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TECHNICAL NOTE

Solvent and Pressure Influences on Air Separation of Liquid Crystalline Triheptyl Cellulose Composite Ethyl Cellulose Membranes

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ABSTRACT

Air separation of a cholesteric liquid crystalline triheptyl cellulose/ethyl cellulose (3/97) binary composite membrane prepared from tetrahydrofuran, chloroform, and dichloromethane solutions was studied at different pressure differences across the membrane by the variable volume method. With an increasing pressure difference in the range from 0.06 to 0.42 MPa, the flux and the oxygen concentration of the oxygen-enriched air through the membrane both increase. The air separation capability depends on the boiling point of the membrane-forming solvent and the membrane thickness.

Key Words. Liquid crystalline triheptyl cellulose; Liquid crystal membrane; Oxygen enrichment membrane; Oxygen-enriched air; Air separation

INTRODUCTION

Membranes for air separation have recently received much attention since membrane processes have the potential for energy efficient operation. Substituted polyacetylenes are well known as polymers excellent in air permeation but poor in air separation and stability (1), while plasma polymers are medium in air permeation but excellent in air separation

(2). Only liquid membranes containing facilitated transport carriers (3–5) possess excellent oxygen permeation (P_{O_2} = 1.11–1.50 × 10^{-7} cm^3(STP)·cm/cm^2·s·cmHg), excellent air separation ability (P_{O_2}/P_{N_2} = 30–80), and excellent oxygen-enriching ability (producing air containing over 88% oxygen at 5.29 × 10^{-3} $cm^3/s \cdot cm^2$ in a single step), but these novel air separations, which can be attained only below 0°C or above 450°C, depend strongly on the operating temperature. Recently, liquid crystal composite membranes have demonstrated better oxygen permselectivity in the temperature range of 25–90°C (6, 7). However, there are only a few reports in the literature concerning the use of liquid crystalline polymers for air separation (7, 8). The object of this paper is to characterize the air separation capability of a cholesteric liquid crystalline triheptyl cellulose (THC)/ethyl cellulose (EC) (3/97) binary composite membrane at 85°C in order to gain some insight into the influence of both solvents and pressure differences (ΔP) on the air separation of a membrane prepared from different solvents.

EXPERIMENTAL

The triheptyl cellulose (THC) used in this study was synthesized according to a previously described method (9). The ethyl cellulose (EC) was purchased from Shantao Xinning Chemical Works, Guangdong Province, in the People's Republic of China. The viscosity of the EC in ethanol/toluene solution is ~0.06 Pa·s. The membrane was prepared by casting from a solution of tetrahydrofuran (THF), chloroform ($CHCl_3$), or dichloromethane (CH_2Cl_2). Compressed air from an air compressor was fed into the upstream side of the membrane. The membrane was prepressurized at 0.4 MPa for ~3 hours before the air separation experiments were started. The method used to measure the air separation capability of the membrane was the variable volume method, wherein the flux, Q_{OEA}, and the oxygen concentration, Y_{O_2}, of the oxygen-enriched air (OEA) were determined by measuring the change in the OEA volume at a constant pressure gradient across the membrane with the help of a 491-type industrial gas analyzer. The effective area of the membrane permeated was 50 cm^2. The oxygen and nitrogen permeability coefficients P_{O_2} and P_{N_2} were calculated by using the following equations:

$$P_{O_2} = \frac{Q_{OEA} \cdot Y_{O_2} \cdot l}{\Delta P_{O_2}} \tag{1}$$

and

$$P_{N_2} = \frac{Q_{OEA} \cdot (1 - Y_{O_2}) \cdot l}{\Delta P_{N_2}} \tag{2}$$

where Q_{OEA} = oxygen-enriched air (OEA) flux [cm^3(STP)/s·cm^2]
Y_{O_2} = oxygen concentration in the OEA (%)
l = membrane thickness (cm)
ΔP_{O_2} or ΔP_{N_2} = the partial pressure difference of oxygen or nitrogen across the membrane (cmHg)

The oxygen/nitrogen separation factor was defined as

$$\frac{P_{O_2}}{P_{N_2}} = \frac{Y_{O_2} \cdot \Delta P_{N_2}}{(1 - Y_{O_2}) \cdot \Delta P_{O_2}} \tag{3}$$

Another way of defining the separation factor is by comparing the compositions of gas mixtures before and after permeating a membrane. Referred to as the actual separation factor (ASF), this quantity is defined by

$$\text{ASF} = \frac{Y_{O_2} \cdot (1 - X_{O_2})}{X_{O_2} \cdot (1 - Y_{O_2})} \tag{4}$$

where X_{O_2} is the oxygen concentration in the feed air (%). The ASF value depends on the pressure difference between both sides of the membrane.

RESULTS AND DISCUSSION

Figure 1(a) shows plots of the flux Q_{OEA} of oxygen-enriched air (OEA) against the pressure difference ΔP across a THC/EC membrane prepared from THF, $CHCl_3$, and CH_2Cl_2 as solvents. It can be seen that Q_{OEA} increases in the order $CH_2Cl_2 < CHCl_3 <$ THF. Among three kinds of membranes, the thinnest (17 μm-thick) membrane cast from THF has the strongest dependence of Q_{OEA} on ΔP. A similar linear relationship between Q_{OEA} and ΔP was observed for the PPO/PAS/PSF multilayer composite membrane (10). We can predict from Fig. 1 that Q_{OEA} should reach 1.1×10^{-3} cm^3(STP)/s·cm^2 for a ΔP of 0.7 MPa, which is as high as the Q_{OEA} through a composite hollow fiber membrane prepared by plasma polymerization (11).

Figures 1(b) and 1(c) show the effects of ΔP on the permeability coefficients of oxygen-enriched air (OEA), oxygen, and nitrogen through THC/EC (3/97) composite membranes from the above three solvents. It is apparent that P_{OEA} and P_{N_2} increase slightly but P_{O_2} decreases with increasing ΔP from 0.06 to 0.42 MPa. The fact that P_{O_2} decreases with ΔP suggests that oxygen transport occurs by dual-mode transport (Henry mode and

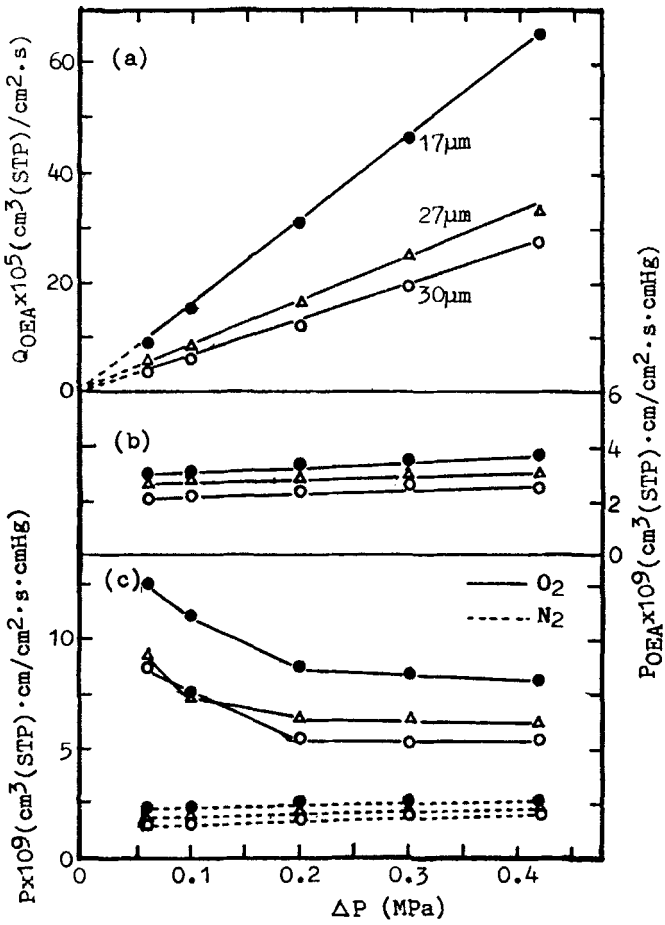

FIG. 1 The flux Q_{OEA} (a), the permeability coefficients P_{OEA} (b), and the P_{O_2} and P_{N_2} (c) of oxygen-enriched air (OEA). Oxygen and nitrogen versus pressure difference across THC/EC (3/97) membranes cast from three solvents: (●) THF, (△) $CHCl_3$, (○) CH_2Cl_2 (85°C).

additive Langmuir mode), just like oxygen transport in a membrane containing a cobalt porphyrin complex as a fixed carrier (12). On the other hand, in the absence of strong plasticization, gas permeability coefficients generally decrease or remain constant with increasing driving pressure (13). In addition, P_{OEA}, P_{O_2}, and P_{N_2} all increase with increasing boiling points of membrane-forming solvents. A similar relationship between oxygen permeability and the boiling points of solvents is shown in Table 1 for an EC membrane without THC. A membrane has variable oxygen

TABLE 1
Air Separation Parameters through EC Membranes Cast from Three Kinds of Solvents (40°C)

Solvents	Boiling point (°C)	l (μm)	ΔP (MPa)	$P_{O_2} \times 10^{10}$ [a]	$Q_{OEA} \times 10^5$ [b]	P_{O_2}/P_{N_2}	Y_{O_2} (%)
THF	66	25	0.4	27.3	16.6	2.60	35.4
$CHCl_3$	61	23	0.4	25.7	19.4	2.11	32.0
CH_2Cl_2	41	30	0.4	18.0	7.32	3.50	40.3

[a] The unit of P_{O_2} is $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$.

[b] The unit of Q_{OEA} is $cm^3(STP)/s\cdot cm^2$.

permeabilities depending upon the boiling points of solvents (14). A solvent with a higher boiling point tends to yield a membrane of higher oxygen permeability.

The THC/EC and EC membranes cast from the highest boiling point THF solution not only have the highest oxygen permeability, but also

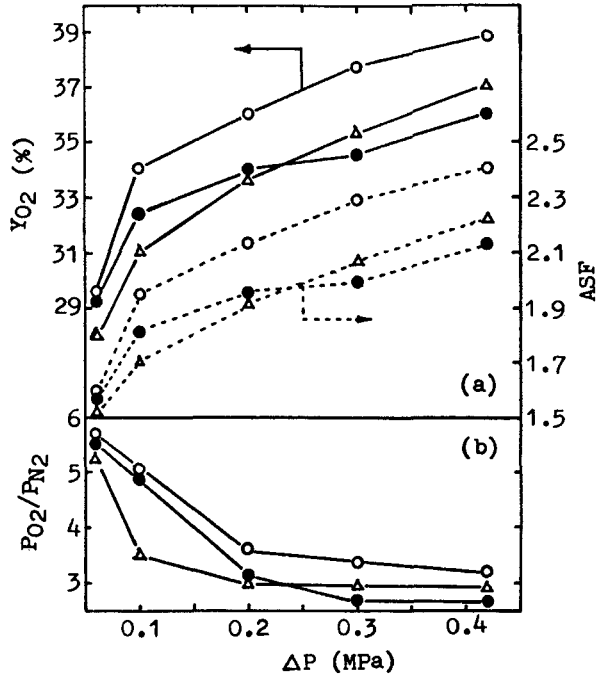

FIG. 2 Air separation parameters versus pressure difference across THC/EC (3/97) membranes cast from three solvents: (○) THF, (△) $CHCl_3$, (●) CH_2Cl_2 *(85°C)*.

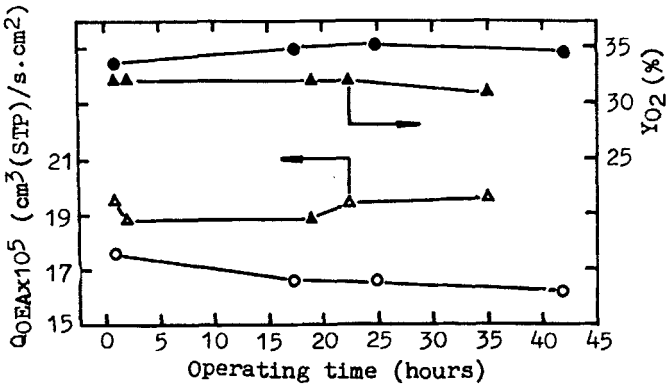

FIG. 3 Flux Q_{OEA} and oxygen concentration Y_{O_2} of oxygen-enriched air (OEA) through EC membranes cast from THF (○) and $CHCl_3$ (△) as a function of operating time at 0.4 MPa net and 40°C.

have a higher air separation ability, as shown in Table 1 and Fig. 2. With an increase of ΔP, Y_{O_2} and ASF increase; on the contrary, P_{O_2}/P_{N_2} decreases. Y_{O_2} and ASF are low at low ΔP but high at high ΔP; that is, Y_{O_2} and ASF are proportional to ΔP, but P_{O_2}/P_{N_2} is inversely proportional to ΔP. The P_{O_2}/P_{N_2} ratio is 5.2–5.8 at a ΔP of 0.06 MPa and 2.6–3.2 at 0.42 MPa, while the highest Y_{O_2} and ASF reach 38.8% and 2.40, respectively. These results show that the THC/EC (3/97) membrane has a better air separation ability than the EC membrane, even better than PPO and fluorinated silicone rubber membranes (15), which may be caused by the

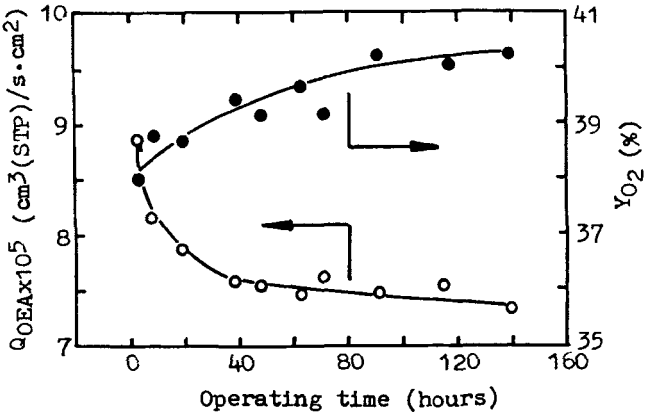

FIG. 4 Flux Q_{OEA} and oxygen concentration Y_{O_2} of OEA through an EC membrane cast from CH_2Cl_2 as a function of operating time at 0.4 MPa and 40°C.

addition of 3 wt% THC exhibiting a cholesteric liquid crystalline state at temperatures in the 20 to 100°C range (9).

In the course of measuring air separation of the membranes, it was noticed that membrane performance changed slightly with time. Flux Q_{OEA} and oxygen concentration Y_{O_2} of oxygen-enriched air (OEA) are plotted as a function of operating time in Figs. 3 and 4 for three typical EC membranes at operating conditions of 40°C and 0.4 MPa. It appears that stable values of Q_{OEA} and Y_{O_2} through thinner EC membranes cast from THF and $CHCl_3$ were obtained within 35–42 hours of operation. For a thicker EC membrane cast from CH_2Cl_2, most of the change in Q_{OEA} and Y_{O_2} took place in the first 40 hours. At the end of 140 hours of operation, it was noted that a slight decline in Q_{OEA} and a slight increase in Y_{O_2} had occurred, probably due to membrane compaction.

Better air separation ability and stability may lead to the practical application of THC/EC and EC membranes as air separation membranes in medical and engineering fields.

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