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Performance of silicone-coated polymeric membrane in separation of hydrocarbons and nitrogen mixtures[☆]

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Abstract

This study reports selectivities and permeances of pure nitrogen, oxygen, ethylene, ethane, propylene and propane and their mixtures through composite poly(dimethylsiloxane) (PDMS)–polysulfone membrane at ambient temperature. It was observed that both propylene and/or propane significantly plasticized PDMS coating in pure as well as mixed gas permeation experiments. Above the plasticization pressure, the permeance order was $P_{C_3} > P_{C_3^=} > P_{C_2} > P_{C_2^=} > P_{O_2} > P_{N_2}$, which matched the solubility order. However, permeance order was changed to $P_{C_3^=} > P_{C_3} > P_{C_2} > P_{C_2^=} > P_{O_2} > P_{N_2}$ below the plasticization pressure, showing that propylene was more permeable than propane. Furthermore, plasticization caused coupling effects for ethylene, ethane and nitrogen in the presence of propylene and propane.

Keywords: Polysulfone; PDMS; Permeance; Selectivity; Membrane; Hydrocarbons; Nitrogen

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1. Introduction

The applications of rubbery polymer-coated membranes for separating volatile organic components (VOCs) from a gas stream have been reported. Various industries are using more than 100 units supplied by Membrane Technology and Research Inc. (MTR), US; GKSS, Germany; and Dalian Institute of Chemical Physics (DICP), China. An average market growth of 8–10% per year has been mentioned for these applications. It has been realized that the membranes are often key separation units resulting in superior high-value products, substantial savings in energy and raw materials. There are possibilities of numerous applications of such processes for recovering hydrocarbons and recycling nitrogen in the petroleum and polymer synthesis industries. More fundamental research has been done to understand the sorption, diffusion and permeation effects of VOCs on the membranes coated with rubbery polymers [1–6]. Among the rubbery polymers, poly(dimethylsiloxane) (PDMS) is a solubility-selective polymer that is more permeable to vapors (condensable) than to gases (non-condensable). Its glass transition temperature is among the lowest values recorded for polymers (−129 °C) indicating a very flexible polymer backbone with long-range segmental motion active event at very low temperatures [7,8]. Many studies of chlorinated and other VOCs/N_2 as well as CO_2/N_2 mixtures through PDMS membranes have been performed [9–12], however, most of the researchers have concentrated on pure component permeations. Merkel et al. [13] reported the permeabilities of pure hydrogen, oxygen, nitrogen, carbon dioxide, methane, ethane, propane and their perflourocarbons through PDMS. They found that there was strong plasticization as propane penetrated the PDMS membrane. An increase in penetrant diffusivity was believed to occur from increased polymer local segmental motion caused by the presence of penetrant molecules in the polymer matrix. As penetrant pressure

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Table 1
Some physical properties of gases and vapors [14]

Gas	Boiling point (101,325 Pa (1 atm = 101,325 Pa))	Critical parameters	
	Temperature (°C)	Temperature (°C)	Volume (cm^3/mol)
Oxygen	−183.1	−118.7	73.0
Nitrogen	−195.9	−147.1	90.0
Ethylene	−103.9	9.5	131.1
Ethane	−88.7	32.0	145.5
Propylene	−47.8	91.6	184.6
Propane	−42.2	96.5	200.0

and, therefore, the penetrant concentration in the polymer increases, the tendency to plasticize a polymer matrix increases particularly for strongly sorbing penetrants. For designing a membrane process to separate a gas mixture, the fundamental permeation parameters of the gases present in the mixture will provide more meaningful data. However, there is a general lack of such data in literature on separation of hydrocarbons from nitrogen. The present work reports the permeation 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 an ambient temperature of 22 °C and a total pressure of 650 kPa (g).

2. Experimental apparatus

The gas permeation apparatus fabricated in our laboratory is a standard constant-pressure permeation design. It comprised of three sections namely feed preparation, membrane cell and data collection. A desired composition and flow rate of a hydrocarbons and nitrogen mixture were produced in the feed preparation section before the membrane cell. There were four mass flow controllers and a readout, which had controls to set a fixed ratio of hydrocarbon/nitrogen mixtures. Three mass flow controllers were rated for 5000 cm^3 (STP)/min of nitrogen equivalent and one for 2000 cm^3 (STP)/min of nitrogen equivalent. The mixture or pure gas was allowed in the ballast volume to prepare constant feed pressure and/or concentration before entering at one end of the membrane cell. The flat sheet membrane with an effective area of 135 cm^2 was evaluated in a stainless SEPA® CF Membrane Cell, supplied by Osmonics Corporation (Minnetonka, MN). Pure gases or mixtures penetrated the membrane in the cell at a desired pressure. The reject gas stream was maintained at nearly the same pressure as feed gas in the cell and was expelled from another end of the SEPA® CF Membrane Cell through a solenoid valve. The data collection section had devices to measure pressures, temperatures and compositions of gas mixtures for feed, reject as well as permeate gas streams. Hewlett-Packard 6890 gas chromatograph equipped with a thermal conductivity detector, a sample injector (six-port valve) and microcapillary column was used to determine the compositions of both permeate and reject streams. The precise thermocouple (type C) and pressure transducer were installed in the feed line. Similarly, temperature, pressure and flow rate in the reject and permeate lines were also recorded. All pressure transducers, mass flow meters and controllers with associated readouts were supplied by MKS Instruments Corporation (Methuen, MA).

3. Materials

Two filler-free composite poly(dimethylsiloxane) membranes labeled as A and B, supplied by different laboratories were used for pure and mixed gas permeation experiments. Membrane A consisted of a highly microporous polysulfone support coated with a 0.20 μm thick PDMS layer. Membrane B consisted of dense homogenous polysulfone support coated with a 0.45 μm thick PDMS layer. They were cast from a polysulfone *N*-methyl pyrrolidone (NMP) solution by gelation in cold water. Nitrogen, oxygen, ethylene, ethane, propylene and propane with at least 99.8% purity were utilized in this work. Some physical properties of these gases are listed in Table 1.

Table 2
Comparison of membranes' properties with reported data for pure gases and hydrocarbons at 275 kPa (g)

	Permeance (GPU)[a]						Selectivity (gas/nitrogen)				
	N_2	O_2	$C_2^{=}$	C_2	$C_3^{=}$	C_3	O_2	$C_2^{=}$	C_2	$C_3^{=}$	C_3
Membrane A	117	217	727	840	1700	1970	1.9	6.3	7.3	16.2	16.8
Membrane B	25	40	94	105	218	143	1.6	3.9	4.3	8.9	5.9
[13][b]	11	23	NA	102	NA	252	2.0	NA	9.0	NA	22.3

NA: not available.

[a] 1 GPU = 10^{-6} cm^3 (STP)/(cm^2 s cmHg).

[b] A filler-free film (35 μm thick) on a highly microporous support by Membrane Technology and Research Inc. at 35 °C.