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Silicone-coated polymeric membrane for separation of hydrocarbons and nitrogen at sub-ambient temperatures☆

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Abstract

Permeation performances of pure and mixed nitrogen, ethylene, ethane, propylene and propane were investigated using a polydimethylsiloxane (PDMS) coated polysulfone composite membrane in the temperature range of −20 to 40 °C. The permeances and selectivities strongly depended on the temperature and feed composition at a constant pressure. Propylene and propane plasticized the PDMS coating with decreasing temperature and increasing hydrocarbon concentrations, which led to significantly high permeances for all mixed hydrocarbons. It also caused positive coupling effects for ethane, ethylene and nitrogen in the presence of propylene and propane. Moreover, pure nitrogen permeances or nitrogen permeance as a mixture component always decreased considerably by lowering the temperature. Consequently, all selectivities for the hydrocarbons to nitrogen increased significantly with the decrease of temperature and increase of total hydrocarbon concentration in feed. A systematic analysis of apparent activation energies to verify the experimental results was also presented.

Keywords: Sub-ambient temperature; PDMS; Membrane; Hydrocarbons; Nitrogen

1. Introduction

Membranes made by coating rubbery polymers on polymeric substrates have been used for separating volatile organic compounds (VOC's) from permanent gases in many commercial applications. These processes have recovered high-value hydrocarbons resulting in substantial savings of energy and raw materials. Membrane Technology Research (MTR), USA, GKSS, Germany and Dalian Institute of Chemical Physics (DICP), P.R. China, have successfully implemented many applications in a wide range of industries. These applications for recovering hydrocarbons and recycling permanent gas in the petroleum and polymer industries have mostly operated at sub-ambient temperature by solubility-selective polymeric membranes [1–6]. Currently, PDMS is the most commonly used rubbery membrane material due to its preferential selectivity for hydrocarbons. Its glass transition temperature is the lowest amongst polymers (−129 °C), indicating a very flexible polymer backbone with long-range segmental motion, which is sufficiently active, even at very low temperatures [7,8]. The permeation properties of thick PDMS films have been evaluated in laboratory for the characteristics of various pure gases, hydrocarbons and some hydrocarbons/permanent gas mixtures over a temperature range of 20–95 °C [9–14]. There are very few research articles dealing with the permeation of pure gases and especially gaseous mixtures through ultra thin asymmetric membranes for industrial separation purposes [15]. Recently Jiang and Kumar [16] reported that propylene and propane significantly plasticized the thin PDMS coating on polysulfone membrane at ambient temperature. Pfromm et al. [17] compared asymmetric polysulfone, polycarbonate and poly(ester carbonate)/PDMS membranes with their isotropic films, showing different plasticization and conditioning behavior for CO_2 permeation due to the fact that the skin layer morphology may contain a different distribution of free volume in asymmetric membranes. Wessling et al. [18] found that the plasticization behavior of polyimide/PDMS composite membranes is also thickness-dependent. Pinnau and He [19] recently reported the permeation properties for a multicomponent mixture of hydrogen, methane, ethane, propane and

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n-butane in a 150 m thick, homogenous PDMS film for the temperature range of −20 to 35 °C. The swelling, induced mainly by propane and *n*-butane sorption, significantly influenced the permeabilities and selectivities of each component in the mixture. An increase in penetrant diffusivity was believed to occur from increased polymer local segmental motion caused by the presence of condensable penetrant molecules in the polymer matrix at a constant temperature. As penetrant pressure and, therefore, the penetrant concentration in the polymer increases, the degree of swelling in a polymer matrix increases for those strongly sorbing penetrant, leading to significant increases in selectivities particularly with the decrease of temperature. It is apparent that there are advantages of combining the condensable pretreatment unit running at sub-ambient temperatures with membrane modules for the removal of extra hydrocarbons from feed gas. This approach could take the benefits of increased permeance and selectivity of hydrocarbons to reduce the required membrane-area for the separation process. Moreover, residual gas could also be maintained at the pressure for recycling to the system. However, there is no published literature on the permeances and selectivities of C_2 and C_3 hydrocarbons and nitrogen mixtures using the thin silicone coated polysulfone composite membranes at sub-ambient temperatures for designing such a process. The present work for the first time reports permeation performances of lower hydrocarbons such as ethylene, ethane, propylene and propane from lean binary, ternary and quaternary mixtures in nitrogen through composite PDMS–polysulfone membrane at a temperature range of −20–40 °C.

2. Experimental

2.1. Materials

A flat sheet PDMS–polysulfone composite membrane described in our earlier work [16] was used for pure and mixed-gas permeation experiment. It consisted of a 0.20 m thick PDMS layer and a highly microporous polysulfone substrate. This composite membrane was cast from a polysulfone—*N*-methyl pyrrolidone (NMP) solution by gelation in cold water. The purities of nitrogen, oxygen, ethylene, ethane, propylene and propane used in our experiments were at least 99.8%.

2.2. Permeation measurements

The manometric laboratory-scale gas permeation apparatus was adapted from the previous work [16]. In addition to the usual gas metering, mixing and pressurizing equipment, this apparatus had a refrigerated/heated circulating bath to maintain a desired operating temperature for the immersed membrane cell. The setting for the fluid bath was selected to achieve the desired temperature in the membrane cell for gas permeation. To ensure a steady state for each temperature setting, the apparatus was allowed to run for sufficient time (up to 48 h) before the data collection was started. A round membrane sheet with an effective membrane area of 1.03×10^{-3} m^2 was used in all experiments. A desired composition of hydrocarbon and nitrogen in feed mixtures was achieved by setting appropriate ratios in mass flow controllers. An on-line Hewlett-Packard 6890 Gas Chromatograph equipped with a thermal conductivity detector, a sample injector (6-port valve) and capillary column was used to determine the composition of permeate stream. All pressures, temperatures and flow rates were also measured precisely by on-line pressure transducers, thermocouples and mass flow meters, respectively.

The membrane performances were characterized in terms of permeance (pressure normalized flux) and selectivity [20,21] and the permeance was presented as GPU in this work (1 GPU = 10^{-5} m^3 (STP)/m^2 s Pa = 10^{-6} cm^3 (STP)/cm^2 s cmHg). In pure gas experiments, permeance was determined by pressure difference between feed and permeate, however, the permeance of each component in the mixture was calculated at a given partial pressure difference over feed to permeate at a constant total pressure of feed gas. The selectivity was defined as the ratio of the permeances of an individual hydrocarbon over nitrogen measured in a mixture simultaneously. The steady state was assumed when the variations in temperature, pressure, flow rate and permeate composition for a selected experimental condition were less than 0.5%. Feed gas flow along the membrane was maintained at a minimum of 8.3×10^{-5} N m^3/s in all mixed-gas permeation experiments, therefore, concentration polarization effects adjacent to membrane surface and the concentration difference between feed and reject gases were minimized. All concentration units were molecular percentages (mol%). Absolute feed pressures were maintained at 390 ± 5 kPa while permeate pressures for both pure and mixed gases were atmospheric. The experiments were performed over a temperature range of −20 to 40 °C.

3. Results and discussion

3.1. Pure gases

Fig. 1 shows the permeances of nitrogen, ethylene, ethane, propylene and propane as a function of reciprocal temperature over a temperature range of −14 to 23 °C at a pressure difference of 133 kPa. For the entire temperature range of study, the highest

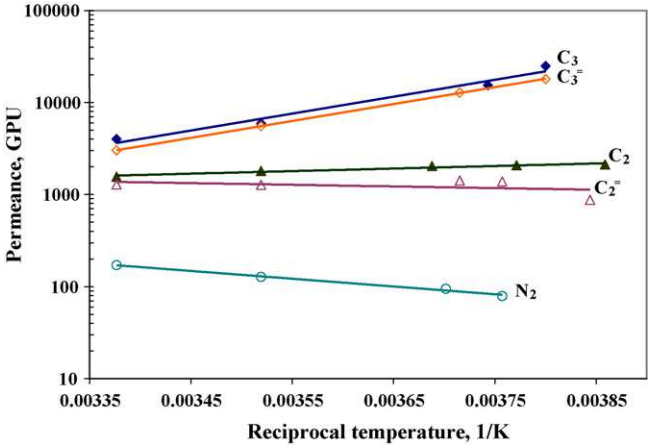

Fig. 1. Effects of temperature on pure gas permeance at a pressure difference of 133 kPa for nitrogen, ethylene, ethane, propylene and propane.

Table 1
Pure gas selectivities and the comparison with a gas mixture at different temperatures

Temp. (°C)	Pure gas selectivity				Pure gas selectivity/mixture selectivity in Fig. 4		
	$C_2^=$	C_2	$C_3^=$	C_3	$C_2^=$	$C_3^=$	C_3
23	7.2	9.0	17.5	23.2	1.0	1.5	1.8
0	12.4	19.7	105.5	126.3	1.16	5.9	6.0
−10	15.1	27.5	235.2	327.1	1.17	10.8	11.9

ratios of propylene and propane pressures to their saturated pressures were 0.3 and 0.39, respectively. It is clear from this figure that permeances of nitrogen and ethylene decreased gradually while permeances of propylene and propane increased significantly with decreasing temperatures. Observed ethane permeances increased only slightly. The apparent activation energies of nitrogen, ethylene, ethane, propylene and propane, calculated from the slopes of Arrhenius plots, were 16.2, 3.5, −5.6, −35.2 and −35.4 kJ/mol, respectively. As a result, the selectivities of hydrocarbons to nitrogen increased significantly as the temperature decreased (see Table 1). In addition, the permeances of various gases as a function of pressure difference at −10 °C (Fig. 2) illustrate that an increase in pressure did not change the permeances of nitrogen, ethylene and ethane significantly whereas the permeances of propylene and propane increased considerably in this pressure range. It could be concluded that permeances of all gases except ethane strongly depended on temperature at a constant pressure difference, however, only propylene and propane depended on the pressure difference at a constant temperature. It appears that the permeations of nitrogen and ethylene remained diffusion-dominant, representing hydrostatic compressive effects which at least did not increase the free volume of the polymer at such a low operating pressure [22]. Conversely, all of the propylene and propane as plasticizing agents contributed to the swelling of the polymer matrix, which caused substantial increase in the degree of swelling with the decrease of temperature due to the temperature dependence of sorption as well as the increase of pressure difference as a result of their higher concentration in the polymer matrix. As mentioned above, however, ethane exhibited a subtle balance between sorption and diffusion in the polymer matrix, thereby maintaining a stable permeance as temperature and pressure difference were varied. Similar observations for the permeabilities of propane, ethane, ethylene and nitrogen have been reported by Stern et al. [23] in 12 different silicone polymer membranes at varying pressure differences and temperatures, and propane diffusion coefficients in some silicone polymer membranes decreased with the decrease of temperature and increased with its increasing concentration in membrane at a constant temperature. This supported the analysis above that increasing solubilities can offset decreasing diffusivities with a result that temperature reduction also can enhance mobilities leading to improved permeation in a swollen polymer membrane. Pinnau and He [19] also reported similar behavior for hydrogen, methane, ethane and propane in a 150 m thick, unfilled, isotropic PDMS film, where reported apparent activation energies were 13.8, 7.1, −5.0 and −30.1 kJ/mol at a pressure difference of 323 kPa over a temperature range of −20 to 35 °C, respectively. Incidentally, these activation energy values were comparable with our work.

4. Gas mixtures

4.1. Effects of temperature on permeance and selectivity

Figs. 3 and 4 show permeances and selectivities for a mixture consisting of nitrogen 80%, ethylene 5%, propylene 7.5%, and propane 7.5% over a temperature range of −20 to 40 °C at a total pressure of 385 kPa (a). The fractions of partial pressure in feed to saturated pressure for propylene and propane at

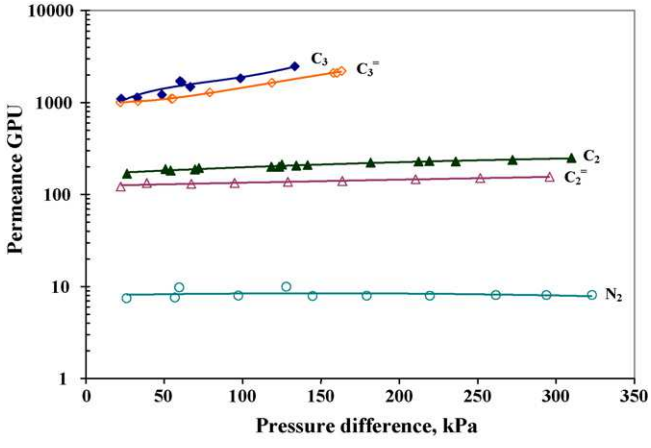

Fig. 2. Effects of pressure difference on permeance of nitrogen, ethylene, ethane, propylene and propane at −10 °C.

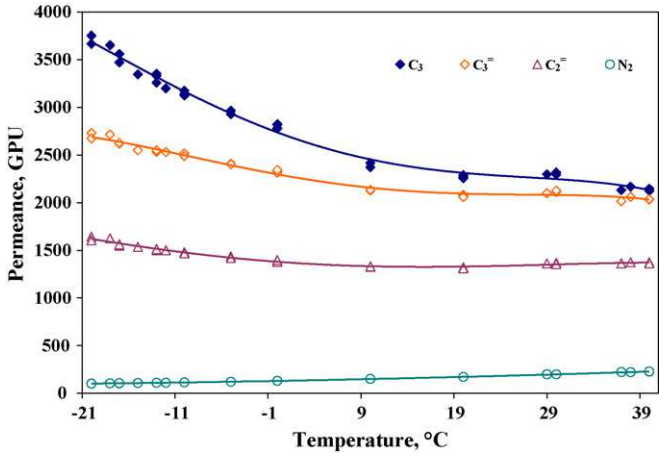

Fig. 3. Effects of temperature on mixed-gas permeance. Feed composition: 80% nitrogen, 5% ethylene, 7.5% propylene and 7.5% propane; feed pressure: 385 kPa; permeate pressure: 101.3 kPa; the stage cuts <0.8%.

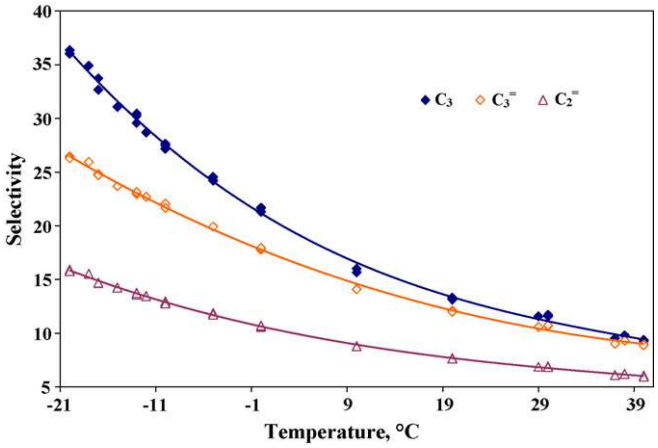

Fig. 4. Effects of temperature on mixed-gas selectivity. (Test conditions were the same as those given in Fig. 3.)

−20 °C were 0.09 and 0.12 in this gas mixture, respectively. The stage cuts were maintained below 0.8%. It is apparent from Fig. 3 that the permeances of all hydrocarbons in the mixture increased as the temperature was decreased, particularly below 0 °C. Nitrogen permeances still decreased with the decrease of temperature as in the case of pure gas. It is interesting to note that ethylene exhibited the opposite permeation behavior in the presence of C_3 components compared to its pure state at varying temperature, whereas the permeances of ethylene remained nearly constant above 0 °C and tended to increase below 0 °C. In addition, the permeance values of ethylene and nitrogen were higher than those obtained for pure gases; for example, the permeances of ethylene and nitrogen in the mixture were 1451.3 and 123.0 GPU instead of 1381.0 and 79.3 GPU at −7 °C as single gases, respectively. Therefore, it could be said that propylene and propane strongly swelled the PDMS coating particularly at lower temperatures, resulting in improved permeances due to simultaneous increases in their solubilities and diffusivities in PDMS. The degree of swelling was enhanced with decreasing temperature to such an extent that it led to a new configuration in polymer matrix where the permeances of ethylene and nitrogen were affected positively: nitrogen still retained diffusion-dominated permeation characteristics but its diffusivity was elevated over the entire temperature range. This proved that the sorption level of nitrogen still was minimal. However, both solubility and diffusivity of ethylene might be elevated. Another explanation by Kamaruddin and Koros [24] for ethylene permeation was that the bulk flux through the membrane could take place for a weakly sorbed penetrant due to a so-called "frame of reference" effect, therefore, contributing to an apparent increased permeances particularly below 0 °C. This permeation behavior is also reflected in the values of apparent activation energies (nitrogen 9.0 kJ/mol, ethylene −1.7 kJ/mol, propylene −3.1 kJ/mol and propane −6.0 kJ/mol) defined as the sum of the activation energy of diffusion, E_d, and the heat of sorption, H_s [25], whereas E_d is always positive in an activated diffusion process. As a result, the selectivities of all hydrocarbons to nitrogen increased significantly with the decrease in temperature. For example, the selectivities of ethylene, propylene and propane increased 165, 198 and 288%, respectively as the temperature was decreased from 40 to −20 °C. However, the selectivities for mixed gases were lower than those for individually measured pure gases. It is clear from Table 1 that ethylene selectivities to nitrogen in pure as well as in the mixture were comparable along the entire temperature range due to the fact that both permeances were elevated in the mixture relative to their pure gas values, which matches the results for the selectivity of ethane over hydrogen in a mixture of hydrogen, methane, ethane, propane and *n*-butane through a 150 m thick, homogenous PDMS film [19]. Furthermore, the selectivities for propylene and propane over nitrogen in the mixture were significantly lower than those in pure state, which were caused by not only significant decrease of permeances for propylene and propane but also the increase of permeances for nitrogen in the mixture based on their pure states. This is different from the decrease in selectivity for propane over hydrogen in a mixture mentioned above, which only resulted from an increase in the mixed-gas hydrogen permeability relative to that measured with pure hydrogen [19]. It could be suggested that different plasticization behavior were perhaps shown in thin PDMS coating supported by an asymmetric substrate at this concentration level. Recently Lin et al. [26] reported another plasticization—enhanced membrane gas separation using poly(ethylene glycol)diacrylate and poly(ethylene glycol)methyl ether acrylate network copolymer.

4.2. Comparison of permeance and selectivity for various mixtures with temperature at constant concentrations

As discussed above, propylene and propane swell the flexible-chain of the PDMS coating. The degree of swelling depends on

Table 2
Mixture name and apparent activation energy

Name	Composition	Apparent activation energy (kJ/mol)				
		N_2	$C_2^=$	C_2	$C_3^=$	C_3
$C_2^=$ binary	8% $C_2^=$, 92% N_2	13.1	7.7			
C_2 binary	8% C_2, 92% N_2	12.2		2.7		
C_2 ternary	8% $C_2^=$, 8% C_2, 84% N_2	10.0	3.6	1.8		
$C_3^=$ binary	8% $C_3^=$, 92% N_2	11.2			−1.0	
C_3 binary	8% C_3, 92% N_2	9.9				−1.9
C_3 ternary	8% $C_3^=$, 8% C_3, 84% N_2	8.1			−2.7	−5.5
$C_2^=$ quaternary	8% $C_2^=$, 8% $C_3^=$, 8% C_3, 76% N_2	7.9	−3.4		−5.5	−8.1
C_2 quaternary	8% C_2, 8% $C_3^=$, 8% C_3, 76% N_2	8.4		−5.3	−5.7	−8.2

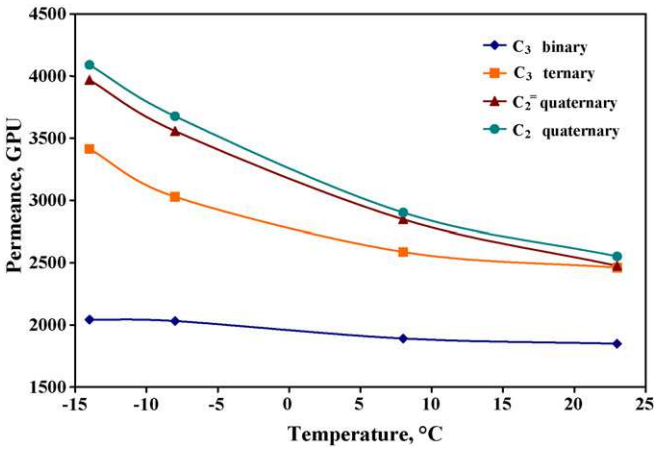

Fig. 5. Comparison of propane permeance in C_3 binary, C_3 ternary, $C_2^=$ quaternary and C_2 quaternary mixtures as a function of temperature. Feed composition as listed in Table 2; feed pressure: 390 ± 5 kPa; permeate pressure: 101.3 kPa; the stage cuts <0.9%.

the sorption level, which is influenced by temperature. Positive coupling effect is associated simultaneously for permanent and/or weakly condensable gases. In order to further investigate the interaction with the membrane, the permeation experiments were conducted with eight different gas mixtures as shown in Table 2 over a temperature range of −14 to 23 °C. Individual hydrocarbon concentration was 8% in each mixture. Total pressure was 390 ± 5 kPa (a). The stage cuts were maintained below 0.9%. Figs. 5 and 6 show the permeances of propane and propylene in five different mixtures. Propane permeances in C_3 binary mixture increased only slightly (10.5%) from 23 to −14 °C. At 23 °C, propane permeances in C_3 ternary, $C_2^=$ quaternary and C_2 quaternary mixtures were almost equal, which were approximately 1.3-fold higher than that in C_3 binary mixture. Furthermore, lowering the temperature led to significant increases for propane permeances in these three mixtures. For example, propane permeances in C_3 ternary, $C_2^=$ quaternary and C_2 quaternary mixtures were 1.7-, 1.9- and 2.0-fold higher than that in C_3 binary mixture at −14 °C, respectively. Similarly, propylene permeances in $C_3^=$ binary mixture increased 6.6% from 23 to −14 °C. Propylene permeances in $C_3^=$ ternary, $C_2^=$ quaternary and C_2 quaternary mixtures were 1.2-, 1.3- and 1.3-fold higher than that in $C_3^=$ binary mixture at 23 °C as well as 1.3-, 1.7- and 1.7-fold higher than that in $C_3^=$ binary mixture at −14 °C, respectively. The variations for propane were greater than those for propylene, showing that solubility-dominated permeation performance depended on the size of hydrocarbon over the entire experimental temperatures [16]. Particularly, the increases in the permeances of propylene and propane in $C_2^=$ quaternary and C_2 quaternary mixtures, whose values were comparable, were even stronger than those in C_3 ternary mixture. Jordan and Koros [22] reported that gas permeabilities in silicone polymers show a trend similar to their mobilities. Furthermore, decreasing temperature diminishes gas permeability due to decreased diffusivity, which is caused by depression of polymer chain mobility [26]. In contrast, our data mentioned above represent that decreasing temperature does not essentially decrease the permeances of propylene and propane particularly at higher total hydrocarbon concentration. Same experimental observations were obtained in the PDMS film for a mixture of hydrogen, methane, ethane, propane and *n*-butane as well as *n*-butane–methane binary mixture [19], and also in the poly(ethylene glycol)diacrylate and poly(ethylene glycol)methyl ether acrylate film for a mixture of hydrogen and carbon dioxide [26]. Therefore, it appears that both propylene and/or propane-induced swelling of PDMS coating caused by increased C_3 sorption would increase significantly by lowering temperature, resulting in a process of loosening the matrix by shifting of relatively short polymer chain segments. Furthermore, long chain rearrangements, made possible by loosening more densely packed entanglements, occur due to C_2 molecule entrapment in the polymer matrix [27]. In this new configuration, not only the diffusivities of propylene and propane might be further improved, but also the diffusivity of either ethylene or ethane could be enhanced adequately, which resulted in opposite behavior to the diffusion-dominated permeation performance with temperature. Of course, the bulk fluxes of ethylene and ethane could not be excluded from permeance contributions in a swollen membrane at a lower temperature due to the variations of diffusivities [24]. Therefore, it can be seen from Figs. 7 and 8 that ethylene or ethane permeances in the presence of C_3 components ($C_2^=$ quaternary and C_2 quaternary mixtures) were apparently higher than those in the mixture without C_3 components ($C_2^=$ binary, C_2 binary and C_2 ternary mixtures), tending to increase with the decrease of the temperature. However, the permeances of ethylene and ethane in $C_2^=$ binary, C_2 binary and C_2 ternary mixtures decreased obviously with the decrease of the temperature. Moreover, ethane permeances in C_2 ternary mixture were higher than those in C_2 binary mixture over the temperature range studied, concluding that ethane permeances could also be enhanced in the presence of ethylene due to its soluble nature. In addition, ethylene permeance in C_2 ternary mixture was lower than that in $C_2^=$ binary mixture at 23 °C, indicating that diffusion competition between ethylene and ethane might take place for the limited activated sites especially as both diffusivities were comparable. However, all nitrogen permeances in individual

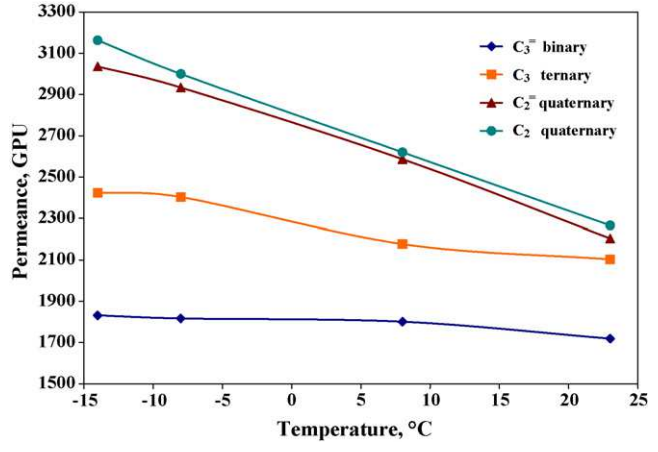

Fig. 6. Comparison of propylene permeance in $C_3^=$ binary, C_3 ternary, $C_2^=$quaternary and C_2 quaternary mixtures as a function of temperature. (Test conditions were the same as those given in Fig. 5.)

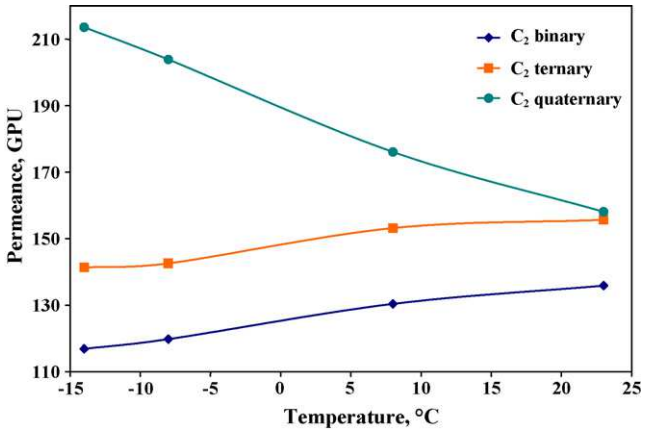

Fig. 7. Comparison of ethane permeance in C_2 binary, C_2 ternary and C_2 quaternary mixtures as a function of temperature. (Test conditions were the same as those given in Fig. 5.)

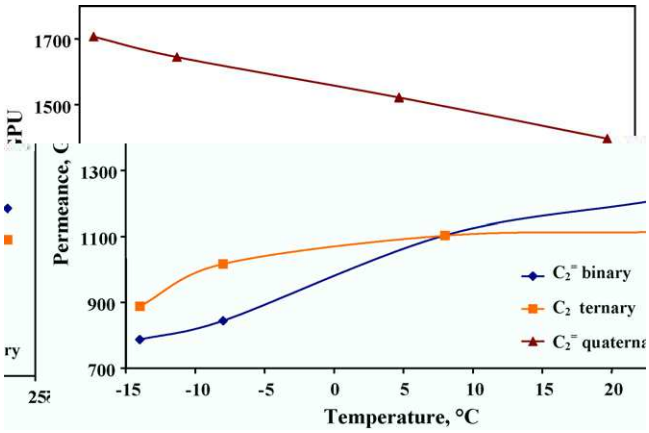

Fig. 8. Comparison of ethylene permeance in $C_2^=$ binary, C_2 ternary and $C_2^=$ quaternary mixtures as a function of temperature. (Test conditions were the same as those given in Fig. 5.)

mixture decreased considerably with the decrease of temperature as shown in Fig. 3 due to the temperature dependence of diffusivity in any configuration of polymer matrix. Apparent activation energies listed in Table 2 can support the above analysis from another angle. Consequently all selectivities of hydrocarbon to nitrogen increased significantly by lowering the temperature (see Tables 3 and 4).

4.3. Effects of composition on permeance and selectivity at −14 °C

It is known that the degree of swelling also depends on hydrocarbon concentration in feed related to its partial pressure at a constant operating pressure and temperature [16,19]. Figs. 9 and 10 demonstrate the effect of increasing total hydrocarbon concentration in feed on permeances and selectivities at −14 °C and 385 kPa (a) for two mixtures. The multicomponent mixture consisted of ethylene, propylene, propane and nitrogen, and the binary mixture contained ethylene and nitrogen, whereas the concentrations of individual hydrocarbons in the mixture were equal. The stage cuts were less than 0.6% in all experiments. The maximum fractions of partial pressure in feed to saturated pressure in the case of multicomponent mixture for propylene and propane were 0.09 and 0.11, respectively. It is clear from Fig. 9 that the permeances of either condensable or permanent gases in the multicomponent mixture increased significantly with the increase of total hydrocarbon concentration in feed. For example, when total hydrocarbon concentration in feed was increased from 5.5 to 24.9%, the permeances of propane, propylene, ethylene and nitrogen were increased by 106, 111, 63 and 16%, respectively. It was observed that the increases in permeances for hydrocarbons were greater than that for nitrogen at same total hydrocarbon concentration in feed. Therefore, it led to significant increases of selectivities by 78, 82 and 60%, respectively (Fig. 10). Moreover in the $C_2^=$–N_2 binary mixture, ethylene permeances increased only 22.4% but nitrogen permeances almost remained constant from 4.8 to 25.7% total hydrocarbon concentration in feed whereas ethylene selectivities

Table 3
The selectivities of ethylene and ethane

Temp. (°C)	Ethylene			Ethane		
	$C_2^=$ binary	C_2 ternary	$C_2^=$ quaternary	C_2 binary	C_2 ternary	C_2 quaternary
23	6.6	6.5	8.1	7.7	9.1	8.5
8	8.0	7.6	10.4	9.4	10.6	11.9
−8	8.1	8.8	13.6	11.3	12.4	16.2
−14	9.5	10.0	15.7	13.8	16.0	19.2

Table 4
The selectivities of propylene and propane

Temp. (°C)	Propylene				Propane			
	$C_3^=$ binary	C_3 ternary	$C_2^=$ quaternary	C_2 quaternary	C_3 binary	C_3 ternary	$C_2^=$ quaternary	C_2 quaternary
23	9.4	11.1	12.8	12.2	9.9	13.0	14.3	13.7
8	11.5	14.3	17.6	17.7	12.4	17.0	19.4	19.6
−8	16.8	18.6	24.2	23.8	18.0	23.5	29.4	29.2
−14	18.7	20.7	27.9	28.5	18.9	29.2	36.5	36.8

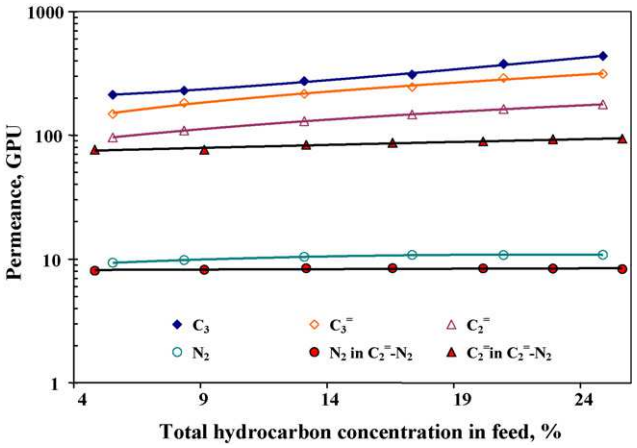

Fig. 9. Mixed-gas permeance as a function of composition at a constant temperature of −14 °C. Feed composition: increasing equal ethylene, propylene and propane concentrations; feed pressure: 385 kPa; permeate pressure: 101.3 kPa; the stage cuts <0.6%.

in the binary mixture still increased by 19.5%. However, both ethylene and nitrogen permeances were considerably lower than those in the multicomponent mixture at the same experimental condition. The selelvtivities, therefore, were lower than those in the multicomponent mixture. For example, ethylene selectivities in the multicomponent mixture were 1.1- and 1.5-fold higher than those in the binary mixture at 5.5 and 24.9% total hydrocarbon feed concentration whereas ethylene partial pressure in the multicomponent mixture was one-third of the value in binary mixture. The PDMS coating was plasticized obviously by increasing propylene and propane concentrations even at lower temperature, resulting in the positive coupling effect for ethylene and nitrogen. It can be concluded that the swelling effect dominates the permeation behavior in the mixture containing higher condensable gases, whereas the degree of swelling could have been impacted adequately by condensable gas concentration in feed. Hydrostatic compressive effect predominately influences penetrant mobility in a polymer for weakly condensable permanent gas mixture. Another example of PDMS film with elevating pressure at 35 °C by Jordan and Koros [22] supports this hypothesis. Nitrogen permeability in the 10:90 CO_2/N_2 mixture was slightly increased due to CO_2 plasticization while in a 50:50 CO_2/N_2 mixture it was higher than the pure gas values and increased with increasing pressure, showing that the swelling nature of CO_2 was able to offset nitrogen's pressurizing effect. Therefore, it demonstrated that hydrostatic compressive control could transfer to swelling control with the increase of partial pressure of CO_2 in feed.

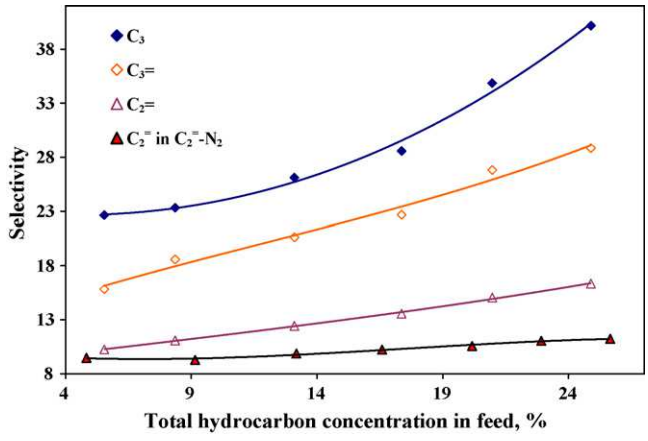

Fig. 10. Mixed-gas selectivity as a function of composition at a constant temperature of −14 °C. (Test conditions were the same as those given in Fig. 9.)

4.4. Effects of concentration in feed on apparent activation energy

The apparent activation energy depends on the physical properties of the penetrants, chemical structure of the polymer and physical properties of polymer matrix. Therefore, apparent activation energy as a function of the feed concentration can illustrate gas permeation behavior in a polymer matrix. Fig. 11 presents ethylene, ethane, propylene and propane in their binary mixtures with nitrogen at a constant pressure of 390 ± 5 kPa over a temperature range of −14 to 23 °C. All stage cuts were less than 0.9%. It can be found explicitly that the apparent activation energy indicated penetrant interaction with the polymer membrane. For example, the apparent activation energies of propylene and propane were negative, demonstrating that they were in an activated sorption process. Moreover, the apparent activation energy of propane was always less than that of propylene at same feed concentration; hence, propane was presumably more effective in loosening the polymer chains for a sorptional uptake. For propylene and propane, relatively less energy might be required with the increase in the degree of swelling, showing that apparent activation energy decreased significantly with the increase of the feed concentration. However, ethane and ethylene were in an activated diffusion process due to their positive apparent activation energies. The apparent activation energy of ethane was always less than that of ethylene at same feed concentration, resulting from the portion of the negative heat of sorption. Consequently, a decreasing apparent activation energy

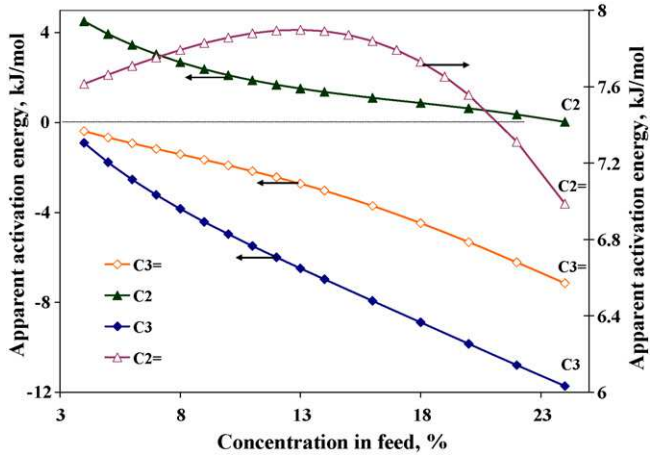

Fig. 11. Apparent activation energy as a function of concentration in feed for $C_2^=$–N_2, C_2–N_2, $C_3^=$–N_2 and C_3–N_2 mixtures at a constant pressure over a temperature range of 23 ∼ −14 °C. Feed pressure: 390 ± 5 kPa; permeate pressure: 101.3 kPa; the stage cuts <0.9%.

with an increasing feed concentration proved that the polymer matrix could already be loosened by ethane even at a lower concentration in feed, thereby, less energy was needed with its increasing concentration in feed for bending of chains in order to create new void volume [27]. This agrees with our experimental results of pure and mixed ethane except for the cases where C_3 components were present. It was interesting to note that ethylene showed a convex response to the apparent activation energies with the increasing feed concentration. Maximum apparent activation energy was at 13% ethylene feed concentration. It can be concluded that more energy was required to shift polymer chains for a diffusional jump at lower ethylene feed concentration. In the ethylene–nitrogen mixture, assuming that there was no swelling in the polymer matrix, the permeation could be based only on their diffusional characteristics.

5. Conclusion

It was concluded that the permeances and selectivities of a PDMS coated polysulfone composite membrane strongly depended on the temperature and feed composition at a constant pressure for most pure and mixed nitrogen, ethylene, ethane, propylene and propane gases. The permeances of propylene and propane in both pure and mixed states increased significantly with decreasing temperature and increasing concentrations in the feed due to C_3-induced swelling of PDMS coating, which caused loosening of the matrix by shifting short polymer chain segments. Possibly long chain rearrangements loosened more densely packed entanglements might have occurred by means of C_2 molecule entrapment in polymer matrix, which led to significant increases in the permeances for ethylene and/or ethane with this increasing degree of swelling. It also caused positive coupling effects for ethane, ethylene and nitrogen in the presence of propylene and propane. Moreover, pure nitrogen permeances or nitrogen permeances as a mixture component always decreased considerably by lowering the temperature. Consequently, all selectivities for the hydrocarbons to nitrogen increased significantly with the decrease of temperature and increase of total hydrocarbon concentration in feed. It was also concluded that relatively less apparent activation energies were required at higher hydrocarbon concentrations due to the increased degree of swelling.

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