Facilitated Transport of Oxygen in Ethyl Cellulose Membranes Containing Cobalt Porphyrins as Oxygen Carriers

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ABSTRACT: Facilitated transport of oxygen was investigated in ethyl cellulose membranes containing cobalt(II) *meso*-tetrakis (substituted phenyl) porphyrins [CoTPP, CoT(2-Cl)PP, CoT(4-Cl)PP, CoT(4-MeO)PP, and CoT(2,4-2MeO)PP] as fixed oxygen carriers. The oxygen permeability (P_{O_2}) and oxygen/nitrogen selectivity (P_{O_2}/P_{N_2}) of the membranes containing oxygen carriers increase with a decrease in the upstream gas pressure, but the nitrogen permeability (P_{N_2}) is almost independent of the upstream nitrogen pressure. This indicates that the fixed oxygen carriers in the polymer membranes can reversibly interact with oxygen and facilitate oxygen transport in the membranes. The study on the influences of the substituents in the cobalt(II) porphyrins and the fifth ligand (imidazole or pyridine) on the membrane permeation behaviors shows that the porphyrin complex with an electron-accepting substituent in the *meso*-phenyl ring or with imidazole as the fifth ligand could increase the permeability and oxygen/nitrogen selectivity of the membranes much more than that with an electron-donating substituent or with pyridine as the fifth ligand. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 484–488, 2000

Key words: facilitated transport; polymeric membranes; oxygen carriers; cobalt porphyrins; substituent effects

INTRODUCTION

The oxygen permeability (P_{O_2}) and oxygen/nitrogen selectivity α ($\alpha = P_{O_2}/P_{N_2}$, where P_{N_2} represents nitrogen permeability) of a polymer membrane could be simultaneously enhanced by the addition of oxygen carriers into the membrane in which oxygen carriers can interact specifically and reversibly with molecular oxygen.[1–3] This concept was successfully applied first in a liquid membrane with hemoglobin[4] and then with a cobalt Schiff base complex[5] as oxygen carriers for oxygen enrichment. However, the uses of a liquid membrane for oxygen enrichment are limited. Therefore, many attempts have been reported in the literature for oxygen transport through a solid polymer membrane containing metal complexes as oxygen carriers; the research in the Tsuchida et al. group is most representative.[6–8]

Tsuchida et al.[8] reported the preparation and characterization of poly(alkyl methacrylate) membranes containing metal [cobalt(II) or iron(II)]

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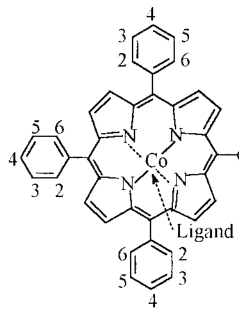

	2	3	4	5	6
CoTPP	H	H	H	H	H
CoT(2-Cl)PP	Cl	H	H	H	H
CoT(4-Cl)PP	H	H	Cl	H	H
CoT(4-MeO)PP	H	H	MeO	H	H
CoT(2,4-2MeO)PP	MeO	H	MeO	H	H

fifth ligand: imidazole or pyridine.

Scheme 1 The structures of five cobalt(II) porphyrins: CoTPP, cobalt(II) *meso*-tetraphenyl porphyrin; CoT(2-Cl)PP, cobalt(II) *meso*-tetrakis(2-chlorophenyl) porphyrin; CoT(4-Cl)PP, cobalt(II) *meso*-tetrakis(4-chlorophenyl) porphyrin; CoT(4-MeO)PP, cobalt(II) *meso*-tetrakis(4-methoxy phenyl) porphyrin; CoT(2,4-2MeO) PP, cobalt(II) *meso*-tetrakis(2,4-dimethoxy phenyl) porphyrin.

meso-tetrakis(alkyl amidophenyl) porphyrin complexes and Schiff base complexes as fixed oxygen carriers, and the oxygen facilitated transport mechanism was discussed using a dual-mode transport model. Although the oxygen facilitated transport in a membrane containing fixed oxygen carriers is dependent upon the structures of the oxygen carriers, the systematic study of the relationship between the structures of oxygen carriers and the oxygen permeation behaviors are little reported in the literature.

In this study five cobalt(II) *meso*-tetrakis (substituted phenyl) porphyrin complexes as oxygen carriers were synthesized; the substituents were varied from an electron-donating group to an electron-accepting group. The influences were studied of different substituted groups and the fifth ligand in the porphyrin complexes, as well as the upstream gas pressure, on the oxygen facilitated transport in ethyl cellulose (EC) membranes.

EXPERIMENTAL

Synthesis of Oxygen Carriers

Five cobalt(II) *meso*-tetrakis (substituted phenyl) porphyrins (CoPors) were synthesized as reported in the literature.[9,10] The structures of these five complexes are shown in Scheme 1.

Membrane Preparation

The CoPors were complexed with imidazole (Im) or pyridine (Py) in chloroform to form CoPorIm or CoPorPy complexes, then the chloroform solution of CoPorIm or CoPorPy was mixed with a chloroform solution of EC (ethoxy content of 45.9%, density of 1.14 g/mL determined from the density gradient tube method using an $H_2O/CaCl_2$ mixture system at 303 K). The complex was carefully cast on a Teflon plate in a vacuum to form a transparent, red-colored membrane with a thickness of about 55 μm and a CoPor concentration of 1.0 wt %.

Permeation Measurement

The gas permeability under various upstream gas pressures was measured using a low-vacuum permeation apparatus with a stable thermostat (Rika Seiki Inc., gas permeation apparatus K-315N); the temperature was kept at 303 K. The pressures on the upstream and downstream sides were detected using a Baratron absolute-pressure gauge (MKS Instruments). The permeabilities were calculated from the slopes of the steady-state straight line of the permeation curves. The experimental error in the gas permeability was estimated to be $\pm 3\%$; the greatest source of error was the membrane thickness. The gas permeabilities P (P_{O_2} and P_{N_2}) are reported below [1 barr = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg].

RESULTS AND DISCUSSION

Figure 1 shows the effect of upstream gas pressure (p_1) on the gas permeability (P_{O_2} and P_{N_2}) and selectivity α in an EC membrane without any CoPor complex. The changes of P_{O_2}, P_{N_2}, and α

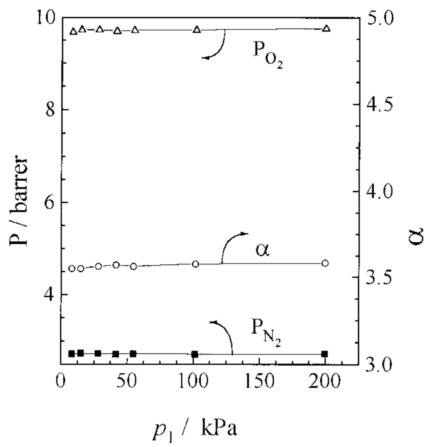

Figure 1 The effect of upstream gas pressure on the permeability and selectivity for the EC membrane without the cobalt–porphyrin complex; 1 barr = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg).

with varying the upstream gas pressure p_1 are very slight. On the contrary, for a membrane containing a CoPor complex as the oxygen carrier, the P_{O_2} increases with a decrease in the p_1 and P_{N_2} is independent of p_1, as shown in Figure 2.

In general, the gas transport model in a membrane could be described according to a dual model,[7,10]

$$J = J_H + J_L \tag{1}$$

where J_H and J_L represent the physical permeation of the ordinary Henry's law mode and the Langmuir mode, respectively. Thus, eq. (1) can be given as follows[7,10]:

$$\begin{aligned} J &= -D_H(dc_H/dx) - D_L(dc_L/dx) \\ &= D_H S_H(p_1 - p_2)/L \\ &\quad + D_L C'_L[b/(1 + bp_1)](p_1 - p_2)/L \end{aligned} \tag{2}$$

and

$$P = D_H S_H + D_L C'_L b/(1 + bp_1) \tag{3}$$

for $J = P\,(p_1 - p_2)/L$, where P is the permeability of the gas in the membrane; D_H and D_L are the diffusion coefficients for the Henry- and Langmuir-type permeations, respectively; c_H and c_L are the gas concentration in the membrane for these two permeation modes; C'_L is the saturated gas concentration in the membrane; S_H is the solubility coefficient for the Henry's law mode; b is an equilibrium constant of gas permeation through a polymer matrix; and p_1 and p_2 are the upstream and downstream gas pressures, respectively.

However, in our experiments the P_{O_2} and P_{N_2} are independent of p_1 in the EC membrane containing no oxygen carrier (Fig. 1). This means that in the conditions in our experiments the b in eq. (3) is very small and $(1 + bp_1) \approx 1$. The P could then be given as eq. (4):

$$P = D_H S_H + D_L C'_L b \tag{4}$$

in which the upstream pressure has no influence on the gas permeability in the membrane as shown in Figure 1.

On the other hand, the oxygen transport in a membrane containing oxygen carriers will be facilitated by the reversible oxygen binding of the carriers in the membrane. The contribution of such oxygen facilitated transport to the P_{O_2} could be given as eq. (5) according to the Langmuir permeation mode,[6–8]

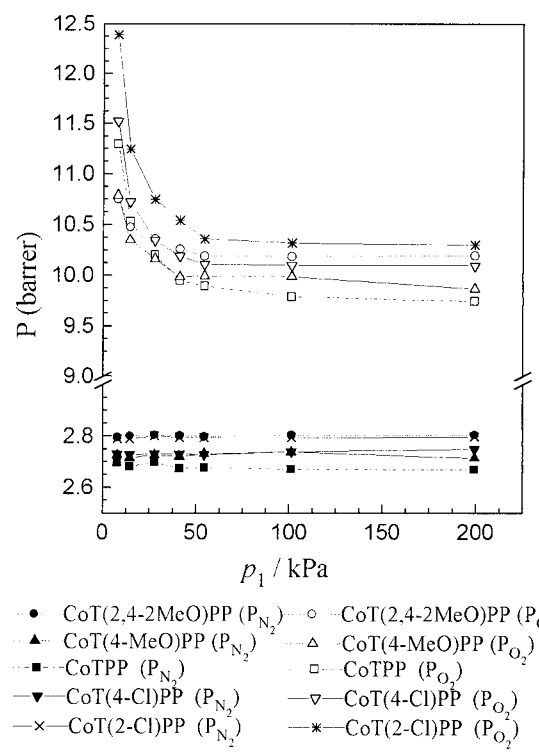

Figure 2 The effect of upstream gas pressure on the permeability for five EC membranes containing cobalt porphyrin complexes; imidazole is the fifth ligand and the concentration of the complex is 1.0 wt %.

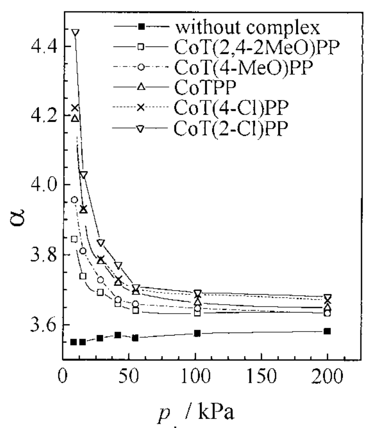

Figure 3 The effect of upstream gas pressure on the permeability and selectivity for six EC membranes; imidazole is the fifth ligand and the concentration of the complex is 1.0 wt %.

$$P'_{O_2} = D_C C'_C K_{O_2}/(1 + K_{O_2} p_1) \quad (5)$$

where C'_C is the saturated concentration of oxygen reversibly bound to a fixed carrier and K_{O_2} is the reversible oxygen-binding equilibrium constant of the carriers in the membranes.

Thus, the total P_{O_2} could be given as eq. (6):

$$P_{O_2} = D_H S_H + D_L C'_L b + D_C C'_C K_{O_2}/(1 + K_{O_2} p_1) \quad (6)$$

According to eq. (6), P_{O_2} is a function of p_1 and increases with decreasing p_1. Because the oxygen carrier does not reacted with nitrogen and does not facilitate the transport of nitrogen in the membrane, P_{N_2} is independent of upstream nitrogen pressure but P_{O_2} and α increase with the decrease of p_1 as shown in Figure 2. This is part of the evidence that the five CoPor complexes could reversibly bind oxygen and can enhance the oxygen transport in EC membranes.

Figure 3 shows the effects of upstream gas pressure (p_1) on the oxygen/nitrogen selectivity α in the EC membranes with or without cobalt(II) porphyrin complexes with imidazole as the fifth ligand. The P_{O_2} of the membrane containing complex CoT(2,4-2MeO)PP with two electron-donating substituents MeO— in its *meso*-phenyl ring is the most weakly affected by the upstream pressure p_1 (Fig. 2), and the selectivity increased only 8.45% compared to the EC membrane without the complex at the upstream pressure of 8.00 kPa (see Table I). On the other hand, the P_{O_2} of the membrane containing complex CoT(2-Cl)PP with an ortho electron-accepting substituent Cl— in its *meso*-phenyl ring is the most strongly affected by the p_1, and the α can increase 25.07% compared to the EC membrane without the complex at a p_1 of 8.00 kPa.

The decrease of the electron-donating effects or the increase of the electron-accepting effects of the substituents in the complexes could increase the selectivity of the membranes. The selectivity increasing order of the five complexes in the membranes is CoT(2,4-2MeO)PP (two electron-donating substituents, MeO—), CoT(4-MeO)PP (one electron-donating substituent, MeO—), CoTPP (no substituent in the phenyl ring), CoT(4-Cl)PP (one para electron-accepting substituent, Cl—), and CoT(2-Cl)PP (one ortho electron-accepting substituent, Cl—). This order implies that the complex with a strong electron-accepting substituent in the *meso*-phenyl ring could increase the selectivity α for EC membranes much more.

The oxygen facilitated transport is also affected by the fifth ligand to the complexes. Figure 4 shows the effects of upstream gas pressure (p_1) on the gas permeability (P_{O_2} and P_{N_2}) and α for the EC membranes containing CoT(2-Cl)PP with pyridine as the fifth ligand [CoT(2-Cl)PP + Py] or CoT(2-Cl)PP with imidazole as the fifth ligand [CoT(2-Cl)PP + Im]. The P_{O_2} of the membrane containing complex CoT(2-Cl)PP + Py is less affected by the upstream pressure p_1, and the selectivity increased only 11.27% compared to the EC membrane without the complex at the pressure of 8.00 kPa (see Table I). However, the P_{O_2} of the membrane containing complex CoT(2-Cl)PP + Im is more strongly affected by the p_1, and the α can increase 25.07% as in the same condition. In

Table I Oxygen-Enriched Characteristics of EC Membranes at p_1 = 8.00 kPa

Membrane Samples	P_{O_2} (barr)	α	$(\alpha - \alpha_{EC})/\alpha_{EC}$ (%)[a]
EC/CoT(2,4-2MeO)PP + Im	10.75	3.85	8.45
EC/CoT(4-MeO)PP + Im	10.78	3.95	11.27
EC/CoTPP + Im	11.29	4.18	17.75
EC/CoT(4-Cl)PP + Im	11.52	4.22	18.87
EC/CoT(2-Cl)PP + Im	12.39	4.44	25.07
EC/CoT(2-Cl)PP + Py	10.82	3.95	11.27

[a] The oxygen permeability of the EC membrane without any complex is 9.68 barr, and its selectivity α_{EC} is 3.55 at p_1 = 8.00 kPa.

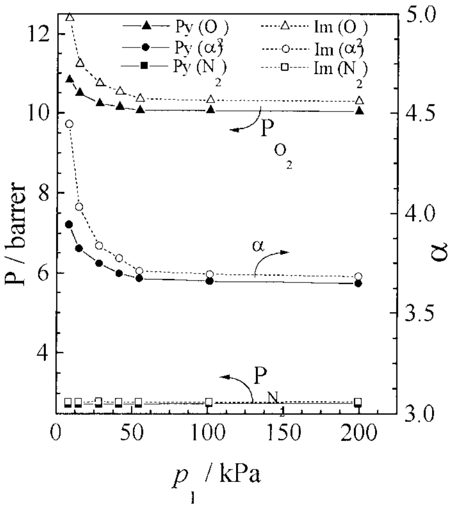

Figure 4 The effect of upstream gas pressure on the permeability and selectivity for EC membranes containing CoT(2-Cl)PP; pyridine (Py) or imidazole (Im) is the fifth ligand and the concentration of the complex is 1.0 wt %.

comparison with pyridine, imidazole as the fifth ligand of CoPor complexes could enhance the oxygen permeability and oxygen/nitrogen selectivity of the membranes much more, and it is a better fifth ligand of CoPor complexes.[9–11]

We investigated the oxygen-binding behaviors of the five CoPor complexes in chloroform solution.[10] It is very interesting that the oxygen-binding rate of the five complexes in chloroform solution decreases according to the same order of CoT(2,4-2MeO)PP, CoT(4-MeO)PP, CoTPP, CoT(4-Cl)PP, and CoT(2-Cl)PP. The measuring results and a detailed discussion will be given elsewhere.[11]

CONCLUSIONS

1. The oxygen permeability and oxygen/nitrogen selectivity of EC membranes containing porphyrin complexes are strongly affected by the upstream pressures, indicating that the CoPors as oxygen carriers could be reversibly bound to the molecular oxygen.
2. The oxygen permeation behaviors of the EC membranes are influenced by the substituents of the CoPor complexes. The stronger electron-accepting affects of the substituents could greatly increase the oxygen/nitrogen selectivity of the EC membranes.
3. As for the fifth ligand, imidazole is more effective than pyridine for the porphyrin complexes in increasing the oxygen permeability and oxygen/nitrogen selectivity of the EC membranes.

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