Composition and Temperature Effects on Air Separation Through Liquid Crystalline Alkyl Cellulose Membranes

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SYNOPSIS

The air separation through triheptyl cellulose (THC)/ethyl cellulose (EC) blend membranes containing no more than 20 wt % THC at the temperature range from 298 to 358 K was investigated using a variable volume method. The air-separation ability for the THC/EC membranes were greater than that for the THC-free pure EC membrane. P_{O_2} for the THC/EC membranes was between 1.06–8.89 × 10^{-9} cm^3 (STP) cm/cm^2 s cmHg and P_{O_2}/P_{N_2} 3.04–3.66. The THC/EC membrane showed a unique trend in its P_{O_2}/P_{N_2}–P_{O_2} relationship, i.e., the magnitude of P_{O_2}/P_{N_2} increased simultaneously with that of P_{O_2}. The THC/EC membrane yielded a maximum oxygen concentration in the oxygen-enriched air (OEA) of 39.5% at an OEA flux of 6.99 × 10^{-4} cm^3 (STP)/s cm^2 for a pressure difference of 0.43 MPa at 358 K. After 300 h of measurement at 0.40 MPa and 313 K, the efficiency of the concentrating oxygen was almost constant.

INTRODUCTION

Air separations with membranes for the production of an oxygen-enriched air (OEA) have attracted attention because of both conceptual and process simplicity of the membrane permeation technique. However, the availability of membranes suitable for air separation is not wide enough to support the above expection because the membranes were so thick that they did not have enough flux to be practical. The recent development of the membranes for air separation is due to the ability to produce thin membranes with higher oxygen permselectivity.[1]

To support this effort in membrane development, a series of 13–30 μm-thick membranes from liquid crystalline triheptyl cellulose (THC)/ethyl cellulose (EC) were prepared and the effects of the liquid crystalline THC content and temperature on their air-separation ability were investigated by the variable volume method.

EXPERIMENTAL

THC with an intrinsic viscosity of 26 mL/g in chloroform at 298 K was used in this study and was identical to that reported in our previous paper.[2] This THC shows fluidity and birefringence and exhibits a grainy appearance characteristic of a cholesteric polydomain structure at room temperature owing to the low molecular weight (low viscosity) of the THC. A flat uniform membrane from the THC/EC with a thickness of between 13 and 30 μm and an effective area of 50 cm^2 was obtained by casting a THC/EC tetrahydrofuran solution on a glass plate. The air-separation abilities across the membrane were measured at a constant pressure gradient of 0.43 MPa according to ASTM D143V. The downstream side of the membrane was atmospheric pressure and the upstream side was filled with compressed air at an absolute pressure of 0.53 MPa. The flux Q_{OEA} of the OEA at atmospheric pressure was measured. The oxygen concentration Y_{O_2} in the OEA was determined using a 491 type industrial gas analyzer. A series of air-separation parameters were calculated using the method reported in our earlier paper.[3] Polarizing microscopic observations were made with a Jiang-Nan XPT-6 polarizing microscope equipped with a hot stage at a heating rate of 5 K/min between 298 and 403 K. To take photomicrograms, the THC sandwiched between the slide and coverglass was allowed to equilibrate for a few hours. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-2C calorimeter at a scanning rate of 20 K/min.

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RESULTS AND DISCUSSION

The THC/EC membranes contained only a small amount of THC (no more than 20 wt %) and were homogeneous visually. Neither pinhole nor defect forms were seen even when the membrane thickness was 17 μm and after the membrane was subjected to a pressure difference of 0.43 MPa and a temperature of above 313 K for 1000 h. No phase-separated aggregates in the membrane were observed based on the bright view of THC, whereas the dark view of amorphous EC under the hot-stage polarizing microscope indicated good compatibility between THC and EC. Therefore, THC should disperse homogeneously in the THC/EC membrane. It should be noted that the dispersion state of THC in the THC/EC membrane might not be established by the DSC method, since this method failed to give any clear information on the phase transition of the THC due to very small transition enthalpy and entropy.[4,5]

Figure 1 shows the temperature effect on the Q_{OEA} of the THC/EC membranes with different compositions at a constant pressure difference of 0.43 MPa. It can be seen that Q_{OEA} increases linearly with increasing temperature below 313 K, but above 313 K, a distinct acceleration in the increase of the Q_{OEA} was observed. On the other hand, the Q_{OEA} depends on the thickness of the membranes, but not on the THC content in the membranes. The thinner the membranes, the more distinct the Q_{OEA} acceleration. At 358 K, the Q_{OEA} through the THC/EC (1.5/98.5) membrane will reach about 7.0×10^{-4} cm^3 (STP)/s cm^2, which is approximately 10 times the size of the Q_{OEA} at 298 K.

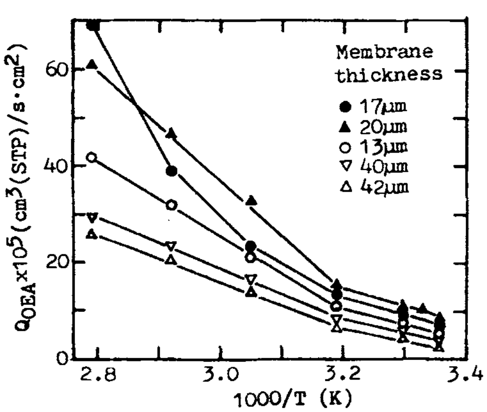

Figure 1 Arrhenius plots of the flux Q_{OEA} of the oxygen-enriched air through the membranes (after operating time of 24 h) with different THC/EC ratios: (○) 0/100; (●) 1.5/98.5; (△) 6/94; (▲) 10/90; (▽) 20/80.

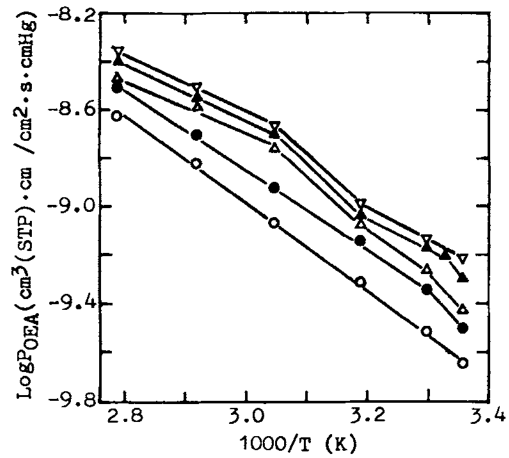

Figure 2 Arrhenius plots of the permeability coefficient P_{OEA} of the oxygen-enriched air through the THC/EC membranes after an operating time of 24 h. For symbols, refer to Figure 1 legend.

The temperature effect on P_{OEA}, P_{O_2}, and P_{N_2} is described in Figures 2 and 3 by an Arrhenius-type law with Log P_{OEA}, Log P_{O_2}, and Log P_{N_2} vs. $1/T$ plots at a constant pressure difference. A jump in P_{OEA}, P_{O_2}, and P_{N_2} through the membranes containing more than 6 wt % THC is observed in the temperature range between 313 and 328 K, possibly as a result of the activation of thermal molecular motion in the membrane and or an enhancement of pore formation. On the other hand, P_{OEA}, P_{O_2}, and

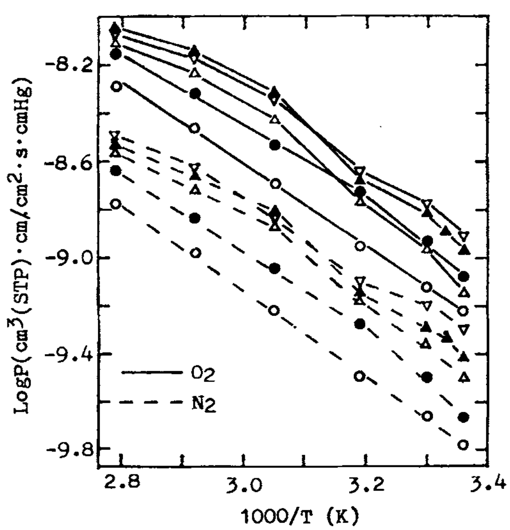

Figure 3 Arrhenius plots of the permeability coefficients P_{O_2} and P_{N_2} of oxygen and nitrogen through the THC/EC membranes after an operating time of 24 h. For symbols, refer to Figure 1 legend.

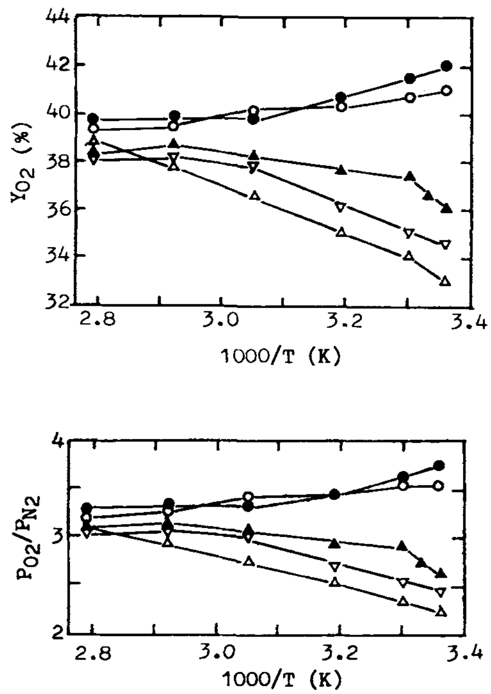

Figure 4 Arrhenius plots of (a) the air-separation capability Y_{O_2} and (b) P_{O_2}/P_{N_2} through the THC/EC membranes after an operating time of 24 h. For symbols, refer to Figure 1 legend.

Figure 6 Photomicrograph of THC showing a "fingerprint" texture for the cholesteric liquid crystalline phase at 298 K at 500× magnification.

P_{N_2} increase slightly as the THC content increases from zero to 20 wt %. When the THC content is between 10 and 20 wt %, P_{O_2} will exceed 4.66×10^{-9} cm^3 (STP) cm/cm^2 s cmHg, which is of the same order as that of P_{O_2} of plasma-polymerized membrane.[1] The THC/EC membrane exhibiting higher P_{O_2} indicates that the introduction of THC can increase the oxygen permeability of the EC membrane, whereas the higher oxygen over nitrogen separation factor P_{O_2}/P_{N_2} can be maintained.

Figure 4 presents plots of the air-separation parameters Y_{O_2} and P_{O_2}/P_{N_2} vs. $1/T$ for the THC/EC membranes. It can be seen that the THC/EC (1.5/98.5) membrane at 298 K exhibits the highest Y_{O_2} and P_{O_2}/P_{N_2}, which decrease with rising temperature from 298 to 358 K, just like the EC membrane. However, the Y_{O_2} and P_{O_2}/P_{N_2} of the membranes containing 6–20 wt % THC increase when temperature rises from 298 to 328 K and remain nearly constant in the temperature range of 328–

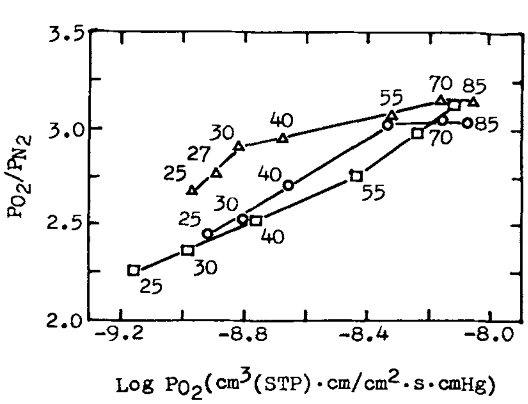

Figure 5 Plots of P_{O_2}/P_{N_2} vs. P_{O_2} for the membranes (after an operating time of 24 h) with different THC/EC ratios: (□) 6/94; (△) 10/90; (○) 20/80 in the temperature range of 298–358 K.

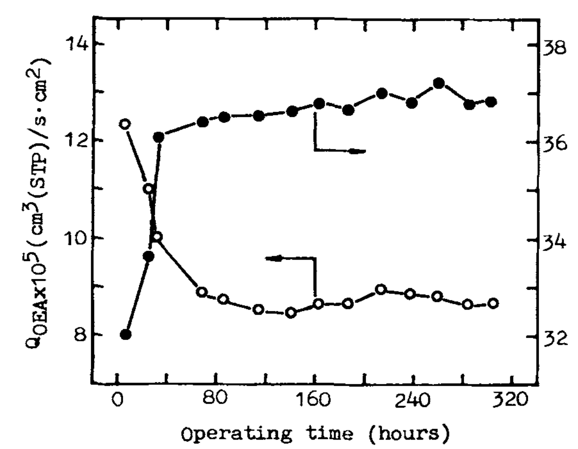

Figure 7 The flux Q_{OEA} and the oxygen concentration Y_{O_2} of the oxygen-enriched air through the THC/EC (1.5/98.5) membrane as a function of operating time at 0.40 MPa net and 313 K.

Table I Comparison of the Oxygen Permselectivities of the THC/EC Membranes with Those of Other Liquid Crystal Membranes

	Membranes					
	THC/EC 1.5/98.5	THC/EC 10/90	LCPMS/PP[a]	LCPMS	EBBA/PVC[b] 60/40	BEP/PC[c] 60/40
Temp (K)	303	343/358	308/348	319	307/348	348
$P_{O_2} \times 10^{10}$ [d]	11.7	68.6/88.9	3.06/46.8	20	5.75/51.9	50.5
P_{O_2}/P_{N_2}	3.66	3.15/3.08	4.33/3.00	2.0	2.95/2.52	2.56
Refs.	This study		6	7	8	9

[a] LCPMS = side-chain liquid crystalline polymethylsiloxane; PP = polypropylene.
[b] EBBA = *N*-(4-ethoxybenzylidene)-4'-butylaniline; PVC = poly(vinyl chloride).
[c] BEP = butyl ethoxyphenoxycarbonylphenyl carbonate; PC = polycarbonate.
[d] Unit: cm^3 (STP) cm/cm^2 s cmHg.

358 K. Hence, P_{O_2}/P_{N_2} increases as P_{O_2} increases with rising temperature (see Fig. 5). Without doubt, this phenomenon is due to the ordered supermolecular arrangement of the cholesteric liquid crystalline THC in a wide temperature range from room temperature up to the isotropization temperature of around 358 K (Fig. 6). The THC exhibits a "fingerprint" texture with fine striation lines, which is similar to that observed for the other low molecular weight ($\bar{M}_n$ = 30,000) THC.[4,5]

For assessment of the process and economic viability of membrane-based air-separation application, membrane stability is an important factor. Long-term tests were performed with the THC/EC (1.5/98.5) membrane with a thickness of 17 μm for a duration of 300 h. A constant transmembrane pressure of 0.40 MPa and a constant temperature of 313 K were maintained throughout the test. The results shown in Figure 7 indicate that most of the change in membrane performance takes place in the first 40 h. This change may be due to membrane compaction. During last 260 h period, Q_{OEA} and Y_{O_2} are essentially constant at 8.6×10^{-5} cm^3 (STP)/s cm^2 and 36.5%, respectively. Therefore, the membrane is good in long-term stability.

Table I compares the oxygen permselectivities of the THC/EC membranes with those of some liquid crystal membranes reported by Chen et al.,[6] Tomoike et al.,[7] and Kajiyama et al.[8,9] It is apparent that the THC/EC membranes exhibit the highest oxygen permselectivity in the liquid crystal membranes shown in Table I at the temperature range from 303 to 348 K. All these results could be due to the ordered supermolecular structure in the cholesteric liquid crystalline state exhibited by the THC.[2,4,5,10]

CONCLUSIONS

It was demonstrated that the air-separation capability of a blend membrane composed of thermotropic liquid crystalline, triheptyl cellulose (THC), and ethyl cellulose (EC) is apparently dependent on the membrane composition and operating temperature. Since THC could exhibit the cholesteric liquid crystalline state with fluidity at room temperature, the THC in the THC/EC membranes may play an important role in transferring or diffusing oxygen. The THC/EC membrane exhibits the unique behavior that P_{O_2}/P_{N_2} increased with increasing P_{O_2} in the temperature range from 288 to 358 K. Stable air-separation parameters (Q_{OEA} = 9.0×10^{-5} cm^3 (STP)/s cm^2 and Y_{O_2} = 37%), which do not change for 310 h, are obtained for the THC/EC membrane. This membrane is the first oxygen-enriching blend membrane containing thermotropic liquid crystalline alkyl celluloses at room temperature.

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