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Shih-Hsiung Chen[a]; Ruoh-Chyu Ruaan[a]; Juin-Yih Lai[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, CHUNG YUAN UNIVERSITY CHUNG LI, TAIWAN, REPUBLIC OF CHINA

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Effect of Nonsolvent/Oxygen Carrier Additives on Gas Separation Performance of Polycarbonate Membranes

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SHIH-HSIUNG CHEN, RUOH-CHYU RUAAN,
and JUIN-YIH LAI*
DEPARTMENT OF CHEMICAL ENGINEERING
CHUNG YUAN UNIVERSITY
CHUNG LI, TAIWAN 320, REPUBLIC OF CHINA

ABSTRACT

N,N'-Dimethylformamide (DMF) and *N,N'*-dialicylidene ethylene diamine cobalt(II) (CoSalen) were added into the casting solution to improve both the gas permeability and oxygen/nitrogen selectivity of polycarbonate (PC) membranes. PC membranes formed by a simple dry method are known to have high oxygen/nitrogen selectivity but low gas permeability. A nonsolvent, DMF, was added into the casting solution to improve the membrane permeability, and an oxygen carrier, CoSalen, was added to improve the oxygen/nitrogen selectivity. The addition of DMF increased the membrane permeability but reduced the oxygen/nitrogen selectivity. On the contrary, the addition of CoSalen raised the selectivity but suppressed the permeability. To make a membrane of selectivity near the value of native PC membrane but with a higher gas permeation rate by adjusting the DMF and CoSalen contents in the casting solution, the highest oxygen permeation flux of CoSalen complexed porous PC membranes was 0.61 GPU(10^{-6} × $cm^3/cm^2 \cdot s \cdot cmHg$) at an O_2/N_2 selectivity of 4.7 at 35°C. This membrane was obtained when 19 vol% of DMF and 4.8 wt% of CoSalen were added into the PC casting solution. This specific membrane, after a long period of storage, 400 days, had a higher oxygen flux (0.88 GPU) which was obtained without any loss in selectivity. At a lower temperature, 5°C, an even higher oxygen selectivity of 7.9 was obtained.

Key Words. Polycarbonate; *N,N'*-Dimethylformamide (DMF); *N,N'*-Dialicylidene ethylene diamine cobalt(II) (CoSalen); O_2/N_2 selectivity

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* To whom correspondence should be addressed.

INTRODUCTION

To make a membrane separation process economically feasible, obtaining a highly permeable and selective membrane plays the most important role (1, 2). In the area of oxygen/nitrogen separation, tremendous efforts were made toward improving two major membrane properties, namely, gas permeability and selectivity. Many tricks of membrane modification were tried; for example, polymer blending (3), grafting (4–6), copolymerization (7), and the incoporation of oxygen affinity ligands. In most cases the above-mentioned techniques can only improve one of the desired properties by sacrificing the other. Polycarbonate membrane was found to have high selectivity and good mechanical strength. Unfortunately, the gas permeability is low. Several efforts were made to improve the membrane permeability. One way was to introduce a metal salt into the casting solution. Micropores were produced through a salt leaching process so as to increase the membrane permeability. However, a decrease in membrane selectivity was found (8–10). Another way was to obtain an asymmetric membrane by using the wet phase inversion method (11, 12). An ultrathin dense layer was obtained and therefore increased the gas permeation. But small pinhole would sometimes appear after prolong use and subsequently killed the selectivity. Pinnau and Koros (14) proposed the use of an integrally skinned asymmetric membrane which was composed of a skinned polycarbonate layer supported by a polysulfone membrane. A tremendous increase in membrane permeability was found without significant loss in oxygen selectivity. Their result was truly impressive except for the complexity of the membrane formation process.

To keep the process simplicity of the dry method, a new approach was proposed by Lai et al. (8). Two additives were added simultaneously into the casting solution. A nonsolvent additive was added to form a porous membrane, while an affinity ligand of oxygen, Cu(II), was incorporated to enhance the membrane selectivity. A high flux membrane was obtained by slightly sacrificing the loss in selectivity. In this study a similar action was taken. A different ligand, *N,N'*-dialicylidene ethylene diamine cobalt(II) (CoSalen), was added into the polycarbonate casting solution. CoSalen is known to be an excellent oxygen carrier. Taking advantage of the high affinity of CoSalen toward oxygen, the selectivity of a porous PC membrane was expected to increase. In addition, the effects of the amount of DMF addition on membrane structure, permeability, and selectivity have never been discussed, and they are investigated in this study. The performance of the modified membrane at various operating temperatures was also studied.

EXPERIMENTAL

Materials

Polycarbonate (Upilon S-2000) was supplied by Mitsubishi Gas Chemical Co. Dichloromethane and *N,N'*-dimethylformamide were supplied by Merck Co. All the above-mentioned chemicals are reagent grade and were used without further purification. The oxygen carrier (CoSalen) was prepared by the method of Bailes and Calvin (13).

Membrane Preparation

The PC membrane was prepared from a casting solution of polycarbonate in dichloromethane. The CoSalen/DMF complexed membranes were prepared by adding both DMF and CoSalen into the PC casting solution. The membranes were formed by casting the solution onto a glass plate to a predetermined thickness using a Gardner knife at room temperature. The membranes were dried in vacuum for 24 hours before gas sorption and permeation measurements.

Gas Permeation Measurement

The apparatus and experimental procedure employed for gas permeability measurements have been described in a previous report (8). The gas permeability was determined by

$$\frac{P}{l} = \frac{1}{(P_1 - P_2)}\left[\frac{q/t}{A}\right]$$

where P/l denotes the gas permeation rate [10^{-6} $\mathrm{cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg}$ (GPU)], q/t is the volumetric flow rate of gas permeation [$\mathrm{cm^3(STP)/s}$], l is the membrane thickness (cm), P_1 and P_2 are the pressures (cmHg) on the high and low pressure sides of the membrane, respectively, and A is the area of membrane tested for gas permeation ($\mathrm{cm^2}$).

SEM Structure Measurement

The structures of membranes were examined with a Hitachi Model S570 scanning electron microscope (SEM). The samples were coating with gold to a thickness of about 150 Å.

Porosity Measurement

In order to calculate the membrane porosity, one must first estimate the polymer volume (V_p) and membrane volume (V_m). The polymer volume was calculated by dividing the weight of polymer by the density of dense polycarbonate (by using a micrometrics Accupyc 1330 pycnometer). The membrane volume was calculated by multiplying the membrane thickness and area. The membrane thickness was measured with a thickness gauge (Teclock MS1201). The porosity is given by

$$\text{Porosity} = \frac{V_m - V_p}{V_m} \times 100\%$$

RESULTS AND DISCUSSION

DMF Addition Resulted in a Highly Porous Membrane Structure

A dense PC membrane was prepared by vacuum drying a 2 g/17 mL polycarbonate/dichloromethane casting solution. This membrane has a smooth appearance and a low porosity. When various amounts of a nonsolvent, DMF, were added into the casting solution, a porous sponge-like membrane structure was formed. Figure 1 shows SEM photographs of the cross section of the porous membranes produced by introducing various amounts of DMF. A homogeneous porous structure with pore sizes ranging from 3 to 6 μm can be clearly observed. Although it seemed that the pore size shown in Fig. 1 was not controlled by the amount of DMF added, the porosity of these membranes did increase with the addition of DMF. As shown in Fig. 2, the porosity increased rapidly at DMF concentrations higher than 10.5 vol% but leveled off at higher DMF concentration (above 20 vol%).

Effect of DMF Addition on Membrane Permeability and Selectivity

It was expected that the porous PC membrane would have a higher gas permeation rate than the nonporous one. To understand how the membrane performance was affected by the added DMF, both the gas permeation rate and gas selectivity were measured and calculated. As can be seen from Fig. 3, the overall gas permeation rate increased as the amount of DMF increased. When the casting solution contained less than 10.5 vol% of DMF, the overall gas flux increased only slightly with an increasing amount of DMF. As the DMF content was raised to above 10.5 vol%, the gas permeation rate increased abruptly. However, the increase in membrane permeability was accompanied by a loss in oxygen selectivity. As shown in Fig. 4, the oxygen selectivities of porous PC membranes were no less than that of the nonporous one when less than 10.5 vol% of

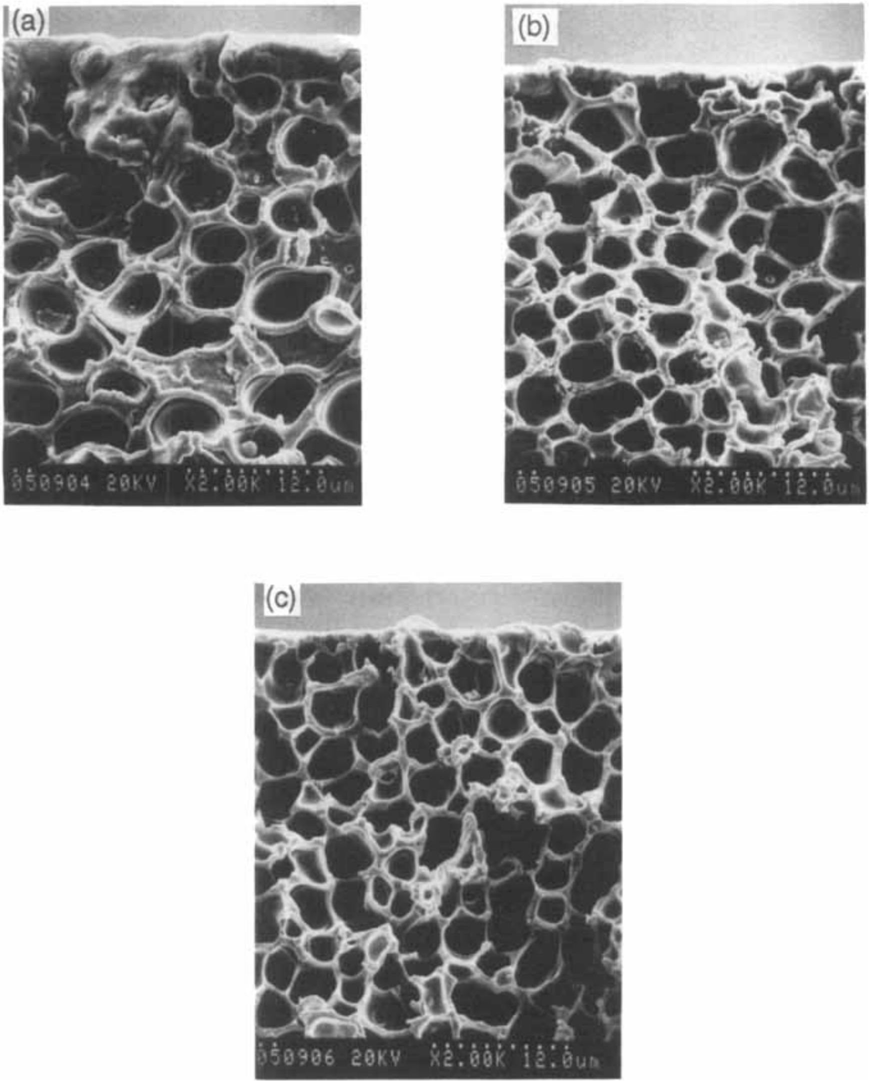

FIG. 1 SEM of PC membrane prepared by nonsolvent additive in the casting (PC, 2 g/17 mL, CH_2Cl_2). DMF added: (a) 2 mL, (b) 4 mL, (c) 6 mL.

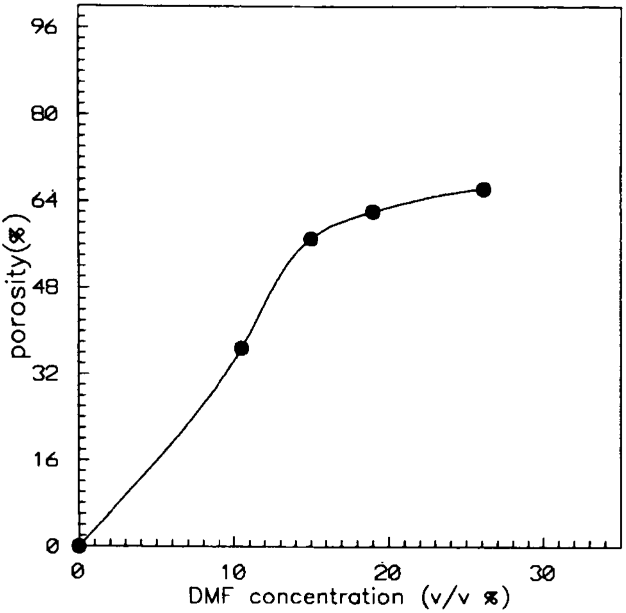

FIG. 2 Effect of added nonsolvent in the casting solution on the porosity of the membrane.

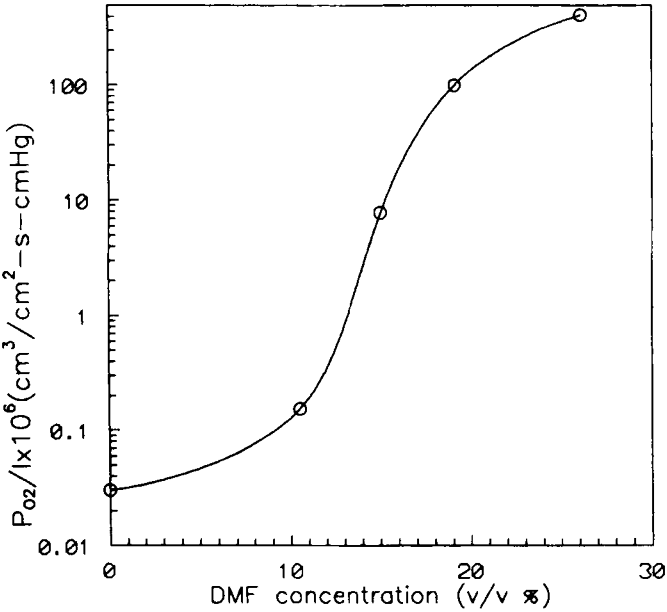

FIG. 3 Effect of added nonsolvent DMF in the casting solution on the oxygen permeation

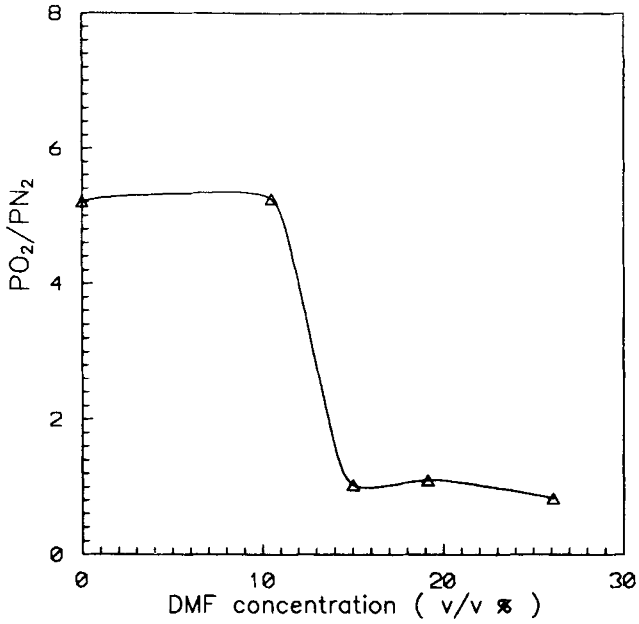

FIG. 4 Effect of added nonsolvent DMF in the casting solution on the selectivity of O_2/N_2.

DMF was added, but a further increase of DMF content led to a drastic decrease in gas selectivity.

The above data show that the gas permeability of PC membranes can be improved by adding a nosolvent, DMF, into the casting solution. Although the permeability seemed to increase indefinitely as we kept increasing the amount of DMF, the oxygen selectivity decreased if we added too much DMF. In order to maintain the oxygen/nitrogen selectivity, the highest oxygen permeation rate obtained was 0.15 GPU, which was achieved by introducing 10.5 vol% of DMF into the PC casting solution.

A High Performance Gas Separation Membrane Can Be Obtained by Incorporating CoSalen into Highly Porous PC Membrane

As was mentioned earlier, the porosity of PC membranes increased when more than 10.5 vol% of DMF was added. These highly porous membranes had high gas permeability but low oxygen selectivity. For example, the oxygen flux through a porous membrane formed by adding 15.0 vol%

DMF was 7.8 GPU and the oxygen selectivity was only 1.03. When CoSalen was added into the casting solution containing 15.0 vol% DMF, the oxygen selectivity was improved. Figure 5 shows that the oxygen selectivity increased along with CoSalen addition. Although the addition of CoSalen increased the oxygen/nitrogen selectivity, the gas permeation rate was affected. Figure 6 shows the decrease of oxygen flux because of CoSalen addition. Nevertheless, even when 3.6 wt% of CoSalen was added, the oxygen permeation rate was still much higher than that of a dense PC membrane. A polycarbonate membrane formed by adding 15.0 vol% of DMF and 3.6 wt% of CoSalen had an oxygen flux as high as 0.4 GPU and a satisfactory oxygen selectivity of 4.9.

A Fixed CoSalen/DMF Ratio to Obtain High Flux PC Membranes While Retaining High Oxygen Selectivity

According to the above results, membranes with a higher gas permeation rate can be obtained by adding more DMF into the PC casting solution. In this circumstance, more CoSalen was needed to sustain the high oxygen selectivity of the original dense PC membranes. A question may

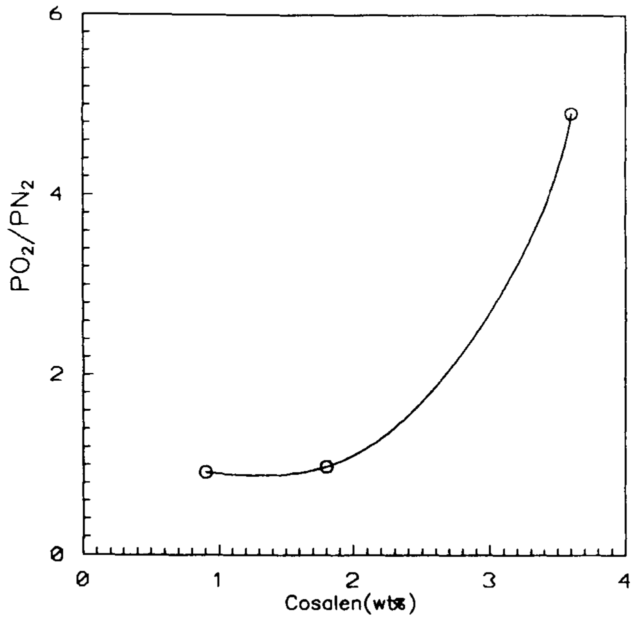

FIG. 5 Effect of additive amount of CoSalen on membrane selectivity of O_2/N_2 (15 vol% DMF additive in casting solution).

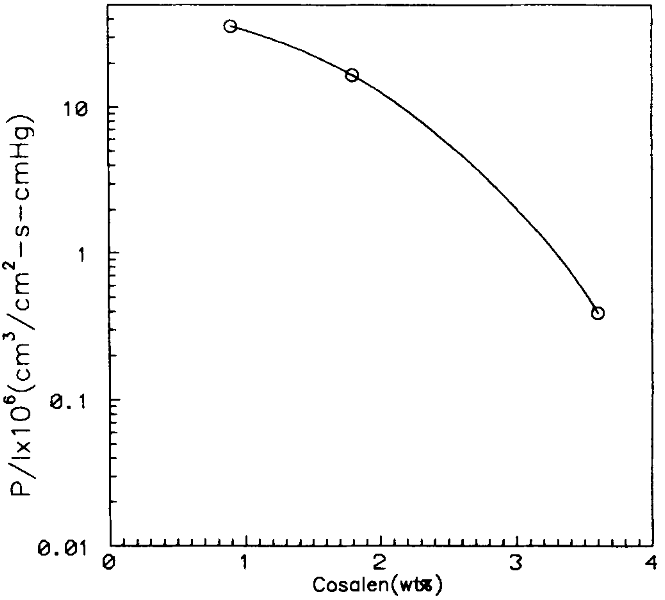

FIG. 6 Effect of additive amount of CoSalen on membrane oxygen flux (15 vol% DMF additive in casting solution).

be raised: How much more CoSalen was needed for a 1% increment of DMF. It was found that as long as a fixed CoSalen/DMF ratio, 0.025 g/mL DMF, was kept, the oxygen selectivity could be maintained. Figures 7 and 8 show the gas permeation rates and oxygen selectivities of membranes produced by adding various amounts of 0.025 g/mL CoSalen in DMF solution in the PC casting solution. It is clear that the selectivity remained constant when less than 19.05% CoSalen/DMF solution was added, as shown in Figs. 7 and 8. But when more than 19.05 vol% of CoSalen/DMF solution was added, the membrane became too porous and it was impossible to obtain any oxygen/nitrogen selectivity. In order to keep the selectivity, the highest attainable oxygen permeation rate, 0.61 GPU, was obtained by adding the 0.025 g/mL CoSalen/DMF solution by 19.05 vol%.

Effect of Storage Time on the Performance of Polycarbonate Membranes

After storage for 400 days at 25°C and 60% RH, the CoSalen-complexed porous PC membranes were tested for their gas permeability and oxygen/

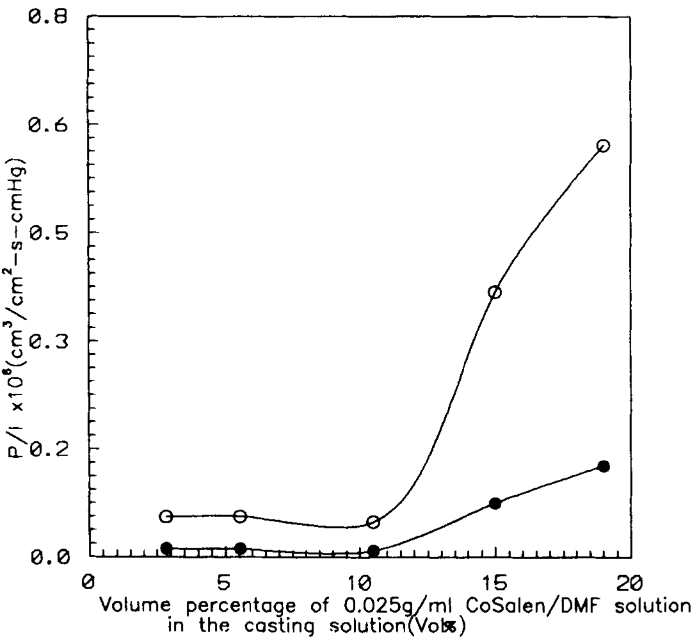

FIG. 7 Effect of volume percentage of 0.025 g/mL DMF solution in the casting solution on the gas permeation flux (0.025 g CoSalen/mL DMF): (○) oxygen, (●) nitrogen.

nitrogen selectivity. It was found that the oxygen selectivity remained unchanged but the gas permeation flux increased 1.5 to 3-fold after long-time storage. The increase in permeability may be due to the evaporation of any remaining DMF trapped inside the porous structure. Table 1 shows the effect of long-time storage on membrane performance. All the membranes showed good stability in terms of oxygen/nitrogen selectivity.

Temperature Effect on Membrane Performance

All the above measurements were performed at 35°C. According to our knowledge, CoSalen has a higher oxygen affinity at a lower temperature. Therefore, the effect of temperature on oxygen selectivity of a membrane made by adding 15 vol% DMF and 3.6 wt% CoSalen was studied. Figures 9 and 10 show that the oxygen selectivity did increase with decreasing temperature, but the oxygen flux decreased. This result provides an operational guideline for using these membranes. If a higher oxygen/nitrogen

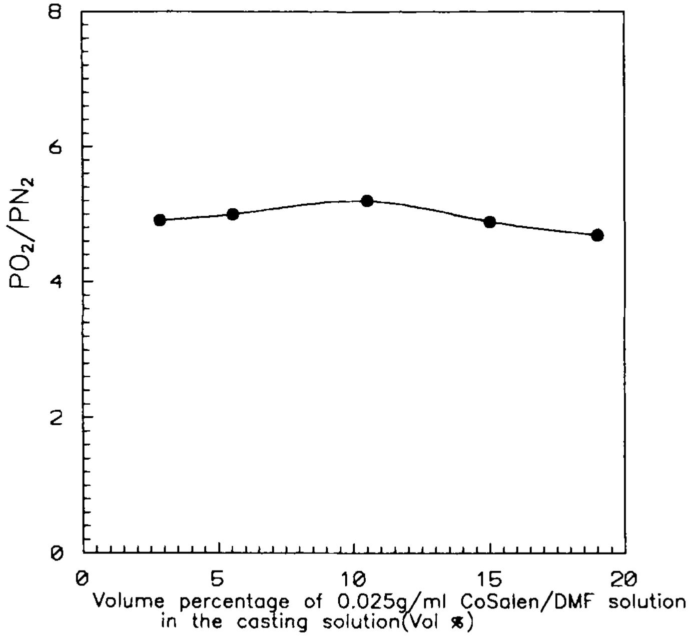

FIG. 8 Effect of volume percentage of 0.025 g/mL DMF solution in the casting solution on the selectivity of O_2/N_2 (0.025 g CoSalen/mL DMF).

TABLE 1
Effect of Storage Time on Gas Separation Performance of Polycarbonate Membranes

CoSalen/DMF additive (mL) (0.025g CoSalen/mL DMF)	Virgin			Storage for 400 days		
	$(P/l)_{O_2}$ GPU[a]	$(P/l)_{N_2}$ GPU[a]	$(P/l)_{O_2}/(P/l)_{N_2}$	$(P/l)_{O_2}$ GPU[a]	$(P/l)_{N_2}$ GPU[a]	$(P/l)_{O_2}/(P/l)_{N_2}$
0.5	0.06	0.01	4.9	0.15	0.03	4.5
1	0.06	0.01	5.0	0.15	0.03	5.3
2	0.05	0.01	5.2	0.15	0.03	5.9
3	0.39	0.08	4.9	0.62	0.13	4.7
4	0.61	0.14	4.7	0.88	0.18	4.8

[a] GPU = $10^{-6}cm^3/cm^2 \cdot s \cdot cmHg$.

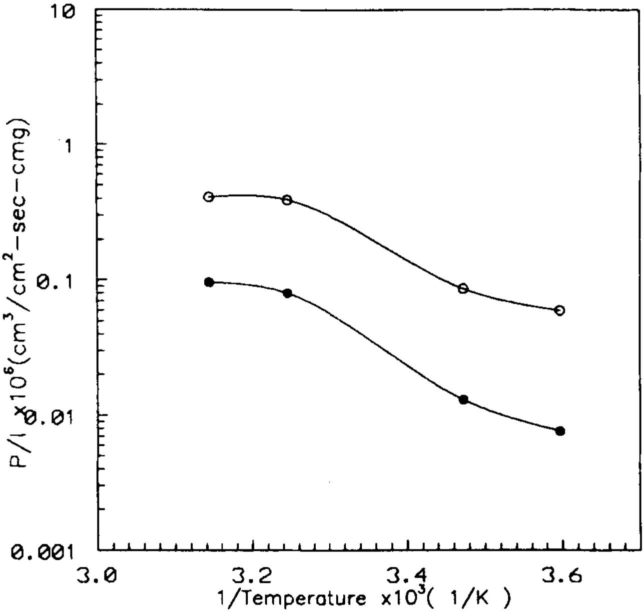

FIG. 9 Effect of operating temperature on gas flux for porous PC membrane (additive 15 vol% DMF, CoSalen/PC 3.6 wt%): (○) oxygen, (●) nitrogen.

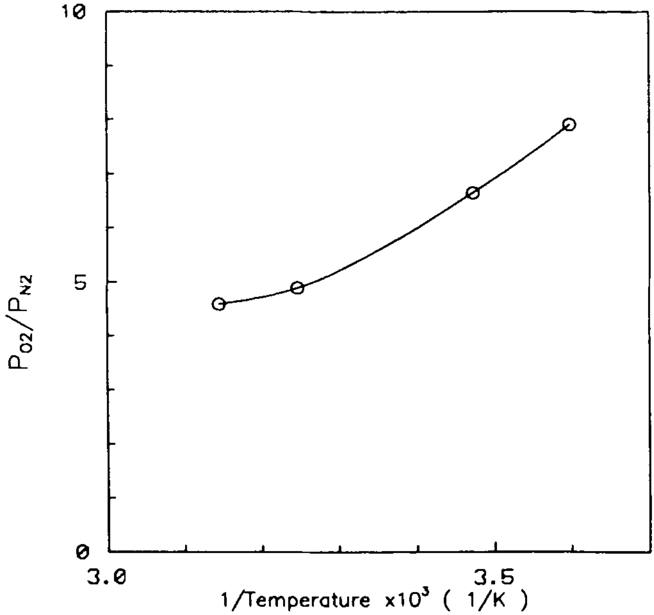

FIG. 10 Effect of operating temperature on selectivity for porous PC membrane (additive 15 vol% DMF, CoSalen/PC 3.6 wt%).

separation factor is desired, the membrane separation process should be operated at a lower temperature. On the other hand, if a higher oxygen flux is desired, a higher operating temperature is required. Unfortunately, we cannot obtain high flux and high selectivity at the same time simply by manipulating the operating temperature.

CONCLUSION

The gas permeation rates of PC membranes were significantly improved by adding DMF and CoSalen simultaneously. The oxygen flux and selectivity of an unmodified PC membrane are 0.03 GPU and 5.1 at 35°C, respectively. The gas permeation rate of a CoSalen/DMF modified membrane (19 vol% DMF, 4.8 wt% CoSalen) can reach 0.61 GPU without significant loss in oxygen selectivity. This is a 20-fold improvement. Although much higher permeability has been achieved through asymmetric membranes made by the wet inversion method, the advantages of the direct drying method, process simplicity, and product stability are still meritorious. The separation performance was also affected by the operating temperature. When a 15.0 vol% DMF, 3.6 wt% CoSalen PC membrane was tested, a high oxygen selectivity, 7.9, could be achieved at 5°C with an oxygen flux of 0.06 GPU.

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