

Development of Thin-Film Composite Membranes for Carbon Dioxide and Methane Separation Using Sulfonated Poly(phenylene oxide)

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ABSTRACT: Novel membranes based on sulfonated poly(phenylene oxide) (SPPO) was developed. SPPO membranes in the hydrogen form were converted to metal ion forms. The effect of exchange with metal ions including monovalent (Li^+ , Na^+ , K^+), divalent (Mg^{2+} , Ba^{2+} , Ca^{2+}) and trivalent (Al^{3+}) ions was investigated in terms of permeation rate and permeation rate ratios for CO_2 and CH_4 gases. Both dense homogeneous membranes and thin-film composite (TFC) membranes were studied for their gas separation characteristics. The effect of membrane preparation conditions and operating parameters on the membrane performance were also investigated. The selectivity of the TFC membrane increased as the cationic charge density increased as a result of electrostatic cross-linking. TFC membrane of very high selectivity was achieved by coating a thin layer of SPPO-Mg on a PES substrate. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 735-742, 2000

Key words: sulfonated poly(phenylene oxide); gas separation membranes; thin film composite membranes; CO_2/CH_4 separation; high selectivity

INTRODUCTION

The membrane-based gas separation processes have been investigated during the past decades, and numerous advancements have been made, leading to industrial applications. Membrane-based gas separations seem to have a tremendous potential as energy-efficient alternatives for cryogenic separations.¹ At present, more than 100

installations, which include various types of applications, are being operated in the world. One such application is separation of CO_2 from various gas mixtures. The removal of carbon dioxide from natural gas is of particular commercial importance in natural gas industries. Recently, studies have been made on the removal of carbon dioxide from flue gas to reduce the amount of greenhouse gas emission to the atmosphere.

There are a number of polymeric materials tested for the purpose of CO_2/CH_4 separation. Among others, Chen and Martin² investigated the separation of CO_2 from CH_4 , in which sulfonated polystyrene (PSS) was used after exchanging the proton of $-\text{SO}_3\text{H}$ with a metal cation. The CO_2/CH_4 permeability ratios were 64.7 and 49.2, respectively, for PSS-Mg and PSS-Na, while that of PSS was 18.1. From these results, they con-

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cluded that exchange by metal cations increases the selectivity of the membrane remarkably due to electrostatic crosslinking. Chen and Martin also measured the permeability data for O₂, N₂, and H₂. Liu and Martin³ prepared defect-free composite membranes using highly ionic polymers involving SO₃⁻Na⁺. The selectivity of 8.0–8.2 for O₂/N₂ was obtained. Chiou and Paul⁴ studied the gas transport properties of Nafion™, a perfluorosulfonic acid polymer. Although their results showed improvement of selectivity by incorporating metal counterions, separation factor of CO₂/CH₄ was 23.8, which was no better than any other polymeric materials. Bikson et al.⁵ coated a lithium form of sulfonated poly(phenylene oxide) (SPPO-Li) onto polysulfone hollow-fiber substrate membranes. They obtained the separation factor of 5.7 for oxygen and nitrogen, with a permeation rate of 22 GPU for oxygen. Moreover, lithiated sulfonated hexafluoro Bis A polysulfone (F6 SPS-Li) membrane showed O₂/N₂ separation factor of 7.1.

Poly(phenylene oxide) is known to be a polymeric material of high permeability with rather low selectivity. Therefore, attempts have been made by several groups to increase the selectivity by polymer modification. Story and Koros⁶ attempted to enhance the permselectivity of poly(phenylene oxide) for CO₂/CH₄ through chemical modifications including carboxylation, esterification, and bromination. Carboxylated PPO (CPPO) membranes showed selectivities from 19.5 to 23.2, depending on the degree of carboxylation, while the selectivity of the base PPO was 15.1. The esterified CPPO and brominated PPO (BPPO) did not increase the selectivity, and their permeability ratios were 17.0 and 15.0, respectively. It is worthy, however, to note that BPPO membrane showed a remarkable increase in permeation rate, from 42 Barrer for PPO to 104 Barrer for BPPO. It is well known that the solubility selectivity for the system CO₂/CH₄ largely depends on the degree of carboxylation and sulfonation. This could be interpreted by chemical interactions between gas and polymer. For example, CO₂, a quadrupolar gas, typically shows a solubility higher than nonpolar gases, including CH₄, in polymers containing polar moieties such as carbonyl, sulfone or hydroxyl substituent groups.⁶ Because the change in the free volume of polymer due to the introduction of substituent has a significant effect on diffusivities of gases, it may lead to reduction in diffusivities, depending

on the property of substituent. Fu et al.⁷ investigated the physical properties of both SPPO and the sodium form of SPPO (SPPO-Na). Glass transition temperatures of SPPO increased remarkably with increasing the sulfonation degree, while the density was only slightly higher than that of PPO in the entire sulfonation range. This may explain the decrease in gas diffusivity with an increase in the degree of sulfonation.

Sakai et al.⁸ examined transport properties of O₂ and N₂ gases for Nafion 117 and 225 membranes in free acid and K⁺ forms. They observed that diffusivities are smaller and solubilities are greater in K⁺ than in acid form for both gases. As for the selectivity, the permeability ratio increased from 2.2 to 7.4 as the acid form was changed to the K⁺ form. For the case of H₂ and O₂, it was suggested that the K⁺ ion in Nafion 117-K⁺ hindered the gas diffusion. Anderson et al.¹ reported permeabilities for a series of gases including CO₂ and CH₄ through conjugated polyaniline by doping and undoping the polymeric membrane with counterions. Polyaniline doped with 4.0 M HBr showed a CO₂/CH₄ selectivity of 640. The morphology of the conjugated polymer film was controlled by changing the size of various dopants, leading to a decrease in permeability in the following order, F⁻ > Cl⁻ > Br⁻ > I⁻. Raymond et al.⁹ investigated sorption and transport of pure CO₂ and CH₄ for membranes in which bisphenol chloral polycarbonate (BCPC) and poly(methyl methacrylate) (PMMA) are blended. As the volume fraction of PMMA increased in the BCPC/PMMA blend, the permeability ratio increased from about 30 (pure BCPC) to 110 (pure PMMA). Sada et al.^{10,11} employed cellulose acetate (cellulose triacetate and cellulose 2,4-acetate) membranes in their studies on the permeation of pure CO₂ and CH₄ gases. Recently, Stern et al.¹² patented the results of the separation of CO₂ and CH₄ gas pair using a family of polyimide homogeneous membranes. Some of polyimides showed very high separation factors varying from about 80 to 100.

The current research efforts are focused on development of novel membranes based on sulfonated poly(phenylene oxide) (SPPO) and improvement of its separation efficiency for commercial use. Since, according to the literature survey, the introduction of counterions into ionic polymers enhances the permselectivity, it was attempted to convert SPPO membranes from hydrogen form to metal ion form. The effect of exchange with metal

ions including monovalent (Li^+ , Na^+ , K^+), divalent (Mg^{++} , Ba^{++} , Ca^{++}), and trivalent (Al^{+++}) ions, was investigated in terms of permeation rate and permeation rate ratios for CO_2 and CH_4 gases. Both dense homogeneous membranes and thin-film composite (TFC) membranes were prepared and tested for their gas-separation performance. The effect of the membrane preparation conditions and the operating conditions on the membrane performance were also studied.

EXPERIMENTAL

Material

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was sulfonated to various sulfonation degrees using chlorosulfonic acid as the reaction agent. PPO was supplied by General Electric Co. and used without any further treatment. A 10 wt % PPO solution was prepared by dissolving PPO in chloroform. Then, a stoichiometric quantity of chlorosulfonic acid was added dropwise to the PPO solution with vigorous stirring. As sulfonation progressed sulfonated PPO in hydrogen form (SPPO-H) precipitated from the solution, because SPPO-H is not soluble in chloroform.¹³ SPPO-H was further isolated from the solution and purified by the method described elsewhere.¹⁴ Ion Exchange Capacity (I.E.C.) values of SPPO-H so prepared were 1.73 and 1.87 mEq./g dry polymer.

Preparation of SPPO Solutions

SPPO-H polymer was mixed with appropriate solvents to make solutions of predetermined polymer concentrations (2.0 and 4.0 wt %). The mixture was left overnight with continuous stirring to complete the dissolution of polymer. The polymer solution was filtered with Fluoropore (Millipore, FSLW 04700, pore size = 3 μm), which was installed in the microsyringe type filter (Millipore, NPT Inlet 25 mm). The amount of every filtered polymer solution was between 10 to 50 mL, depending on whether the solution was used for the preparation of the TFC membrane or the dense homogeneous membrane. For the preparation of the TFC membranes, 2.0 and 4.0 wt % solutions were used, while only 4 wt % solution was used for the preparation of the dense homogeneous membrane. Methanol, ethoxyethanol (EE), butoxyethanol (BE), and dimethyl acet-

amide (DMAc) were used to make coating solutions for the preparation of TFC membranes, while only methanol was used as solvent for the casting dope of dense homogeneous membrane. All the chemicals used in this study were of analytical grade.

Preparation of SPPO Composite Membranes in Hydrogen Form

Commercial polyethersulfone (PES) and laboratory made polyetherimide (PEI) ultrafiltration (UF) membranes were used as porous substrate membranes. PES UF membranes with MWCO = 7000–10,000 were supplied by the Fluid Systems Co. Glycerol filled in the pores of commercial PES membranes was removed by soaking the membrane in deionized water for at least 24 h before being dried in the air overnight and cut into coupons for further use. PEI UF membranes were laboratory prepared from the casting solution with a composition of PEI/*N*-methylpyrrolidone/ γ -butyrolactone = 25/55/20.¹⁵ The membrane was dried overnight in the air before further use. A coating solution (about 0.3 mL) was spread over skin side of the substrate membrane before being dried in a forced convection oven at 60°C overnight. When methanol was used as a solvent for coating solution, the coated layer was dried at room temperature. The TFC membranes so prepared were stored in a vacuum oven before use.

Preparation of SPPO Composite Membranes in Metal Cation Form

The SPPO membrane in hydrogen form was immersed in a solution of alkali metal hydroxide or alkaline earth metal hydroxide of 0.1 to 1 *N*, depending on the solubility of hydroxide in water. When the solubility was low, the solution saturated with hydroxide was used. The membrane was kept immersed for 48 h at room temperature to complete the exchange of the proton to metal cation. Exceptions were Mg^{++} and Al^{+++} , for which magnesium nitrate and aluminum chloride were used, respectively. The membranes after ion exchange were dried in air and then stored in a vacuum oven for at least 5 days before use.

Experimental Apparatus

The gas permeation system used in this work was a constant pressure system (CPS), the detail of

Table I Effect of the Number of Coating Layers on the Permeance and Permeance Ratio of SPPO-H TFC Membrane^a

| Number of Coating Layers | Permeance (GPU ^b) | | Permeance Ratio CO ₂ /CH ₄ |
|--------------------------|-------------------------------|-----------------|--|
| | CO ₂ | CH ₄ | |
| 2 | 11.46 | 0.44 | 26 |
| 3 | 5.34 | 0.21 | 25 |
| 4 | 3.75 | 0.15 | 25 |

^a Ion exchange capacity of SPPO = 1.81 mEq/g polymer; solvent in coating solution, methanol; polymer concentration in coating solution, 4 wt %; substrate membrane, PEI UF; operating pressure, 100 pig.

^b 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg.

which was given elsewhere.¹⁶ Six gas separation cells were connected in series. The effective membrane area varied from cell to cell, and ranged from 12.6 to 13.5 cm².

Gas Permeability Measurement

The permeability measurement for TFC membranes was conducted first for CO₂ after 5 days membrane exposure to CO₂ gas. This was followed by the permeability measurement of CH₄ after the exposure of the membrane to CH₄ gas for 4 days. The order in the gas permeability measurement for dense homogeneous membranes was the same as that for the TFC membranes. The membrane exposure periods for CO₂ and CH₄ gases were 8 and 6 days, respectively. The measurement of the permeation rate was repeated 5 to 10 times by bubble flow meters, and the average value was calculated. The error in the permeation rate measurement was less than 3%. Gas permeation rate was converted to permeability (Barrer = 10⁻¹⁰ cm³ (STP) cm/cm² s cmHg) for the dense homogeneous membrane and to permeance (GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg) for the TFC membranes.

RESULTS AND DISCUSSION

SPPO TFC Membranes Prepared Using Methanol in Coating Solution

Table I shows the effect of the number of coating layers on the TFC membrane performance. The membrane was prepared by coating a 4 wt %

SPPO solution in methanol. Although the permeance of the TFC membrane decreases with an increase in the number of coated layers, the permeance ratio remains almost constant. The increase in the ideal separation factor (carbon dioxide/methane permeability ratio) from PPO (15.1) to SPPO has already been reported.⁷ The effect of sulfonation of PPO on its T_g , density and d-spacing was studied thoroughly by Kruczek and Matsuura.¹⁷

Table II shows the effect of operating pressure on the permeance. There was a slight increase in the permeance of both CO₂ and CH₄. As a result, the permeance ratio remained almost constant.

Although some TFC membrane performance data could be obtained by these preliminary experiments, methanol was found to be inappropriate as a solvent for the preparation of the coating solution, because the coated layer was very brittle. This was particularly so when SPPO with the metal ion was used for the coating material. Different solvents were, therefore, tested for alternatives. At the same time, the substrate membrane was changed from a laboratory made PEI membrane to a commercial PES membrane.

In Table III, some experimental results of both dense homogeneous and TFC membranes are given based on SPPO-Na material. Although permeability (Barrer) data are given for the dense homogeneous membrane, permeance (GPU) data are given for TFC membranes. Permeation rates of both CO₂ and CH₄ were determined under the operating pressure of 100 psig, except for permeation rates of CH₄ gas through the dense homogeneous membrane, which were measured at 250

Table II Effect of Operating Pressure on Permeance and Permeance Ratio of SPPO-H TFC Membranes^a

| Operating Pressure (pig) | Permeance (GPU ^b) | | Permeance Ratio CO ₂ /CH ₄ |
|--------------------------|-------------------------------|-----------------|--|
| | CO ₂ | CH ₄ | |
| 100 | 11.46 | 0.44 | 26 |
| 150 | 13.50 | 0.51 | 26 |
| 200 | 15.47 | 0.58 | 27 |

^a Ion exchange capacity of SPPO = 1.81 mEq/g polymer; solvent in coating solution, methanol; polymer concentration in coating solution, 4 wt %; number of coating layer, 1; substrate membrane, PEI UF; operating pressure, 100 pig.

^b 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg.

Table III Effect of Solvent on Permeability of SPPO-Na Dense Homogeneous Membranes and on Permeance of SPPO-Na TFC Membranes^a

| Solvent | Permeability (Barrer ^b) | | Permeability Ratio CO ₂ /CH ₄ |
|-----------------------------|--|------------------------------|---|
| | CO ₂ ^d | CH ₄ ^e | |
| Dense Homogeneous Membranes | | | |
| EE | 36.32 | 0.84 | 43 |
| BE | 11.93 | 0.42 | 28 |
| DMAc | 10.94 | 0.20 | 55 |
| TFC Membranes | | | |
| EE | 4.66 | 0.07 | 68 |
| BE | 3.20 | 0.09 | 34 |

^a Ion exchange capacity of SPPO polymer, 1.87 mEq./g polymer; polymer concentration in coating solution, 4 wt %; number of coating layer, 1; substrate membrane, PES UF.

^b 1 Barrer = 10⁻¹⁰ cm³ (STP)/cm² s cmHg.

^c 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg.

^d operating pressure, 100 psig.

^e operating pressure, 250 psig.

psig. Therefore, the permeability ratios reported for dense homogeneous membranes include permeability data at 100 psig for CO₂ and at 250 psig for CH₄ gas. Table III indicates that there is indeed an effect of the solvent. For the TFC membrane, ethoxyethanol (EE), was better than butoxyethanol (BE) in terms of both permeance and selectivity. For the homogeneous membrane, DMAc was the best solvent, showing a very high selectivity. But the permeability of the dense homogeneous membrane prepared from DMAc solvent was the lowest. Comparing TFC and dense homogeneous membranes, the selectivity of the former membrane was higher. But, because the TFC membrane data include those at 250 psig, this conclusion should be reexamined. Another interesting observation was that EE showed higher permeation rate and higher selectivity than BE for both TFC and dense homogeneous membranes. Dimethyl acetamide (DMAc) could not be tested for the TFC membrane because the PES substrate membrane was dissolved in DMAc solvent.

In Table IV, two methods of ion exchange are compared; in one method, ion exchange was done before the SPPO polymer layer was coated on top of the substrate membrane; in the other, it was done after the SPPO layer was coated on the substrate membrane. The table clearly indicates that the ion exchange after the coating resulted in

superior data both for sodium and potassium exchanged SPPO membranes. This is due to more complete ion exchange of a thin SPPO layer coated on the substrate membrane. On the other hand, the diffusion of metal hydroxide took place only slowly in the shredded polymer sheet, which was used for the ion exchange of the polymer before coating, leaving an unreacted proton in the sulfonate group.

Effect of Metal Cations

Protons of the sulfonic group of SPPO were exchanged with various metal ions after the SPPO-H layer was coated and the TFC membranes so prepared were tested for their performance. The results are summarized in Table V: The following conclusions can be drawn from Table 5 with few exceptions. (1) The (CO₂/CH₄) permeance ratio for divalent cation is higher than that for monovalent cation when ions of similar sizes are compared (Fig. 1). For example, comparing Li⁺ and Mg⁺⁺ that have ionic radii of 0.059 and 0.072 nm, respectively; the ratio for SPPO-Mg (146) is greater than the ratio for SPPO-Li (94); similarly, comparing Na⁺ and Ca⁺⁺ that have ionic radii of 0.102 and 0.100 nm, respectively, the ratio for SPPO-Ca (92) is greater than the ratio for SPPO-Na (68). K⁺ and Ba⁺⁺ have ionic radii of 0.151 and 0.142 nm. The ratio for SPPO-Ba (54) is greater than that of SPPO-K (53.9). (2) Among a series of either monovalent cations or that of divalent cations, the permeance ratio decreases as the ionic radius increases.

Table IV Comparison of Ion Exchange Before and After Coating^a

| Material | Ion Exchange | Permeance (GPU ^b) | | Permeance Ratio CO ₂ / CH ₄ |
|----------|----------------|----------------------------------|-----------------|---|
| | | CO ₂ | CH ₄ | |
| SPPO-Na | Before coating | 1.90 | 0.03 | 59 |
| | After coating | 4.66 | 0.07 | 68 |
| SPPO-K | Before coating | 6.20 | 0.11 | 54 |
| | After coating | 5.01 | 0.06 | 83 |

^a Ion exchange capacity of SPPO, 1.73 mEq./g polymer; solvent of coating solution, ethoxyethanol; polymer concentration in coating solution, 4 wt %; number of coating layer, 1; substrate membrane, PES UF; operating pressure, 100 psig.

^b 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg.

Table V Effect of Metal Cations on the Performance of Cation-Exchanged SPPO Membranes^a

| Ion Exchanged SPPO | Ionic Size (nm) | Permeance (GPU ^b) | | Permeance Ratio CO ₂ /CH ₄ |
|--------------------|-----------------|-------------------------------|-----------------|--|
| | | CO ₂ | CH ₄ | |
| SPPO-Li | 0.06 | 3.37 | 0.04 | 94 |
| SPPO-Na | 0.10 | 4.66 | 0.07 | 68 |
| SPPO-K | 0.15 | 6.20 | 0.11 | 54 |
| SPPO-Mg | 0.07 | 4.98 | 0.03 | 146 |
| SPPO-Ca | 0.10 | 5.73 | 0.06 | 92 |
| SPPO-Ba | 0.14 | 5.06 | 0.09 | 54 |
| SPPO-Al | — | 5.51 | 0.06 | 94 |

^a Ion exchange capacity of SPPO = 1.73 mEq./g polymer; solvent of coating solution, ethoxyethanol; polymer concentration in coating solution, 4 wt %; number of coating layer, 1; operating pressure, 100 psig.

^b 1 GPU = cm³ (STP)/cm² s cmHg.

The conclusions stated above infer that there is a general correlation between the ionic charge density of cation and the pure gas permeance ratio; i.e., the permeance ratio increases with an increase in the charge density of cations. This is probably due to the enhancement of the electro-

Table VI Effect of Operating Pressures on the Permeance of SPPO-Metal Membranes^a

| Membrane | Permeance (GPU ^b) | | Permeance Ratio CO ₂ /CH ₄ ^c |
|----------|-------------------------------|-----------------|---|
| | CO ₂ | CH ₄ | |
| 100 psig | | | |
| SPPO-K | 6.20 | 0.11 | 54 |
| SPPO-Mg | 4.98 | 0.03 | 146 |
| SPPO-Ca | 5.73 | 0.06 | 92 |
| 200 psig | | | |
| SPPO-K | | 0.15 | 42 |
| SPPO-Mg | | 0.04 | 116 |
| SPPO-Ca | | 0.07 | 82 |
| 237 psig | | | |
| SPPO-K | | 0.15 | 42 |
| SPPO-Mg | | 0.04 | 116 |
| SPPO-Ca | | 0.06 | 89 |

^a Ion exchange capacity of SPPO = 1.73 mEq./g polymer; solvent in coating solution, ethoxyethanol; polymer concentration in coating solution, 4 wt %; number of coating layer, 1; substrate membrane, PES UF, operating pressure, 100 psig.

^b 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg.

^c Based on CO₂ permeance at 100 psig.

Table VII Effect of Polymer Concentration in Coating Solution on Permeance of SPPO-Mg TFC Membrane^a

| Polymer Concentration (wt %) | Permeance (GPU ^b) | | Permeance Ratio CO ₂ /CH ₄ |
|------------------------------|-------------------------------|-----------------|--|
| | CO ₂ | CH ₄ | |
| 4 | 4.98 | 0.03 | 146 |
| 2 | 6.75 | 0.05 | 127 |

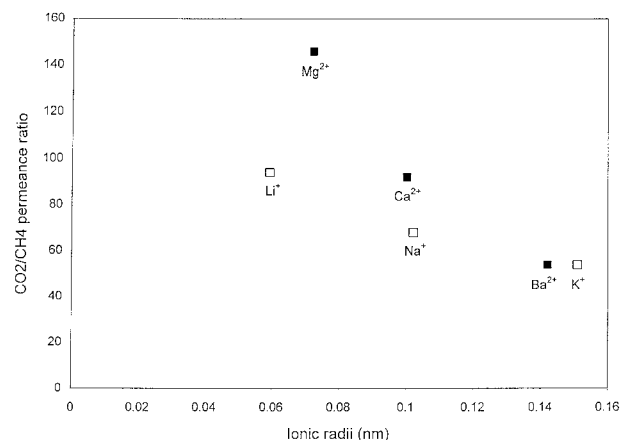
^a Ion exchange capacity of SPPO = 1.73 mEq./g polymer; solvent in coating solution, ethoxyethanol; number of coating layer, 1; substrate membrane, PES UF; operating pressure, 100 psig.

^b 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg.

static crosslinking between charged polymers and metal cations with an increase in the cationic charge density.

It is then expected that the trivalent cation AL⁺⁺⁺ will show an even higher selectivity than the divalent cations. However, as the data in Table V shows, the selectivity data of SPPO-Al is not necessarily higher than those of the divalent cations.

It is interesting to compare the selectivity of SPPO-metal-coated TFC membranes for gas separation and the selectivity of those membranes in sodium chloride separation from water. It was found in our earlier work¹⁸ that sodium chloride separation decreased, while water flux increased as the cationic charge density increased. For example, comparing SPPO-Li, SPPO-Na, and SPPO-K TFC membranes, the pure water permeation rate was in

**Figure 1** Ionic radii vs. CO₂/CH₄ permeance ratio.

the order of SPPO-Li > SPPO-Na > SPPO-K, while the sodium chloride separation was in the order of SPPO-Li < SPPO-Na < SPPO-K. The performance of both reverse osmosis and gas separation membranes, therefore, seem to be affected by the charge density of cations, but the effect on the selectivity is opposite.

Effect of Operating Pressure

At the operating pressure of 100 psig, the permeation rate of carbon dioxide was high enough to be measured accurately by the bubble flow meter. However, the flow rate of methane was very low, rendering the experimental data less reliable. Therefore, attempts were made to measure methane flow rate at higher pressures. The results of such experiments are summarized in Table VI. The table shows CO₂ permeance data measured at 100 psig. The permeance data of CH₄ are given, on the other hand, for the operating pressures of 100, 200, and 237 psig. The latter data show that there were some changes in CH₄ permeance from 100 to 200 psig; however, the data for 200 and 237 psig were almost the same. The data at 200 and 237 psig seem to be more reliable. The pure gas permeance ratios are also given based on the CO₂ permeance data obtained at 100 psig.

Effect of Skin Layer Thickness

The selectivity of TFC membrane based on SPPO-Mg material was extremely high, encouraging an attempt to increase the flux by decreasing the thickness of the SPPO-Mg layer. For this purpose, the polymer concentration in the coating solution was decreased from 4 to 2 wt %. It was expected that the coated layer thickness would become one-half, resulting in twice as large a permeance. The data shown in Table VII indicates that there was only a 36% increase in CO₂ permeance. Regarding the selectivity of the membrane, it decreased slightly, but no definite conclusion could be made because the comparison was made on the basis of the data obtained at 100 psig, where the methane permeation rate was extremely low. The lower than expected increase of permeance at 2% polymer concentration is either due to the penetration of the coating solution in the pore of the substrate membrane or due to a higher degree of crosslinking in the thinner coating layer

because more Mg(NO₃)₂ solution could have chance to reach the bottom of the coating layer when the coating layer was thinner.

CONCLUSIONS

1. TFC membranes of high selectivities for CO₂/CH₄ gas pair can be prepared by using SPPO polymer with I.E.C. values of 1.7–1.9 mEq./g polymer. Ethoxyethanol is the most appropriate for a solvent in the coating solution. A commercial PES membrane can be used as a substrate membrane.
2. The selectivity can be further increased by exchanging the sulfonate proton with metal cations.
3. Ion exchange after thin film coating is more effective to prepare membranes of high selectivity than before coating.
4. The selectivity of the TFC membrane increases as the cationic charge density increases, probably due to electrostatic crosslinking between cations and SPPO molecules. As a result, a TFC membrane of very high selectivity can be prepared by coating a thin layer of SPPO-Mg material.

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