

# Chelate Membrane from Poly(vinyl alcohol)/Poly(*N*-salicylidene allyl amine) Blend. II. Effect of Co(II) Content on Oxygen/Nitrogen Separation

MOON JAE CHOI, CHANG KYU PARK, and YOUNG MOO LEE\*

Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 133-791, South Korea

## SYNOPSIS

Facilitated transport of oxygen was performed through chelate membranes containing cobalt with selective oxygen binding ability as a fixed oxygen carrier. Chelate membranes were obtained from Schiff base membranes after treating a poly(allyl amine) (PAAM) and poly(vinyl alcohol) (PVA) blend with salicylaldehyde. It is confirmed that the O—O stretching peak through a frequency change in FTIR could be seen at  $1150\text{ cm}^{-1}$  between cobalt in the membrane and incoming oxygen. The permeability of oxygen through Schiff base membranes was  $2.01\text{--}2.98 \times 10^{-13}\text{ [cm}^3\text{ (STP) cm}^2\text{/cm s cmHg]}$  and oxygen permselectivity was in the range of 1.83–3.27. For chelate membranes, both the permeability of oxygen and oxygen selectivity increased to  $2.15\text{--}2.82 \times 10^{-12}\text{ [cm}^3\text{ (STP) cm}^2\text{/cm s cmHg]}$  and around 8, respectively. Permselectivity of chelate increased as a result of facilitation of  $\text{O}_2$  and inhibition of  $\text{N}_2$  transport. Detailed results and the mechanism of facilitation of oxygen are discussed on the basis of molecular interactions. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

In oxygen/nitrogen separation, most of the polymers are selective toward oxygen. Extensive reviews on molecular transport of oxygen and nitrogen through polymer films have been published and an inverse relationship appears to exist between oxygen permeability and selectivity.<sup>1</sup> Many researchers have focused on simultaneously enhancing both permeability and selectivity. These efforts have been developed in the forms of a facilitated transport using transition-metal complexes,<sup>2–11</sup> preparation of asymmetric membranes in which extraordinarily thin, defect-free synthetic films with high gas selectivity on the surface of the microporous substrates by UV and plasma,<sup>12–15</sup> and electrically conductive polymers.<sup>16–19</sup> Facilitated transport using a metal complex acts such that transition metal bound in the membranes acts as a fixed oxygen carrier which enhances the oxygen selectivity through the reversible and selective binding with oxygen.

Nishide et al. prepared the combination membrane of poly(1-trimethylsilyl-1-propyne) with oxygen permeability of  $148.0 \times 10^{-10}\text{ cm}^3\text{ (STP) cm}^2\text{/cm s cmHg}$  (barrer) and selectivity of 2.9 and polyvinylimidazole-bound porphinatocobalt (CoP) with selective oxygen-binding ability that showed reversible and highly selective oxygen adsorption and desorption.<sup>3</sup> They also studied the selective sorption and facilitated transport of oxygen in the polymer membranes of CoP as the chemical sorption site or the fixed carrier of oxygen. CoP was coordinated to various polymers such as poly(octyl methacrylate-co-4-vinylpyridine) or poly(octyl methacrylate-co-1-vinylpyridine).<sup>4–6</sup> Baker et al. synthesized liquid membranes which showed the oxygen permeability of 260 barrer and selectivity of 20. In this system, the transition metals were fixed in the pore of microporous membranes and were dissolved by proper solvents.<sup>7</sup>

Delaney et al. incorporated the reversible oxygen-binding metal complexes into polymer matrices by blending the carrier with the polymer, poly(styrene-4-vinylpyridine), or grafting the carrier onto the polymer backbone, poly(styrene-vinylbenzyl chloride).<sup>2</sup> Hsiue et al. used two kinds of modified sty-

\* To whom correspondence should be addressed.

rene-butadiene-styrene triblock copolymers as polymeric axial ligands. One was modified by radiation-induced graft polymerization and the other was modified by epoxidation to obtain high oxygen permeability and high selectivity.<sup>8-11</sup> They also reported the effect of axial ligand and the equatorial chelate group on chelate membranes. On the other hand, Wohlré et al. synthesized Schiff base-type chelates and explained relations between chelates and oxygen in terms of a monomolecular superoxo complex and a bimolecular  $\mu$ -peroxo complex.<sup>20-22</sup> They reported that in the beginning of the experiment oxygen transport was carried out first in the monomolecular superoxo complex state. However, the complex becomes a bimolecular  $\mu$ -peroxo complex state and Co(II) converts irreversibly into Co(III), resulting in the loss of the oxygen-binding ability of the metal

complex. Studies on enhancing oxygen permeability and selectivity are summarized from the literature and listed in Table I.

In our previous article, we reported on the synthesis and properties of cobalt-containing PAAM and PVA chelate membrane.<sup>23</sup> In another report, we already investigated the separation of benzene/cyclohexane by pervaporation processes using the same membrane.<sup>24</sup> In the present study, we report on the oxygen/nitrogen separation results through a novel cobalt-containing chelate membrane. Chelate membrane was made by first blending PAAM and PVA in varying blending ratios. PAAM was chosen because it has a high reactivity to form a Schiff base, and PVA, because of a good membrane property. PAAM was converted to a Schiff base type to incorporate transition metals and to bind with

**Table I** Summary of Gas Permeability and Selectivity in Various Membranes

Membranes	CoPIIm (Wt %)	$P_{O_2}$ <sup>a</sup>	$P_{N_2}$ <sup>a</sup>	$\alpha_{O_2/N_2}$	Ref.
PS-VBC-CoSaphen · NEt <sub>3</sub> <sup>b</sup>	—	1.39	0.135	10.3	2
PS-IPO-CoSalphen · NEt <sub>3</sub> <sup>c</sup>	—	3.99	0.326	12.2	2
POIm/PMSP(3/7) <sup>d</sup>	2	14.80	5.00	2.9	3
POIm/PMSP(3/7)	6	7.87	1.74	4.5	3
Cobalt porphyrin polymer <sup>e</sup> (CoPIIm)complex <sup>f</sup>	1.3-5 0-4.5	1.8-2.9 6.4-23	3.1-2.4 2.0-1.92	5.8-12 3.2-12	4 5
CoP-OPy membrane <sup>g</sup>	25	5.8	0.95	6.1-8.3	6
ESBS-Co3 <sup>h</sup>	—	2.94	0.47	6.2	9
ESBS-Co4 <sup>i</sup>	—	2.10	0.47	4.5	9
SBS-g-CoS <sup>j</sup>	—	3.4	1.4	2.34	10
Polymer film <sup>k</sup>	—	0.54-0.57	0.066-0.071	8.2-8.0	12
Polyarylsulfone <sup>l</sup>	—	0.387	0.050	7.74	15
Polyetherimide <sup>m</sup>	—	0.367	0.040	9.13	15
CoPoly(acrylonitrile/styrene) <sup>n</sup>	—	0.217	0.023	9.48	15
Polyamide <sup>o</sup>	—	0.0767	0.008	9.07	15
Doped/undoped PA <sup>p</sup>	—	0.172	0.00323	53.2	16
PMPy-NO <sub>3</sub> <sup>q</sup>	—	1.26	0.16	7.9	17
Redoped PA <sup>r</sup>	—	0.79	0.16	5.05	17

<sup>a</sup> Permeability in  $10^{-9}$  cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.

<sup>b</sup> Co(II) complex of a styrene-vinylbenzyl chloride-vinylbenzyl-*N,N'*-disalicylidene-3,4-diaminobenzoate copolymer with triethylamine as axial base.

<sup>c</sup> Co(II) complex of a styrene-methacrylamidoethyl-*N,N'*-disalicylidene-3,4-diaminobenzoate copolymer.

<sup>d</sup> Poly(octylmethacrylate-co-vinylimidazole)/poly(1-trimethylsilyl-1-propyne)-bound *meso*-tetrakis- $\alpha,\alpha,\alpha,\alpha$ -(*o*-pivalamido-phenyl)porphinate-cobalt(II) (CoP).

<sup>e</sup> *meso*-tris( $\alpha,\alpha,\alpha$ -*o*-methacrylamidophenyl)mono( $\beta$ -*o*-methacrylamidophenyl)porphinate cobalt etc.

<sup>f</sup> [ $\alpha,\alpha',\alpha'',\alpha'''$ -*meso*-Tetrakis(*o*-piralamidophenyl)porphinate]cobalt(II)-1-methylimidazole complex (CoPIIm).

<sup>g</sup> CoP coordinated to poly(octylmethacrylate-co-4-vinylpyridine).

<sup>h</sup> *N,N'*-Ethylenebis(3-methyl-7-phenylsalicylidendiminato)cobalt(II).

<sup>i</sup> *N,N'*-Phenylenebis(3-methyl-7-phenylsalicylidendiminato)cobalt(II).

<sup>j</sup> Styrene-butadiene-styrene-*g*-vinylpyridine graft copolymer(SBS-*g*-VP) membrane containing 10 wt % CoS at 30°C.

<sup>k</sup> Polymer film was photopolymerized from a solution 7.9 wt % sodium styrene sulfonate and 30 wt % technical-grade divinylbenzene in dimethyl sulfoxide (62.1 wt %).

<sup>l-o</sup> Ozonated polymers.

<sup>p</sup> Poly(*N*-methylpyrrole) was contacted an aqueous solution of an oxidative polymerization reagent [e.g., 2.0M Fe(NO<sub>3</sub>)<sub>3</sub>].

<sup>r</sup> Polyaniline.

oxygen. Gas permeation results through a Schiff base and chelate membranes are investigated and reported here.

## EXPERIMENTAL

### Reagent and Membrane Preparation

PVA ( $M_w$ : 66,000, degree of hydrolysis: 88%) and PAAm ( $M_w$ : 100,000) were purchased from Shin Yo Pure Chemicals (Japan) and Aldrich Chemicals Co. (U.S.A.), respectively. Dianion SA 10A, strong base ion-exchange resin, was purchased from Samyang Co. (Korea). Distilled and deionized water treated with a Milli-Q water purification system (Millipore Co., U.S.A.) were used as a blending solvent. Salicylaldehyde, dimethylformamide (DMF), triethylamine (TEA), methanol, and  $\text{Co}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$  were used for the preparation of the chelate membrane without further purification. All reagents were from Junsei Chemicals (Japan, GR grade). Membranes were prepared according to the same procedure reported in a previous study.<sup>23</sup> The chemical structure of chelate membrane is shown in Figure 1.

### Measurement of Gas Permeability

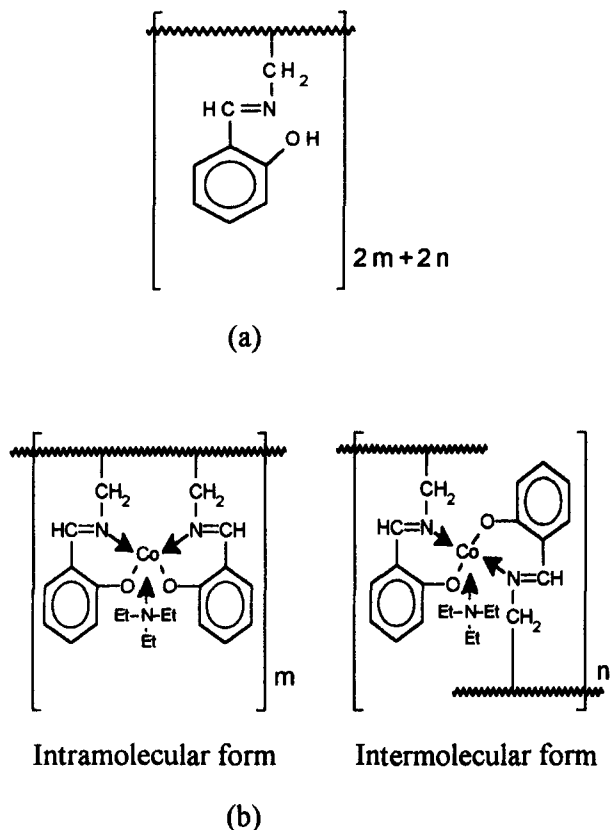
Single-gas permeabilities of Schiff base and chelate membranes were determined by initially evacuating the downstream volume of the membrane to about  $1 \times 10^{-3}$  mmHg and providing the upstream side with  $\text{O}_2$  and  $\text{N}_2$  at 10 Torr for the test. The change of pressure in the downstream side was measured by a pressure transducer and plotted against operating time.<sup>2,25</sup>

Permeability was calculated using the equation

$$P = \frac{dp}{dt} \times \frac{V(273)}{760(273 + t)A} \times \frac{1}{\Delta P} \times \frac{l}{60} \quad (1)$$

where  $P$  is the permeability coefficient [ $\text{cm}^3$  (STP)  $\text{cm}/\text{cm}^2$  s mmHg],  $dp/dt$  is a gradient of pressure vs. time curve at the steady state;  $t$ , the temperature ( $^\circ\text{C}$ );  $V$ , the volume of the downstream side ( $9.7 \text{ cm}^3$ );  $A$ , the membrane area ( $13.416 \text{ cm}^2$ );  $l$ , the membrane thickness; and  $\Delta P$ , the difference between upstream pressure and downstream pressure. Permeability may also be defined as the multiplicity of the diffusion and solubility coefficient. Apparent diffusivity is represented as follows:

$$D = l^2/6\theta \quad (2)$$



**Figure 1** Schematic of the structure of PAAm in (a) Schiff base form and (b) chelate form.

where  $\theta$  is an intercept obtained from the linear portion of the pressure vs. time plot. Apparent solubility,  $S$ , and oxygen selectivity,  $\alpha$ , was calculated using eqs. (3) and (4), respectively:

$$S = P/D \quad (3)$$

$$\alpha = P_{\text{O}_2}/P_{\text{N}_2} \quad (4)$$

### Characterization

FTIR (Nicolet Magna IR 550) was used to confirm the selective adsorption of oxygen onto the chelate membrane. The density of membrane was measured by a density gradient column containing a mixture of  $n$ -heptane and carbon tetrachloride as a cosolvent and PET as a reference.

## RESULTS AND DISCUSSION

In our previous study,<sup>23</sup> we reported on the detailed procedure for the membrane preparation and char-

**Table II** Designation, Density,  $T_g$ , and Cobalt Contents of Membranes

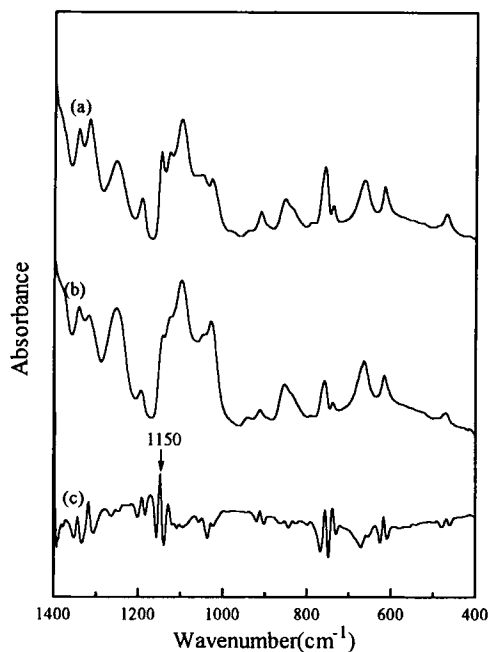
	Initial Weight Ratio of PVA/PAAm	Density (g/cm <sup>3</sup> ) <sup>a</sup>	$T_g$ (°C)	Co(II) Content (Wt %) <sup>b</sup>
<b>Sch 3 : 1</b>	3	1.22	39	—
<b>Sch 4 : 1</b>	4	1.23	47	—
<b>Sch 5 : 1</b>	5	1.24	47	—
<b>Sch 6 : 1</b>	6	1.24	48	—
<b>Che 3 : 1</b>	3	1.36	—	15.75
<b>Che 4 : 1</b>	4	1.36	—	12.48
<b>Che 5 : 1</b>	5	1.37	—	11.28
<b>Che 6 : 1</b>	6	1.39	—	9.82

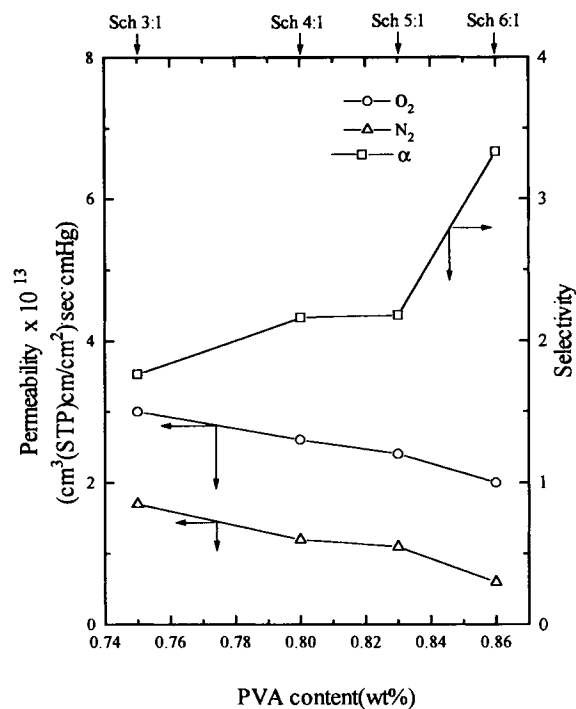
<sup>a</sup> Density of PVA: 1.26 g/cm<sup>3</sup>.<sup>b</sup> Determined by elemental analysis.

acterization of Co(II) chelate membrane from PAAm/PVA blend. Abbreviations, glass transition temperature, density, and Co(II) content are shown in Table II. As an intermediate step, the blend membrane was modified to a Schiff base type. Structures + 2 of the blend and Schiff base membrane were confirmed by the FTIR subtraction method. Differential scanning calorimetric thermograms of blend and Schiff base membranes showed that the glass transition temperature ( $T_g$ ) ranges between 40 and 50°C. Co(II) content in chelate membrane was determined by energy-dispersive X-ray spectroscopy, elemental analysis, and thermogravimetric analysis (TGA) and ranged between 9.82 and 15.75 wt %. As the membrane becomes chelate with Co(II), density increased as measured by a density gradient column. During the process of becoming chelate membrane, the Schiff base membrane is an effective intermediate step for the preparation of chelate membrane containing cobalt. The membrane becomes more amorphous in the process of preparing chelate membrane as evidenced by X-ray diffraction patterns.

Morosoff et al. confirmed the ability of cobalt chelates to bind oxygen reversibly at room temperature by FTIR.<sup>25</sup> They observed the selective adsorption of oxygen onto the metal-containing polymer by comparing FTIR stretching frequencies before and after oxygen exposure in the membrane. In the present study, Morosoff's method was adopted to investigate the oxygen-binding ability of the present Co(II) chelate membrane. As a result of comparing the FTIR frequency before [Fig. 2(b)] and after [Fig. 2(a)] oxygen exposure, the difference spectrum [Fig. 2(c)] showed a new absorbance at 1150 cm<sup>-1</sup> attributed to an O—O stretching for oxygen complexed to the cobalt center of chelate membrane as the sixth site.

Measurement of gas permeability was performed on the Schiff base and chelate membranes as shown in Figure 3. The permeability of oxygen and nitrogen decreased and selectivity increased with PVA content in the blend membrane. This result is understandable because PVA is a semicrystalline polymer. The content of bulky salicylaldehyde bound with —NH<sub>2</sub> of PAAm in Schiff membranes decreased from **Sch 3 : 1** to **Sch 6 : 1**. Therefore, the free volume in the membrane decreased from **Sch 3 : 1** to **Sch 6 : 1** during the process of becoming the Schiff base membrane and the crystalline region in

**Figure 2** FTIR spectra of (a) oxygen-adsorbed **Che** membrane, (b) **Che** membrane in N<sub>2</sub> atmosphere, and (c) the subtraction result.



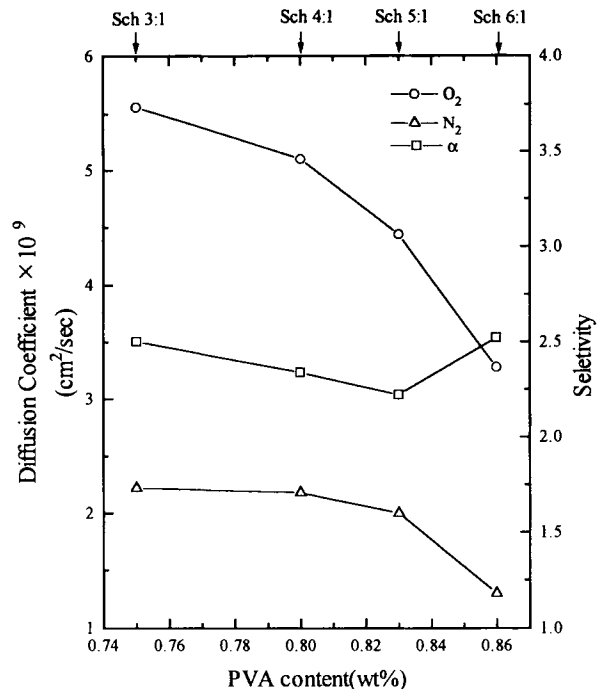
**Figure 3** Effect of PVA content on gas permeability of **Sch** membrane.

PVA was more or less destroyed. In other words, the gas permeability of the **Sch 3 : 1** was increased more than that of the **Sch 6 : 1** because of more free volume of **Sch 3 : 1** than that of **Sch 6 : 1**.<sup>26</sup>

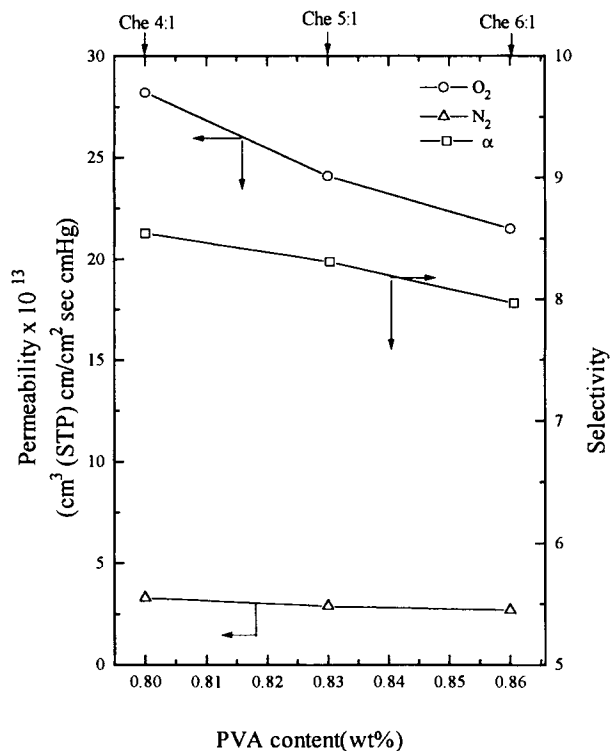
These increments of free volume can be inferred from changes of  $T_g$  and density. Generally,  $T_g$  decreased with increase in the free volume in the polymer.<sup>27</sup> Therefore, the  $T_g$  of **Sch 3 : 1** is 39°C, which is lower than that of **Sch 6 : 1** (48°C) as shown in Table II.

Also, the change of free volume can affect the diffusion coefficient of polymer membranes under the assumption that the gas diffusion can occur only through the amorphous region in polymers. The diffusion coefficients of Schiff base membranes are represented in Figure 4. The diffusion coefficient of **Sch 3 : 1** is larger than that of **Sch 6 : 1**. Also, the diffusion coefficient of oxygen was larger than that of nitrogen, but the solubility coefficient of nitrogen was similar to that of oxygen. This result indicates that gas permeability in the Schiff base membranes is affected by the mobility or the free volume but not by the solubility.

The permeation results of chelate membranes are shown in Figure 5. In the case of **Che 3 : 1**, the membrane was too brittle to measure the gas permeability. Note that as Co(II) was incorporated into the membranes nitrogen permeability was not af-



**Figure 4** Effect of PVA content on diffusion coefficient of **Sch** membrane.



**Figure 5** Effect of PVA content on gas permeability of **Che** membrane.

**Table III** Permeability, Diffusion Coefficient, and Solubility Coefficient of Schiff Base and Chelate Membranes

Sample	Sch 4 : 1	Che 4 : 1	Sch 5 : 1	Che 5 : 1	Sch 6 : 1	Che 6 : 1
<b>P<sup>a</sup></b>						
Oxygen	2.56	28.20	2.40	24.10	2.01	21.50
N <sub>2</sub>	1.17	3.30	1.03	2.90	0.61	2.70
$\alpha_{\text{Oxygen/N}_2}$	2.19	8.50	2.34	8.31	3.27	7.69
<b>D<sup>b</sup></b>						
Oxygen	5.02	1.30	4.44	1.61	3.30	2.00
N <sub>2</sub>	2.13	6.87	1.87	6.74	1.33	6.75
$\alpha_{\text{Oxygen/N}_2}$	2.36	0.19	2.37	0.24	2.48	0.30
<b>S<sup>c</sup></b>						
Oxygen	0.51	21.70	0.54	14.91	0.61	10.72
N <sub>2</sub>	0.55	0.48	0.55	0.43	0.46	0.40
$\alpha_{\text{Oxygen/N}_2}$	0.93	43.99	0.98	34.67	1.33	26.80

<sup>a</sup> Permeability in  $10^{-13}$  cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.

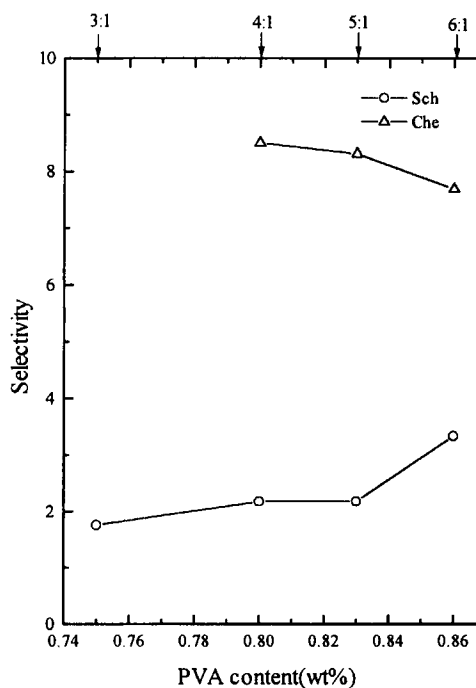
<sup>b</sup> Diffusivity in  $10^{-9}$  cm<sup>2</sup>/s.

<sup>c</sup> Solubility in  $10^{-4}$  cm<sup>3</sup>/cm<sup>3</sup> atm.

fects but oxygen permeability increased with increasing Co(II) contents. The gas permeability and oxygen selectivity decreased for samples from **Che 4 : 1** to **Che 6 : 1**. These results were because the more Co(II)-containing **Che 4 : 1** membrane bound more easily with oxygen compared with the less Co(II)-containing **Che 6 : 1** membrane. It also showed that oxygen permeability steeply decreased compared with nitrogen permeability for samples from **Che 4 : 1** to **Che 6 : 1**. Therefore, the higher permeability of **Che 4 : 1** than that of **Che 6 : 1** and the similar selectivity resulted from the solubility coefficient which had much influence on the permeability as the Co(II) content in the membrane increased. Reversible and selective binding of Co(II) with oxygen, not nitrogen, enhances oxygen permeability rather than nitrogen.

The gas permeability, diffusion coefficient, and solubility coefficient of Schiff base and chelate membranes are summarized in Table III. By comparing the Schiff base and chelate membranes, the selectivity increased when Schiff base membranes were converted into chelate membranes. The fact that the increase of oxygen permeability is larger than that of nitrogen is a direct cause of an increased amount of cobalt-fixed carriers incorporated in the membranes. By comparing diffusion coefficients of gases, when Schiff base membranes changed into chelate membranes, the nitrogen diffusion coefficient increased in proportion to an increase of free volume, as we confirmed in X-ray diffraction<sup>23</sup> and density measurements. However, the oxygen diffusion coefficient represented an opposite tendency

because Co(II) incorporated in the chelate membrane inhibited the diffusion of oxygen.<sup>2,11</sup> In other words, the oxygen diffusion coefficient in chelate membrane decreased, but, on the other hand, nitrogen diffusion coefficients are almost constant. In comparing the solubility coefficients, however, the oxygen solubility coefficient increased much but nitrogen solubility did not change as the membrane



**Figure 6** Effect of PVA content on selectivities of Sch and Che membranes.

became chelate. Therefore, even though the nitrogen diffusion coefficient is larger than that of oxygen, the selectivity increased under the influence of the enhanced oxygen solubility of oxygen in the chelate membrane.

The selectivity of Schiff base and chelate membranes are shown in Figure 6. As the Co(II) was fixed in the Schiff base membranes, the selectivity increased. In comparing oxygen and nitrogen permeabilities of Schiff base and chelate membranes, nitrogen permeability does not change but oxygen permeability is much different (Table III). Accordingly, the increase of selectivity in the chelate membrane resulted mainly from the increase of oxygen permeability as oxygen had been bound with a fixed carrier, Co(II), incorporated in the chelate membrane and had been facilitated through. Therefore, an increase of measured selectivity between the Schiff base and chelate membranes is due mainly to an increase in the solubility selectivity. The effects of the change of upstream pressure and of other metals on the permeability coefficient of the membranes are ongoing and will be presented shortly.

## CONCLUSIONS

In this study, we synthesized novel chelate membranes containing a fixed carrier, Co(II), as a selective oxygen-binding ability. A selective O—O stretching peak binding with the Co(II) atom in the chelate membranes was confirmed by FTIR analysis. Those selective bindings exerted a beneficial influence upon the gas permeability. The permeability of Schiff base membranes increased with the increase of free volume in the membrane as evidenced by the glass transition temperature and density measurements. Both the permeability and selectivity of chelate membranes containing Co(II) increased with the Co(II) content. Their maximum increases are about 10 and four times greater than those of the Sch membrane, respectively. An increase of measured selectivity in chelate membrane is due mainly to the solubility increase upon cobalt incorporation.

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