Korean J. of Chem. Eng., **10**(4), 207-210 (1993)

SELECTIVE MOLECULAR OXYGEN TRANSPORT THROUGH A CELLULOSE ACETATE MEMBRANE CONTAINING AN ELECTRON-POOR IRON(II) PORPHYRIN COMPLEXES

Sung-Wook Im, Byung-Soo Yu* and Suk-In Hong

Dept. of Chem. Eng., Korea University, Anam-dong, Sung Buk-Ku, Seoul 136-701, Korea
*Dept. of Chemistry, Wonkwang University, Shinyong Dong, Iri 570-749, Korea
(*Received 21 April 1993 • accepted 14 August 1993*)

Abstract—Molecular oxygen diffusion in the cellulose acetate membranes containing the 5,10,15, 20-tetrakis(pentafluorophenyl)-21H,23H-porphine iron(II) was studied. Both the permeability coefficient and the separation factor for oxygen in the membrane containing the iron(II) porphyrin complex were increased with decreasing the upstream gas pressure which correspond to a dual-mode oxygen transport. The effects of the axial ligands of the iron(II) porphyrin on oxygen permeation was also examined in the same cellulose acetate membrane. The fluoride and 2-methyl imidazole ligands coordination to the iron(II) porphyrin induce to increase the oxygen permeability coefficient and the value of ideal separation factor.

INTRODUCTION

Oxygen and nitrogen gas separation by many polymers containing various transition metal complexes have been studied extensively over the years [1-5]. Metalloporphyrin complexes are the most interesting inorganic complexes as model compound for biological oxygen carriers [6-11]. The iron porphyrins are present as a common active site or a prosthetic group in hemoglobin and myoglobin. The binding ratio of O_2 and heme protein is known as 1:1. Generally synthetic iron(II) porphyrin complexes react reversibly with molecular oxygen to form 1:1 dioxygen adduct at low temperatures:

$$Fe(II)(Por)(B) + O_2 \rightleftharpoons Fe(Por)(B)(O_2)$$

In contrast to the oxygen-carrying ability of hemoglobin and myoglobin, simple iron(II) synthetic porphyrin complexes are rapidly and irreversively oxidized to form dinuclear iron(III) complex by molecular oxygen at room temperature [12-14]:

$$PFe(II)(B) + O_2 \rightleftharpoons PFe(II)(B)(O_2)$$
$$PFe(II)(B)(O_2) + PFe(II)(B) \rightleftharpoons (B)PFe\text{-}O_2\text{-}Fe(III)P(B)$$
$$(B)PFe\text{-}O_2\text{-}FeP(B) \xrightarrow[\text{rapid}]{} 2PFe(IV)(B)(O^{2-})$$
$$2PFe(IV)B(O^{2-}) + PFe(II)(B) \xrightarrow[\text{rapid}]{} PFe(III)\text{-}O\text{-}Fe(III)P + 2(B)$$

In order to prevent autoxidation of iron(II) porphyrin complexes, sterically hindered iron(II) porphyrins having appended bulky substituents such as 2-methylimidazole and 1,2-dimethylimidazole were synthesized and utilized as a-model compound of a molecular oxygen carrier [15-18].

Tsuchida and coworkers have reported the facilitated oxygen transport through a polymeric membrane containing cobalt(II) or iron(II) α, α′, α″, α‴-meso-tetrakis(O-pivalamidophenyl) porphyrin complex as a fixed carrier of oxygen [19-23]. Recently, it was reported very electron deficient pentafluorinated ion(II) porphyrin (F_{20}-TPP)Fe(II) with fluoride ligand showed a unique spectral properties and unusual molecular oxygen activation chemistry [24-25]. In order to improve the facilitated oxygen transfer through a polymeric membrane containing metalloporphyrins, less sterically hindered porphyrin such as very electron poor pentafluorinated porphyrin, (F_{20}-TPP)Fe(II) was expected as a very useful molecular oxygen carrier. It was already discussed that the oxygen transport was improved by using a metalloporphyrin having a short picket-fence [19-22]. At this point of view, the (F_{20}-TPP) Fe(II) complex which was used in this experiment may be one of the most ideal oxygen carrier in the facilitated molecular oxygen transport. In this paper, selective molecular oxygen transfer in cellulose ace-

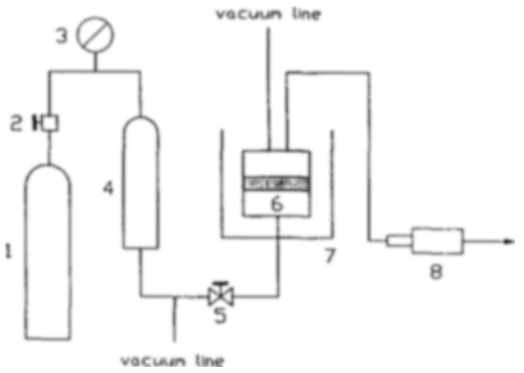

Fig. 1. The experimental apparatus for permeation measurement.

1. Gas bomb
2. Metering valve
3. Pressure gauge
4. Cylinder for volume increase
5. On/Off valve
6. Permeation cell
7. Water bath
8. Pressure transducer

tate membrane containing 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(II) with fluoride and 2-methyl imidazole have been described.

EXPERIMENTAL

1. Materials

Toluene, acetone, and dichloromethane were used after further purification according to the published methods [26-27]. All solvent were degassed using a nitrogen purge after or during purification. Cellulose acetate (Aldrich Co.) with acetyl content 39.8% was used. Chloroiron(III) 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin was prepared by modifications of literature methods [28, 29]. Crystalline iron(II) pentafluorophenylporphyrin, (F_{20}-TPP)Fe(II), was prepared under the nitrogen atmosphere by zinc amalgam reduction of the chloroiron(III) complex [30]. Crystalline fluoroiron(II) and 2-methyl imidazole iron(II) pentafluorophenylporphyrin, [Bu_4N][(F_{20}-TPP)FeF], [Bu_4N][(F_{20}-TPP)Fe(2-MeIm)], were prepared by the literature methods [24]. Typically, 5 equivalent of fluoride or 2-MeIm was added in the iron(II) porphyrin solutions. The membranes was prepared in a following procedure. The casting solutions were made by mixing the solvents, the cellulose acetate, and either the (F_{20}-TPP)FeF^- or (F_{20}-TPP)Fe(2-MeIm)$^-$ a certain ratio. This solution was carefully cast on a glass plate under a nitrogen atmosphere and then dried for at least one day and further dried in vacuum dryer for one day. The thickness of membrane was measured as about 40 μm. About 2.4 wt% of the metalloporphyrin as an oxygen carrier was contained in the membranes.

Table 1. The mean permeability coefficients and ideal separation factors for oxygen and nitrogen in CA membrane with (F_{20}-TPP)Fe at various pressures, 28°C

Upstream pressure (mmHg)	Mean permeability[a]		Ideal separation factor
	P_{O2}	P_{N2}	P_{O2}/P_{N2}
30	1.204	0.398	3.03
80	1.132	0.393	2.88
150	1.080	0.396	2.73
300	1.055	0.397	2.66
450	1.046	0.398	2.63

[a]Mean permeability is in 10^{-10} cm^3 (STP) cm $sec^{-1}cm^{-2}$ $cmHg^{-1}$ (Barrer)

2. Permeation measurement

Oxygen and nitrogen permeation coefficients for various upstream gas pressures were measured with a low vacuum permeation apparatus shown in Figure 1 with a constant gas pressure chamber in order to keep a constant gas pressure. The permeation cell (Millipore Co., USA) was purchased and used. The downstream gas pressure was recorded by pressure transducer. The permeation coefficient was calculated from the slope of the steady-state straight line of the permeation curve. All measurements were carried out at 28℃ and the upstream gas pressures were ranged from 30 mmHg to 450 mmHg.

RESULT AND DISCUSSION

1. Cellulose acetate membrane

The measurement of permeabilities of oxygen and nitrogen was carried out with the cellulose acetate membrane without metalloporphyrin as an oxygen carrier. The upstream gas pressure was increased from 30 mmHg to 450 mmHg. Increasing pressure of upstream gas does not affect the permeabilities of oxygen and nitrogen. The ideal separation factor for oxygen and nitrogen in cellulose acetate membrane without porphyrin complex at 28℃ was found to be constant as 2.63 for the whole range of pressure used in this experiment. This value was smaller than that of previously published one [31].

2. Effect of metalloporphyrin on facilitated transport of oxygen

Pentafluorophenyl iron(II) porphyrin, (F_{20}-TPP)Fe (II): Table 1 shows the permeability coefficients and permeability ratios (P_{O2}/P_{N2}) of the cellulose acetate membrane containing 2.4 wt% (F_{20}-TPP)Fe(II) com-

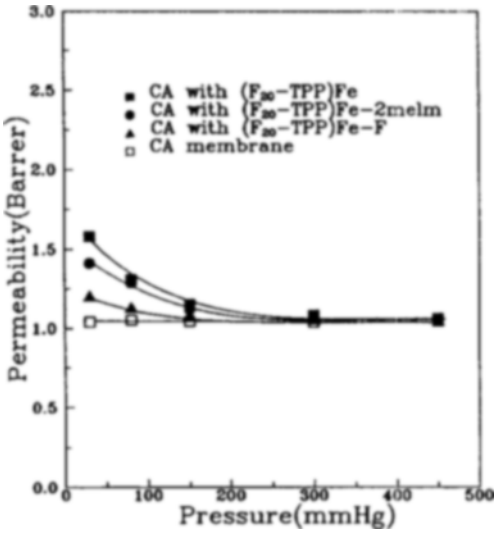

Fig. 2. The permeability coefficients for oxygen in various membranes at 28°C.

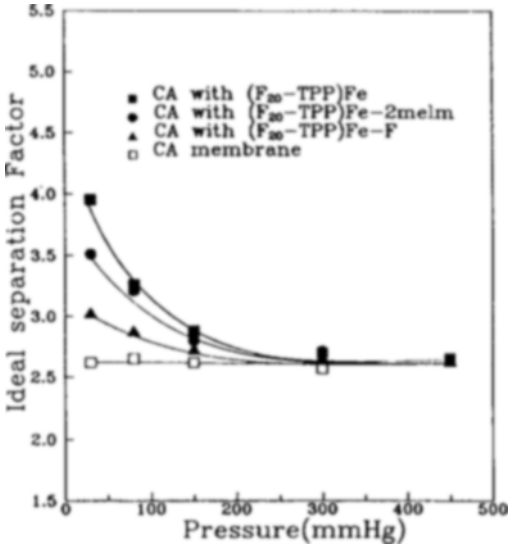

Fig. 3. The ideal separation factors for oxygen and nitrogen in various membranes at 28°C.

plex. The permeability coefficients for oxygen in this membrane at 28℃ are gradually increased with decreasing the upstream pressure. The permeability ratio (P_{O2}/P_{N2}) of the membrane containing 2.4 wt% (F_{20}-TPP)Fe(II) at low upstream pressure was almost twice larger than that of a polymer membrane containing same amount of cobalt porphyrin complex [19]. In this case, the facilitation of oxygen transport is remarkable for the lower upstream pressure, which corresponds to a dual mode transport model as similar to the other oxygen permselective polymer membranes [32].

3. Trans ligand effects on facilitated oxygen transport in cellulose acetate membrane containing pentafluorophenyl iron(II) porphyrins

Coordinations of 2-methyl imidazole and fluoride lignads to the (F_{20}-TPP)Fe(II) porphyrin induce to change the electronic configurations from intermediate spin state to high spin state [24-25] and O_2 affinity of the iron(II) porphyrin. Permeability coefficients for oxygen and nitrogen in cellulose acetate membranes containing the pentafluorophenyl iron(II) porphyrins with the fifth ligands (2-MeIm, F) are shown in Figure 2. Figure 2 shows that the fifth ligand ligation on iron (II) porphyrin causes the permeability coefficient of oxygen to increase as the upstream pressure decreases. At a higher upstream pressure than 300 mmHg, there is no change in the permeability coefficient of oxygen which is consistent with the other oxygen permselective polymer membranes due to a dual-mode transport mechanism. And the ideal separation factors

Table 2. The oxygen permeability coefficients and ideal separation factors in various membranes at 30 mmHg at 28°C

Membrane	O_2 permeability[(a)]	P_{O2}/P_{N2}
Cellulose acetate (CA)	1.040	2.63
CA with (F_{20}-TPP)Fe	1.204	3.03
CA with (F_{20}-TPP)Fe-2MeIm	1.410	3.51
CA with (F_{20}-TPP)Fe-F	1.581	3.95

*(F_{20}-TPP)Fe-X = 2.4 wt%

*[(a)]permeability is in 10 ^{10}cm^3 (STP) cm sec ^{1}cmHg ^{1} (Barrer)s

for oxygen in cellulose membranes containing various pentafluophenyl iron(II) porphyrins are shown in Figure 3. The ideal separation factors for oxygen are remarkably increased by coordinations of 2-methyl imidazole and fluoride to the iron(II) porphyrins at the low upstream pressure. The calculated values of the oxygen permeability coefficients and ideal separation factors in cellulose acetate membrane with various iron(II) porphyrins are summerized in Table 2. All of the data clearly shows that the fluoride and 2-methyl imidazole ligands ligations to the very electron-poor pentafluophenyl iron(II) porphyrins in cellulose acetate membranes result in increasing the facilitatd transport of oxygen at the low upstream gas pressure.

It is known that very acidic pentafluorinated iron(II) porphyrin complexes have the unusual molecular oxygen activation chemistry and the relatively stable property against oxygen [24]. Furthermore, the ligand

coordination such as the fluoride ion to the pentafluorinated iron(II) porphyrin induces to increase the significant stability for the molecular oxygen. It should be noted that the small size and very electronegative fluoride ligand ligation to the very electron-poor iron (II) porphyrin results in remarkable increasing both the stability for the molecular oxygen and the degree of efficiency on the facilitated transport of oxygen.

CONCLUSION

Cellulose acetate membrane containing 2.4 wt% pentafluorophenyl iron(II) compound was examined for the transport of the molecular oxygen. The oxygen permeability coefficient and the separation factor through this membrane are remarkably larger than those through the polymer membrane without iron(II) prophyrin complex. The oxygen permeabilities and selectivities in the membranes containing the (F_{20}-TPP)Fe(II) coordinated with fluoride and 2-MeIm ligands were also examined. At the low upstream pressure, the fluoride ligand coordination to the (F_{20}-TPP)Fe (II) causes to increase the oxygen permeability coefficient and the ideal separation factor significantly for the cellulose acetate membrane with the iron porphyrin complex.

REFERENCES

1. Norman, H.: *Inorganic. Chem.*, **25**, 4714 (1986).
2. Hernmingesn, E. and Scholander, P. F.: *Science*, **132**, 1379 (1960).
3. Kemena, L. L., Noble, R. D. and Kemp, N. J.: *J. Membrane Sci.*, **15**, 259 (1983).
4. Jonhson, B. M., Baker, R. W., Matson, S. L., Smith, K. L., Roman, I. C., Tuttle, M. E. and Lonsdale, H. K.: *J. Membrane Sci.*, **31**, 31 (1987).
5. Kawakami, H., Tsuda, K., Nishide, H. and Tsuchida, E.: *Macromolecules*, **24**, 3310 (1991).
6. Nishide, H., Ohyanagi, M., Okada, O. and Tsuchida, E.: *Macromolecules*, **19**, 494 (1986).
7. Nishide, H., Ohyanagi, M., Okada, O. and Tsuchida, E.: *Macromolecules*, **20**, 417 (1987).
8. Ohyanagi, M., Nishide, H., Suenaga, K. and Tsuchida, E.: *Macromolecules*, **21**, 1590 (1988).
9. Tsuchida, E., Nishide, H., Ohyanagi, M. and Okada, O.: *J. Phys. Chem.*, **92**, 6461 (1988).
10. Tschida, E., Hasegawa, E., Chika, Y., Babe, T. and Nishide, H.: *Chem. Lett.*, 1727 (1989).
11. Hasegawa, E., Fukuzumi, M., Nishide, H. and Tsuchida, E.: *Chem. Lett.*, 123 (1990).
12. Cohen, I. A. and Caugey, W. S.: *Biochemistry*, **7**, 636 (1968).
13. Chang, C. K., Powell, D. and Traylor, T. G.: *Croat. Chem. Acta.*, **49**, 295 (1977).
14. Chen, D.-G., Del Gaudio, J., La Mar, G. N. and Balch, A. L.: *J. Am. Chem. Soc.*, **99**, 5486 (1977).
15. Almog, J., Baldwin, J. E. and Huff, J.: *J. Am. Chem. Soc.*, **97**, 227 (1975).
16. Chang, C. K.: *J. Am. Chem. Soc.*, **99**, 2819 (1977).
17. Collman, J. P.: *Acc. Chem. Res.*, **10**, 265 (1977).
18. Collman, J. P., Gagne, R. R., Halbert, T. R., Marchen, J. C. and Reed, C. A.: *J. Am. Chem. Soc.*, **95**, 7868 (1973).
19. Nishide, H., Ohyanagi, M. and Okada, O.: *Macromolecules*, **19**, 494 (1986).
20. Nishide, H., Ohyanagi, M. and Tsuchida, E.: *Macromolecules*, **20**, 417 (1987).
21. Ohyanagi, M., Nishide, H., Suenaga, K. and Tsuchida, E.: *Macromolecules*, **21**, 1950 (1988).
22. Nishide, H., Ohyanagi, M., Okada, O. and Tsuchida, E.: *Macromolecules*, **21**, 910 (1980).
23. Tsuchida, E., Nishide, H., Ohyanagi, M. and Okada, O.: *J. Phys. Chem.* **92**, 6461 (1988).
24. Yu, B.-S. and Goff, H. M.: *J. Am. Chem. Soc.*, **111**, 6558 (1989).
25. Yu, B.-S.: Ph.D. Dissertation, University of Iowa, Iowa city (1989).
26. Perrin, D. D., Armarego, W. L. F. and Perrin, D. R.: "The Purification of Laboratory Chemicals", 2nd ed., Pergamon Press, New York (1980).
27. Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. and Tatchell, A. R.: "Vogel's Textbook of Practical Organic Chemistry", 4th ed., The Chaucer Press, Ltd., Suffolk, p. 278 (1978).
28. Eaton, S. S. and Eaton, G. R.: *J. Am. Chem. Soc.*, **97**, 3660 (1975).
29. Woon, T. C., Shirazi, A. and Bruice, T. C.: *Inorg. Chem.*, **25**, 3845 (1986).
30. Landrum, J. T., Atano, K., Scheidt, W. R. and Reed, C. A.: *J. Am. Chem. Soc.*, **102**, 6729 (1980).
31. Brandrup, J. and Immergut, E. H.: "Polymer Handbook", 3rd ed., John Wiley & Sons, New York, VI 435 (1989).
32. Kawakami, H., Tsuda, K., Nishide, H. and Tsuchida, E.: *Macromolecules*, **24**, 3310 (1991).