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ORIGINAL CONTRIBUTION

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Effect of pressure on oxygen enrichment of liquid crystalline cellulose ether membranes at elevated temperature

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Abstract Cholesteric liquid crystalline triheptyl cellulose (THC)/ethyl cellulose binary blend membranes were prepared and the effect of pressure on their oxygen enrichment at elevated temperature was investigated using a constant pressure-variable volume method. The oxygen enrichment increased with the increase of transmembrane pressure difference or with slight increase of the THC content in the blend membranes. The oxygen concentration through the membranes increased linearly with decreasing pressure ratio. Air was directly separated through a 17 μm-thick THC/EC(1.5/98.5) membrane to prepare an oxygen-enriched air containing 39.5% oxygen at the flux of 6.99×10^{-4} cm^3(STP)/s.cm^2 at the pressure difference of 0.43 MPa and 85 °C.

Key words Liquid crystalline cellulose ether – liquid crystal membrane – oxygen enrichment membrane – air separation – pressure dependency

Introduction

Membrane gas separation is generally targeted at low volume application where the relative simplicity of membrane system is advantageous because it results in low capital cost. Polydimethyl siloxane reported to be more permeable to oxygen and nitrogen has an oxygen/nitrogen selectivity ratio of about 2, therefore it cannot be used to enrich the oxygen in the air to more than 30%. Ethyl cellulose exhibits higher oxygen/nitrogen selectivity of 3.43, but moderate to oxygen permeability of 1.5×10^{-9} cm^3(STP)·cm/cm^2·s·cmHg. Blend membrane may provide a simple method for improving the oxygen enriching properties of the membranes. Low molecular liquid crystal blend membranes for air separation have been reported by Kajiyama and Huang et al. [1, 2]. High molecular polysiloxane exhibiting liquid crystallinity has demonstrated a good gas separation capability [3, 4]. However, there are very few reports in the literature concerning cellulose ether liquid crystal blend membranes for gas separation, especially at high temperature. The goal of this paper is to present the effect of pressure difference and ratio on the oxygen enrichment through cholesteric liquid crystalline triheptyl cellulose (THC)/ethyl cellulose (EC) binary blend membranes at elevated temperature.

Experimental procedure

The experimental technique used in the synthesis of THC is identical to that reported in our previous papers [5, 6]. A flat uniform THC/EC blend membrane with a thickness of between 13–45 μm was obtained by casting the THC/EC from a 2 wt% tetrahydrofuran solution on a glass plate. The solvent was evaporated slowly at room temperature. Oxygen enrichment measurements were performed at 85° and 40 °C using a constant pressure-variable volume method according to ASTM D143V. The membrane effective area was 50 cm^2.

Compressed air from an air compressor was supplied into the upstream side. The pressure on the upstream side was always constant and greater than the atmospheric pressure on the downstream side [7]. The flux (Q_{OEA}) and oxygen concentration (Y_{O_2}) of the oxygen-enriched air (OEA) or the permeated air across the membrane were measured by a 491-type industrial gas analyzer. The details of the measurements were described elsewhere [6, 8, 9]. On the basis of the data of the Q_{OEA} and Y_{O_2}, the OEA permeability coefficient P_{OEA}, oxygen and nitrogen permeability coefficients P_{O_2} and P_{N_2}, and oxygen over nitrogen separation factor P_{O_2}/P_{N_2} were calculated by using the following equations (from Fick's law):

$$P_{OEA} = Q_{OEA} \cdot 1/\Delta P \quad (1)$$

$$P_{O_2} = Q_{OEA} \cdot Y_{O_2} \cdot 1/\Delta P_{O_2} \quad (2)$$

$$P_{N_2} = Q_{OEA} \cdot (1 - Y_{O_2}) \cdot 1/\Delta P_{N_2} \quad (3)$$

$$P_{O_2}/P_{N_2} = Y_{O_2} \cdot \Delta P_{N_2}/((1 - Y_{O_2}) \cdot \Delta P_{O_2}) \quad (4)$$

where 1 is the membrane thickness, ΔP is the transmembrane pressure difference, and ΔP_{O_2} or ΔP_{N_2} is the partial pressure difference of oxygen or nitrogen between the upstream and downstream membrane faces. The relationship between pressure ratio and the oxygen concentration in a single operation can be given as [2]:

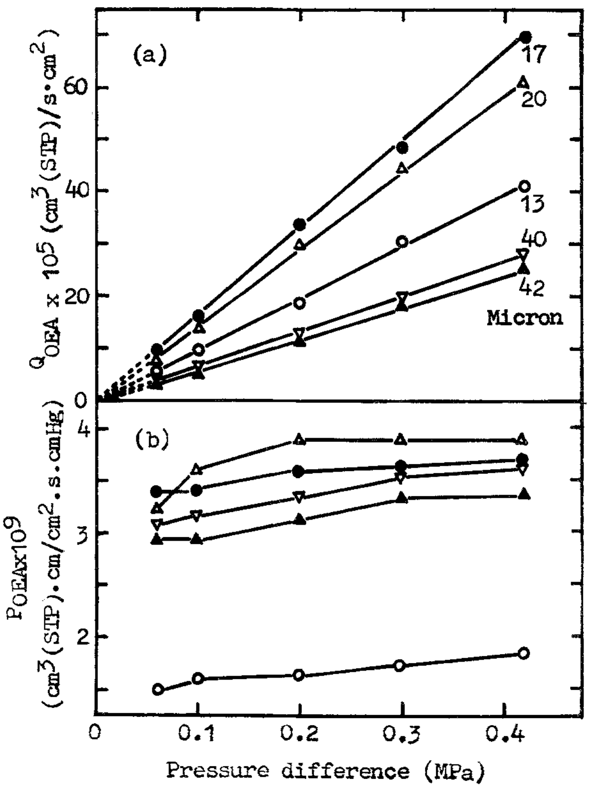

Fig. 1

$$Y_{O_2} = \frac{[(\alpha - 1)(\phi + X_{O_2}) + 1] - \{[(\alpha - 1)(\phi + X_{O_2}) + 1]^2 - 4\phi X_{O_2}(\alpha - 1)\ \alpha\}^{1/2}}{2\phi(\alpha - 1)} \quad (5)$$

where X_{O_2} is the oxygen concentration in the feed air, α is the oxygen/nitrogen separation factor from pure oxygen and pure nitrogen, and ϕ is the total permeate pressure divided by the total feed pressure. The reproducibility was within 5%.

Results and discussion

Effect of pressure difference on an oxygen-enriched air (OEA) flux

Figure 1a shows the pressure difference dependency of the flux Q_{OEA} of oxygen-enriched air (OEA) across the membranes in the pressure difference range of 0.06 – 0.42 MPa for THC/EC binary blend membranes with different compositions at 85 °C. The Q_{OEA} data increase linearly with increasing pressure difference. Low molecular liquid crystal blend membrane also exhibits a similar increase in the Q_{OEA} with increasing pressure difference [10]. The rate of the increase in the Q_{OEA} with pressure difference is nearly independent of membrane compositions within the range of 1.5–20 wt % THC, and is inversely proportional to the membrane thickness. These results could be explained by the solution-diffusion model.

Effect of pressure difference on the P_{OEA}, P_{O_2} and P_{N_2}

As shown in Figs. 1b and 2, the P_{OEA} and P_{N_2} increase slightly with increasing pressure difference, on the contrary, the P_{O_2} decreases first and then remains essentially constant at the pressure difference above 0.2 MPa. These results indicate that oxygen molecules through the THC/EC blend membranes seem to permeate in a special process different from nitrogen molecules [11]. Oxygen transport might occur by dual mobility model. The faster oxygen mobility might decrease with increasing pressure difference due to hydrostatic compressive effects that cause a reduction in the free volume of the membranes. This reduction in free volume results in a corresponding decrease in P_{O_2}. On the other hand, when transmembrane

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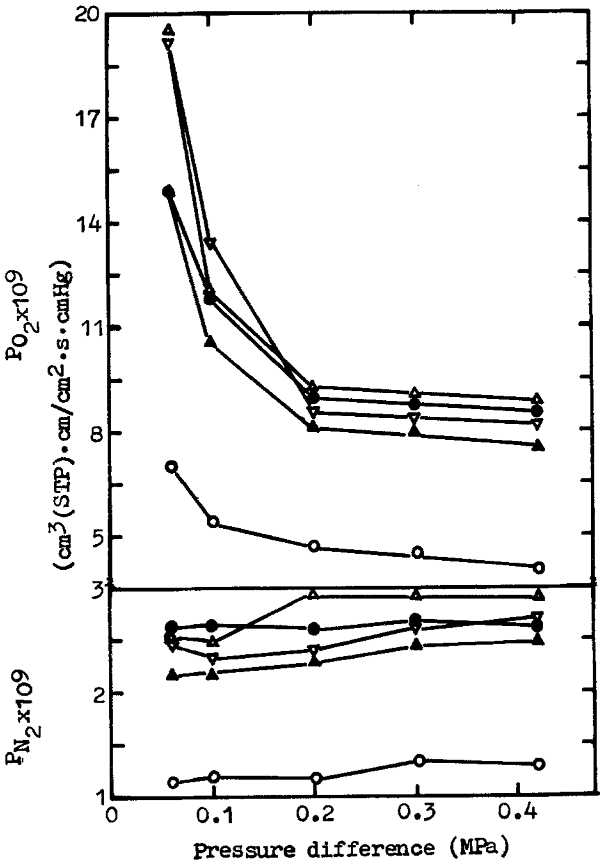


Fig. 2

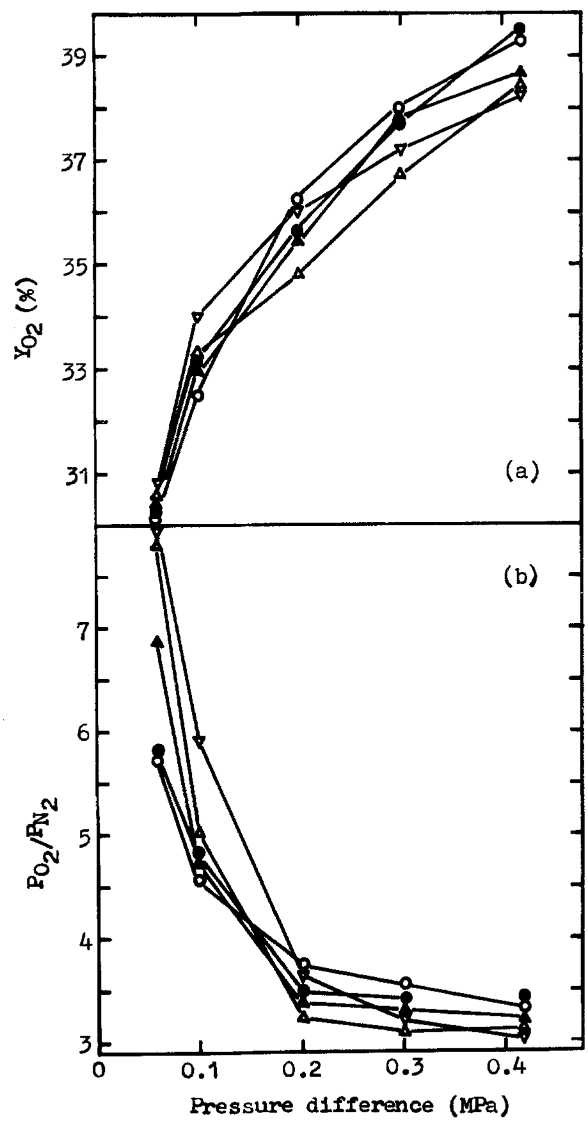
pressure difference is above 0.2 MPa, the P_{OEA} and P_{O_2} of the THC/EC (10/90) membrane could reach 3.9×10^{-9} and 9.0×10^{-9} cm^3(STP)·cm/cm^2·s·cmHg, respectively, which are much higher than those for pure EC membrane. This result suggests that an addition of a small amount of THC to EC is effective in the improvement of the oxygen permeability. The improvement might be contributed to the changes of the THC/EC membrane in the cohesive energy density.

Effect of pressure difference on the Y_{O_2} and P_{O_2}/P_{N_2}

The oxygen concentration Y_{O_2} in the OEA permeated through the membranes increases up to 38.2–39.5% as pressure difference increases up to 0.43 MPa (see Fig. 3a), quite the contrary, the P_{O_2}/P_{N_2} value decreases with increasing pressure difference (Fig. 3b), and then the P_{O_2}/P_{N_2} remains at a practically constant value of 3–4 at the pressure difference higher than 0.2 MPa, i.e. the pressure dependencies of the Y_{O_2} and P_{O_2}/P_{N_2} are inverse, which is presumably due to much higher P_{O_2} than P_{N_2} at lower pressure difference. The P_{O_2}/P_{N_2} value, as a result, is surprising high at low pressure difference, but low at high pressure difference.

Apparently, the introduction of a small amount of THC can enhance the P_{OEA} and P_{O_2} of EC membrane, while the high oxygen over nitrogen selectivity is maintained. When the THC content is in the range of 0–20 wt %, the derivatives of the Y_{O_2} and P_{O_2}/P_{N_2} are 1.6% and 0.5 at the pressure difference above 0.2 MPa, respectively. Additionally, if permeability measurements with pure oxygen and nitrogen are performed respectively at 24 °C, the ideal P_{O_2}/P_{N_2} of THC-free EC membrane is 3.74, which is essentially the same as the P_{O_2}/P_{N_2} obtained from the air permeability measurements.

Fig. 3



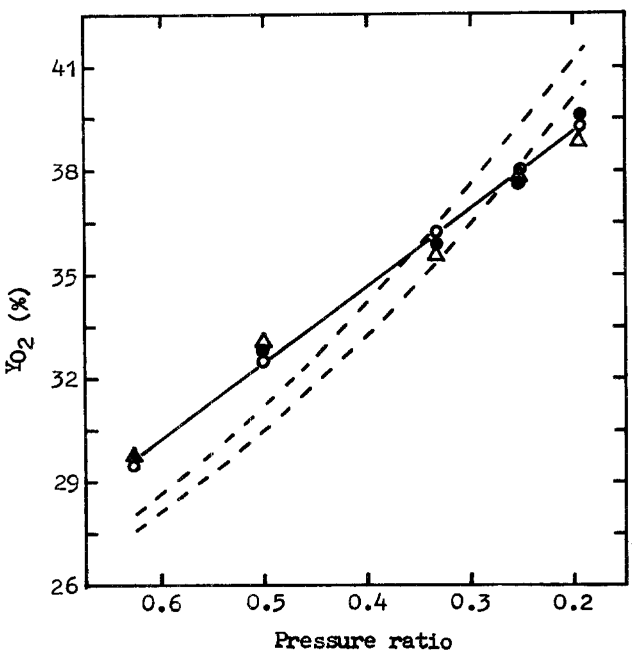
Effect of pressure ratio on the Y_{O_2}

The experimental Y_{O2} is compared with the Y_{O_2} value calculated for the α_{O_2/N_2} (3.43–3.74) of pure EC by using Eq. (5) in Fig. 4. It can be seen that the pressure ratio dependence of the experimental Y_{O_2} is weaker than that of the calculated Y_{O_2} in the pressure ratio range from 0.19 to 0.63. When the pressure ratio is larger than 0.35, the experimental Y_{O_2} is larger than the calculated Y_{O_2}. A good agreement between the experimental and calculated Y_{O_2} is found in the pressure ratio range from 0.25 to 0.35. The agreement obtained indicates that the Y_{O_2} could be predicted using Eq. (5) for a certain pressure ratio.

Effect of time on the membrane performance

In the course of measuring the oxygen enrichment of the membrane, it is noticed that the membrane performance is changing with measuring time. The Q_{OEA} and Y_{O_2} data for the THC/EC (10/90 and 20/80) typical membranes are plotted as a function of measuring time in Fig. 5. It appears that the increase in the Y_{O_2} takes place in the first 3–5 h, and small changes in the Q_{OEA} and Y_{O_2} occur after this. The increase in the Y_{O_2} is probably due to membrane compaction. Based on these results, a standard testing of approximately 3–5 h is established.

Fig. 4



Comparison of oxygen enrichments of THC/EC membranes with other membranes

Table 1 compares the oxygen enrichments of the THC/EC membranes with those of some liquid crystal membranes, plasma-polymerized membranes and pure EC membrane reported in the literature. The capacity and degree of the oxygen enrichments in the THC/EC membranes are as high as those in plasma-polymerized membranes [7, 11]. The THC/EC membranes, however, show higher oxygen permselectivity than low molecular liquid crystal membranes [10, 12, 13] and liquid crystalline polysiloxane membrane [4, 14]. All these results could be due to the ordered supermolecular structure of the cholesteric liquid crystalline state exhibited by the THC [5, 6].

Fig. 5

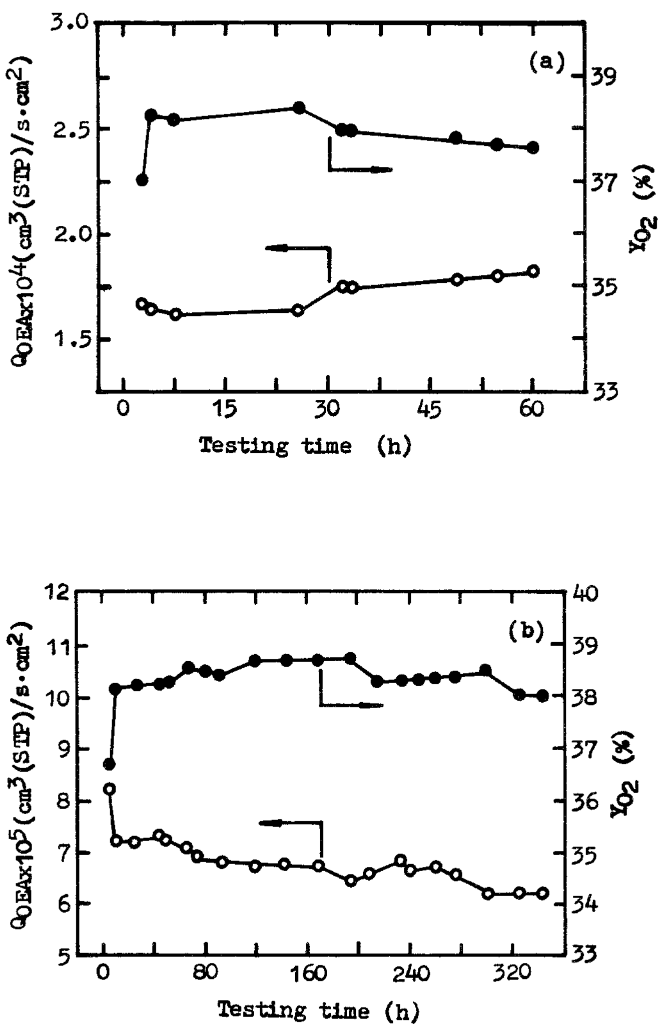


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Table 1 Comparison of the oxygen enrichment of the THC/EC membranes with those of other liquid crystal membranes and plasma-polymerized membranes

Membranes (wt%)	ΔP (MPa)	Temp. (°C)	$Q_{OEA}10^4$ (cm^3(STP)/s·cm^2)	Y_{O2} (%)	Refs.
THC/EC					
1.5/98.5	0.43	40	1.39	40.3	This
1.5/98.5	0.43	85	6.99	39.5	study
3/97	0.41	40	1.85	36.8	
3/97	0.41	85	6.87	38.8	
10/90	0.41	40	1.48	37.5	
10/90	0.41	85	6.07	38.3	
20/80	0.40	40	0.65	39.2	
20/80	0.43	85	2.97	38.3	
Pure EC	0.80	30	0.94	32.6	2
7CB/almite[a]	0.17	35	8.50	25.6	10
PCH/PVC[b]	0.10	46	2.80	24.1	13
Plasma	0.20		0.95	36.1	11
polymerized	0.69		10.0	33.0	7
membranes					

[a] 7CB = 4-*n*-heptyl-4′-cyanobiphenyl liquid crystal
[b] PCH = 4-amyl-4′-cyanophenylcyclohexane liquid crystal
PVC = poly(vinyl chloride)

Conclusions

The oxygen enrichment of the THC/EC membrane is found to depend strongly on transmembrane pressure difference and pressure ratio, and also to depend on the THC content in the membrane and the thickness of the membrane. The THC/EC membrane yields a maximum oxygen concentration Y_{O2} in the OEA of 39.5% at the OEA flux Q_{OEA} of 6.99×10^{-4} cm^3(STP)/s·cm^2 for an applied pressure difference of 0.43 MPa across the membrane at 85 °C. The preliminary results obtained in this study, demonstrate the possibility to achieve a highly effective oxygen enriching membrane with heat resistance simply based on the cholesteric liquid crystalline cellulose ethers.

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