

Oxygen/Nitrogen Transport in Ionomer Composite Membranes Containing a Cobalt Schiff Base Complex

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ABSTRACT: Different amounts of (*N,N'*-disalicylideneethylenediamin)cobalt (CoS) were blended to a cobalt (II)-neutralized sulfonated EPDM (Co^(II)-S-EPDM) ionomer membrane to enhance its oxygen-enriching ability. Various influence factors on permeabilities and selectivities of the composite membranes, such as the gas pressure difference, the CoS content, and the testing temperature have been investigated. Oxygen permeability coefficients (P_{O_2}) and oxygen/nitrogen separation factors (α_{O_2/N_2}) increased simultaneously by decreasing the gas pressure difference or by increasing the CoS content. In comparison with the EPDM matrix, P_{O_2} and α_{O_2/N_2} of Co^(II)-S-EPDM-CoS (85/15) composite membrane increased from 11.0 Barrer and 4.38 to 37.0 Barrer and 9.60. Obvious enhancement in the oxygen-enriching property shows that the dual actions of cobaltous ion crosslinking and addition of an abundant cobalt complex may be an effective way to improve a rubbery polymer membrane. As high as 15 wt % of the CoS could be blended. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1071–1077, 1999

Key words: oxygen/nitrogen separation membrane; ionomer membrane containing cobaltous ions; (*N,N'*-disalicylideneethylenediamin)cobalt; facilitated oxygen transport

INTRODUCTION

Polymer gas separation membranes almost exhibit an inverse permeability/selectivity behavior; that is, as gas permeability of a polymer decreases, its selectivity to different gas pairs generally increases.¹ There are two ways to enhance both the permeability and selectivity of polymer membranes for oxygen enrichment from air. One approach is to blend a liquid crystal and a high oxygen affinity substance into a polymer membrane.^{2,3} When the membrane is heated to a temperature above the liquid crystal phase, a simul-

taneous increase in both the permeability and selectivity can occur.

Another way is to incorporate an oxygen carrier into a polymer membrane.⁴ The oxygen carrier, being almost cobaltous complexes such as Schiff base or porphyrin complexes, which were blended with a suitable polymer or attached to a polymer backbone chain as pendent groups, can absorb and selectively transport oxygen. This type of membranes exhibits a few characteristics that the selectivities are improved distinctly, and the permeability coefficients and separation factors increase at the same time with a decreasing gas pressure difference. Used membrane materials reported by the literature have been concerned with polymethacrylates,^{5–7} a styrene and diene three-block copolymer,^{8,9} polystyrene,¹⁰ polycarbonate,¹¹ and poly(1-trimethylsilyl-1-propyne).¹² The oxygen carrier contents in the membranes are generally below 10 wt %.

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We previously reported the preparation and oxygen-enriching properties of the rubbery Co^(II)-S-EPDM ionomer membrane.¹³ It is interesting to note that a facilitated oxygen transport through the membrane was observed due to cobaltous ion action and suggested that a polymer cobalt complex could be formed in the ionomer. However, it was unable to incorporate more amounts of the cobalt ions into the ionomer as there was a limit to the sulfonic group content in the polymer membrane. In order to enhance further its oxygen-enriching ability several composite membranes, Co^(II)-S-EPDM-CoS of different weight ratio, have been prepared and investigated.

EXPERIMENTAL

Material and Preparation

EPDM was obtained from Mitsui Chemical Co. (EPT-4045). The diene is 5-ethylidene-2-norbornene (ENB) and its content is 0.9 mmol/g copolymer, $[\eta] = 1.45$ dL (decahydronaphthalene, 135°C). Acetic anhydride, sulfuric acid, ethylenediamine, cobaltous acetate, and salicylaldehyde (all from Shanghai Chemical Reagent Co.) were used as received. CoS was synthesized by a method in the literature.¹⁴ Co^(II)-S-EPDM ionomer was synthesized by our previous method.¹³ Its degree of sulfonation of Co^(II)-S-EPDM was determined by the sulfur content of 0.20 mmol/g.

Preparation of Co^(II)-S-EPDM-(CoS) Composite Membranes

Co^(II)-S-EPDM ionomer was dissolved in toluene-tetrahydrofuran (volume ratio: 85/15) at a concentration of 2.0 wt %. A certain amount of the CoS was added into the above solution weighted and dissolved fully to form a mixed solution. Several Co^(II)-S-EPDM-CoS composite membranes of different weight ratio, designated 100/0, 95/5, 90/10, and 85/15, respectively, were prepared by casting from the mixed solution on glass plates in a container filled with nitrogen. The resulting membranes were carefully stripped from the glass plate and then dried in vacuum. The transparent and flexible rubbery membranes of approximately 60 μm thickness were obtained.

Permeation Measurement

Oxygen and nitrogen permeability coefficients (P_{O_2} , P_{N_2}) of the composite membranes were mea-

sured according to the variable-volume method of Stern et al.¹⁵ The gas was supplied at a constant, and the volume changes of the permeated gas with time were recorded. Thus, the permeability coefficient P can be calculated from the following expression:

$$P = \frac{(\Delta V/\Delta t) \cdot l}{\Delta p \cdot A}$$

where ΔV and Δt are the change in volume of the permeated gas and time; A and l are the area and thickness of the membrane, respectively; Δp is the gas pressure difference across the membrane; P is usually corrected to standard conditions (STP) of temperature (273 K) and pressure (76 cm Hg). The oxygen/nitrogen separation factor was calculated by

$$\alpha_{\text{O}_2/\text{N}_2} = \frac{P_{\text{O}_2}}{P_{\text{N}_2}}$$

Thermal Analysis, Scanning Electron Microscope Observation, and Spectroscopic Measurement

Glass transition temperatures (T_g) of the rubbery membranes were measured by using a Perkin-Elmer DSC-2C. The heating rate was 5°C/min.

The membrane surface and the fracture surface of the 95/5 composite membrane coated with gold was observed by using a Hitachi Scanning Electro Microscope (S-520).

The oxygen-binding property of the composite membranes was monitored by electron spin resonance (ESR) spectroscopy (Bruker ECS-106). A toluene-tetrahydrofuran (volume ratio: 85/15) solution of the Co^(II)-S-EPDM-CoS blend was exhausted and filled with nitrogen alternately and repeatedly and then was measured at X-band at 0°C. After the solution was exposed from nitrogen to air, the same operation was repeated.

RESULTS AND DISCUSSION

Effects of Gas Pressure Difference on the Permeability and Selectivity

The composite membranes are wine-red and in the rubbery state at room temperature. The T_g of EPDM, S-EPDM, Co^(II)-S-EPDM, and Co^(II)-S-EPDM-CoS (95/5) membranes measured by differential scanning calorimetry (DSC) (Table I) show little change in their elasticity. Figures 1

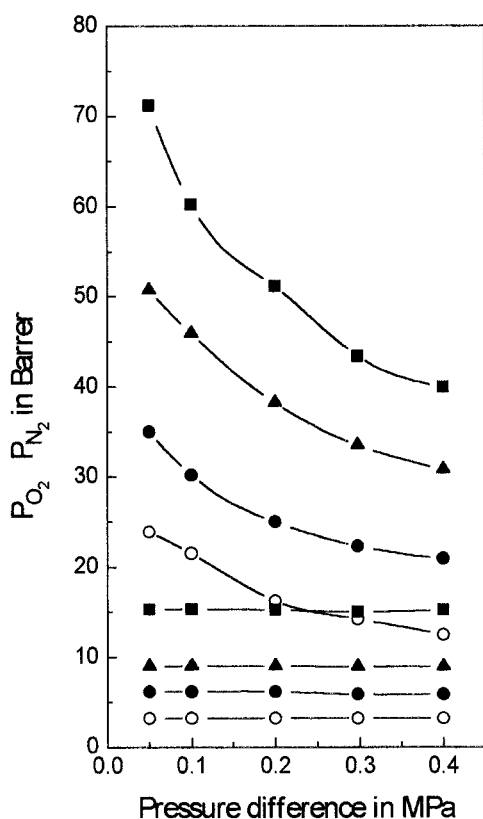
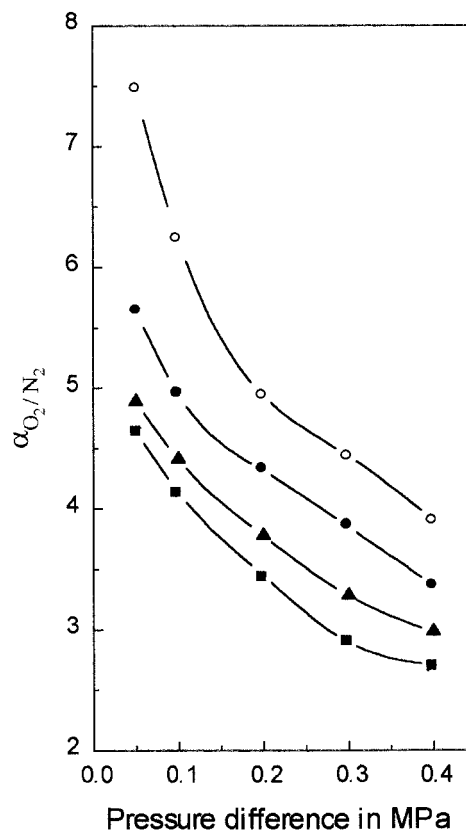
Table I Glass Transition Temperatures (T_g) and Oxygen-Enriching Properties of the EPDM, S-EPDM, Co^{III} -S-EPDM Membranes, and the Co^{III} -S-EPDM-CoS (95/5) Composite Membrane

Membrane	T_g (°C)	Δ_p (mPa)	Temperature (°C)	P_{O_2} (Barrer) ^c	$\alpha_{\text{O}_2/\text{N}_2}$
EPDM ^{a,b}	-54.6	0.05	25	11.0	4.38
S-EPDM ^a	-55.1	0.05	25	15.7	3.68
Co^{III} -S-EPDM ^a	-55.3	0.05	25	22.4	6.79
		0.40	25	11.9	3.80
Co^{III} -S-EPDM-CoS (95/5)	-52.8	0.05	60	49.0	3.33
		0.05	25	23.9	7.47
		0.40	25	12.5	3.91
		0.05	60	71.2	4.26

^a From Zhang and Lin.¹³^b Vulcanized with S_2Cl_2 vapor at 40°C for 30 min.^c 1 Barrer = $10^{-10} \text{ cm}^3 \cdot (\text{SPT}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

and 2 give the effects of gas pressure difference (Δ_p) on P_{O_2} , P_{N_2} , and $\alpha_{\text{O}_2/\text{N}_2}$ for Co^{III} -S-EPDM-CoS (95/5) composite membrane at several temperatures. The composite membrane shows a clear increase in P_{O_2} and $\alpha_{\text{O}_2/\text{N}_2}$ with decreasing Δ_p . For example, P_{O_2} increases from 12.5 to 23.9

Barrer when $\Delta_p(\text{O}_2)$ decreases from 0.40 to 0.05 mPa at 25°C, while at a higher temperature of 60°C, a more obvious increase from 41.5 to 71.2 Barrer occurs. In contrast to P_{O_2} , P_{N_2} versus $\Delta_p(\text{N}_2)$ curves exhibit horizontal lines. It indicates that P_{N_2} is independent of the nitrogen pres-

**Figure 1** Effect of the gas pressure difference on P_{O_2} (—) and P_{N_2} (---) for the Co^{III} -S-EPDM-CoS (95/5) composite membrane at (○) 25, (●) 40, (▲) 50, and (■) 60°C.**Figure 2** Effect of the gas pressure difference on $\alpha_{\text{O}_2/\text{N}_2}$ for the Co^{III} -S-EPDM-CoS (95/5) composite membrane at (○) 25, (●) 40, (▲) 50, and (■) 60°C.

sure difference. The different influences of Δ_p on P_{O_2} and P_{N_2} lead to a distinct increase in α_{O_2/N_2} (Fig. 2). The α_{O_2/N_2} increases from 3.91 to 7.47 as Δ_p decreases from 0.40 to 0.05 mPa at 25°C. This exhibits a high selectivity feature of the membranes containing cobalt complexes. As expected, a characteristic phenomenon of simultaneous enhancements of both P_{O_2} and α_{O_2/N_2} occurs with decreasing Δ_p . In our previous studies, the Co^(II)-S-EPDM membrane without the CoS also show the same behavior, but the composite membrane gives better oxygen-enriching properties.

Some data of oxygen enrichment for the EPDM, S-EPDM, Co^(II)-S-EPDM membranes and the 95/5 composite membrane under the same conditions are also summarized in Table I. As compared with EPDM and S-EPDM, P_{O_2} and α_{O_2/N_2} values of the composite membrane increase to a some extent at 25°C and, more distinctly, under 0.05 mPa at 60°C. But this increase is smaller in comparison to Co^(II)-S-EPDM. The reason could be concerned with morphology of the composite membrane and coordinate structure of the CoS.

Scanning electron microscopy (SEM) was used to examine the morphology of the 95/5 composite membrane. Figure 3(a) is a photograph of the air-facing surface. It can be seen that the CoS in the form of a crystal particle with different size gathered together on the membrane surface. This is probably due to the fact that the chemical structure difference of the CoS and the ionomer matrix results in poor compatibility between them. Figure 3(b) presents a fracture surface and shows that internal structure of the membrane appears denser and that the CoS amount inside is less than the exterior. This nonuniform distribution of the CoS crystal particles in the membrane is in prejudice of facilitated transport for oxygen. Besides, the CoS is a four-coordinate structure complex and not better in oxygen-binding ability, which can be enhanced if an axial base was added and combined with its vacant coordinate site.¹⁶

The mechanism of oxygen transport through the polymer membranes containing the cobalt complex has been described by some literature.⁵⁻⁷ It has been reported that oxygen sorption and desorption to and from the cobalt complex in the membranes is rapid and reversible and that oxygen transport is facilitated by this additional pass. This process can be detected by means of an ESR spectroscopy or a high-sensitivity UV spectrophotometer. In this study, a toluene-tetrahydrofuran solution of Co^(II)-S-EPDM-CoS (95/5)

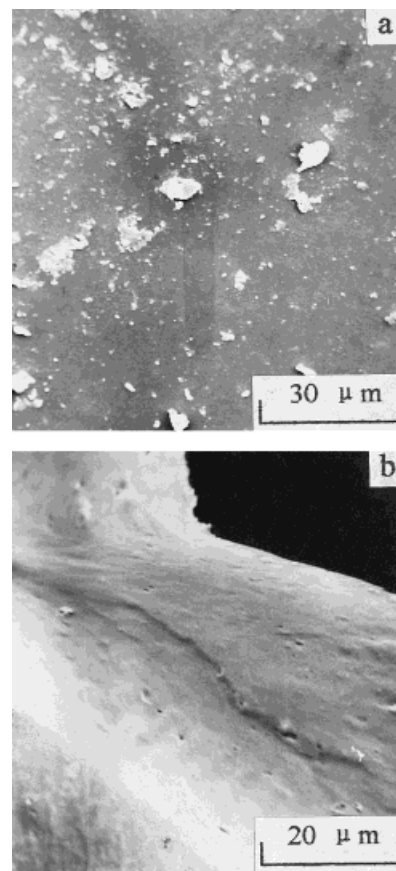


Figure 3 Scanning electron micrographs of the Co^(II)-S-EPDM-CoS (95/5) composite membrane: (a) air-facing surface; (b) fracture surface.

was exhausted and filled with N₂ alternately and repeatedly, and then was measured by ESR spectroscopy at the X-band at 0°C. The results are shown in Figure 4(a). It exhibits that a signal in the vicinity of $g = 2.0$ is nearly a horizontal line in N₂, which indicates the absence of an oxygen adduct. A new strong signal occurs within 10 min under the same conditions after the solution was exposed from N₂ to air. This signal is assigned to the cobalt-oxygen adduct by the literature.⁵⁻⁷ The cyclic experiment was repeated quite a few times, and the N result remains unchanged. Reversible ESR spectral change of the solution of Co^(II)-S-EPDM-CoS (95/5) shows that the oxygen-binding equilibrium process is reversible. This behavior is similar to the Co^(II)-S-EPDM membrane reported previously [Fig. 4(b)], but the signal is stronger than its. The stronger signal should include two parts of the Co^(II)-S-EPDM itself and the CoS to bind oxygen.

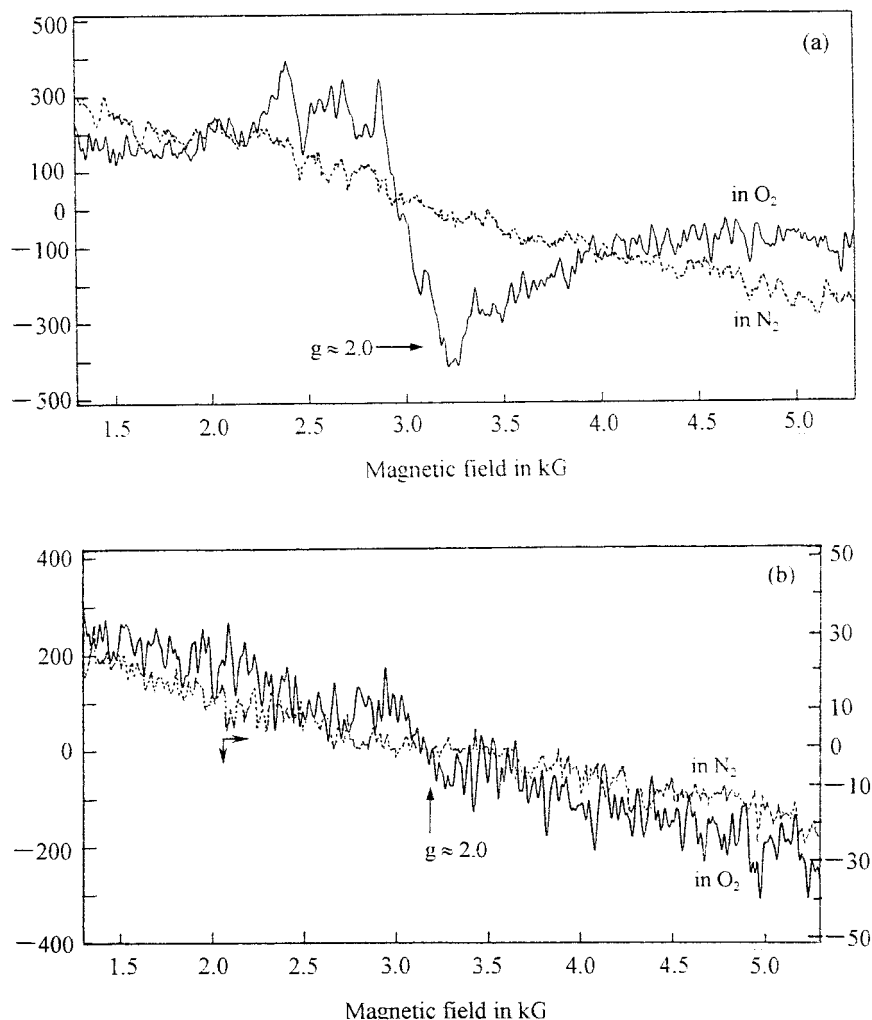


Figure 4 Reversible ESR spectral change of (a) $\text{Co}^{\text{II}}\text{-S-EPDM-CoS}$ (95/5) and (b) $\text{Co}^{\text{II}}\text{-S-EPDM}$ in toluene-tetrahydrofuran (volume ratio: 85/5) at 0°C .

Effects of the CoS Content on the Permeability and Selectivity

In order to examine the influence of the oxygen carrier content, more amounts of the CoS were added into the membranes. Thus, 90/10 and 85/15 composite membranes were prepared and measured. Figure 5 presents P_{O_2} versus Δ_p curves for the 85/15 membrane. P_{O_2} increases still and more obviously with decreasing Δ_p . Figure 6 gives further effect of the CoS content on P_{O_2} and $\alpha_{\text{O}_2/\text{N}_2}$ under lower Δ_p of 0.05 mPa. The P_{O_2} of the composite membrane basely increase linearly with increasing the CoS content at 25 and 60°C . The $\alpha_{\text{O}_2/\text{N}_2}$ are also increase but P_{O_2} and $\alpha_{\text{O}_2/\text{N}_2}$ increase trends are different and have the reverse behavior for 25 and 60°C . It is also found from Figures 5 and 6 that some good oxygen-enriching results

for the 85/15 membrane can be obtained. For instance, P_{O_2} and $\alpha_{\text{O}_2/\text{N}_2}$ are about 37 Barrer and 9.6 at 25°C and 100 Barer and 5.0 at 60°C , respectively. By comparing with data of the EPDM, $\text{Co}^{\text{II}}\text{-S-EPDM}$ membranes listed in Table I, the modification effect for oxygen-enriching ability is obvious. The reason probably is due to the formation of the CoS dimer and the microvoids on interfaces between the ionomer matrix and the CoS crystal with blending more CoS crystal in the composite membranes. From this, dual actions of the cobaltous ion crosslinking and addition of abundant cobalt complex may be an effective way to improve the oxygen-enriching abilities for a rubbery polymer membrane. The CoS content as high as 15 wt % in the composite membranes is higher than the polymer membranes containing

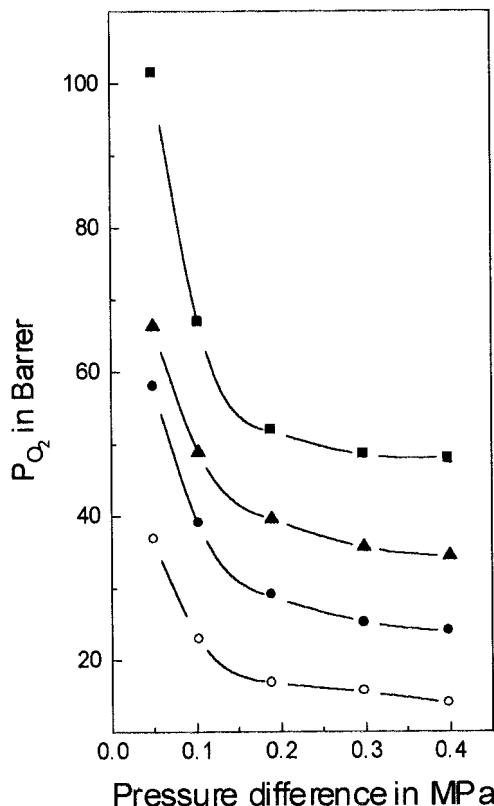


Figure 5 Effect of the gas pressure difference on the $\text{Co}^{\text{III}}\text{-S-EPDM-CoS}$ (85/15) composite membrane at (○) 25, (●) 40, (▲) 50, and (■) 60°C.

cobalt complexes reported by the literature⁵⁻¹² are. Nevertheless, the CoS above 15 wt % could not be blended into the ionomer membrane due to limits of compatibility and solubility of the CoS for the ionomer and the mixed solvent.

Effects of Testing Temperature on the Permeability and Selectivity

The above-mentioned discussion, in fact, has been partly dealt with testing temperature. P_{O_2} versus Δ_p curves at a higher temperature, either the 95/5 or the 85/15 composite membrane, always perch on or above in the figures but the $\alpha_{\text{O}_2/\text{N}_2}$ versus Δ_p curve shows just the reverse. It indicates that P values increase and that $\alpha_{\text{O}_2/\text{N}_2}$ values decrease with increasing temperature. This is in accordance with a general law of the effects of temperature on the permeability and selectivity.

The activation energies of oxygen and nitrogen permeation through the membrane can be obtained according to the Arrhenius equation. The Arrhenius diagrams of the 95/5 composite are

shown in Figure 7. Under two Δ_p of 0.05 and 0.40 mPa, the P_{N_2} curves merge into one straight line, and the P_{O_2} exhibit two lines, above which the one under low Δ_p lies above. The slopes measured by the lines and the activation energies calculated from these slopes are collected in Table II. The activation energy of P_{N_2} is 37.7 kJ/mol and those of P_{O_2} are 26.1 and 28.0 kJ/mol under Δ_p of 0.40 and 0.05 mPa, respectively. This evidences that not only the potential energy barriers for oxygen and nitrogen permeation through the composite membrane are different, but also that of oxygen under a lower $\Delta_p(\text{O}_2)$ is lower than under a higher $\Delta_p(\text{O}_2)$. Figure 7 shows also that decreasing trends of $\alpha_{\text{O}_2/\text{N}_2}$ with temperature are different for different $\Delta_p(\text{O}_2)$.

CONCLUSIONS

The $\text{Co}^{\text{III}}\text{-S-EPDM-CoS}$ composite membranes were prepared by blending the CoS into the iono-

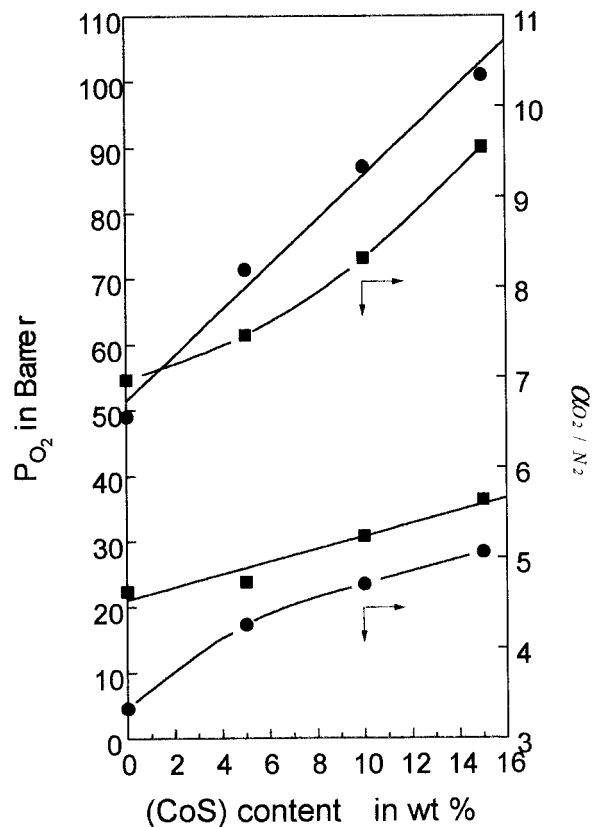


Figure 6 Effect of the CoS content in the composite membranes on P_{O_2} and $\alpha_{\text{O}_2/\text{N}_2}$ under a pressure difference of 0.05 mPa at (■) 25 and (●) 60°C.

mer containing cobaltous ions. Their P_{O_2} and α_{O_2/N_2} increase simultaneously with decreasing the gas pressure difference or increasing the CoS content. As high as 15 wt % of the CoS could be blended into the membranes, and this content is higher than that of the membranes containing cobalt complex reported by previous literature. The potential energy barriers of oxygen permeation through the 95/5 composite membrane are about lower 10 kJ/mol than that of nitrogen through the same membrane but have small differences in their values for different $\Delta_p(O_2)$. By comparison with the ionomer matrix, the oxygen-enriching abilities of the composite membranes were enhanced distinctly by crosslinking of cobaltous ions and blending abundant cobalt complex. These dual actions may be an effective way to improve oxygen/nitrogen separation properties for a rubbery polymer membrane, especially with high permeability.

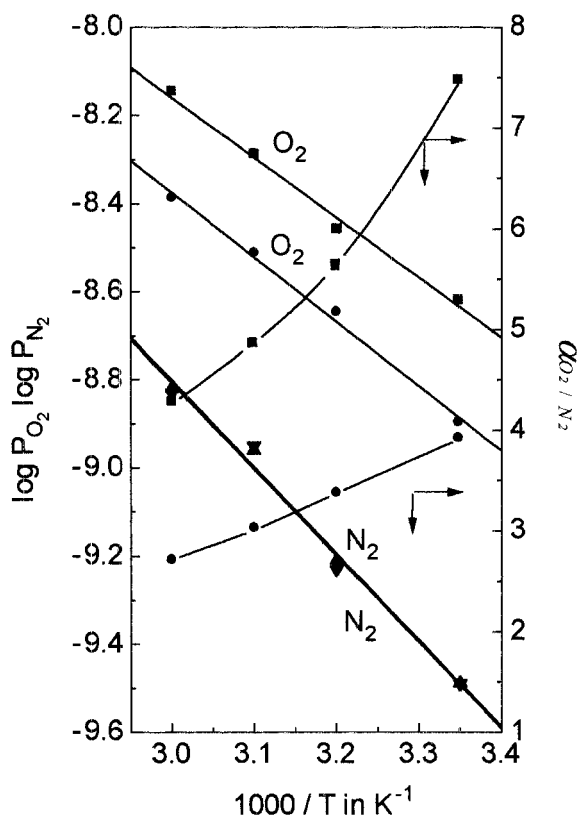


Figure 7 The Arrhenius plots of P_{O_2} and P_{N_2} and the relationship between α_{O_2/N_2} and $1/T$ for the Co^(III)-S-EPDM-CoS (95/5) composite membrane under a pressure difference (■, ▲) 0.05 and (●, ▼) 0.40 mPa.

Table II Slopes of Arrhenius Plots and Activation Energies for Oxygen and Nitrogen Permeation Through the Co^(III)-S-EPDM-CoS (95/5) Composite Membrane

Permeation Gas	Pressure Difference (MPa)	Activation Energy (kJ/mol)	
		Slope $\times 10^3$	Activation Energy (kJ/mol)
O ₂	0.05	-1.3608	26.1
O ₂	0.40	-1.4636	28.0
N ₂	0.05	-1.9664	37.7
N ₂	0.40	-1.9664	37.7

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REFERENCES

1. Stern, S. A. *J Membr Sci* 1994, 94, 1.
2. Kajiyama, T.; Ohmori, Y. *Chem Soc Jpn* 1985, 10, 1897.
3. Kajiyama, T.; Takahara, A.; Kikuchi, H. *Polym J* 1991, 23, 347.
4. Zhang, Z. Y.; Lin, S. A. *Polym Bull (Chinese)* 1994, 4, 200.
5. Nishide, H.; Ohyanagi, M.; Okado, O.; Tshchida, E. *Macromolecules* 1987, 20, 417.
6. Tsuchida, E.; Nishide, H.; Ohyanagi, M.; Kawakami, H. *Macromolecules* 1987, 20, 1907.
7. Nishide, H.; Kawakami, H.; Suzuki, T.; Azechi, Y.; Tsuchida, H. *Macromolecules* 1990, 23, 3714.
8. Yang, J. M.; Hsiue, G. H. *J Membr Sci* 1994, 87, 233.
9. Hsiue, G. H.; Hsu, W. L. *Angew Macromol Chem* 1993, 211, 21.
10. Delaney, M.; Reddy, D.; Wessling, R. *J Membr Sci* 1990, 49, 5.
11. Chen, S. H.; Lai, J. T.; Ruaan, R. C.; Wang, A. A. *J Membr Sci* 1997, 123, 197.
12. Nishide, H.; Kawakami, H.; Sasame, T.; Ishiwata, K.; Tsuchida, E. *J Polym Sci, Part A: Polym Chem* 1992, 30, 77.
13. Zhang, Z. Y.; Lin, S. A. *Macromol Rapid Commun* 1995, 16, 927.
14. Bailes, R. H.; Calvin, M. *J Am Chem Soc* 1947, 69, 1886.
15. Stern, S. A.; Sinclair, T. F.; Gareis, P. J. *Mod Plast* 1964, 42, 154.
16. Jones, T. D.; Summerville, D. A.; Basolo, F. *Chem Rev* 1979, 79, 139.