

Comparative studies on the effects of casting solvent on physico-chemical and gas transport properties of dense polysulfone membrane used for CO₂/CH₄ separation

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ABSTRACT: The effects of casting solvents on the physico-chemical and transport properties of polysulfone membranes were investigated. Comparative analysis of the properties of membranes prepared from a new solvent (diethylene glycol dimethylether, DEG) and other commonly used solvents (1-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, dimethyl sulfoxide and *N,N*-dimethylformamide) were performed using gas permeation, X-ray diffraction, scanning electron microscopy, thermogravimetric, and Fourier transform infrared spectroscopy analyses. The degree of polymer-solvent interaction was evaluated using the solvent molar volume, and Hansen and Flory-Huggins parameters. Membrane prepared from DEG displayed a relatively higher permeability of 29.08 barrer and CO₂/CH₄ selectivity of 23.12 compared to membranes prepared from other solvents. This improved performance was attributed to the better interaction between the DEG solvent and polysulfone than other solvents that were considered. DEG has the highest molar volume of 142.280 cm³/mol and the lowest Flory-Huggins parameter of 0.129. Thus a thorough evaluation of polymer-solvent interaction is very crucial in preparing membranes with optimum performance. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42205.

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INTRODUCTION

Membrane gas separation technology is now of great practical and fundamental interests due to the increasing role of natural gas (NG) in the generation of clean energy.^{1,2} This technology is now commercially employed in NG processing industry for CO₂ removal from NG. However, the market share of membrane gas separation technology in NG processing is still very low compare to other processing methods such as absorption, cryogenic distillation and others.³⁻⁵ This is due to the low flux at which some of the membranes are operated.⁶ One of the proposed solutions to this problem is the operation of the CO₂ membrane separation system at high feed pressure.⁷ Increasing the pressure will increase the flux and reduce the membrane area requirement that is needed to achieve certain product purity.^{4,8} Many polymeric materials and membrane preparation methods have been investigated for this purpose.^{5,9-17} While many of the polymers that have been developed are still in the laboratory stage, some of the methods are too complicated to be commercially implemented. One of the commercially feasible

options is the modification of the method of membrane preparation using commercially available polymers. Polysulfone (PSF) is one of the most widely investigated commercially available glassy polymers for CO₂ removal from NG. This is due mainly to its commercial availability, low market price, high chemical and heat resistance, good mechanical properties, good stability, biocompatibility, and ease of processing.^{5,18,19}

The properties of polymeric membranes have been reported to be dependent on the preparation protocol as well as the casting solvents that are employed for the preparation.²⁰⁻²⁸ Moreover, in addition to other costs, the economy of membrane preparation using solution casting also depends on the costs of the polymer as well as the casting solvent used. To minimize the cost of preparation, solvent with high polymer solubility, high molar volume and low cost forms a good candidate. There are two classes of membrane structure, namely: the physical structure and the chemical structure. The type of casting solvent plays a major role in the nature of the physical structure.²⁶ The effect of casting solvent on the membrane properties such as

Table I. Physical Properties and the Costs of Various Solvents^{25,33}

Solvent name	Molecular formula	Mole weight (g/mol)	Molar volume (cm ³ /mol)	BP (°C)	Price (\$/L)
Chloroform	CHCl ₃	119.38	80.013	60.5–61.5	115.60
Dichloromethane	CH ₂ Cl ₂	84.93	64.098	39.8–40.0	141.87
Tetrahydrofuran	C ₄ H ₈ O	72.11	81.114	65–67	187.85
Dimethyl sulfoxide	(CH ₃) ₂ SO	78.13	71.027	189	150.14
N-Methyl-2-pyrrolidone	C ₅ H ₉ NO	99.13	96.430	202–204	207.34
N,N-Dimethylacetamide	CH ₃ CON(CH ₃) ₂	87.12	92.978	164.5–166	142.81
N,N-Dimethylformamide	HCON(CH ₃) ₂	73.09	77.426	152–154	139.18
Diethylene glycol dimethyl ether	C ₆ H ₁₄ O ₃	134.17	142.280	155–165	120.34

Solvent prices were obtained from <http://www.thomassci.com>, Honeywell Burdick & Jackson, and Sigma-Aldrich.

permeability has been documented by Kesting *et al.*^{29,30} According to the authors, there appeared to be some trend for gas permeability to increase with increase in molar volume of solvents. This is due to the fact that the intra- and the internodular chain segment displacements are strongly related to the size of the transient molecular spacers or templates that sheath the macromolecules in solution.³⁰ The intranodular chain displacement represents the Henry's site while the internodular represents the Langmuir site.









Varieties of other research works have been published on the effect of casting solvents on membrane performance. The effect of casting solvents (cyclohexane, toluene, and tetrahydrofuran (THF)) on the free volume size distribution of PTMSP membranes was investigated by Bi *et al.*²⁶ Results obtained by the authors revealed that permeability of oxygen through the membranes cast from cyclohexane solution was about five times larger than those from THF solutions. Results of PALS analysis on the membranes showed that the increase in permeability was due increase in pore size and number density of the free volume. It has been reported that solvents have various chemical and physical properties that induce different interactions with polymer chains which then result in different membrane performance responses. Consequently, it is possible for membranes to have solvent-dependent morphologies and separation performances.²³ Study on the effect of the type of casting solvent on the gas permeation properties of ethylene vinyl acetate (EVA) copolymer was performed by Mousavi *et al.*³¹ for variety of pure gases. The authors found that the casting solvent acts as a transient template which controls the packing density of the final membrane product by covering the polymer molecules with a layer of solvent in the nascent membranes. Investigation on the effect of type of solvent on the morphology and gas separation performance of 6FDA/PMDA-TMMDA copolyimide membranes showed that membranes cast using CH₂Cl₂ or N-methyl pyrrolidone (NMP) have an amorphous structure, while film samples cast from N,N-dimethyl formamide (DMF) have a crystalline structure. In addition, the gas transport properties of membranes cast from DMF showed the lowest permeabilities for the gases CO₂, N₂, and CH₄.³² This is despite the fact that DMF has a solubility parameter that is closer to that of the copolyimide used than to those of CH₂Cl₂ and NMP.

The main objective of this work is to perform a comparative study on the physico-chemical properties of dense PSF membranes prepared from various solvents and those of DEG. Variety of solvents with a range of solubility parameters was chosen. Three of these solvents NMP, DMAc, and DMF had previously been used by many authors in membrane preparation. The remaining two, DMSO and DEG, have not been previously used.

EXPERIMENTAL

The right selection of suitable solvent for membrane preparation has been reported to play a very crucial role in the optimization of the developed membrane performance.^{20,22} Thus, there are many factors that have prompted a study on the use of DEG for membrane casting. At first, attempts were made to prepare a thin dense top layer using the casting method. Varieties of solvent were listed for this task. Solvent screening was done based on the molecular weights, molar volume, boiling points, and the market prices of the solvents. Table I contains the selected properties and market prices of some commonly used solvents for membrane preparation. From this table, it was observed that these solvents can be put into two classes based on their boiling points. Solvents such as NMP, DMF, DMSO, and DMAc can be put into one class because of their boiling points being all greater than 150°C. In addition, they also have very close range of molecular weights values of less than 100 g/mol. On the other hand, low boiling point solvents such as chloroform, DCM, and THF can form another group of class with boiling point less 100°C. Their molecular weight values are also less than 100 g/mol except for Chloroform. Interesting information from this table is that DEG seems to possess unique physical properties among the solvents. The molecular weight of DEG is the highest on the table and its boiling point falls between those of the two classes of solvents on Table I. Above all, it was found to be among the cheapest of all the solvents. Moreover, DEG also has the largest molar volume among all the solvents. On a practical sense, it was the only solvent that has the smallest thickness of 3.5 μm among of the membranes prepared using various solvents. Thus, a further research into the use of such solvent in membrane preparation is worthwhile. To our knowledge, no previous research works

Table II. Molar Attraction Constants and the Overall Solubility Parameters for Polymer and the Solvent

Material	Functional group	Components			Frequency of occurrence	Total solubility (MPa) ^{1/2}
		F_{di} (MJ ^{1/2} m ^{3/2} mol ⁻¹)	F_{pi} (MJ ^{1/2} m ^{3/2} mol ⁻¹)	E_{hi} (Jmol ⁻¹)		
DEG		420	0	0	2	19.447
		100	401	3000	3	
		270	0	0	4	
PSF		420	0	0	2	20.324
		100	401	3000	2	
		-70	0	0	1	
		1270	110	0	4	
		591	0	13,490	1	

have been reported on the use of this solvent for preparation of membrane as thin as 3.5 μm using solvent knife casting method. DMSO did not dissolve PSF after stirring for more than 48 h at room temperature (25°C).

MATERIAL AND METHODS

PSF (Udel-P1700) by Amoco Chemicals was used for this study. The solution casting membrane fabrication technique was used to prepare dense flat sheet membranes using diethylene glycol dimethylether (DEG), 1-methyl-2-pyrrolidone (NMP), (*N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF) as solvents. CH₄ and CO₂ gases were also used. Detailed description of the membrane preparation is presented elsewhere.³⁴ Figures 1 and 2 show the chemical structure of the new solvent and PSF that were used in this work, respectively.

Scanning Electron Microscopy

The surface and cross sectional morphologies of the membrane were observed using scanning electron microscopy (SEM, JEOL JSM-6610L). The dried dense membrane was fractured under cryogenic condition using liquid nitrogen and then sputtered with a thin layer of gold.

Estimation of Solubility Parameters

In order to get some insight into the level of interaction between DEG and the polymer, its solubility parameters were calculated and compared with other solvents. The dispersive, polar, and hydrogen bonding solubility parameters were deter-

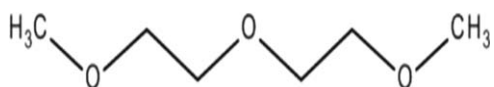


Figure 1. Chemical structure of diethylene glycol dimethyl ether.

mined using the group contribution approach as documented in Ref. 35. Solubility parameters were calculated using the following equations:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (1)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (2)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad (3)$$

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (4)$$

where F , E , V , δ_d^2 , δ_p^2 , δ_h^2 and δ_t are the molar attractive constant, cohesive energy, molar volume, dispersive, polar, and hydrogen bonding solubility parameters, and total solubility parameter, respectively.

Table II contains the overall solubility parameters and the molar attraction constants that were used as input into the group contribution model. The numerical values of the total solubility parameters for other solvents were readily available from literature. Also, the Flory–Huggins Interaction parameters (χ_{s-p}) were calculated for all the solvents. The parameter was calculated using the numerical values of the Hansen solubility parameters and the following relation.³⁶

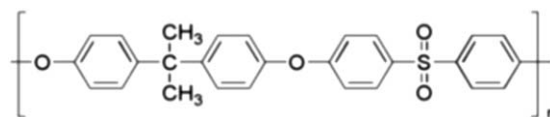


Figure 2. Chemical structure of polymer.

Table III. Solubility and Flory–Huggins Parameters of Various Solvents

Name	δ_d (MPa) ^{1/2}	δ_p (MPa) ^{1/2}	δ_h (MPa) ^{1/2}	δ_t (MPa) ^{1/2}	χ_{s-p}
Dimethyl sulfoxide	18.400	16.400	10.200	26.700	1.105
N-Methyl-2-pyrrolidone	15.970	16.281	8.520	24.346	0.995
N,N-Dimethylacetamide	12.369	16.886	8.677	22.658	0.707
N,N-Dimethylformamide	14.853	20.277	9.508	26.874	1.197
Diethylene glycol dimethyl ether	15.603	8.455	7.953	19.447	0.129
Polysulfone	18.610	3.480	7.390	20.324	-

$$\chi_{s-p} = 0.34 + \frac{V_s}{RT} (\delta_s - \delta_p) \quad (5)$$

where δ_s , δ_p , V_s , R , and T are solubility parameter of the solvent, solubility parameter of the polymer, specific volume of solvent, gas constant, and absolute temperature.

Gas Permeation Measurement

Gas permeability was measured by a constant pressure/variable volume apparatus. Permeate flow rate was measured using a bubble flowmeter. At steady-state condition, gas permeability was calculated using the following equation:

$$P = \frac{22,414}{A} \frac{l}{(p_2 - p_1)} \frac{p_1}{RT} \frac{dV}{dt} \quad (6)$$

where A is the membrane area (cm²), p_2 and p_1 are feed or upstream and permeate or downstream pressures, respectively, R is the universal gas constant (6236.56 cm³cmHg/molK), T is the absolute temperature (K), $\frac{dV}{dt}$ is the volumetric displacement rate of the soap-film in the bubble flowmeter (cm³/s) and 22,414 is the number of cm³ (STP) of penetrant per mole.^{37,38}

Thermo Gravimetric Analysis

Thermogravimetric analysis (TGA) was used to check the residual solvent remaining after drying the membranes. It was also used to examine the effect of the new solvent on the thermal properties of the membranes. TGA was done from room temperature to 800°C using NETZSCH STA 449F3 analyzer at heating rate of 10°C/min under nitrogen atmosphere with flow rate of 20 mL/min using ~10 mg membranes samples. The weight loss between 10°C below and 10°C above the boiling points of solvent was used to calculate residual solvents within the membranes from the TGA curves. These ranges of temperature were chosen to account for solvents that might have evaporated before reaching the boiling points.

X-ray Diffraction

X-ray diffraction (XRD) test was conducted on dense membranes made from all the solvents using a diffractometer with Cu K α radiation of $\lambda = 1.5406$ Å, voltage of 40.0 kV and current of 30.0 mA. Samples were scanned in 2θ from 5 to 40° at the rate of 1°/min. The broad peak on each of the membrane X-ray pattern was attributed to the average intersegmental distance of polymer chains.¹¹ The XRD patterns were used to calculate values of d -spacing of the membranes using Bragg's law:

$$n\lambda = 2d \sin \theta \quad (7)$$

where θ is the X-ray diffraction angle.

Peak maxima were identified by curve fitting as well as by digitally reading out the intensity values. Results from both methods are identical.

RESULTS AND DISCUSSIONS

Solubility and Flory–Huggins Parameters

The level of polymer–solvent interaction was first investigated using the Hansen's solubility parameter and the Flory–Huggins solution theory. The values of these parameters were estimated and presented on Table III. The closer the total solubility parameter between a solvent and a polymer, the better the interaction between them. DEG was observed to be the closest to PSF and therefore is expected to have the best interaction with PSF. The Flory–Huggins parameter is commonly used to determine the miscibility of two polymers. The lower the value of this parameter, the better its interaction with the polymer. From the table, DEG was observed to have the smallest value of the Flory–Huggins parameter.

Scanning Electron Microscopy

Membrane separation performance was known to be directly related to the dope composition from which the membrane has been prepared. Furthermore, the gas transport in membrane (both porous and nonporous dense) are often explained based on four different mechanisms, namely: the solution diffusion, viscous flow, Knudsen flow, and molecular sieving.⁴ On a general note, the mode of permeation and separation in membrane is dictated by its morphology.³⁹ For dense membrane, the tight surface is an indicative of dense selective skin.³⁹ Thus the solution diffusion is the widely accepted mechanism for it. Moreover, it has been reported that the membrane permeability changes from solution-diffusion to Knudsen diffusion separation as the membrane pore size increases.⁶ In this study, nonporous dense nature or the tight surfaces of the membranes were probed using scanning electron microscopy (SEM).

SEM images of the surface and the cross-section of the DEG membrane are shown in Figures 3 and 4, respectively. The SEM images of the surface displayed in Figure 3 revealed a continuous defect-free surface. The dense nature of the thin cross section was clearly revealed by the micrograph in Figure 4. In addition, cross-section micrographs of PSF membranes made from other solvents were also included in Figure 4 for comparison. From Figure 4, the SEM images of all the membranes do

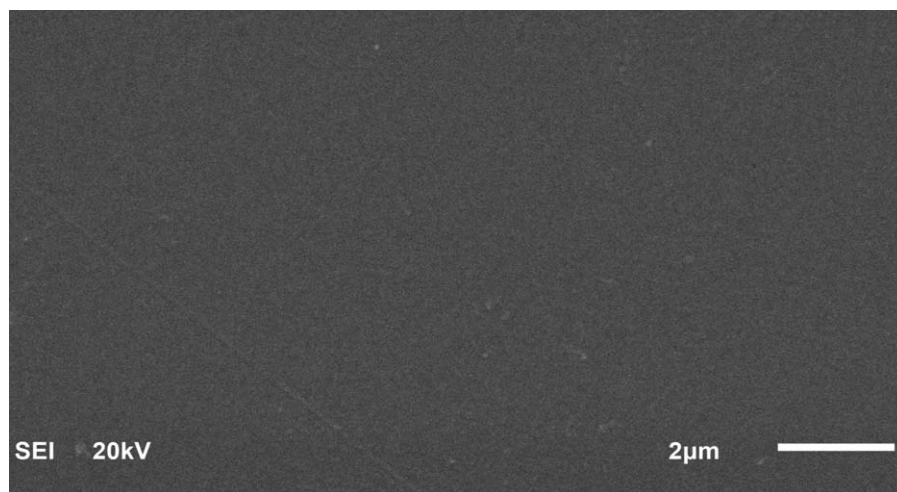


Figure 3. Surface morphology of PSF-DEG.

not reveal any detectable micro pores. Rather, it showed membranes with densely packed micro structure. Consequently, the mechanism of gas transport through the membrane can be taken to follow the solution diffusion mechanism.

Gas Permeability

Solution knife casting method was used to prepare the dense thin layer using DEG membrane. Several attempts were made to apply this same method to prepare dense thin layer of the same thickness using other commonly used solvents such as NMP, DMF, and DMAc in order to compare their permeabilities with the DEG membrane. All the attempts were not successful because the resulting membranes contained some surface defects and not as thin. The lowest defects free thickness that was successfully prepared was about 25 μm . Permeability properties of membrane of such thickness could not be compared with DEG

membranes whose thickness is 3.5 μm . Besides, permeability of such membrane thickness and solvents are already available in the literature, spending time determining the permeability again may not be worthwhile effort. However, due to the fact that every experiment has its own conditions, permeabilities of membranes prepared from other solvents and under the same condition as that of DEG-membrane are also presented. Table IV contains the results for the permeabilities of CO_2 and CH_4 , and the ideal selectivities from this study and that from literature.^{40–43} The DEG membrane was observed to display a higher permeability for both CO_2 and CH_4 . The permeability values are about six times higher than the permeability of membrane prepared from other solvent using the same Udel 1700 PSF (sample nos. 2, 4, 5, and 7 on Table IV). The ideal selectivity was observed to be same as that of sample 4. Thus, the new solvent can be said to have improved membrane productivity but

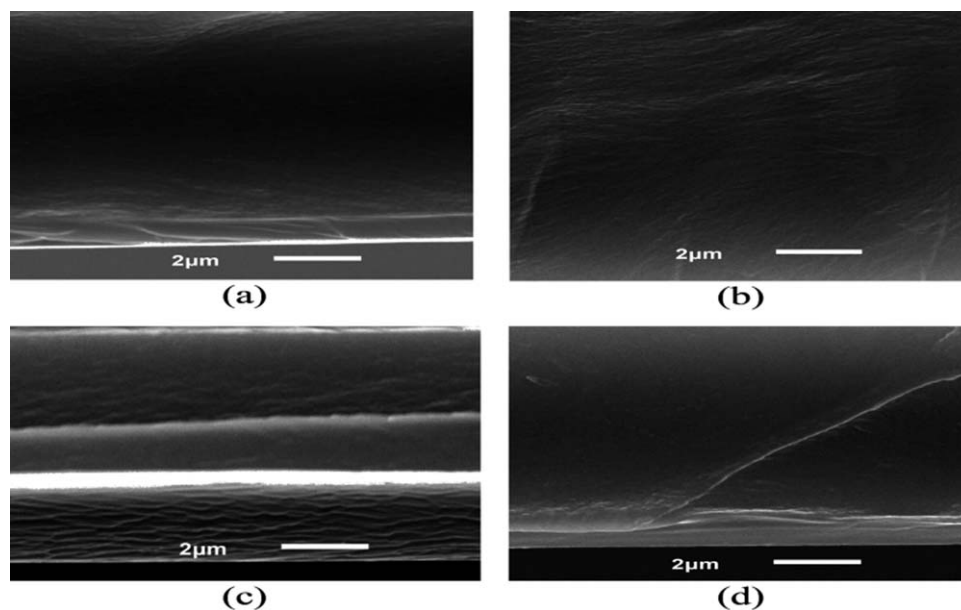


Figure 4. SEM micrograph of the cross-section of membranes prepared using various casting solvents. (a) PSF-DEG, (b) PSF-DMAc, (c) PSF-DMF, and (d) PSF-NMP.

Table IV. Pure CO₂ and CH₄ Permeability of Dense PSF Membrane Sample at 35°C

No.	Pressure (bar)	P_{CO_2} (barrer)	P_{CH_4} (barrer)	Ideal selectivity $P_{\text{CO}_2}/P_{\text{CH}_4}$	Thickness (μm)	Solvent	Ref.
1	5.0	29.08	1.258	23.12	3.5	DEG	This work
2	6.0 ^a	7.8	-	-	2.0	TCM	40
3	5	13.2	0.66	20	-	DCM	41
4	5	6.3	0.27	23.33	-	DCM	41
5	1.0	7.92	-	-	30-40	THF	42
6	5	11	-	26	50-75	s-TCE	43
7	2	7.1	-	22	-	s-TCE	43
8	10	4.01	-	-	23	DMF	This work
9	5	3.44	-	-	23	NMP	This work
10	5	3.35	-	-	32	DMAc	This work

TCM, chloroform; THF, tetrahydrofuran; s-TCE, s-tetrachloroethane; DMF, *N,N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide.

^aPrepared by spin coating onto a polytetrafluoroethylene (PTFE) porous support.

has no effect on the selectivity. Previously, chemical modification has been reported to increase membrane permeability and selectivity. For example, sample 6 was made by substitution of phenyl rings in PSF in place of the methyl groups in the connector unit and this led to permeability coefficient that is about twice those observed for unmodified PSF.⁴³ Although, the selectivity of this membrane was higher than the DEG membrane, however, its permeability is lower. Similarly, another modified PSF, hexafluorobisphenol A PSF (sample no. 3) has both the selectivity and permeability lower than the DEG membrane.⁴¹

The enhancement in the performance of this membrane is best explained using the solution–diffusion mechanism. In the field of membrane technology for gas separation, it has been established that permeability (P) of membrane is a function of both the diffusion coefficient (D) and the solubility coefficient (S). That is:

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

Also, for two components A and B, the ideal selectivity $\alpha_{A/B}$ of membranes is defined as:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B} \right] \times \left[\frac{S_A}{S_B} \right] \quad (4)$$

Thus, both the permeability and the ideal selectivity of membrane can be increased by changing either D or S or both D and S . When permeability change is brought about by increase in D , then it can be attributed to a change in the membrane degree of porosity and as a result, the selectivity may be destroyed. For solubility selective membranes, permeability increase is caused by increase in solubility. This does not require any change in the degree of porosity. In this study, one or both scenarios are suspected to be responsible for the enhancement in the membrane performance. Specifically, permeability increase may be attributed to increase in diffusivity of CO₂. The nondestruction of membrane selectivity may be attributed to the increase in solubility of CO₂ or a corresponding increase in the diffusivity of CH₄ due to increase in free volume caused by

high molar volume of the casting solvent. In addition, the low thickness of the membrane plays a very essential role. This observation is similar to what have been reported previously. For example, increased permeability with little or no change in selectivity has been reported by Aguilar-Vega and Paul.⁴³ Chemical modification of PSF (replacement of methyl groups in PSF with the phenyl rings in the connector unit) lead to higher permeability coefficient and selectivity that is similar or slightly higher than those observed for unmodified PSF.

Definitely, further studies are needed to confirm the factors that are responsible for these kinds of behaviors. For this reason, detailed studies into the transport properties of the DEG membrane using other more sophisticated characterization methods is part of future research works in our laboratory.

The increase in the CO₂ permeability as compared to other solvents can be explained using the solvent template effect. As explained earlier, template effect is used to describe the role of casting solvent in the nature of the physical structure of membrane. During preparation, the solvent acts as a transient template which controls the packing density of the final membrane material. On a molecular level, this phenomenon is due to the fact that the intra- and the internodular chain segment displacements are strongly related to the size of the transient molecular spacers that sheath the macromolecules in solution. The template effect was documented by Kesting *et al.*³⁰ using the permeability of O₂ in PSF membrane. The permeability of O₂ in PSF was reported to increase with increase in molar volumes of the casting solvents. However, there is critical molar volume (V_c) below which there is a modest template effect and above which there is an appreciable template effect. For permeability of O₂ in PSF, V_c was observed to be 147 cm³/mol. The increase in the permeability of O₂ was modest before 147 cm³/mol, whereas above this value, the permeability increased sharply with no comprise to the selectivity up to 188 cm³/mol. Similar observation was detected in this study. Permeability data on Table IV was combined with the properties of the solvents on Table I to develop a graph of permeability against the molar volume of

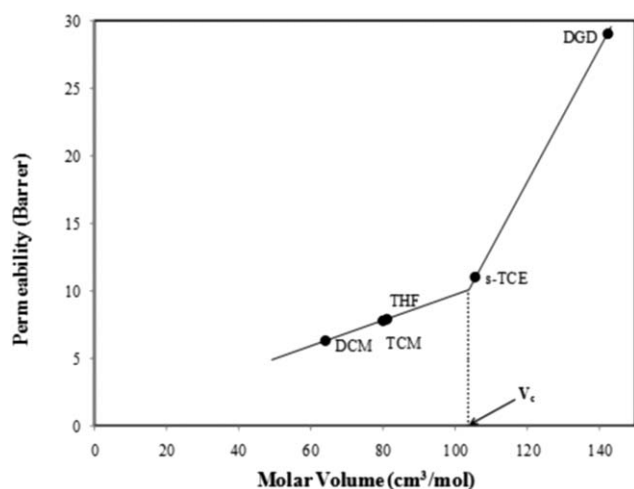


Figure 5. Relationship between the CO₂ gas permeability and molar volume of the casting solvents.

the solvents as presented in Figure 5. From this figure, the critical molar volume for CO₂ in PSF is 103.5 cm³/mol. Thus, the appreciable template effect is apparent when the permeability of DEG membrane is compared with those from other solvents. Based on this, the difference in the permeability of DEG membrane can be explained based on the appreciable template effect above the V_c . Another observation from this figure is that, it can be deduced that the V_c for CO₂ in PSF is less than 147 cm³/mol. Thus the V_c was suspected to be dependent on both the penetrant gas involved and the polymer through the permeation is taking place. In the work of Bi *et al.*²⁶ on the effect of casting solvent on the permeability of gases in poly[1-(trimethylsilyl)-1-propyne] (PTMSP), the authors concluded that the use cyclohexane resulted in larger size and number density of polymer free volume while THF resulted in polymer with smaller size and number density. However, the authors did not consider the molar volume of the respective solvents. On

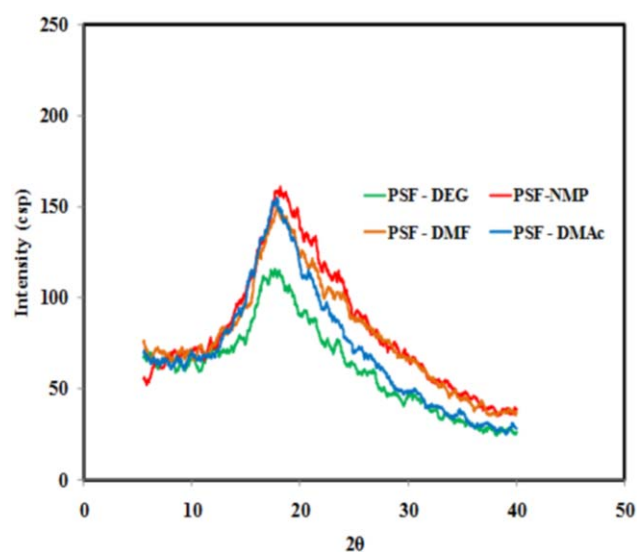


Figure 6. X-ray diffraction patterns of membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Calculated d -spacings for PSF Membranes Made from Various Solvents

Membranes	d -spacing (Å)
PSF-DEG	5.972
PSF-DMAc	5.602
PSF-DMF	5.5855
PSF-NMP	5.529

the basis of the solvent molar volume, the permeability of CO₂ in PTMSP are 7.02, 3.81, and 2.08 cm³ STP cm/cm² s cmHg while the molar volume of solvents are 108.161, 105.908, and 81.114 cm³/mol for cyclohexane, toluene and THF, respectively. Thus, these results are in line with the template effect. There is need for more research works on the dependent of V_c on the type of polymers and penetrant gases.

Average Interchain Distances Using XRD

The X-ray diffraction spectra of all membranes are shown in Figure 6. All the patterns contain only broad peaks. This is an indication that the samples are amorphous. The 2θ values at the maximum peak of the PSF-DEG samples were observed to be positioned to the left hand side in relative to membranes from other solvents. This means that the average interchain distance (d -spacing) of this sample is more than others. The values calculated for the d -spacing are shown in Table V. From this table, it was observed that the DEG membrane has the highest value of d -spacing. This could have contributed to the reasons why its permeability is higher than membranes from other solvents as reported in Table IV.

The relationship between the d -spacing and the gas permeability could be explained from a molecular point of view. The most widely accepted molecular representation of polymer is the Chain model. Thus, the chain–chain attraction is one of the factors that have been reported to be responsible for gas permeability in polymer. The d -spacing is a measure of the molecular distance between chains. This is inversely proportional to the chain–chain attraction. That is, polymers having lower van der Waals attraction are expected to have a larger interchain distance. The low intermolecular attraction may lead to higher gas permeability as explained by Salamone.⁴⁴ Infact, direct relationship between the d -spacing and gas transport properties in membrane have been reported by Wang *et al.*⁴⁵

Fourier Transform Infrared

Fourier transform infrared (FTIR) test was used to access possible change in the PSF chemical structure and functional groups due cross-linking or other chemical interaction between the DEG and the PSF. Solvents such as NMP, DMF, DMAc, and DCM have been used previously for preparing PSF membranes. The effects of these solvents on separation performance of PSF have also been investigated. The FTIR spectra that have been reported for the membranes made from these solvents did not reveal any chemical interaction between the solvents and the membrane.^{25,46–51} The spectra obtained in this study were shown in Figure 7 for membranes prepared from DEG as well other solvents. The spectra of the DEG membrane are similar to

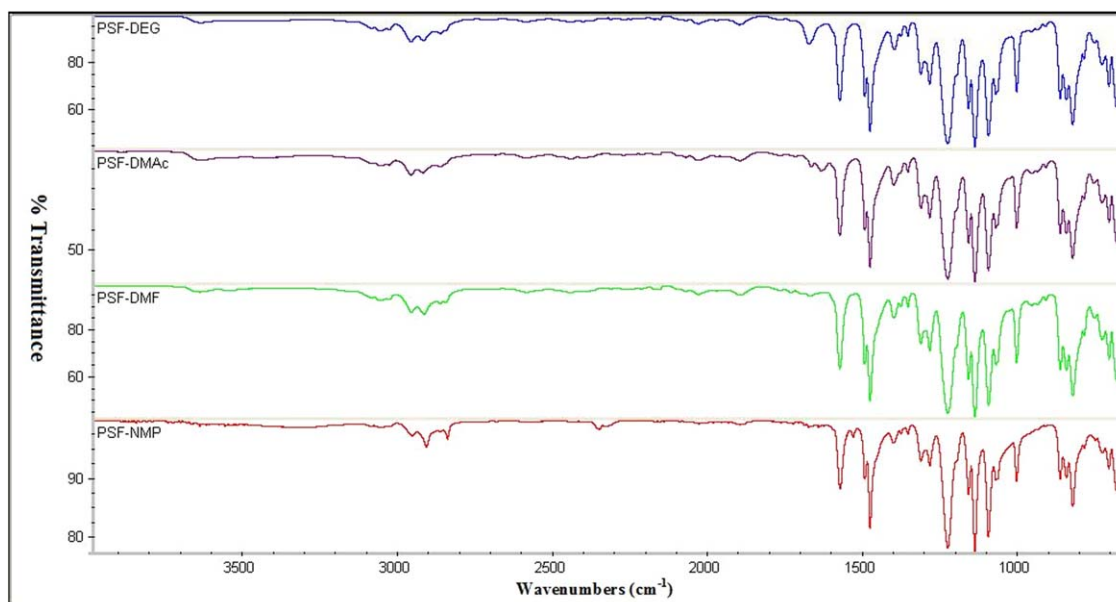


Figure 7. FTIR spectra of membranes prepared using various casting solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. Infrared Spectra of Polysulfone Membranes

Functional group	Associated group frequency wave number (cm^{-1})	Wave number from this work (cm^{-1})
Aryl ethers (C-O-C)	1270-1230	1235.26
Aryl sulfones (-SO ₂ -)	1170-1135	1147.48
Methyl (-CH ₃)	2970-2950	2966.18

that of other solvents with all functional group remaining unchanged. All the spectra are similar to one another and to those reported in previous literature.^{25,46,49} This confirms the absence of chemical interaction between the DEG and PSF. A molecule of PSF is known to consist of backbone made of diaryl sulfone (that is Ar-SO₂-Ar) and diaryl ether (Ar-O-Ar) groups. The interpretations of the characteristics absorption peak observed in Figure 7 are displayed on Table VI. The associated group frequency wave numbers were obtained from Ref. 52.

Thermo Gravimetric Analysis

TGA was performed in order to quantify the residual solvent within the membrane after drying and to evaluate the effect of casting solvent on the thermal stability of the membranes. The thermo gravimetric curves of the all the membranes samples are shown in Figure 8. The membrane samples that were used for the TGA were dried under the vacuum for 9 days. All membranes were found to display similar thermal stability behaviors. Their thermal stability was maintained up to a temperature of about 550°C for all the membranes. A major change in weight loss began to appear after this temperature. This is due to decomposition of main chains of the polymers. The decomposition temperatures are the same for all the membranes. This is thus an indication that the solvents have no effect on the thermal stabilities of the membranes. The overall weight loss at

temperature below the degradation temperature showed that the residual solvent in each of the polymer is very small. Table VII showed the boiling point of each of the solvents and the

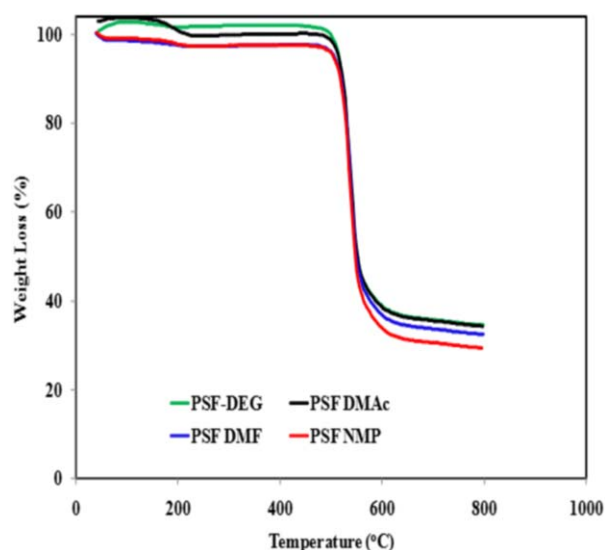


Figure 8. TGA spectra of membranes made from various solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VII. Residual Solvent in Membrane Samples after Drying

Membrane sample	Solvent	Boiling point (°C)	Residual solvent (wt %)
PSF-DEG	DEG	155-165	0.383
PSF-DMAc	DMAc	164.5-166	0.870
PSF-DMF	DMF	152-154	0.206
PSF-NMP	NMP	202-204	0.631

percentage weight losses at the boiling point range that were extracted from the TGA results. To quantify residual solvents, weight losses were estimated within temperature interval of 10°C above and below the boiling points of each membrane. The amounts of residual solvent are very small and within the values assumed to be negligible in the literature.^{22,53} Thus, the improved performance cannot be attributed to the presence of residual solvent.

CONCLUSION AND RECOMMENDATION

The effects of polymer–solvent interaction on membrane performance were investigated by comparing the properties of membranes prepared from a new commercially available solvent, diethylene glycol dimethylether (DEG) and other commonly used solvents. Results obtained revealed that there exists a trend between the molar volume of the solvent and gas permeability of PSF membranes. Gas permeability increase with increase in molar volume. In addition, there exist a critical volume above which the increase in the permeability is very rapid. This value was determined to be 103.5 cm³/mol for permeability of CO₂ in PSF. DEG has the highest molar volume and it was the cheapest of all the solvents considered. It was concluded that the critical molar volume is most likely dependent on penetrant gas as well as the polymer involved in making the membrane. Also, gas separation performance of polymeric membranes can be enhanced by careful selection of casting solvent. Moreover, the cost of membrane preparation can be minimized by performing a thorough evaluation of the polymer–solvent interaction prior to membrane dissolution. Future research works on the polymer–solvent interaction and the determination of the critical molar volume of various solvents and gases are recommended.

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