Oxygen Enrichment Across Blend Membranes of Bipyridine and Ethyl Cellulose

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ABSTRACT: Blend membranes of 2,2′-bipyridine (2BP) or 4,4′-bipyridine (4BP) with ethyl cellulose (EC) containing no more than 25 wt % BP are prepared and evaluated for their oxygen enrichment by both the constant pressure–variable volume method and the constant volume–variable pressure method. The actual air-separation ability through the 2BP/EC blend membrane containing 1.5–7 wt % 2BP are enhanced while the permeated flux is slightly increased in comparison with the virgin EC membrane. Among the 2BP/EC blend membranes examined, the 2BP/EC blend membrane containing 3 wt % 2BP offers the best oxygen/nitrogen permselectivity and yields the highest oxygen concentration of 42.7% at the transmembrane pressure difference of 0.75 MPa and 25°C. Like other homogeneous dense membranes, the BP/EC blend membrane demonstrates strong dependencies on the transmembrane pressure difference, retentate/permeate flux ratio, and operating temperature. It possesses higher activation energy of oxygen and nitrogen permeation than those of the virgin EC membrane in the tested temperature range of 9.7–60°C. The CO_2 over CH_4 permselectivity through EC membranes can be improved by introducing 4BP, and the ideal oxygen over nitrogen separation factor through the 4BP/EC (10/90) membrane increases 16% at the upstream pressure of 10 bar compared with the virgin EC membrane. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1371–1381, 2003

INTRODUCTION

The membrane-separation technique has continued to enjoy tremendous attention due to its relative simplicity and lower cost for several decades.[1–7] The advantages that the membrane-based gas-separation process affords can only be achieved if the membrane meets the required selectivity, permeability, and stability for a particular application.[1–4,8–13] Within the air-separation field, only a relatively small number of membranes processes have realized any commercial success to date, and this may essentially be due to a number of problems with the membrane materials that still need to be addressed, particularly those relating to selectivity. One simple approach to minimize these problems is to employ additives. In recent years, the method of introducing some additives into traditional polymers possessing moderate O_2/N_2 selectivity, such as ethyl cellulose (EC),[14] cellulose ester,[15] and polycarbonate,[16] to improve the permselectivity has attracted considerable attention due to its simplicity and convenience. The thermogravimetry and liquid crystallinity of typical polymers for gas separation including cellulose ester,[17] polyphenyleneoxide,[18] polymethylpentene,[19] polyvinylpyridine,[20] and polysiloxane[21] have been studied to elaborate their thermostability and structural order. The additives employed already in the literature include cobalt-containing oxygen carriers, such as α, α', α'', α'''-mesotetrakis(*o*-pivalamidophenyl)porphinato cobalt(II), *N*,*N*′-dialicylidene ethylenediamine cobalt(II), and cobalt di-(salicylal)-3,3′-diimino-di-*n*-propylamine,[16] and liquid crystalline materials, such as low molecular nematic liquid crystals.[22–24] The effect of improvement for O_2/N_2 selectivity through the blend polymer membrane is altered greatly with various additives. Most of additives could elevate the ideal O_2/N_2 separation factor to a magnitude of 3–4, and exceptionally high selectivity for oxygen and nitrogen could reach to 10. In the actual air-separation process, the oxygen concentration of permeated oxygen-enriching air can be attained to 39.5% in this way.

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To further improve the O_2/N_2 permselectivity of the EC membrane, another two additives, 2,2′-bipyridine (2BP) and 4,4′-bipyridine (4BP), are considered. The thought originates from the fact that the polymers containing one or more aromatic heterocyclic nitrogen atom(s) either in their main chains or in their side groups have previously been shown to facilitate the separation of oxygen over nitrogen. For example, the ladder polypyrrolone, which has two nitrogen atoms in its repeated structure unit,[4,25] poly(4-vinylpyridine), which has one nitrogen atom in its repeated side unit,[26,27] and polytriazole, which has three nitrogen atoms in its structure unit,[28] have shown excellent O_2/N_2 selectivities of 6.5, 7, and 9, respectively. Two important conducting polymers, polyaniline[29,30] and polypyrrole,[31–33] containing one nitrogen atom in their main chain units, have exhibited an extremely high O_2/N_2 selectivity of higher than 10 and 7.9 after a careful doping with inorganic acid.

According to the above understanding of the relationship between O_2/N_2 selectivity and the molecular structure of the employed materials, both 2BP and 4BP, which have two nitrogen atoms within their molecules, were selected to act as modification additives for the purpose of improving the air-separation ability of the EC membrane, which is believed to possess excellent flexibility and a good membrane-forming ability besides moderate O_2/N_2 selectivity. It was our objective in this work to prepare BP/EC blend membranes and to investigate their intrinsic actual oxygen-enriching ability and gas permselectivity in more detail.

EXPERIMENTAL

Materials

EC, with a degree of substitution of 2.3–2.4, was purchased from the Shantou Xinning Chemical Works of Guangdong Province (China) and its 5 wt % solution viscosity in ethanol/toluene (50/50) is about 0.04–0.08 Pa s. 2BP, 4BP, and tetrahydrofuran (THF) were commercially obtained. All were analytical grade and were used as received.

Membrane preparation

BP/EC blend membranes with different BP/EC weight ratios were prepared by pouring the casting solutions with concentrations of 4–6 wt % in THF onto glass plates and evaporating the solvent at the room temperature for several days. These membranes, thus obtained, had a thickness of about 40–67 μm.

WAXD characterization

The BP/EC membranes were characterized by wide-angle X-ray diffraction (WAXD) in a Bragg angle range of 3–40° using the wavelength of 0.154 nm of the CuKα election beam in a step-by-step scanning region and recorded using nickel-filtered radiation at room temperature with a Bruker Analytical X-ray Systems D8 Advance X-ray diffractometer (Germany). The scanning rate was 3°/min.

Mechanical properties characterization

The tensile properties of the BP/EC membranes were examined by an Instron tensile tester Model 5565 (USA).

Actual oxygen-enriching measurements

Actual oxygen-enriching properties through the 2BP/EC membranes were measured by a constant pressure–variable volume approach. The employed apparatus had a permeation cell with an effective permeate area of 73.9 cm^2. The feed gas was compressed air with an oxygen concentration of 20.9 vol % from an air compressor. The permeate flux, Q_{OEA}, of the oxygen-enriched air (OEA) through the membranes was determined by measuring the change in the volume of the OEA at a constant pressure gradient across the membrane. The measurements of the oxygen concentration Y_{o_2} in the OEA permeated were performed on a 491-type industrial gas analyzer. The actual oxygen enrichment parameters can be calculated by the equations listed in our previous article.

Gas-permeation measurements

The gas-permeation performance of the 4BP/EC blend membranes was measured using a constant volume–variable pressure approach with a vacuum time-lag apparatus.[14,27] An increase in the permeate pressure with time was recorded by two pressure sensors that were connected directly to a computer. The permeability coefficient P of the 4BP/EC membranes was calculated from the slope of the straight line in the steady-state region, and the ideal selectivity for a gaseous mixture of A and B was calculated from a ratio (P_A/P_B) of two permeabilities of A and B. The experimental errors varied with the magnitudes of the permeability and the time lag and were about 5% for O_2, CO_2, and H_2 and about 10% for N_2 and CH_4.

RESULTS AND DISCUSSION

Characteristics of BP/EC membranes

BP/EC blend membranes are all smooth and flexible and look transparent and homogeneous in visible light when the BP content is no more than 7 wt %. Beyond this, the membrane appearance, including transparency and homogeneity, becomes worse, espe-

TABLE I
WAXD Characteristics and Mechanical Properties of 2BP/EC Blend Membranes

Parameter	2BP/EC ratio (wt/wt)							
	0/100	3/97	5/95	7/93	10/90	15/85	20/80	25/75
Membrane appearance								
Transparency	Best	Best	Best	Better	Better	Better	Fair	Fair
Homogeneity	Best	Best	Best	Better	Fair	Worse	Worst	Worst
Bragg angle (degree)	8.1,19.1	8.2,19.2			8.3,19.2			
Tensile strength (MPa)	48	45	45	43	40	37	36	39
Initial modulus (MPa)	560	1130	958	1210	724	840	748	806
Elongation at break (%)	28	8	10	8	25	10	10	21

cially for 2BP/EC (25/75) (Table I) and 4BP/EC (20/80) membranes (Table II). A similar phenomenon was observed for the poly(4-vinylpyridine)/EC blend membrane.[27] The rich-BP phases can be observed with a naked eye as when the BP content is higher than 10 wt %. Generally, the homogeneity of a mixture is related to the mixture methods besides the properties of the components themselves. In this experiment, a mixed-methods in solution was employed, by which two materials are easily miscible. However, in the following period of evaporation of the solvent, BP materials have enough time to move and come out to form some aggregates in a macroscopic scale when the BP content is higher than 10 wt %. These aggregates tend to lead to an inferior permselectivity through the blend membranes since some pinholes would be easily formed in this domain under an operating pressure difference, as discussed below.

It can be seen from the WAXD diagrams of the BP/EC membranes shown in Figure 1 that the BP/EC blend membranes are nearly amorphous. Two major diffraction peaks at a Bragg angle of approximately 8.1° (stronger) and 19.2° (weaker) are observed for 2BP/EC membranes. The intensity of the former is enhanced slightly while that of the latter is weakened slightly with increasing 2BP content. Like the virgin EC membrane, the 2BP/EC blend membranes with a 2BP content of no more than 10 wt % show a very low crystallinity.[14,27] It is this similar low crystallinity that offers the 2BP/EC membrane a constant permeability in comparison with the EC virgin membrane, as discussed below. However, a big change in the crystalline structure has taken place in the 4BP/EC (10/90) membrane, especially in the 4BP/EC (20/80) membrane, which exhibits more than two diffraction peaks (Fig. 1). The weaker peak at a Bragg angle of 19.2° for the EC virgin membrane is shifted toward a higher angle of 19.7° and becomes the strongest, while the stronger peak at an angle of 8.1° for the EC membranes is

TABLE II
WAXD Characteristics and Mechanical Properties of 4BP/EC Blend Membranes

Parameter	4BP/EC ratio (wt/wt)		
	0/100	10/90	20/80
Membrane appearance			
Transparency	Best	Fair	Fair
Homogeneity	Best	Worse	Worst
Bragg angle (degree)	8.1, 19.1	9.5, 19.7	9.9, 12.8, 19.7
Tensile strength (MPa)	48		37
Initial modulus (MPa)	560		709
Elongation at break (%)	28		21

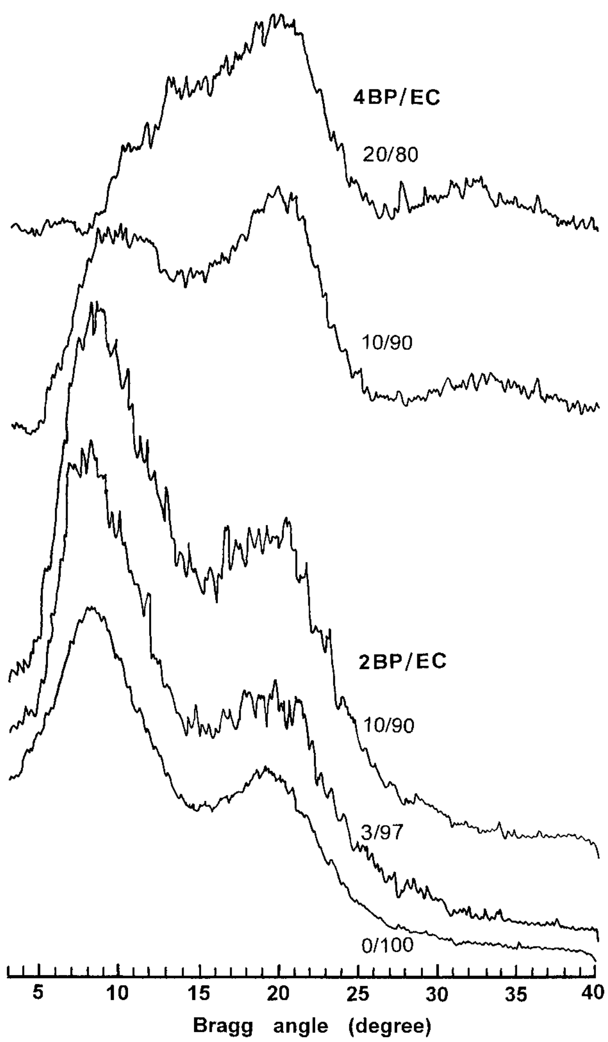

Figure 1 WAXD diagrams of the 2BP/EC and 4BP/EC blend membranes with different BP/EC weight ratios.

shifted toward a higher angle of 9.5° for 4BP/EC (10/90) or breaks into other weaker peaks at higher respective Bragg angles of 9.9° and 12.8° for the 4BP/EC (20/80) membrane. Additionally, a new wide peak at the highest Bragg angle of approximately 32° is observed in both of these 4BP/EC membranes. All the information implies that 4BP/EC blend membranes have a different crystalline structure. Compared with virgin EC or 2BP/EC membranes, a more compact structure or more efficient packing exists in the 4BP/EC membranes. The content of the compact structure in the 4BP/EC membrane is higher than that in the pure EC or 2BP/EC membrane. The characteristic crystalline structure can be used to explain the lower gas permeability of the 4BP/EC blend membrane than that of the virgin EC membrane, as described below.

The effect of BP on the mechanical performance of the EC membrane was also investigated to examine the stability of the membrane in the course of the oxygen-enriching operation. In the examined BP content range, the introduction of BP leads to a slight decrease in the tensile strength, a significant increase in the initial modulus, and an apparent decrease in the elongation at break in comparison with the pure EC membrane[14] (Tables I and II). For 2BP/EC membranes, the tensile strength decreases gradually as the 2BP content increases, except for 2BP/EC (25/75). It is well understood that a small diminution in tensile strength is observed. However, it is difficult to understand that a continuous diminution in tensile strength for 2BP/EC (25/75) is not observed. Perhaps the abnormal behavior may be due to the lower 2BP content in a sample selected for testing than to the feed content owing to its inhomogeneity. Obviously, the enhancement in the modulus for BP/EC blend membranes resulted from the rigidity of rigid BP particles. These changes in the mechanical performance are responsible for the stability in oxygen enrichment.

Effect of 2BP content on actual oxygen enrichment from air

The effect of the 2BP content in the blend membranes on the actual oxygen enrichment from air at three transmembrane pressure differences is shown in Figure 2. It can be seen that, in the testing range of 2BP content from 0 to 15 wt %, the oxygen concentration Y_{o_2} of the OEA first increases with increasing 2BP content in the EC membrane and then decreases when more than 3 wt % of 2BP was added. The corresponding OEA flux Q_{OEA} of OEA remains unchanged essentially until 5 wt % of 2BP, and a distinguished increase in the OEA flux occurs after that, especially at the transmembrane pressure of 0.65 MPa [Fig. 2(b)]. In comparing the 2BP/EC blend membranes with a virgin EC membrane, it can be found that when no more than 7 wt % 2BP was added the oxygen concentration Y_{o_2} of OEA is enhanced, while the OEA flux Q_{OEA} is substantially maintained at their individual values at three operating pressure differences. On the contrary, when more than 7 wt % 2BP was added, a decline in oxygen concentration Y_{o_2} and an enhancement in flux Q_{OEA} are observed. Thus, it could be concluded that when 3 wt % of 2BP is introduced, the modification extent on the actual oxygen-enrichment properties from air for the EC membrane reaches the maximum. The oxygen concentration Y_{o_2} of the 2BP/EC (3/97) membrane reached 42.3% at the transmembrane pressure difference of 0.65 MPa and 20°C, while the virgin EC membrane exhibits an oxygen concentration Y_{o_2} of 39.6% at the same operating conditions. Moreover, the OEA fluxes for both membranes are almost the same, which results from the same amorphous feature verified by the WAXD diagram in Figure 1.

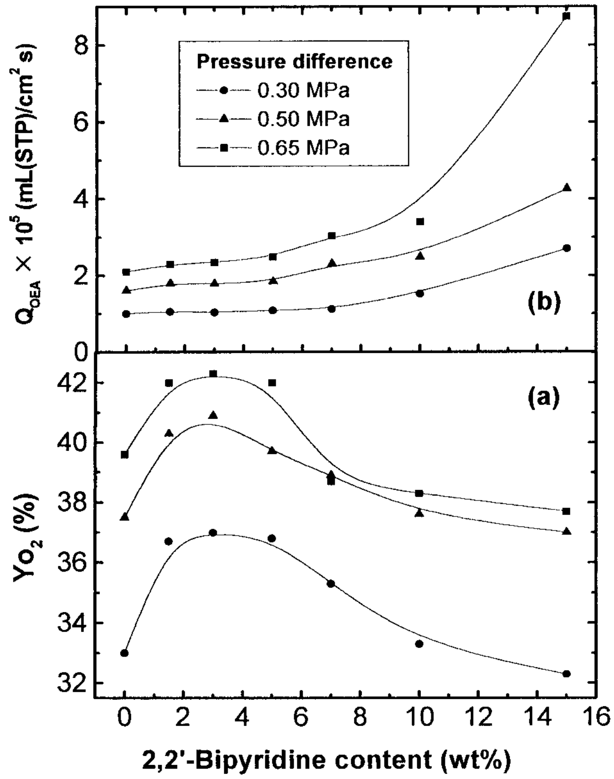

Figure 2 Effect of 2BP content in 2BP/EC blend membranes cast from 4 wt % in THF solution on (a) Y_{o_2} and (b) OEA flux Q_{OEA} at three transmembrane pressure differences and 20°C in a retentate/permeate flux ratio range from 300 to 700.

This result suggests that an addition of a small amount of 2BP to EC is effective for improvement of the actual oxygen-enrichment properties from air for the EC membrane. It is obvious that the introduction of an appropriate amount of 2BP is a key factor for this improvement. If a smaller quantity of 2BP is introduced, the improvement of the actual oxygen-enrichment properties from air across the obtained 2BP/EC

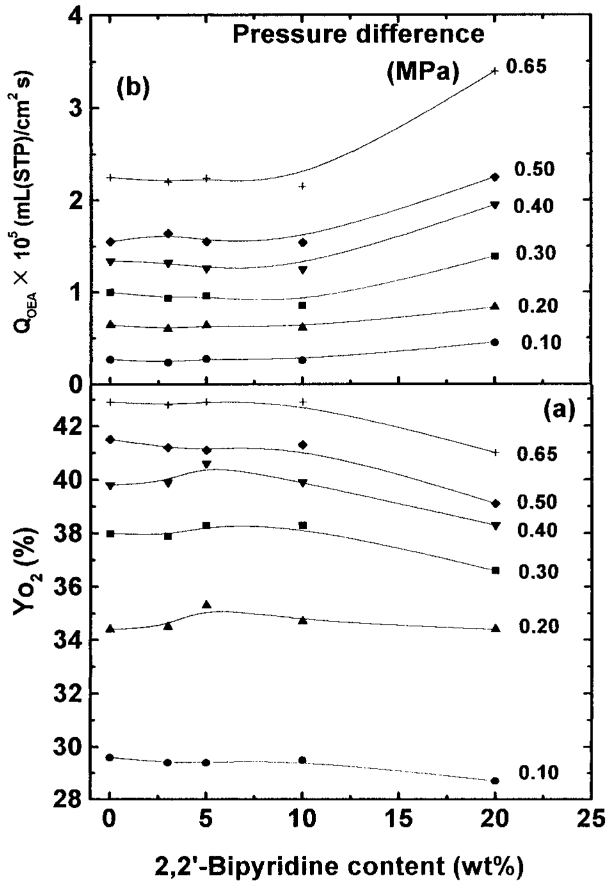

Figure 3 Effect of 2BP content in thicker 2BP/EC blend membranes cast from 6 wt % in THF solution on (a) Y_{O_2} and (b) OEA flux Q_{OEA} at six transmembrane pressure differences and 20°C in a retentate/permeate flux ratio range from 250 to 650.

membrane is not considerable. On the contrary, if a greater quantity of 2BP is introduced, the actual oxygen-enrichment properties from air is impaired and even lost compared with the EC membrane. 2BP/EC (20/80) and (25/75) membranes with a thickness of 40 μm, for instance, have no oxygen-enriching ability at all. This undesirable effect seems to result from the BP aggregates described above because they cannot withstand the pressure difference applied in the examination and even leak out from the interior to the exterior of the membranes. It can be predicted that if the miscibility between 2BP and EC is good enough no BP aggregates will be observed; the performance of the blend membrane with high 2BP content would also be improved significantly. Additionally, the OEA flux is hardly ever dependent on the membrane composition and is inversely proportional to the membrane thickness within the range of 0–7wt %, which implies that the permeated behavior of gas through the 2BP/EC membranes could be elucidated by the solution–diffusion model.

The phenomena that the actual oxygen-enrichment properties across the EC membrane can be modified by 2BP could be explained by the fact that there are two nitrogen atoms in the 2BP molecule which may reduce the solubility of nitrogen gas from the feed air in the membrane via repulsion of the same kinds of atoms and, thus, furthermore hinder a portion of the nitrogen molecules from permeating through the membrane.

Effect of membrane thickness on actual oxygen enrichment from air

Some thicker 2BP/EC blend membranes with a 2BP content from 0 to 20 wt % and about 67-μm-thick casting from a 6 wt % concentration in THF were measured for their oxygen enrichment. The results are shown in Figure 3. Compared with thinner membranes, the actual oxygen-enrichment performance through thicker BP/EC membranes is enhanced for all the tested membranes including pure EC. The behavior is coincident with that of other dense membranes.[27] The obvious reason is that thicker membranes usually have fewer defects than do thinner membranes for the same kinds of membranes. In comparing the 2BP/EC membranes with the pure EC membrane having almost the same thickness, however, the oxygen enrichment is only slightly enhanced for the 5 wt % 2BP/EC membrane and even diminished for the 20 wt % 2BP/EC membrane [Fig. 3(a)]. A smaller enhancement in oxygen enrichment for thicker membranes may be explained by the schematic model shown in Figure 4. It can be speculated that a small amount of 2BP (no more than 10 wt %) in a thicker EC membrane tends to form some separated microphases wrapped in the EC matrix rather than continuous microchannels from one side to the other side of the membrane that could easily occur in thinner membranes (Fig. 4). Hence, the effect of 2BP on modifying the oxygen enrichment of the EC membrane is impaired. In other words, the improvement of a small amount of 2BP on oxygen enrichment across the EC membrane is diminished as the membrane thickness increases. On the other hand, if a high 2BP content up to 20 wt % is employed in a thicker EC membrane, an inhomogeneous distribution for 2BP phases is frequently obtained. In this circumstance, BP had a tendency of becoming some of aggregates. These aggregates are easily impacted and, thus, some pinholes

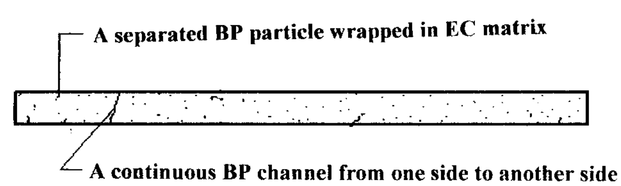

Figure 4 Proposed schematic showing separated particles and continuous channels for 2BP phase in EC matrix.

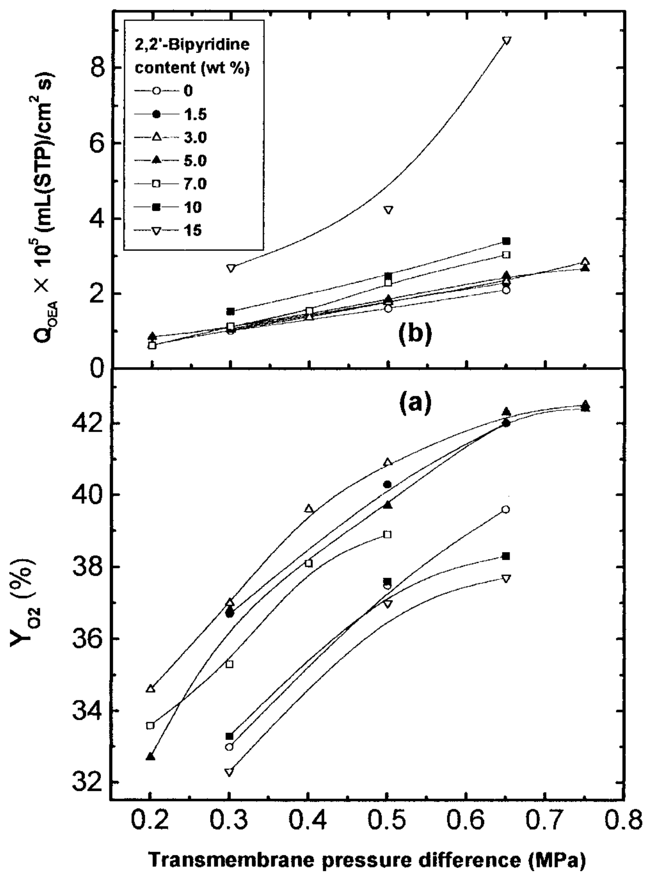

Figure 5 Effect of transmembrane pressure difference on (a) Y_{o_2} and (b) OEA flux Q_{OEA} through 2BP/EC blend membranes with different 2BP content at 25°C in a retentate/permeate flux ratio range from 300 to 700.

would be formed, so the oxygen-enrichment performance across a 20 wt % 2BP/EC membrane is inferior [Fig. 3(a)]. If a higher content of 2BP could be dispersed homogeneously in the thicker 2BP/EC blend membrane by a special method, fine channels could be formed and the modification of 2BP on the oxygen-enrichment properties of pure EC would be remarkable. It could be concluded that a small amount of 2BP has a better effect on oxygen enrichment across the thinner 2BP/EC membrane than that across the thicker membrane.

Effect of operating parameters on actual oxygen enrichment from air

Effect of transmembrane pressure difference on oxygen enrichment

Figure 5 shows the pressure-difference dependencies of the oxygen concentration Y_{o_2} and the OEA flux Q_{OEA} across the 2BP/EC blend membranes with different 2BP contents from 0 to 15 wt % at the pressure difference of 0.2–0.75 MPa. It is seen that the oxygen concentration Y_{o_2} in OEA permeated through the 2BP/EC blend membranes increased to 37.7–42.7% as the pressure difference increased to 0.65–0.75 MPa for all 2BP/EC membranes. Among them, the 2BP/EC blend membrane containing 3 wt % BP yields the highest oxygen concentration of 42.7% at the transmembrane pressure difference of 0.75 MPa and 25°C. Additionally, the oxygen concentration Y_{o_2} data tend to come close to each other for 1.5–5 wt % 2BP/EC blend membranes when a high pressure difference of 0.75 MPa is applied. In comparing all 2BP/EC blend membranes with each other in Figure 5(a), it is found that the 3 wt % 2BP/EC membrane has the highest Y_{o_2} and the 15 wt % 2BP/EC membrane has the lowest oxygen concentration Y_{o_2} value in the testing pressure difference range of 0.2–0.75 MPa, which coincides with the above results.

The flux Q_{OEA} increases linearly with an increasing pressure difference except for the 15 wt % 2BP/EC blend membrane [Fig. 5(b)]. The rate of the increase in the OEA flux with the pressure difference remains at a practically constant value and is nearly independent of the membrane compositions within the 2BP content range of 0–5 wt %. Beyond this composition range, the increased rate will become slightly large and eventually increases abruptly for the high 2BP content blend membrane due to the existence of 2BP aggregates which cannot withstand the higher pressure difference applied. Low and high molecular weight liquid crystalline blend membranes also exhibit similar enhancement in the oxygen concentration and flux as the pressure difference increases.[22,24]

Effect of retentate/permeate flux ratio on oxygen enrichment

The retentate/permeate flux ratio is defined by the rejection flux F_1 in the upstream side over the permeate flux F_2 in downstream side The rejection flux F_1 can be controlled by a needle valve assembled in the outlet pipe of nitrogen-enriched air in the feed side. If the rejection flux F_1 is set small enough, more and more nitrogen gases will cut off in the upstream side and polarization in the concentration will become serious in the course of permeation of compressed air through the membrane. Conversely, if the rejection flux F_1 is set large enough, the upstream gas will be kept as fresh air with an oxygen content near 20.9%; thus, the polarization in the concentration will be eliminated substantially. However, more energy is exhausted in the latter circumstance. Therefore, a reasonable retentate/permeate flux ratio must be established. For this purpose, the dependence of oxygen enrichment on the retentate/permeate flux ratio was investigated. The results show that oxygen concentrations through the 2BP/EC blend membranes at a 0.5 pressure difference and 27°C increase dramatically in the retentate/permeate flux ratio range of 0–100. Beyond this range, oxygen concentrations are kept at

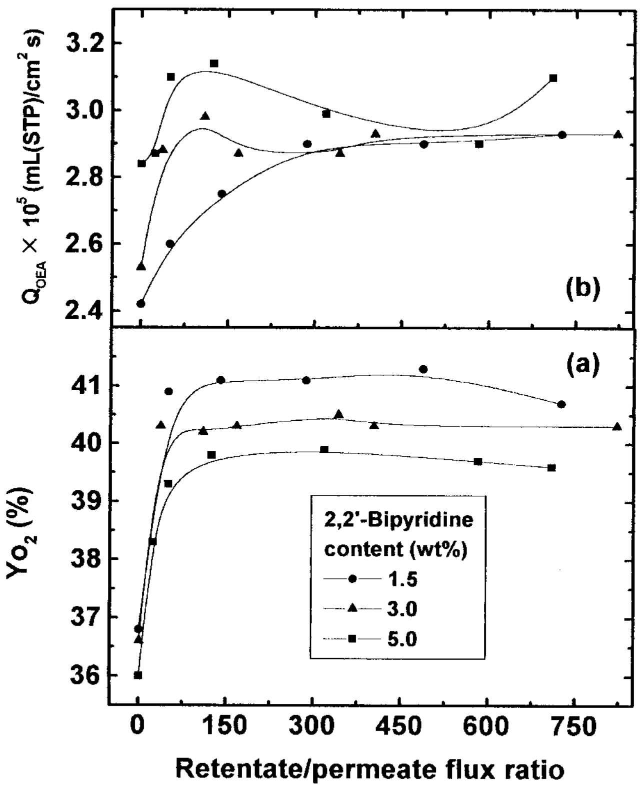

Figure 6 Effect of retentate/permeate flux ratio on (a) Y_{O_2} and (b) OEA flux Q_{OEA} through 2BP/EC blend membranes with different 2BP content at 27°C and the transmembrane pressure difference of 0.5 MPa.

their individual values [Fig. 6(a)]. The corresponding OEA flux exhibits a similar retentate/permeate flux ratio dependency [Fig. 6(b)]. It should be pointed out that the 2BP/EC blend membrane containing 1.5 wt % 2BP possesses the highest Y_{O_2}, whereas the 2BP/EC blend membrane containing 5 wt % 2BP possesses the lowest Y_{O_2} among the three 2BP/EC membranes in the retentate/permeate flux ratio range of 100–800. It seems that the result is in contradiction with that from Figure 2. The diversity of the magnitude of the oxygen concentration shown in Figures 2 and 6 through the three blend membranes could be explained by the stability or the mechanical performances (Table I) of these blend membranes. It must be appreciated that the measurements in Figure 6 were taken after the blend membranes were subjected to several dozens of cyclic examinations under a higher transmembrane pressure difference. Some defects may be formed in these blend membranes after a certain number of measurements. The inferior extent of oxygen enrichment through the blend membranes is generally proportional to the 2BP content. The stability of the blend membrane, of course, is the opposite. The phenomenon that the OEA flux through the 2BP/EC (5/95) membrane increases abruptly at a retentate/permeate flux ratio of 700 also indicates inferior mechanical properties of the membrane after more times of testing [Fig. 6(b)].

It can be speculated that the inferior oxygen enrichment resulting from the stability of the blend membranes could be overcome by an enhancement of uniformity of the BP and EC mixture. Additionally, the stability of the blend membranes would be improved by sandwiching them between two support membranes such as polysulfone and polyethersulfone, based on our experience. Further investigation should be done in the future.

Effect of temperature on oxygen enrichment

Figure 7 presents plots of the air-separation parameters including the actual air-separation factor for the virgin EC membrane with a thickness of 67 μm at the transmembrane pressure difference of 0.5 MPa and the retentate/permeate flux ratio range of 200–380. It is shown that the Y_{O_2} and the actual air-separation factor P_{O_2}/P_{N_2} decrease almost linearly, whereas the OEA flux Q_{OEA} increases obviously when the temperature increases. Without doubt, all these behaviors of the virgin EC membrane are similar to other homogeneous dense membranes.

The plots of $\mathrm{Ln}P_{O_2}$ and $\mathrm{Ln}P_{N_2}$ versus $1/T$ [Fig. 7(b)] show a good linear relationship that coincides with an Arrhenius law. Based on the two plots, the activation

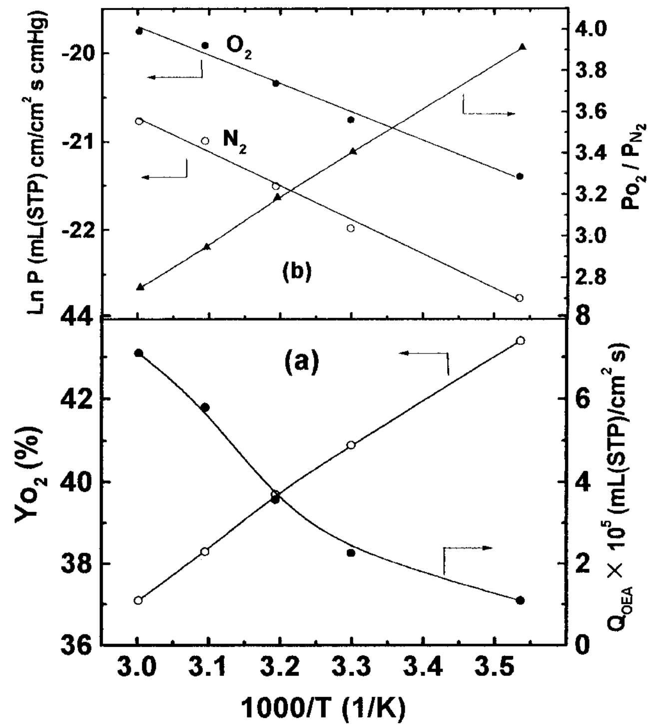

Figure 7 Effect of temperature on (a) Y_{O_2} and OEA flux Q_{OEA} as well as (b) P_{O_2}, P_{N_2}, and P_{O_2}/P_{N_2} through virgin EC membrane at the transmembrane pressure difference of 0.5 MPa and the retentate/permeate flux ratio range of 200–380.

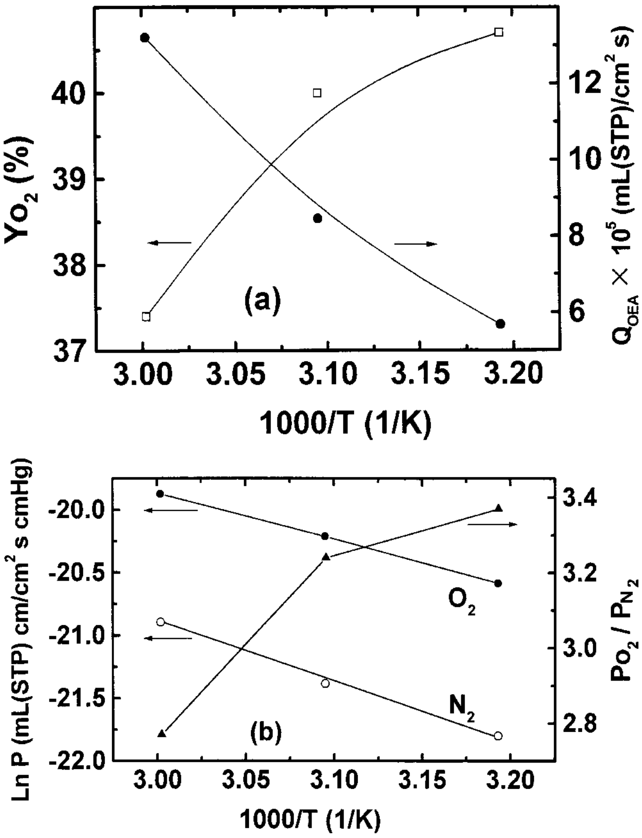

Figure 8 Effect of temperature on (a) Y_{o_2} and OEA flux Q_{OEA} as well as (b) P_{o_2}, P_{N_2}, and P_{o_2}/P_{N_2} through 2BP/EC (1.5/98.5) blend membrane at the transmembrane pressure difference of 0.5 MPa and the retentate/permeate flux ratio range of 90–320.

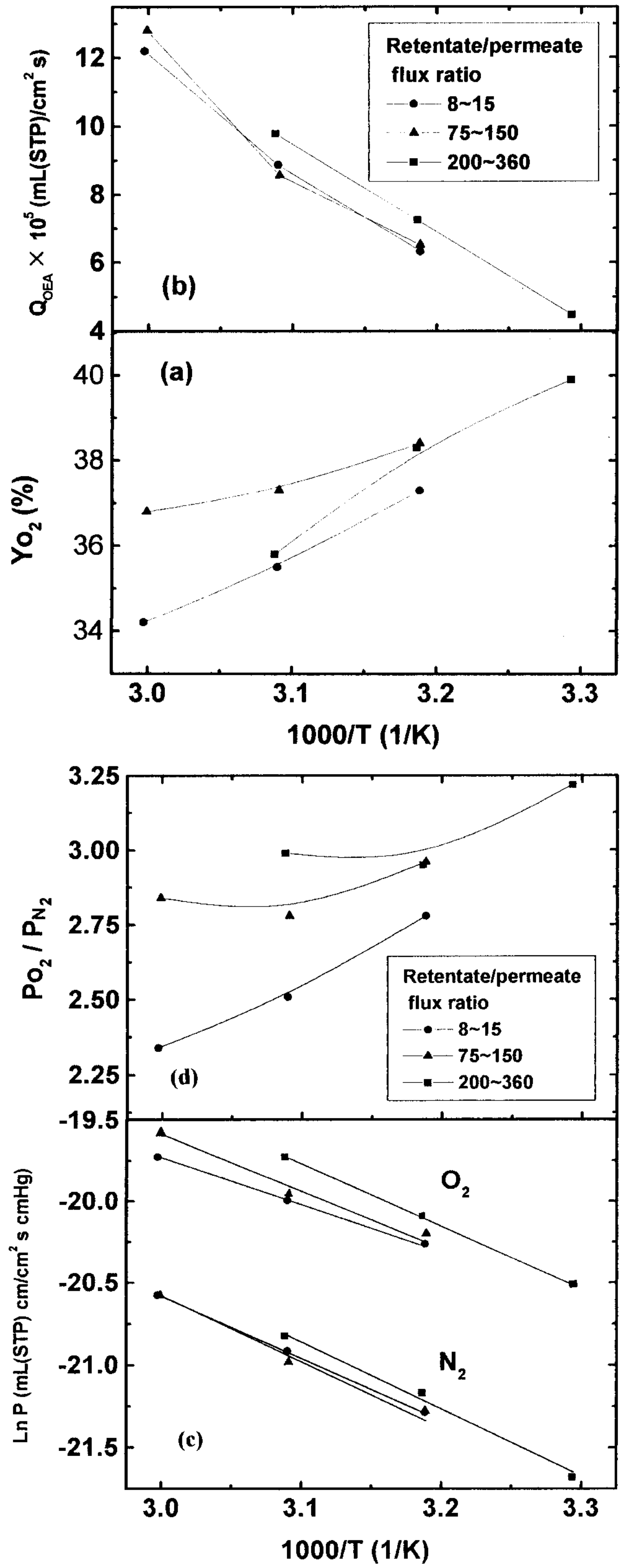

Figure 9 Effect of temperature on (a) Y_{o_2}, (b) OEA flux Q_{OEA}, (c) P_{o_2} and P_{N_2}, and (d) P_{o_2}/P_{N_2} through 2BP/EC (5/95) blend membrane at the transmembrane pressure difference of 0.5 MPa and the retentate/permeate flux ratio range of 8–360.

energy of oxygen and nitrogen permeation listed in Table III can be calculated according to the following Arrhenius equations:

$$\ln P_{o_2} = \ln(P_{o_2})_0 - \frac{E_{o_2}}{RT} \quad (1)$$

$$\ln P_{N_2} = \ln(P_{N_2})_0 - \frac{E_{N_2}}{RT} \quad (2)$$

The activation energy of oxygen and nitrogen permeation across the virgin EC membrane in the temperature range of 9.7–60°C are 26.7 and 32.2 kJ/mol, respectively. The former is lower and the latter is slightly higher than the literature data,[14] which are, respectively 29.9 and 31.2 kJ/mol, obtained from a thinner virgin EC membrane with a thickness of 18 μm in the higher temperature range of 25–85°C.

The temperature effects on oxygen-enrichment parameters through the 1.5 and 5.0 wt % BP/EC blend membranes are described in Figures 8 and 9. Similar behavior is observed in the blend membranes. Likewise, the activation energy of oxygen and nitrogen

TABLE III
Activation Energy of O_2 and N_2 Permeation Through 2BP/EC Blend Membranes at Temperature Range of 9.7–60°C and the Retentate/Permeate Flux Ratio Range from 100 to 380

	Membrane		
Active energy	Virgin EC	2BP/EC (1.5/98.5)	2BP/EC (5/95)
E_{O_2}	26.7	30.9	31.7 27.0[a] 23.2[b]
E_{N_2}	32.2	39.4	34.7 30.8[a] 30.8[b]

[a] The retentate/permeate flux ratio range was from 75 to 150.
[b] The retentate/permeate flux ratio range was from 8 to 15.

permeation through the blend membranes listed in Table III can be calculated from the almost linear plots of Ln $P \sim 1/T$. Apparently, the 2BP/EC blend membranes exhibit stronger sensitivity to temperature than do the virgin EC membrane in the retentate/permeate flux ratio range from 100 to 380. Being a small molecular weight material having a melting point of 69.7°C, the 2BP phase tends to deform easily under the operating transmembrane pressure difference compared with the EC phase, especially at a temperature higher than ambient temperature. In other words, the 2BP phase is more sensitive to temperature than is EC. Hence, it is easy to understand the stronger sensitivity of the 2BP/EC blend membranes to temperature than that of the virgin EC membrane.

Note that the activation energy of oxygen and nitrogen permeation measured in this method is slightly changeable with the retentate/permeate flux ratio (Table III). When the retentate/permeate flux ratio decreases to the range of 75–150 or 8–15, E_{O_2} and E_{N_2} decline 11–15% or 11–27%, respectively. The phenomenon is related to the decline in the oxygen concentration in the OEA permeated.

Gas permselectivity of 4BP/EC membranes

To further survey other aromatic nitrogen-containing materials on gas-separation properties, the gas permeabilities of 4BP/EC blend membranes cast from 6 wt % in THF were measured. A typical variation of the downstream pressure of five pure gases through the 4BP/EC (10/90) blend membrane with time at 25°C and the upstream pressure of 10 bar is shown in Figure 10. The permeation parameters calculated from the same membrane at the same temperature and respective upstream pressure of 1, 2, 5, and 10 bar are listed in Table IV. It is seen that five gases permeate the membrane in different ways.[14,27] Among the five gases, CO_2 exhibits the fastest permeation rate after a longer time lag of 30 s, while H_2, with the smallest molecular size, exhibits the second fastest permeation rate after the shortest time lag of 1 s. N_2 exhibits the slowest permeation rate after a longer time lag of 29 s. Compared with virgin EC membrane,[14,27] the rank of these permeation rates for the five gases through the 4BP/EC blend membrane is not altered, but magnitudes of these permeability coefficients decreases unexpectedly in the examined upstream pressures, especially for the 4BP/EC (20/80) blend membrane (Table IV). The decline in the permeability coefficients for the five gases should be attributed to a more compatible morphological structure of the 4BP/EC blend membranes verified by the WAXD diagrams shown in Figure 1, as discussed above.

The oxygen permeation through the 4BP/EC (20/80) blend membrane was recorded with an increasing

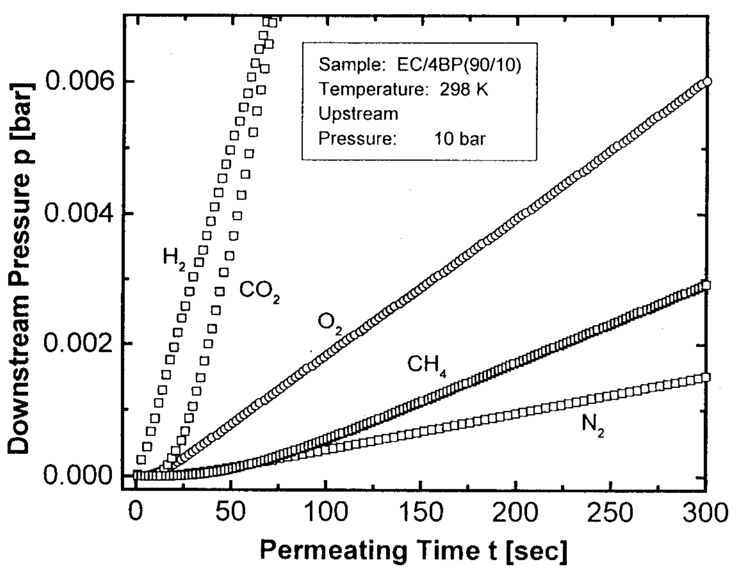

Figure 10 Relationship between downstream pressure and permeating time for the permeation of five gases through 4BP/EC (10/90) membrane at an upstream pressure of 10 bar and 298 K.

TABLE IV
Gas-permeation Performance [mL (STP) cm cm^{-2} s^{-1}cmHg^{-1}] of 4BP/EC (wt/wt) Membranes at 25°C and Upstream Pressure of 5 and 10 Bar, Respectively

Membrane	Pressure (bar)	P_{O_2}	P_{N_2}	P_{CO_2}	P_{CH_4}	P_{H_2}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}	P_{H_2}/P_{N_2}
EC (virgin)	5	12.6	2.95	63.0	5.98	54.8	4.27	10.5	18.6
	10	12.0	2.91	68.2	5.99	55.4	4.12	11.4	19.0
4BP/EC (10/90)	5	9.37	2.42	60.9	5.26	44.4	3.87	11.6	18.8
	10	9.11	2.40	68.6	5.20	44.4	3.80	13.2	18.5
4BP/EC (20/80)	1	7.17	1.98	48.0	4.61	34.5	3.62	10.4	17.4
	2	7.07	1.88	48.0	4.43	33.9	3.73	10.8	18.0
	5	6.97	1.89	50.2	4.33	33.7	3.69	11.6	17.8
	10	7.06	1.87	53.8	4.35	34.5	3.78	12.4	18.4

upstream pressure from 1 to 10 bar and is shown in Figure 11. It can be seen that the downstream pressure of the membrane increases rapidly after a small initial time lag. The increased rate of downstream pressure with the permeating time is strongly dependent on the upstream pressure. Certainly, the permeability coefficient of the five gases through the blend membrane can be calculated from the slope of the straight line of the downstream pressure versus the permeating time in a steady-state region. It can be seen from Table IV that the permeability of the five gases through the 4BP/EC (20/80) blend membrane does not change essentially with the upstream pressure. A similar relationship was observed for virgin EC membrane,[14,27] but the magnitude of the EC membrane is larger than that of the 4BP/EC (20/80) membrane.

On the other hand, the permselectivity for the H_2 over N_2 pair decreases slightly and that for the CO_2 over CH_4 pair increases as 4BP introduced (Table IV). Unfortunately, the permselectivity for the O_2 over N_2 pair decreases obviously after 4BP is introduced into the EC virgin membrane (Table IV). Since the five gases permeate the BP/EC blend membranes with their individual permeated rates as with the EC virgin dense membrane,[14] rather than with the same permeated rates as with the porous membrane, there should be no defect or pinhole in the 4BP/EC blend membranes. Thus, the decline in permselectivity for O_2 over N_2 should not increase from the defect or pinhole. One of the reasons is that the diffusivity calculated from Figure 10 for N_2 is larger than that for O_2, although the permeability coefficients for O_2 and N_2 both decrease.

It is interesting that the CO_2 over CH_4 permselectivity through the EC membranes increases with introducing 4BP, and the ideal separation factor increases 16% at the upstream pressure of 10 bar (Table IV). Without doubt, this is related to the remarkable decline of the permeability coefficient of CH_4. Apparently, CH_4, with a large molecular size, is different in

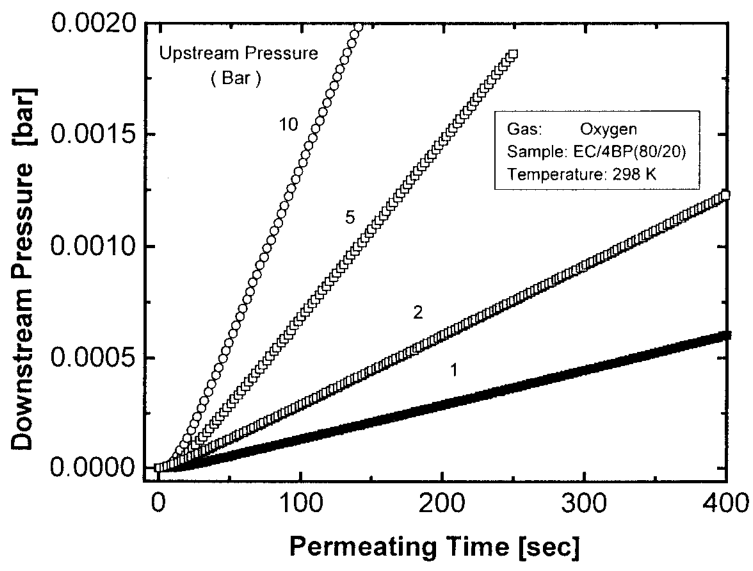

Figure 11 Relationship between the downstream pressure and permeating time for oxygen permeation through 4BP/EC (20/80) membrane at different upstream pressures and 298 K.

permeating through the more compacted 4BP/EC membrane, verified by the WAXD diagram in Figure 1.

Summarizing, the different positions of two nitrogen atoms in the BP molecule would result in a different effect on the gas permselectivity. A small amount of 2BP can improve the O_2 over N_2 permselectivity through the EC membrane, while a small amount of 4BP can improve the CO_2 over CH_4 permselectivity through the EC membrane. It seems that the fine crystalline structure of the dense membrane is responsible for the diversity. Additionally, the position of two nitrogen atoms in 2BP and 4BP molecules should be a key factor, which results in a different crystalline structure and a different repulsion or solution to the same gas. An incisive analysis could be done in the future.

CONCLUSIONS

New oxygen-enriching blend membranes composed of 2BP or 4BP and EC with different composition ratios were evaluated for their gas-separation properties. It was demonstrated that the addition of a small amount of 2BP to EC is an effective and simple method for improving the actual oxygen-enrichment properties from air for the EC membrane. When 3 wt % of 2BP was introduced, the modification extent is up to the maximum for the thinner EC membrane while the permeated flux remains substantially constant. The oxygen concentration Y_{O_2} through the blend membrane reached 42.3% at the transmembrane pressure difference of 0.65 MPa and 20°C, whereas the virgin EC membrane exhibits an oxygen concentration Y_{O_2} of 39.6% at the same operating conditions. The oxygen enrichment of the 2BP/EC blend membrane was found to depend strongly on the transmembrane pressure difference, retentate/permeate flux ratio ranging from 0 to 100, and operating temperature. The activation energies of oxygen and nitrogen permeation through the 2BP/EC membranes are, respectively, 30.9–31.7 and 39.4–34.7 kJ/mol in the retentate/permeate flux ratio range from 100 to 380, the temperature range of 9.7–60°C, and the pressure difference of 0.5 MPa, which are higher than that through the virgin EC membrane. The O_2 over N_2 permselectivity through the 4BP/EC membranes decreases, but the CO_2 over CH_4 permselectivity through the same membrane increases as compared with the pure EC membrane.

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