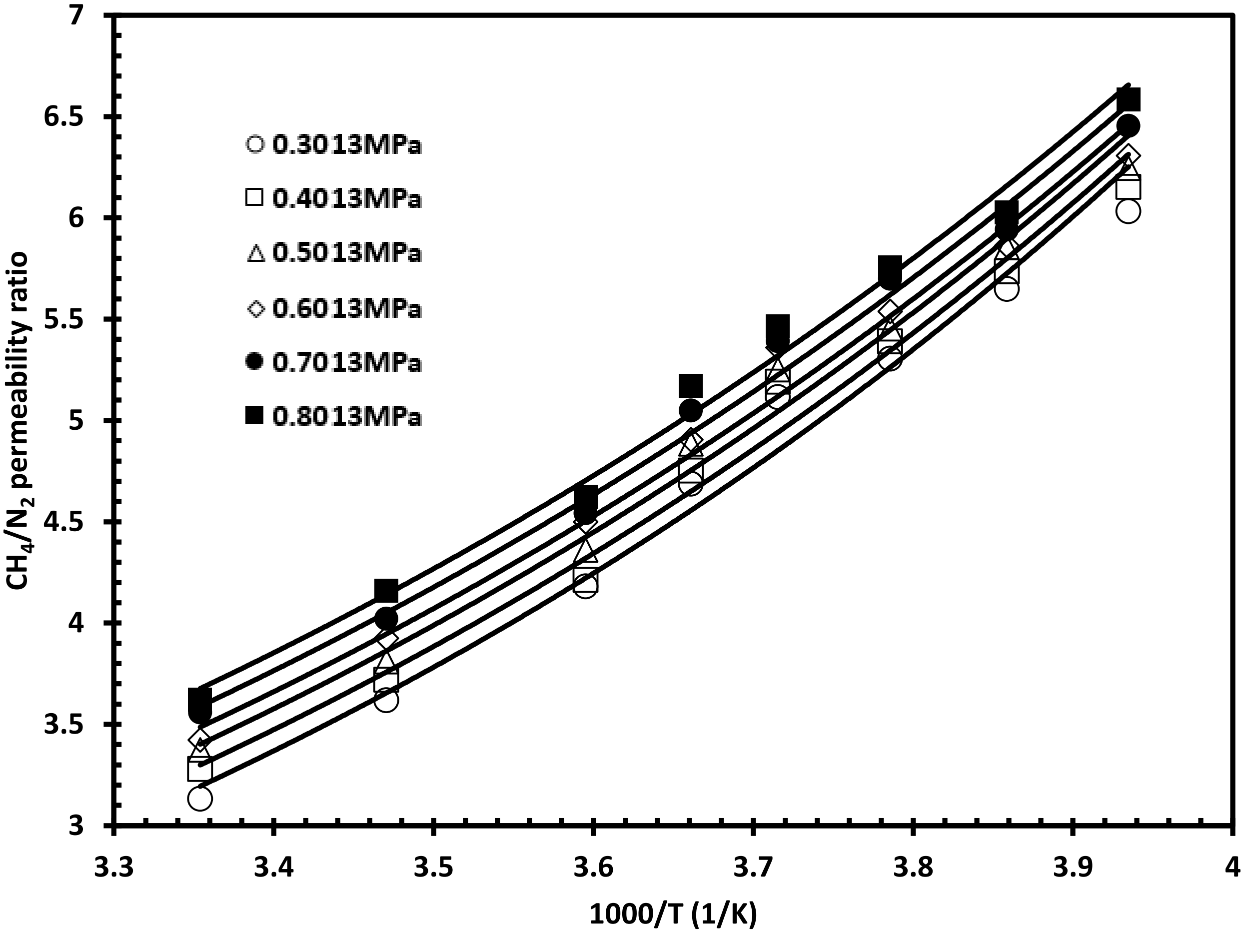

Figure B.26 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=37.5/62.5 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

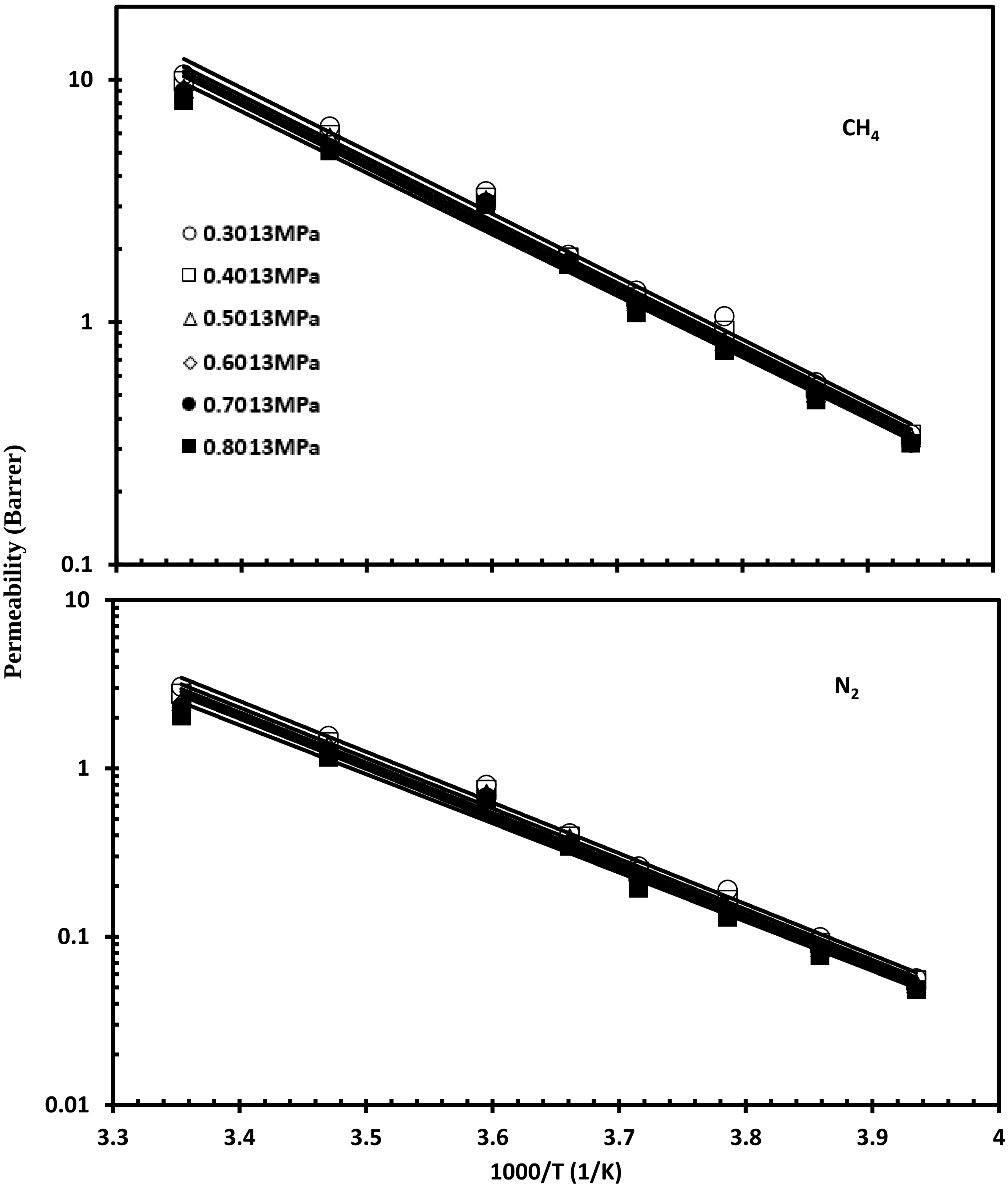

Figure B.27 Effect of temperature on the permeability of the gases permeate through PEBA 2533/1074=25/75 membrane. Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute

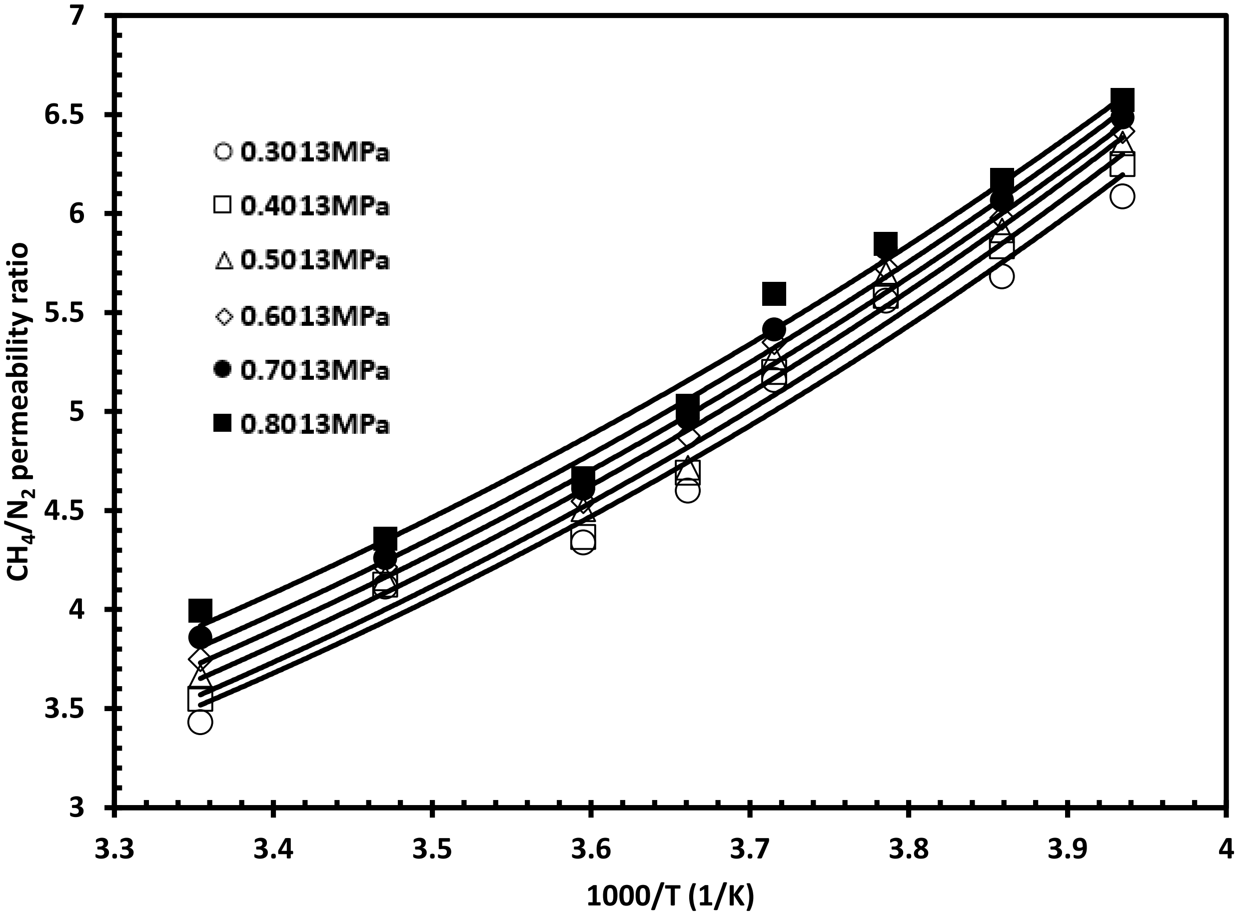

Figure B.26 Effect of temperature on the CH_4/N_2 permeability ratio for PEBA 2533/1074=25/75 membrane. . Note the applying pressure varies from 0.3013 to 0.8013 MPa absolute.

B.4 Binary Gas Permeation Tests with PEBA 2533/1074=50/50 Blend Membrane

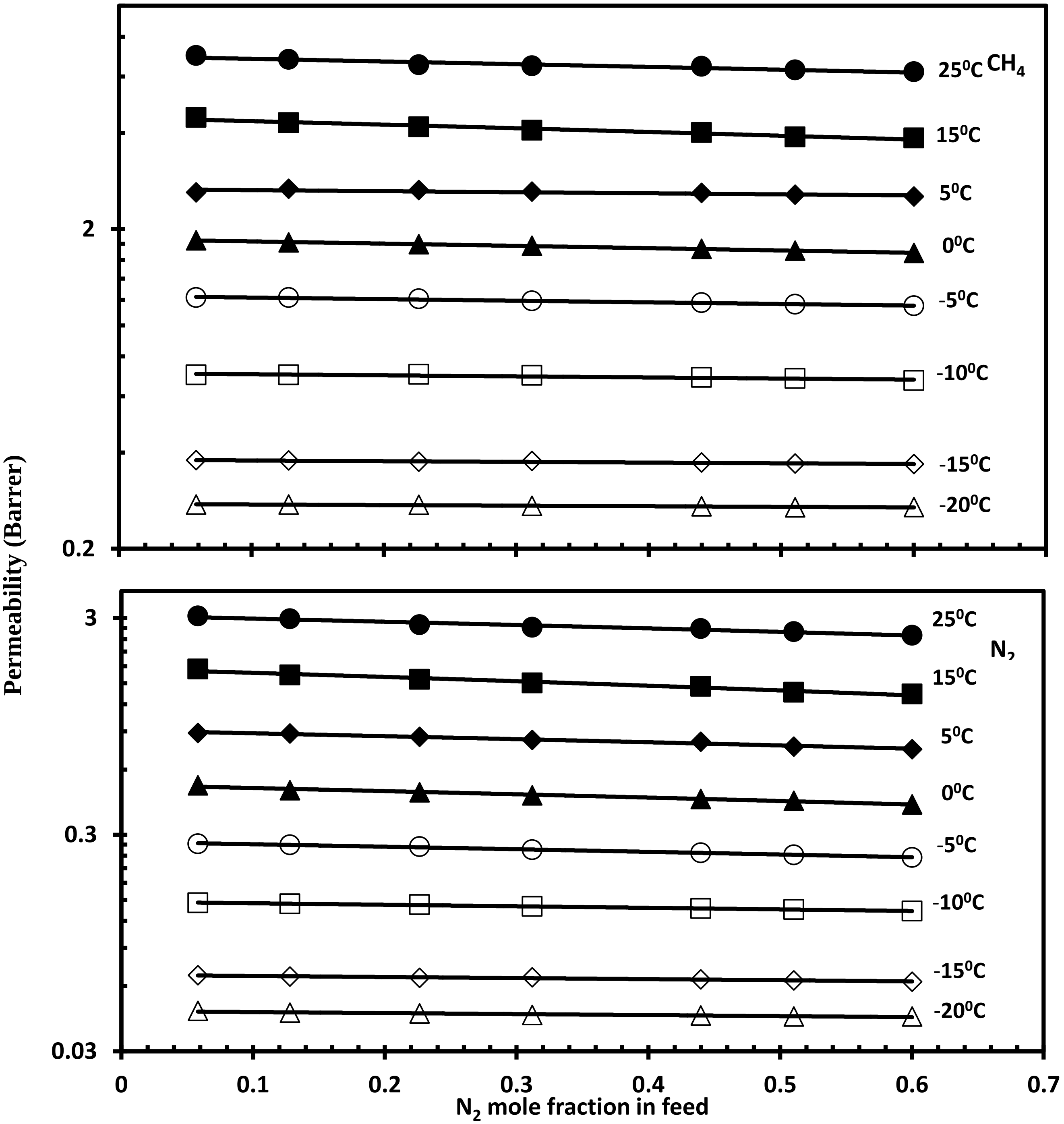

Figure B.27 Effect of N_2 mole fraction in feed on the permeability of the gases permeate through PEBA 2533/1074=50/50 membrane in binary system. Note the applying pressure is 0.7013 MPa absolute, temperature varies from 25⁰C to -20⁰C.

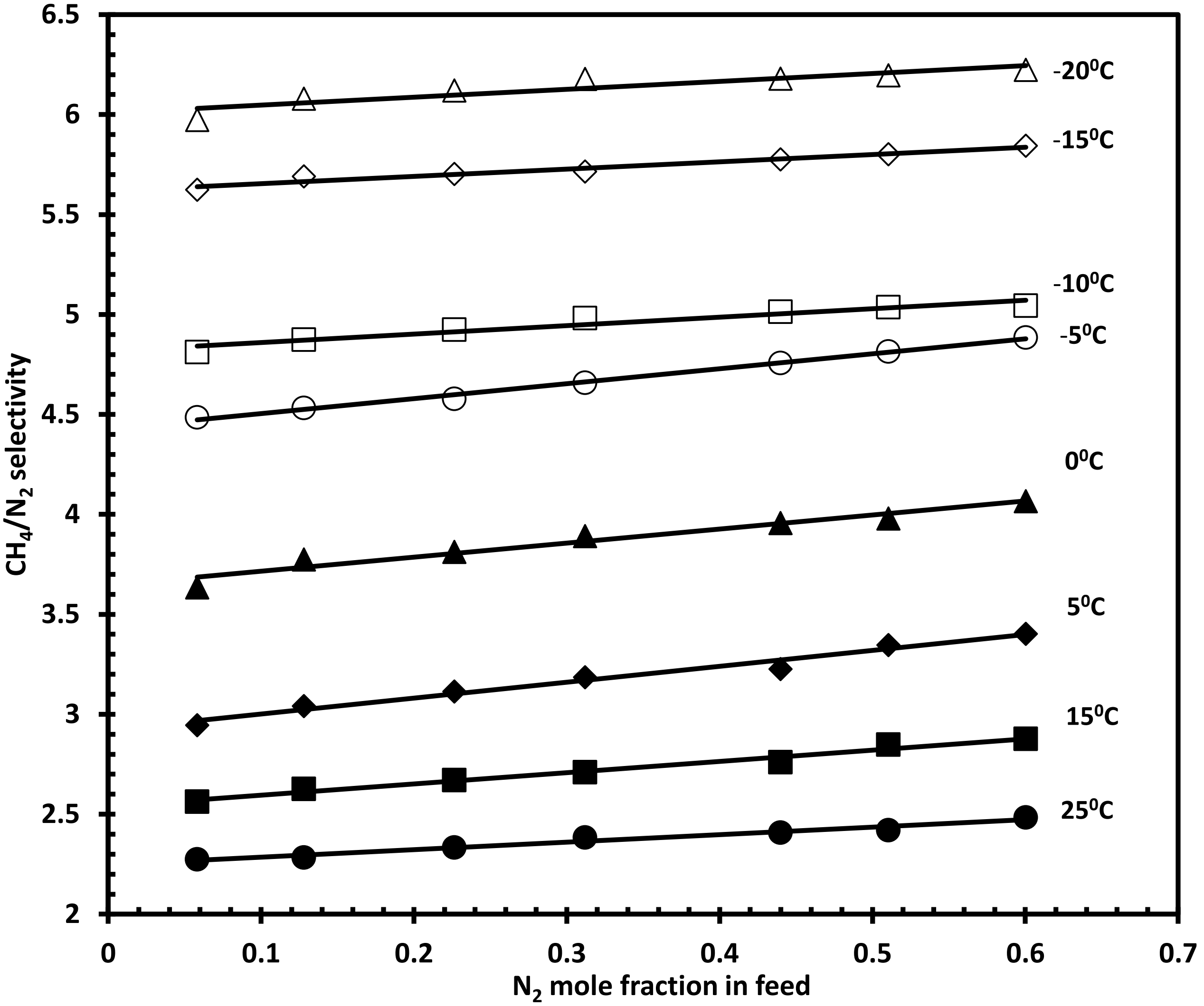

Figure B.28 Effect of N_2 mole fraction in feed on CH_4/N_2 selectivity of PEBA 2533/1074=50/50 membrane in binary system. Note the applying pressure is 0.7013 MPa absolute, temperature varies from 25^0C to -20^0C.