

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

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**ABSTRACT:** Facilitated transport of oxygen through Co(II) and Mn(II) chelate membranes from poly(vinyl alcohol)/poly(*N*-salicylidene allyl amine) was investigated. As the membranes became chelated, oxygen diffusivity decreased and the solubility toward oxygen was enhanced. The oxygen permeability of the base poly(vinyl alcohol)/poly(*N*-salicylidene allyl amine) membrane was  $2.6 \times 10^{-3} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ cm Hg sec}$  (barrer), and the selectivity toward oxygen was 2.2. As Co(II) was introduced into this membrane, oxygen permeability and oxygen selectivity increased to  $2.82 \times 10^{-2}$  barrer and 8.5, respectively. The permeability and selectivity of Mn(II) chelate membrane were  $3.28 \times 10^{-2}$  and 5, respectively. A major reason for the increased selectivity was the enhanced solubility of oxygen in chelate membrane upon chelation. The transport behavior of chelate membranes followed a dual-mode transport, and the parameters were estimated and compared between Co(II) and Mn(II) membranes. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 483–490, 1997

**Key words:** chelate membrane; gas separation; facilitated transport; oxygen separation

## INTRODUCTION

In membrane processes using polymeric membranes, many efforts have been concentrated on improving both selectivity and permeability because these two parameters usually show an inverse relationship.<sup>1–18</sup> One of these efforts was a facilitated transport using transition metal embedded in the polymeric membrane.<sup>1–10</sup> To pre-

pare the facilitated transport membranes using transition metals, liquid and solid membranes have been used. In the case of liquid membranes, Baker et al. noted that oxygen selectivity of more than 3 was reported for the membrane employing ethylene glycol and glycerol as immobilized liquid membrane.<sup>1</sup> However, liquid membranes possess several problems such as instability of the membrane itself, design of the device, instability of the complexes, and carrier saturation. Polymeric chelate membrane, on the other hand, can solve these problems to some extent.

Nishide et al. prepared a membrane consisting of cobalt–porphyrin dispersed in poly(1-trimethylsilyl 1-propyne) and reported that oxygen permeability of the membrane with 4.5 wt % metal content was 23 barrer with oxygen selectivity of 12.<sup>2</sup> But those values were obtained at the cost of decreased permeability upon chelation. Hsuie et

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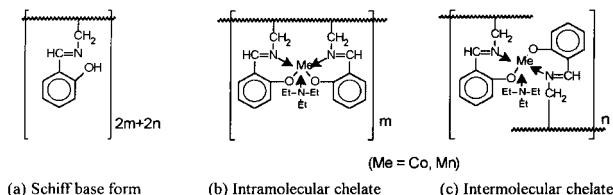
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**Figure 1** Schematic structure of Schiff base and chelate forms.

al. obtained the decreased permeability and increased selectivity using modified block copoly-(styrene-butadiene-styrene) membranes containing a series of low-molecular-weight Schiff base–Co(II) chelates.<sup>8,9</sup> A possible reason for the decrease of permeability was that the blended Co(II)–porphyrin or low-molecular-weight Schiff base–Co(II) chelate occupied the free volume of the base polymer and restricted the transport of gases. The rotation of the backbone and side chain was limited by the coordination of the side Lewis base group with Co(II). However Delaney et al. obtained a twofold increase of both oxygen permeability and selectivity using Schiff base–Co(II) chelate grafted to a styrenic copolymer.<sup>10</sup> In the case of grafted chelates, it seems that the ligand group makes the free volume in polymer enlarge, and thus the decrease in permeability is not observed.

We have already reported on the preparation and characterization of a poly(vinyl alcohol)/poly(*N*-salicylidene allyl amine)–Co(II) chelate membrane,<sup>19</sup> its gas permeabilities with variable Co(II) contents,<sup>20</sup> and separation of benzene/cyclohexane by pervaporation through this membrane.<sup>21</sup> Generally, in gas separation, cobalt was used for the central metal in Schiff base ligands.<sup>1–10</sup> Yano et al. reported the selective oxygen gas sorption of complex Mn(II) salts of ethylene–methacrylic acid copolymer with 1,3-bis(aminomethyl)cyclohexane.<sup>22</sup> They used acetic acid as a ligand. No studies on the application of Schiff base–Mn(II) chelate membranes to oxygen/nitrogen separation have been reported. In the case of Schiff base–Mn(II) chelate, because Mn(II) is more liable than Co(II) in the same ligands, as shown in Irving–Williams order, it is expected that the decrease of diffusivity will be small compared with Co(II) chelates.

This article discusses an attempt to increase both permeability and selectivity by preparing the grafted Schiff base membrane using poly(vinyl alcohol)/poly(allyl amine). We also report on the facilitation transport ability of Mn(II) chelate

membrane by varying the feed pressure and comparing it with Co(II) chelate membrane.

## EXPERIMENTAL

### Materials and Membrane Preparation

Poly(vinyl alcohol) (PVA; MW: 66,000; degree of hydrolysis: 88%) and poly(allyl amine) (PAAM; MW: 100,000) were purchased from Shin Yo Pure Chemicals (Japan) and Aldrich Chemicals Co. (USA), respectively. Dianion SA 10A, a strong base ion exchange resin, was purchased from Samyang Co. (Korea). Distilled and deionized water treated with the Milli-Q water purification system (Millipore Co., USA) was used as a blending solvent. Salicylaldehyde, dimethylformamide (DMF), triethylamine (TEA), methanol, Co(acetate)<sub>2</sub>·4H<sub>2</sub>O, and Mn(acetate)<sub>2</sub>·4H<sub>2</sub>O were used for the preparation of chelate membrane without further purification. All reagents were from Junsei Chemicals (Japan, GR grade).

Procedures for preparing Co(II) chelate membrane were reported in our previous study.<sup>19</sup> Mn(II) chelate membrane was prepared in the same manner with the exception of treating time (30 mins) in metal solution. Initial weight ratio of PVA and PAAM was 4 : 1.

The chemical structure of chelate membrane is described in Figure 1. Sample designations and metal contents are listed in Table I.

### Measurement of Gas Permeability

Single-gas permeabilities of Schiff base and chelate membranes were determined by the time-lag method, which entailed initially evacuating the downstream volume of the membrane to about  $1 \times 10^{-3}$  mmHg and providing the upstream side with O<sub>2</sub> and N<sub>2</sub> at 10 torr for the test. The change of pressure in the downstream side was measured

**Table I** Sample Designation of Chelate Membranes

Sample	Initial Weight Ratio of PVA/PAAM	Metal Content (wt %) <sup>a</sup>
Sch	4	—
Sch–Mn	4	8.8
Sch–Co	4	10.5

<sup>a</sup> Determined by thermogravimetric analysis at a temperature of 900°C.

by a Baratron pressure transducer (MKS Inc., U.S.A.) and plotted against time.

Permeability of the membrane was calculated by using the equation

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

where  $P$  is the permeability coefficient ( $\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{sec cm Hg}$ ),  $dp/dt$  is a gradient of pressure versus time curve at steady state,  $T$  is temperature ( $^{\circ}\text{C}$ ),  $V$  is the volume of the downstream side ( $20.5 \text{ cm}^3$ ),  $A$  is the membrane area ( $13.416 \text{ cm}^2$ ),  $l$  is the membrane thickness, and  $\Delta p$  is the difference between upstream pressure and downstream pressure. From the solution-diffusion model, permeability may also be defined as the multiplicity of diffusion and solubility coefficient. Apparent diffusivity is represented as follows:

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

where  $\theta$  is an intercept obtained from the linear portion of the pressure time plot. Apparent solubility  $S$  and  $\text{O}_2$  selectivity were calculated using eqs. (3) and (4), respectively.

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

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

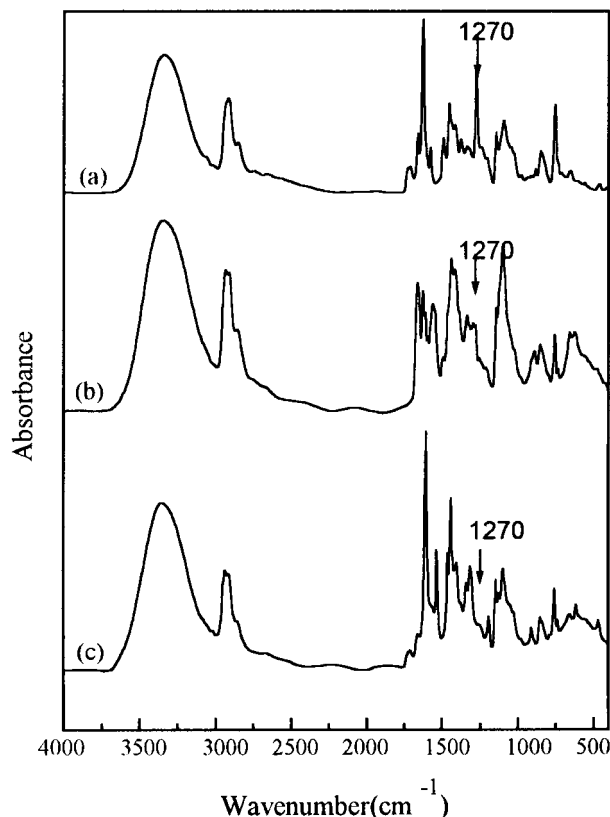
In general, the facilitated transport membrane follows a dual-mode transport model.<sup>23</sup> The model equation is as follows:

$$P = k_D D_D + D_C C'_C K / (1 + K p_2) \quad (5)$$

where  $P$  is the permeability of the gas,  $k_D$  is Henry's law coefficient,  $D_D$  and  $D_C$  are the diffusion coefficients, respectively,  $C'_C$  is the saturation amount of gas reversibly bound to the binding site,  $K$  is the gas binding and dissociation equilibrium constant, and  $p_2$  is the upstream gas pressure.

### Characterization

Fourier transform infrared spectroscopy (FTIR) (Nicolet Magna IR 550) was used to compare differences of the characteristic peaks between Co(II) and Mn(II) chelate membranes. Differential scanning calorimetry (DSC) (Du Pont Model 910) was used to characterize the thermal proper-



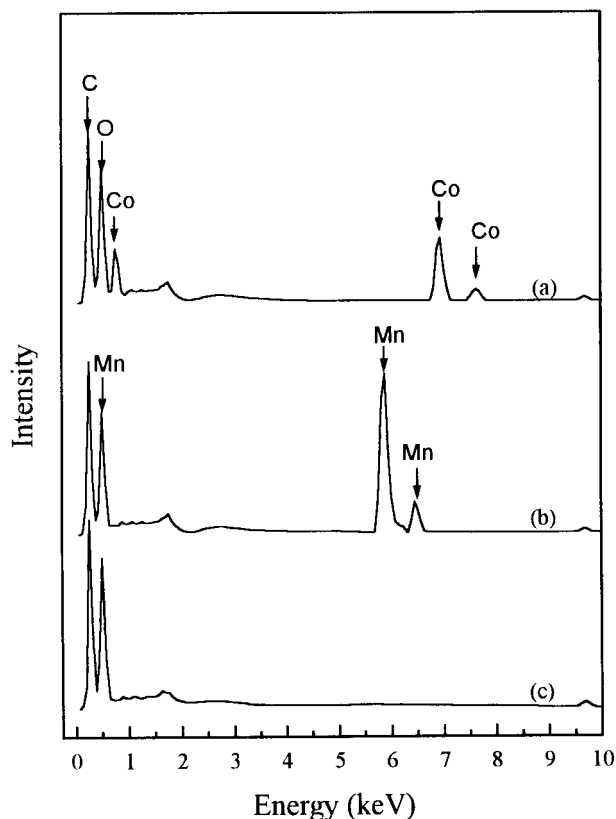
**Figure 2** FTIR spectra of (a) Sch, (b) Sch-Mn, and (c) Sch-Co membranes.

ties of Co(II) and Mn(II) chelate membranes. The metal content was measured by thermogravimetric analysis (TGA) (Du Pont Model 951) at a temperature of  $900^{\circ}\text{C}$ . The metals in the membranes were confirmed using an energy dispersive X-ray spectrometer (EDX, Noran Co., Voyager, U.S.A.).

## RESULTS AND DISCUSSION

### Characteristic Differences of Co(II) and Mn(II) Chelate Membranes

Figure 2 shows the FT IR spectra of Sch, Sch-Co, and Sch-Mn membranes. The  $\nu_{\text{-OH}}$  peak of Sch at  $1270 \text{ cm}^{-1}$  disappeared completely in Sch-Co. However, the  $\nu_{\text{-OH}}$  peak of Sch-Mn at  $1270 \text{ cm}^{-1}$  did not disappear completely, and the peak at  $1550 \text{ cm}^{-1}$  corresponding to the antisymmetric stretching band of carboxylic salt appeared. From this result, it appears that Mn(II) coordinated with the  $-\text{OH}$  of PVA to some degree. The peak at  $1550 \text{ cm}^{-1}$  appeared also in the case of PVA



**Figure 3** EDS spectra of (a) Sch-Co, (b) Sch-Mn, and (c) Sch membranes.

soaked in Mn(II) solution. According to the study of Wöhrle et al., excessive cobalt in the polymer does not influence the reversible binding of dioxygen in divinylsalen-Co(II) chelate, and only Schiff base ligand-bound cobalt is active.<sup>24</sup>

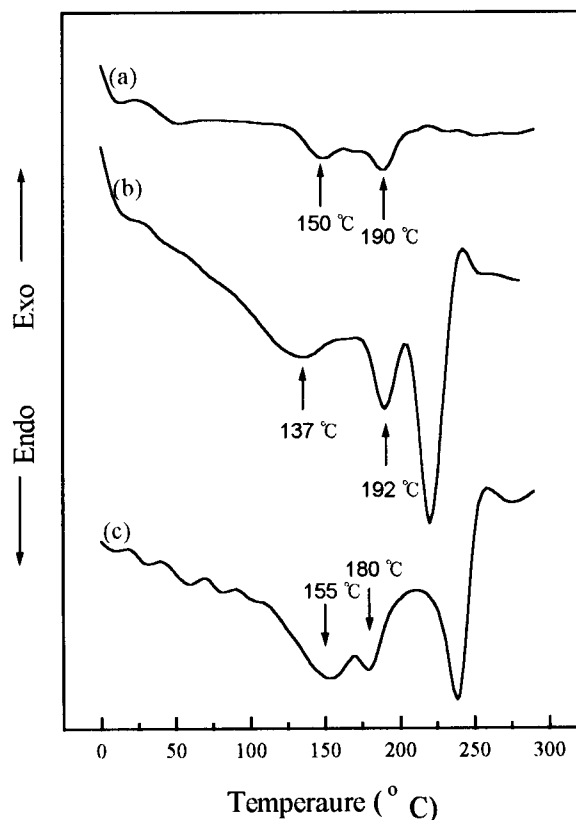
Energy dispersive X-ray (EDX) was used to identify the type of metals in the membranes (Fig. 3). The characteristic peaks of Co(II) in the chelate membrane were identified at 6.9 and 7.2 keV and in Mn(II) at 5.9 and 6.4 keV, respectively.

Figure 4 shows DSC thermograms of Sch, Sch-Co, and Sch-Mn membranes. Melting peaks of PVA are observed at 180–190°C. Moreover, melting peaks of ionic crystals were observed near 130–150°C in all samples. Notice that the melting peak of ionic crystals in Sch-Co is larger than that of Sch-Mn, probably owing to the difference in metal content in chelate membranes (Table I). Also note that the melting peaks of an ionic cluster in Sch-Mn and in Sch-Co appeared at 137 and 155°C, respectively, which means that the ionic interaction between metal and Schiff base is stronger for the cobalt-containing membrane and thus that the strength of the ionic cluster of Sch-

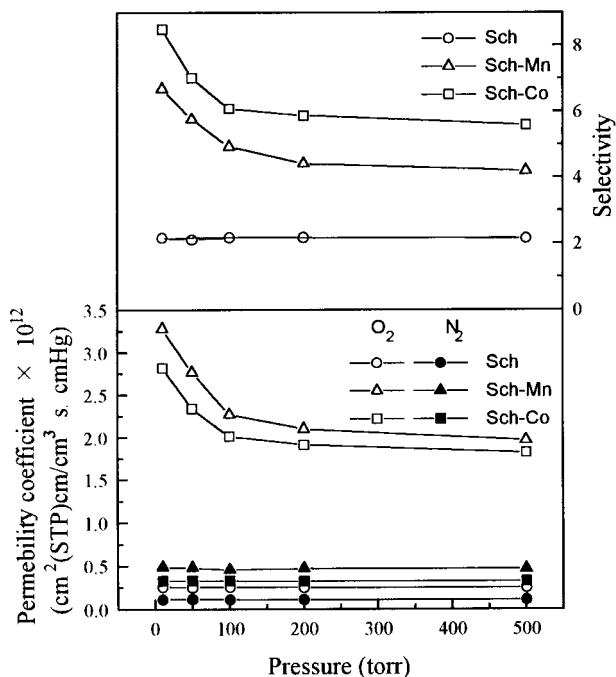
Co is stronger than that of Sch-Mn. The present result corresponds to that reported by Hirasawa et al.,<sup>25,26</sup> who found that the complex Mn salt in the ethylene-methacrylic acid copolymer with 1,3-bis(aminoethyl)cyclohexane is weaker than the complex salts Co(II), Cu(II), and Zn(II) transition metal-ion complexes. The strength and content of ionic clusters in the chelate membranes may affect the gas permeability and will be discussed later.

### Gas Permeation

Figure 5 shows the permeabilities and selectivities of Sch, Sch-Co, and Sch-Mn membranes with the variation of feed pressure from 1.3 ~ 66.7 kPa. Permeabilities increased for chelate membranes (Sch-Co and Sch-Mn) compared with virgin Sch. The permeability of Sch-Mn is greater than that of Sch-Co in all feed-pressure ranges tested. The difference between the permeabilities of Sch-Mn and Sch-Co can be explained by the strength and content of the ionic cluster, as mentioned above. The stronger and more ionic the cluster is in the



**Figure 4** DSC thermograms of (a) Sch, (b) Sch-Mn, and (c) Sch-Co membranes.



**Figure 5** Gas permeabilities and selectivities of Sch, Sch-Mn, and Sch-Co membranes.

membrane, the less the gas permeability is. As observed in DSC melting thermograms in Figure 4, the Sch-Co membrane has a stronger and more ionic cluster. Therefore, the permeability of Sch-Co is less than that of Sch-Mn. The enhanced permeabilities of the two chelate membranes may also be caused by the different membrane preparation procedures. Chelating was carried out by swelling Sch in the metal solutions and later drying it. During this step, one central metal bonds with two salicylidene groups, and upon drying the sample, the free volume of the chelate membrane increases.

As shown in Figure 5, the permeability coefficient of oxygen for both chelate membranes decreases exponentially with pressure. We conclude that the Sch-Mn and Sch-Co membranes have an affinity toward oxygen. If a membrane has an affinity with a permeant gas, the permeability coefficient of the membrane decreases exponentially with pressure. In the case of the membrane having no affinity with a permeant gas, the permeability decreases slightly and linearly.<sup>27</sup>

### Sorption Amount of Oxygen

For the interpretation of the dual-mode transport shown in eq. (5), the sorption amount should be

known. We determined the sorption amount of oxygen from upstream pressure times the solubility coefficient calculated from eq. (3). Figure 6 represents the pressure dependence of the sorption amount of oxygen obtained by the method mentioned above.

The Langmuir-type oxygen solubility coefficient,  $C_C$ , and equilibrium constant,  $K$ , in eq. (5) were obtained from the dual-mode sorption equations shown below.<sup>28</sup>

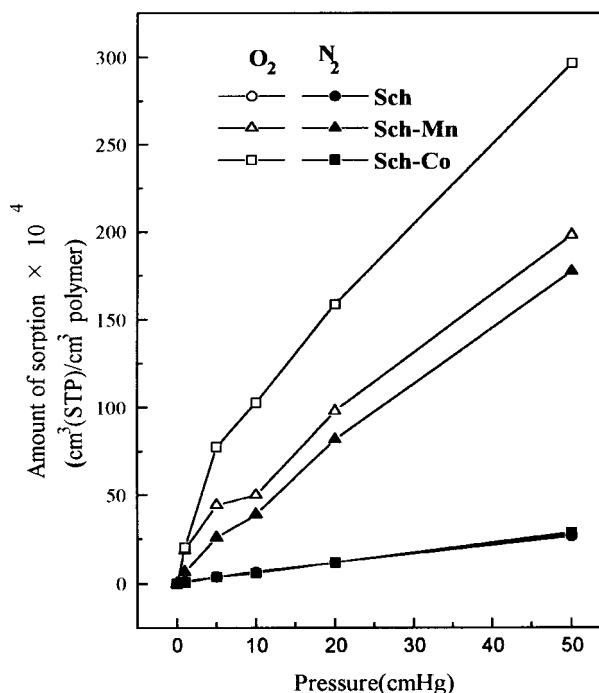
$$C = C_D + C_C \quad (6)$$

$$C_D = k_D p_2, \quad C_C = C'_C K p_2 / (1 + K p_2) \quad (7)$$

$$1/C_C = 1/C'_C + 1/C'_C K p_2 \quad (8)$$

where  $C$  is the total amount of sorption and  $C_D$  and  $C_C$  are the sorbed amount of gas by Henry mode and Langmuir mode, respectively.

From the above equations, if we know  $C_D$ , we can obtain  $C'_C$  and  $K$ . We obtained  $C_D$  from the sorption test of nitrogen (that is, the amount of Henry-mode sorption of oxygen, which has no interaction between membrane and permeant, would be the same as that for nitrogen). This is evident by comparing the solubility coefficients of



**Figure 6** Sorption isotherms of Sch, Sch-Mn, and Sch-Co membranes.

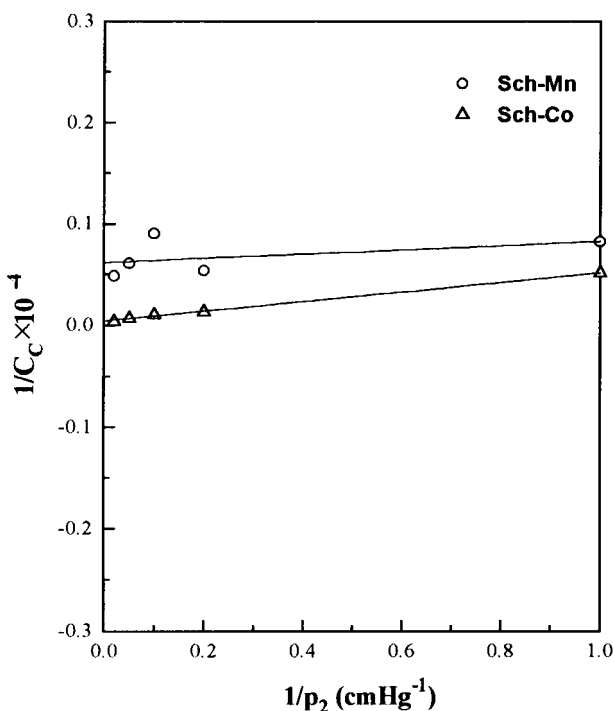
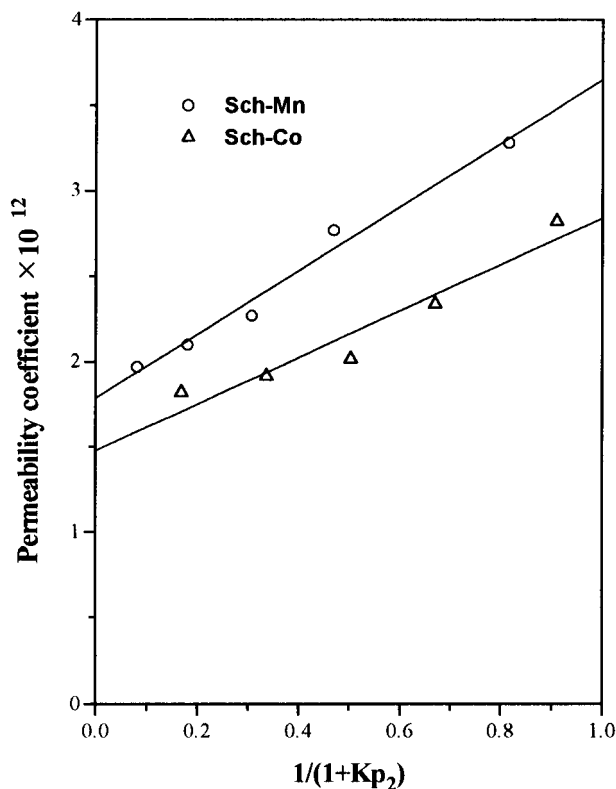
**Table II Solubility Coefficients (S) of Sch Membranes**

Pressure (torr)	Solubility Coefficient, $S^a \times 10^3$	
	O <sub>2</sub>	N <sub>2</sub> <sup>a</sup>
10	0.135	0.128
50	0.080	0.078
100	0.068	0.066
200	0.060	0.059
500	0.055	0.052

<sup>a</sup>cm<sup>3</sup> gas (STP)/cm<sup>3</sup> polymer cmHg

the Sch membrane (Table II). Some researchers obtained the  $C_D$  value from the oxygen uptake of the base membrane. However, in the chelate membranes, as the metal is introduced to the membrane, the ionic clusters are formed, and these ionic clusters change the free volume of the membrane.<sup>25,26</sup> In addition to that, as chelate is formed, the central metal atom acts as a short-range crosslinking agent and restricts the chain rotation.<sup>29</sup> Therefore, it is expected that the sorption amounts of oxygen before and after chelation may differ.

Figures 7 and 8 show the plots for obtaining

**Figure 7**  $1/C'_C$  versus  $1/p_2$  of Sch-Mn and Sch-Co membranes.**Figure 8**  $P_{O_2}$  versus  $1/(1 + Kp_2)$  of Sch-Mn and Sch-Co membranes.

parameters in dual-mode transport equations. The results are summarized in Table III. Henry-mode diffusion coefficients ( $D_D$ ) of chelate membranes are greater than those of Sch. This can be explained from the fact that one Co(II) or Mn(II) atom draws two salicylidene groups, and some of those chelates form ionic clusters, resulting in shrinkage of polymer chains in the membrane. As the membrane is dried from such a state, the free volume of the chelate membranes increases. Another fact derived from Table III is that the  $k_D$  of Sch-Mn is much larger, and the  $D_D$  of Sch-Mn is smaller, than those of Sch-Co. We knew that the ionic interaction between metal and the Schiff base is stronger for the cobalt-containing membrane and thus, the strength of the ionic cluster of Sch-Co is stronger than that of Sch-Mn. Therefore, the increase of free volume caused by the shrinkage of the main chain upon chelation is less for Sch-Mn. Therefore,  $D_D$  is less and  $k_D$  is larger for Sch-Mn compared with those of Sch-Co.

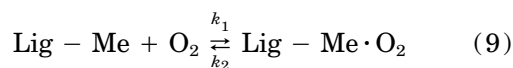
Langmuir-type transport behavior is somewhat different from Henry's mode in chelate membranes. Here,  $C'_C$  is smaller and  $D_C$  is larger for

**Table III Dual-Mode Parameters of Sch–Mn and Sch–Co Membranes**

Membrane	$k_D \times 10^3$ cm <sup>3</sup> gas (STP)	$D_D \times 10^9$ cm <sup>2</sup>	$C'_C \times 10^3$ cm <sup>3</sup> gas (STP)	$D_C \times 10^9$ cm <sup>2</sup>	$K \times 10^2$ 1
	cm <sup>3</sup> polymer cmHg	s	cm <sup>3</sup> polymer cmHg	s	cmHg
Sch	0.06	0.41	—	—	—
Sch–Mn	0.35	5.10	1.62	0.39	29.82
Sch–Co	0.06	25.97	23.26	0.06	9.2

Sch–Mn compared with those of Sch–Co. Mn(II) is more labile than Co(II), as shown in Irving–William's order. When Mn(II) is unstable, it is believed that residence time of oxygen in the chelate membrane is relatively short compared with Co(II), contributing to a small solubility coefficient of Sch–Mn. Moreover, oxygen molecules can easily dissociate from the Mn(II) chelate membrane, resulting in a large diffusion coefficient in the Langmuir mode.

The equilibrium constant,  $K$ , of Sch–Mn is larger than that of Sch–Co as compared in Table III. Here,  $K$  is defined as



$$K = \frac{k_1}{k_2} = \frac{[\text{Lig} - \text{Me} \cdot \text{O}_2]}{[\text{Lig} - \text{Me}][\text{O}_2]} \quad (10)$$

where Lig represents ligand and Me is Co(II) or Mn(II).

In the case of Sch–Mn, Mn(II) is introduced to a hydroxyl group in PVA to some degree. However, Co(II) is scarcely attached to PVA, as explained above. When dioxygen binds with those Mn(II), attached to hydroxyl group of PVA, Mn(II) may be oxidized to Mn(III), and dioxygen forms peroxy complexes with Mn metals irreversibly.<sup>24</sup> Therefore, the concentration of Lig–Mn·O<sub>2</sub> in Sch–Mn membrane is greater than the concentration of Lig–Co·O<sub>2</sub> in Sch–Co. Therefore, it is clear from eq. (10) that  $K$  of Sch–Mn is larger than that of Sch–Co.

## CONCLUSIONS

Mn(II)- and Co(II)-containing chelate membranes have been prepared using Schiff base as a ligand. Mn(II) coordinated with the hydroxyl group in PVA to some degree, as evidenced from

FT IR spectral analysis. DSC thermograms of Schiff base and chelate membranes showed that melting peaks of ionic clusters appeared near 130–150°C. Sch–Co membrane exhibited a larger and higher ionic crystal melting temperature than that of Sch–Mn. The strength and higher content of ionic clusters in chelate membrane affect the gas permeability. Both permeability and oxygen selectivity have been enhanced by chelating Schiff base membranes. Increased permeabilities for two chelate membranes may be caused by the strong ionic interactions and enhanced free volumes in chelate membranes. Since the permeability coefficient of oxygen through two chelate membranes decreased exponentially with pressure, chelate membranes should have an affinity for oxygen rather than nitrogen and contributed to an increase in oxygen selectivity upon chelation of the Schiff base membrane. Permeation behavior of gases through chelate membranes were interpreted by dual-mode transport theory. Independent parameters in dual-mode transport theory were evaluated.  $D_D$  of chelate membranes were greater than that of Sch owing to the large free volume in chelate membranes. The  $k_D$  of Sch–Mn is much larger, and  $D_D$  is smaller, than those of Sch–Co.

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