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Transport Analysis of olefins & nitrogen through PDMS membranes

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Introduction

Annually, 60 millions tons of polyolefins including polyethylene and polypropylene, etc. are produced in the world. During the manufacturing process, 1-2wt% of olefin gases of total feedstock remains unreacted and incinerated into air. Because of high cost of olefins and hazardous emission of carbon dioxide and toxic gases in incineration process, it is of important to recover them efficiently.

Polyolefin off-gases mainly are divided into two classes; condensable olefin gases – ethylene, propylene and butylenes, and non-condensable, permanent gases - nitrogen and hydrogen. The separation of condensable gases from non-condensable gases by membrane is often called 'vapor permeation'. In this separation, rubbery polymers such as polydimethysiloxane(PDMS), etc., have been used well. Due to the wide applications, many studies have been done to develop good membrane materials and membrane process for this vapor separation. Finally, Membrane Technology and Research (MTR) Inc. has successfully developed the profitable membrane-based vapor permeation process for olefin off-gas recovery and VOC(volatile organic compound) recovery. But, the published studies have mainly focused on separation of saturated VOC s from VOC-laden waste-streams or hydrocarbons from gasoline-off gas. In spite of MTR's commercialization, the systematic permeation behaviors for olefin off-gases have not reported yet. In academic point of view, it is of interest to show the permeation behaviors of olefins and nitrogen as functions of operation pressure and temperature and how they are influenced by sorption- and diffusion-related terms through PDMS membranes.

In this study, we report the permeability, sorption and diffusivity behaviors of three olefins and nitrogen through PDMS membrane

Experimental

PDMS membranes were prepared from SYLGARD™ (Dow Corning Co.). Casting solutions were prepared by dissolving 5wt% of base A/curing agent B mixture(9:1) in n-hexane and curing at 110℃ to complete cross-linking. The thickness of prepared membranes was about 200㎛.

Permeation test was done with bubble flowmeter for ethylene, propylene, 1-butylene and nitrogen. Their physical properties are listed in Table 1. Operation temperature and pressure, depending on the critical temperature were controlled from -30 to 50℃ and from 1 to 25 atm, respectively.

Table 1. Critical Temperature and Lennard Johns Diameter of Test Gases

	Nitrogen	Ethylene	Propylene	1-Butylene
Critical Temp. (K)	126.21	282.34	364.90	419.50
σLJ *	3.9	4.1	4.7	5.2

Gas permeability P_A of gas A and gas selectivity, $\alpha_{A/B}$ are calculated as the following two equations;

$$P_A = J_A L/(p_2 - p_1) \quad , \qquad \alpha_{A/B} = (P_A / P_B)$$

Solubility coefficient, S_A and solubility selectivity, S_A / S_B through PDMS membrane were obtained with a high-pressure barometric sorption apparatus. Diffusion coefficient, D_A and diffusion selectivity, D_A / D_B were calculated, from following two equations, respectively, by using the permeability and solubility data:

$$P_A = D_A S_A \quad , \qquad \alpha_{A/B} = \left(\frac{P_A}{P_B}\right) = \left(\frac{S_A}{S_B}\right) \times \left(\frac{D_A}{D_B}\right)$$

Results and Discussion

Figure 1 shows the permeability and selectivity behaviors of three olefins and nitrogen through PDMS membranes as a function of operation pressure from 1 to 20atm at 25℃. The permeability of olefins increases with increasing feed pressure, while that of nitrogen decreases slightly and thus, the selectivity of olefin/nitrogen increases. The permeability of olefins and their selectivities over nitrogen are in the following order: 1-butylene > propylene > ethylene, which is the same order of critical temperature of olefins, not the order of olefin size

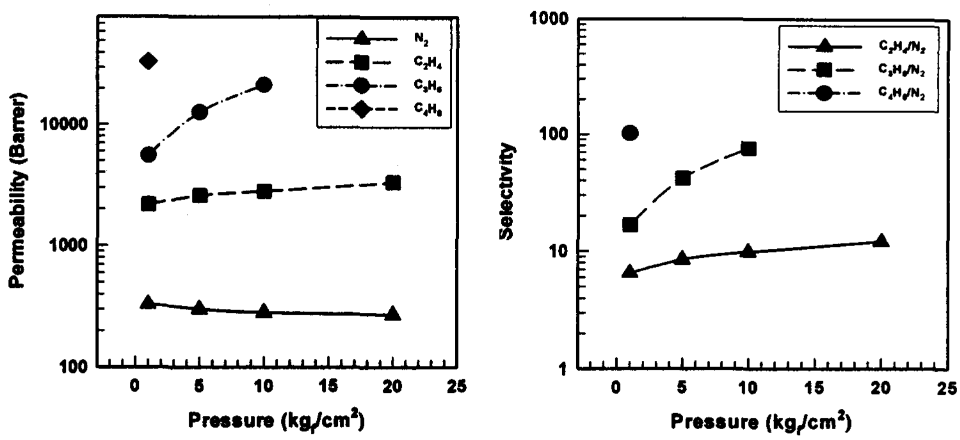

Figure 1. Permeability and selectivity of olefins & nitrogen vs operation pressure.

Figure 2 shows the permeability and selectivity behaviors of three olefins and nitrogen through PDMS membranes as a function of operation temperature from 25 to -25℃ at 1 atm. Typical vapor permeation behaviors are observed; as temperature decreases, the permeability of propylene and 1-butylene increases highly, that of ethylene increases slightly and that of nitrogen deceases highly. Permeability of olefins and their selecitivity over nitrogen with decreasing operation temperature are same order of critical temperature.

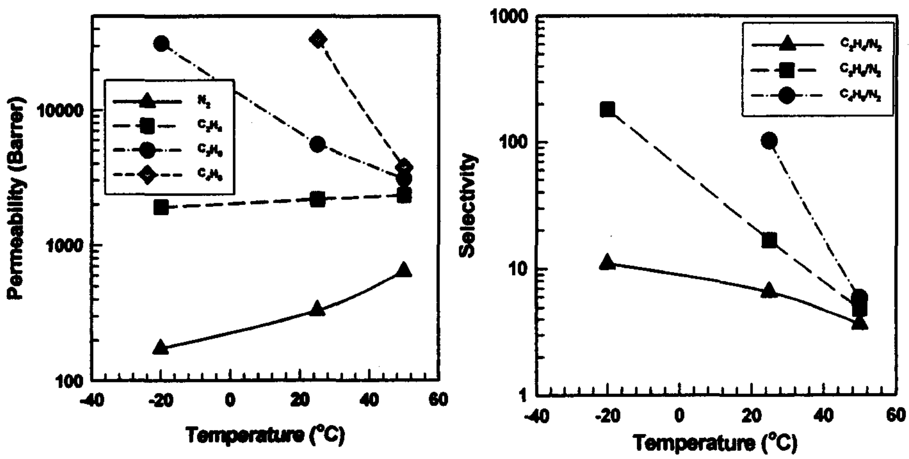

Figure 2. Permeability and selectivity of olefins & nitrogen vs operation temperature.

Figure 3 presents the diffusivity and solubility behavior of olefins and nitrogen through PDMS membranes as a function of critical temperature and Lennard-Johns diameter. Figure 4 shows the solubility selectivity and diffusion selectivity for three olefin/nitrogen pairs. As critical temperature increases in X-axis, both the diffusivity and solubility increase. Olefins with higher critical temperature show higher solubility in PDMS membranes. This can plasticize the membranes highly to decrease the diffusion resistance for large olefins and thus, shows reverse-size dependent diffusivity & diffusion selectivity(>1). This study clearly explains typically high permeability and selectivity of large, condensable gases over permanent gas through rubbery polymeric membranes.

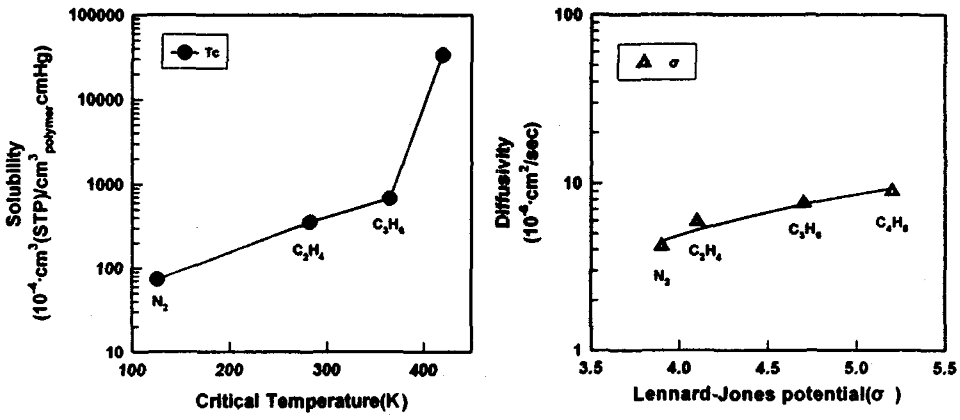

Figure 3. Solubility of olefins & nitrogen vs critical temp. and diffusivity. vs L-J diameter

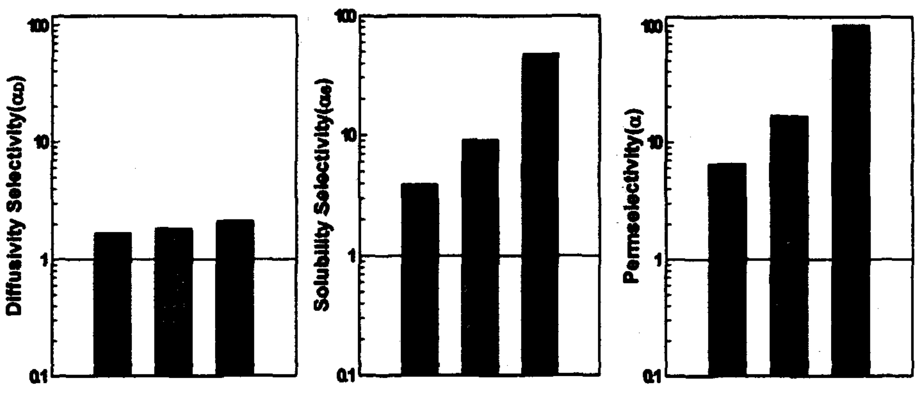

Figure 4. Diffusion selectivity, solubility selectivity and perm-selectivity of olefins & nitrogen

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