Morphology and permeation properties of polysulfone membranes for gas separation: Effects of non-solvent additives and co-solvent

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ARTICLE INFO

Article history:
Received 9 September 2009
Received in revised form
31 December 2009
Accepted 10 February 2010

Keywords:
Gas separation membranes
Polymeric additives
Co-solvent
Non-solvent additives

ABSTRACT

The effects of non-solvent additives, polymeric additives, polymer concentration and volatile solvent on the performance and morphology of polysulfone flat sheet gas separation membranes have been investigated. The isothermal phase diagram of polysulfone (PSF)–(NMP/additive)–(water) ternary system at 25 °C was provided based on the visual cloud point experiment. Flat sheet membranes were fabricated by the phase inversion technique. Scanning electron microscope (SEM) was used to analyze the morphology of fabricated membranes and their gas separation properties characterized by gas permeation test using pure carbon dioxide and methane as test gases. The results showed that addition of additives to the polymer solution brought the cloud point curves closer to the (polymer)–(solvent/additive) axis in the following order: PEG < ethanol < PVP < glycerol. The gas permeation test results showed that ideal CO2/CH4 separation factor of the membranes improved by the presence of the additives in the following order: PEG < ethanol < PVP < glycerol. This was in accordance with the shift of binodal line to the (polymer)–(solvent/non-solvent) axis. The critical concentration of polysulfone in 1-methyl-2-pyrrolidone (NMP) solvent was determined by viscometry experiment to be about 30 wt.%. Addition of tetrahydrofuran (THF) as a volatile solvent into the polymer solution increased the membrane selectivity, which was attributed to elimination of the macro-void formation during instantaneous demixing and selective loss of highly volatile solvent from the outermost surface of the membrane during polymer solution casting.

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1. Introduction

Asymmetric membranes are used for reverse osmosis, ultrafiltration and gas separation processes because of their high permeability, selectivity and mechanical strength in high pressure application [1]. Among different membrane fabrication methods, phase separation is the most common method for fabrication of hollow fiber and flat sheet asymmetric membranes [2]. In this method, a homogeneous solution of polymer, solvent, non-solvent and additives is cast into a film and then converted to a solid state by one of the following methods [2,3]:

1. Immersion precipitation.
2. Precipitation from the vapor phase.
3. Thermal precipitation or TIPS.
4. Air casting of the dope solution.
5. Precipitation by controlled evaporation.

Making a high-performance separation membrane by studying the membrane formation procedure is an important issue in membrane research [4].

For the fabrication of high-flux and defect-free flat sheet membranes, it is usually necessary to bring the dope composition to the vicinity of the cloud point or the precipitation point by adding a proper non-solvent additive into the dope [4–6]. In addition, adding non-solvent additives into the casting or spinning solution can decrease macro-void formation in the sub-layer [7–10].

When a non-solvent additive is used as a third component in the polymer–solvent solution, it can decrease the dissolving power of the solvent and thus increase polymer–polymer interaction. Therefore, adding a non-solvent additive into a polymer solution increases the tendency of polymer chains to approach a more tightly coiled conformation [11]. Addition of non-solvent into the dope solution can bring the initial composition of the casting solution nearer to the precipitation point. In other words, non-solvents can alter the phase separation behavior during the phase inversion process and can accelerate the coagulation process.
from solution to gel state when the casting solution is immersed in a coagulant [12,13]. On the other hand, when non-solvents are added to the polymer solution, polymer solidification can occur rapidly at the membrane surface and, as a result, membranes with a thinner skin layer and a more uniform structure can be formed [13].

Although the addition of a non-solvent is very desirable, addition of water is not recommended because its non-solvent power is too strong. Instead, ethanol was suggested as a better non-solvent [14–19].

Polymeric additives such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) are also known to affect membrane performance favorably [20–22]. Although, several investigations have been made on the effect of polymeric additives on the phase inversion behavior and the results were related to morphology and performance of ultrafiltration and nanofiltration membranes [23–28], to our knowledge, systematic investigations have not yet been conducted with regard to gas separation membranes.

It is also known that the properties of solvent affect the morphology and performance of the membrane. For example, addition of a volatile solvent into a polymeric solution, along with a non-solvent, can change liquid–liquid demixing behavior, and as a result can cause a change in the membrane morphology and performance. Besides, adding a co-solvent to a polymeric solution can eliminate macro-void formation during instantaneous demixing and change the morphology of the membranes from finger-like to sponge-like structure despite of instantaneous demixing [29,30].

The objectives of the present work are to investigate systematically the effect of ethanol, polyethylene glycol (PEG400), polyvinylpyrrolidone (PVPK15) and glycerol as additives on the morphology and separation properties of flat sheet gas separation membranes. Also, the effect of the addition of a volatile solvent to the casting solution is investigated.

2. Theoretical background

As mentioned above, phase inversion by immersion precipitation is one of the most widely used methods for asymmetric membrane fabrication. In this technique, a polymer solution is immersed in a non-solvent (coagulant) bath and solvent–non-solvent exchange will occur between the polymer solution and the non-solvent. This exchange forms the nascent pores and the polymer matrix surrounding the pores. Depending on the formation conditions, a variety of different morphologies can be prepared as will be discussed later. Traditionally, casting dopes are ternary polymeric solutions, containing a mixture of polymer(s), solvent(s), and non-solvent [31–33].

A ternary diagram is used for describing the phase separation process of a system composed of polymer/solvent/coagulant. In this diagram the equilibrium curve known as the binodal curve, divides the area of the triangle into the 2 following regions.

1. One-phase region: every composition of solvent/polymer/coagulant in this region forms a homogeneous one-phase solution. It is obvious that the dope composition must lie in this region.
2. Two-phase region: every composition of solvent/polymer/coagulant in this region separates into two equilibrium rich and lean polymer phases whose compositions are given by the two ends of the tie lines.

On the other hand, the spinodal curve represents the curve where all possible fluctuations lead to phase separation [34]. The region between the binodal and spinodal curves implies metastable compositions where phase separation by nucleation and growth takes place. As has been shown in Fig. 1, the intersection point of these two curves is defined as the critical point (C).

The morphology and properties of the membrane are strongly related to the dope position, critical point position and precipitation path. If the precipitation path crosses the binodal curve, phase separation starts with nucleation and growth of the polymer-rich or polymer-lean phase [29,30]. Usually when the polymer concentration is low, the precipitation path crosses the equilibrium line below the critical point and nucleation of a polymer-rich phase initiates the phase separation process. But when the polymer concentration is high, the mentioned path passes through the binodal curve above the critical point. In this case, nucleation of the polymer-lean phase may occur. On the other hand at high polymer concentrations, the precipitation path bypasses the binodal curve and phenomena such as vitrification, gelation or crystallization will occur without polymer-lean phase growth.

In addition to the precipitation path and the mechanism for membrane formation, the time of phase separation initiation after immersion is very important in order to predict the morphology and separation properties of the resulting membrane. If precipitation is initiated immediately after immersion (instantaneous demixing), the resulting membranes have a porous top layer and if precipitation begins after measurable time (delayed demixing) one can expect a membrane with a dense skin layer [2,13,33,35].

Therefore, the membrane formation path and the demixing process are influential parameters that can affect skin layer formation of asymmetric membranes [36–40]. That is, by changing the demixing time and the precipitation path during membrane preparation one can improve the membrane morphology and separation property. Adding a non-solvent additive (NSA) to the dope solution is an effective way to change the precipitation path and the demixing behavior [34,41].

It has been shown that non-solvent additives can play a very important role in determining membrane structure and gas separation properties [11–13]. Usually, the addition of a non-solvent to the membrane casting solution brings the initial composition of the dope solution nearer to the precipitation point [12] and thus in the presence of a non-solvent additive one can expect that the binodal curve moves toward the polymer/solvent axis and the single phase region decreases with increasing non-solvent additive concentration in the solution. Therefore, the addition of a suitable non-solvent additive into the membrane casting solution shortens the precipitation path and accelerates the coagulation process and thus membranes with thinner skin layer and more uniform structure could be obtained [13,30,36,42,43]. It is necessary to note, non-solvent additives should be miscible with the coagulant and the concentration of NSA in the polymer dope is quite different.
for different non-solvent additives [11]. In addition to non-solvent additives, salts, inorganic acids, organic acids and co-solvents can be used as additives. These additives can change membrane property and morphology just like non-solvent additives. Commonly used additives can be classified into the following categories [28]:

1. Polymer additives (PVP and PEG).
2. Low-molecular-weight chemicals including salts (LiCl), inorganic acids (acetic acid and phosphoric acid), organic acids (propionic acid).
3. Weak co-solvents (ethanol and acetone).
4. Weak non-solvents (glycerol and ethylene glycol).
5. Strong non-solvents such as water.

Among non-solvent additives, formamide, glycerol, ethyl acetate, triethyl phosphate, ethylene carbonate, acetic acid, propionic acid, butyric acid, isobutyric acid, glutaric acid, sulfuric acid, methanol, ethanol, propanol, butanol, ethylene glycol, diethylene glycol, water and lithium chloride have been tested as non-solvent additives [11–14,17,28,30,36,42,44–51]. Table 1 reviews the application of additives in the different membranes.

As has been shown in the above table, alcohols (methanol, ethanol, propanol, butanol, pentanol) and ethylene glycol, diethylene glycol are the most widely used additives for gas separation applications. In contrast, polymer additives are used usually for nanofiltration and ultrafiltration applications [27,31,34,41,43,52] and their effect on the performance of gas separation membranes has rarely been investigated.

These polymer additives (polymethylpentylpolylidenechloroform (PVP), polyethylene glycol (PEG), tetra ethylene glycol (TEG)) are often used to accomplish the following tasks: increase the viscosity, introduce hydrophilicity, improve pore formation and suppress macro-void formation in order to create membranes with high-pure water fluxes. Besides, non-solvent additives can be added with polymer additives in order to bring the solution composition closer to the binodal composition. As an example, PEG is a very weak non-solvent and can be added in large amounts to polymer–solvent solutions [43] and PVP is a well-known additive that can increase the viscosity of the polymer solution. This additive can influence macro-void formation and dopes containing PVP have higher permeability [27,31,34,41]. Other hydrophilic polymers such as poly(ethylene oxide) have similar effects on membranes [31].

In addition, solvents as well as non-solvents and polymeric additives can also change the membrane properties and morphology. As mentioned earlier, the membranes which have been prepared under an instantaneous L–L demixing process have a thin top layer of porous nodular structure and macro-void-filled open cell substructure and can be used for ultrafiltration and hyperfiltration applications. On the other hand, under delayed L–L demixing process, a membrane with a dense, thick top layer and a closed cell substructure are always formed. These kinds of membranes are suitable for gas separation and pervaporation applications if the substructure resistance can be kept low [53].

Usually adding a volatile solvent into the casting dope, along with non-solvents, can change liquid–liquid demixing behavior of the dope during membrane fabrication and as a result can change the membrane morphology and separation properties. As an example, adding tetrahydrofuran (THF) into the cellulose acetate–NMP–water system can induce delayed L–L demixing and as a result a denser membrane structure with small tear-drop type macro-voids and a substructure of large pore size can be prepared [30]. Also, due to the fact that the viscosity of a polymer solution is higher in a thermodynamically suitable solvent, THF can affect (decrease) dope viscosity and as a result affect the separation property of membranes [30]. Hence, addition of volatile solvents into the dope can not only change the kinetic parameters but also can alter thermodynamics properties and the L–L demixing behavior of membrane fabrication processes.

Besides, adding a co-solvent to the dope solution (e.g. dimethylformamide (DMF)) into the polymer–NMP solution system can eliminate macro-void formation during instantaneous demixing and change the morphology of the membranes from macro-voidal to sponge-like structures despite instantaneous phase demixing [29].

Usually the skin layer of asymmetric membrane is generated from a region with locally elevated polymer concentration. Volatile solvents (e.g. dichloromethane (DCM), chloroform or tetrahydrofuran (THF)) in the casting dope can rapidly be driven off under-forced

<table>
<thead>
<tr>
<th>Additive</th>
<th>Solvent(s)</th>
<th>Polymer</th>
<th>Application</th>
<th>Reference, year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, ethanol</td>
<td>NMP</td>
<td>PSF</td>
<td>Gas separation</td>
<td>[11], 2002</td>
</tr>
<tr>
<td>Methanol, ethanol, propanol, butanol, pentanol, ethylene glycol, diethylene glycol</td>
<td>NMP</td>
<td>PES</td>
<td>Gas separation</td>
<td>[12], 1996</td>
</tr>
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<td>Methanol, diethylene glycol, deionized water</td>
<td>NMP, DMAc</td>
<td>PSF, PES</td>
<td>Modeling</td>
<td>[13], 1995</td>
</tr>
<tr>
<td>Ethanol</td>
<td>NMP</td>
<td>Polyimide</td>
<td>Gas separation</td>
<td>[14], 2002</td>
</tr>
<tr>
<td>Water</td>
<td>NMP</td>
<td>PES</td>
<td>Gas separation</td>
<td>[17], 2000</td>
</tr>
<tr>
<td>PVP K30</td>
<td>NMP</td>
<td>PES</td>
<td>Nanofiltration</td>
<td>[27], 2007</td>
</tr>
<tr>
<td>LiCl, glycerol</td>
<td>NMP</td>
<td>PVDF-HFP</td>
<td>Microporous membrane fabrication</td>
<td>[28], 2008</td>
</tr>
<tr>
<td>PVP K90, K30</td>
<td>NMP</td>
<td>PES</td>
<td>Ultrafiltration</td>
<td>[31], 1995</td>
</tr>
<tr>
<td>PVP</td>
<td>DMAc</td>
<td>Poly (bis phenol-A-sulfone)</td>
<td>Modeling</td>
<td>[34], 1999</td>
</tr>
<tr>
<td>Ethanol, propanol, butanol, chloroform</td>
<td>NMP</td>
<td>PSF</td>
<td>Pervaporation</td>
<td>[36], 2007</td>
</tr>
<tr>
<td>PVP</td>
<td>DMAc, NMP</td>
<td>PSF</td>
<td>Ultrafiltration</td>
<td>[41], 2008</td>
</tr>
<tr>
<td>Ethanol</td>
<td>DMAc</td>
<td>PSF</td>
<td>Gas separation</td>
<td>[42], 2006</td>
</tr>
<tr>
<td>PEG + water</td>
<td>NMP</td>
<td>PES</td>
<td>Ultrafiltration</td>
<td>[43], 2003</td>
</tr>
<tr>
<td>Ethanol</td>
<td>THF</td>
<td>PSF</td>
<td>Gas Separation</td>
<td>[44], 2002</td>
</tr>
<tr>
<td>Ethanol</td>
<td>THF + DMAc</td>
<td>PSF</td>
<td>Gas separation</td>
<td>[45], 2002</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>NMP</td>
<td>PSF + 4-PVP</td>
<td>Gas separation</td>
<td>[46], 2006</td>
</tr>
<tr>
<td>Branched and linear alcohols</td>
<td>Chloroform</td>
<td>PPO</td>
<td>Gas separation</td>
<td>[47], 1999</td>
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<tr>
<td>LiCl</td>
<td>DMAc</td>
<td>Cardo polyamide</td>
<td>Gas separation</td>
<td>[48], 2004</td>
</tr>
<tr>
<td>Water, ethanol</td>
<td>NMP, DMAc</td>
<td>PES, PES, PEI, CAB</td>
<td>Morphological aspect of dual layer hollow fibers</td>
<td>[49], 2000</td>
</tr>
<tr>
<td>Water</td>
<td>DMAc + THF</td>
<td>PSF</td>
<td>Gas separation</td>
<td>[50], 1999</td>
</tr>
<tr>
<td>Ethanol, propanol, butanol</td>
<td>Dichloromethane (DCM), Chloroform</td>
<td>Polycarbonate</td>
<td>Gas separation</td>
<td>[51], 2008</td>
</tr>
<tr>
<td>PEG 400</td>
<td>NMP</td>
<td>AN-MA-SSA</td>
<td>Ultrafiltration</td>
<td>[52], 2006</td>
</tr>
</tbody>
</table>
convection conditions (dry–wet phase inversion) and thus, due to a selective loss of highly volatile solvent from the outermost surface of the membrane, the polymer-rich regions are forced to coalesce by capillary pressures. This phenomenon causes the polymer-rich phase to undergo rapid vitrification and hence an oriented membrane skin with few pores or defects will be formed [50, 51]. On the other hand, the evaporation step prior to immersion in the coagulation bath in the dry/wet technique also influences the thickness of the membrane. A longer evaporation step generally leads to a thicker membrane while a shorter evaporation time results in a thinner skin layer with significantly different separation performance. Therefore, presence of a volatile and less volatile solvent (e.g. NMP) in the casting dope can affect solvent evaporation rate as well as skin formation during dry phase inversion induced by forced convection [44]. Also, since the thickness and the integrity of skin layer are intimately related to solvent evaporation, the ratio of the less volatile solvent to the more volatile solvent, called solvent ratio, is a crucial parameter for development of defect-free and ultrathin-skinned asymmetric membranes for gas separation processes. It has been reported that the reduction of the solvent ratio in polymer solutions increases the volatile component concentration in the dope and can increase the thickness of the selective skin of the membrane while it decreases the membrane surface porosity [44]. Therefore, a membrane with higher selectivity and lower permeability will be formed when the volatile solvent concentration is increased in the polymer solution. On the other hand, some of the thinnest skin layers can be observed in membranes prepared from polymer solutions with a high solvent ratio; however, these skin layers are usually highly porous [44].

3. Experimental

3.1. Materials

Polysulfone (PSF (Udel-P1700)) was supplied by Amoco Chemicals. 1-Methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) and ethanol (EtOH) were supplied by MERCK. Polyvinylpyrrolidone (PVPK15) was supplied by FLUKA. Polyethylene glycol (PEG400) was supplied by SIGMA–ALDRICH and glycerol was supplied by QREC.

Tap water was used as the coagulation medium. The polymer was dried in an oven at 80 °C overnight before use. Other organic chemicals (solvents and non-solvents) were used as received.

3.2. Preparation of asymmetric flat sheet membranes

Asymmetric polysulfone flat sheet membranes were prepared by the phase inversion method. The details of the membrane casting method were described by Ismail and Lai [44]. The precisely prepared dope solution was cast on a glass plate with a casting knife for a gap setting of 200 μm in ambient conditions (30 °C and 84% relative humidity) and was then immediately immersed in the coagulant bath (immersion precipitation method).

3.3. Cloud point measurement

Cloud points were determined by means of the titration method. Distilled water was gradually added to a solution of polymer and solvent/non-solvent additive mixtures. The ratio of non-solvents to solvent was kept constant at 1/6 (by weight) and the solution was kept at a constant temperature (25 °C). After adding each droplet of water to the solution, local coagulation was observed in the surface of solution. Then, the solution was mixed to become homogeneous. This process was repeated until the solution became turbid.

3.4. Gas permeation test

Gas permeation rate was measured by the constant pressure method as described elsewhere [44]. The pressure-normalized fluxes of the fabricated flat sheet membranes were measured for pure carbon dioxide and methane at 25 °C and the feed gas pressure of 8 bar. Circular membrane discs with a 5 cm diameter and an effective permeation area of 13.5 cm² were used. The standard permeate volumetric flow rate at atmospheric conditions was measured by a soap bubble flow meter. Each set of data represents an average of 5 replicates. Eq. (1) was normally used to determine the pressure-normalized flux, called permeance, through the membranes:

$$\frac{P}{T} = \frac{Q}{A \Delta P}$$

where Q is the measured volumetric flow rate (at standard pressure and temperature), P is permeability, I is membrane skin layer thickness, A is effective membrane area and ΔP is the pressure difference across the membrane. The common unit of permeance is GPU and 1 GPU is equal to 10⁻⁰⁶ cm³ (STP)/cm² s cmHg.

Eq. (2) can be used for calculating the ideal gas separation factor (α):

$$\alpha = \frac{P_i}{P_j}$$

where $P_i$ and $P_j$ are permeation rate of i and j components, respectively.

3.5. Characterization of flat sheet polysulfone membranes

The morphology of the polymeric membrane was observed by low vacuum scanning electron microscope (JEOL JSM-6390LV). The samples for SEM characterization were prepared in liquid nitrogen followed by Pt coating.

4. Results and discussion

4.1. Dope formulation

The separation performance of asymmetric membranes is directly related to the initial dope composition. Separation properties are influenced by membrane morphology, which is derived by phase separation during membrane preparation. The phase separation is further controlled by the thermodynamic interaction between the casting solution and the non-solvent in the coagulant bath. As mentioned earlier, thermodynamics and kinetics of solvent/non-solvent exchange are both important, making the composition of the dope crucial for the final fiber morphology [54].

The addition of a NSA (non-solvent additive) into the polymer solution has been shown to play an important role in the development of membranes with improved separation characteristics. In formulating these polymeric solutions, it was recognized that the solution composition could be brought to the vicinity of the binodal line by adjusting the addition of a NSA [12]. Hence, in this study binodal lines were obtained for various non-solvent additives based on the cloud point measurement, wherein the polysulfone concentration and the solvent/additive ratio were fixed at 25 wt.% and 6/1, respectively. This means that the dope position in the triangle coordinate lied on the (polymer)–(solvent/additive) axis as is shown in Fig. 2.

4.2. Effect of the additives on the isothermal phase diagram

Based on the cloud-point experiment, the equilibrium phase diagram of polysulfone (polymer)–NMP (solvent)–water (coagulant) at 25 °C with and without additives was made (Fig. 3).
As shown in the figure, adding non-solvent additives to the polymer solution brought the cloud-point curves closer to the (polymer)–(solvent/additive) axis, making the one-phase region narrower. That is, the presence of the non-solvent decreases the solvent power and thus polymer–polymer interactions increase. Therefore, when additives are added to the casting dope, less water (non-solvent) is needed to precipitate the polymer [28].

Fig. 3 indicates that adding ethanol to the polymer–solvent system can bring the binodal line closer to the (polymer)–(solvent/non-solvent) axis as compared to polymer–NMP system without addition of ethanol. The same effect was observed for PEG400, PVPK15 and glycerol. It was found that the shift of the binodal line is the most significant for glycerol. The strong effect of glycerol on the phase behavior of polysulfone–NMP–water system might be attributed to its weak solvent property and good affinity for NMP, which reduces polymer solubility in NMP [55].

4.3. Effect of additives on the gas permeance and ideal separation factor

Table 2 shows the effect of different additives on the permeance of methane and carbon dioxide and the ideal CO2/CH4 separation factor at 8 bar.

As shown in Table 2, ideal CO2/CH4 separation factor is increased by the addition of an additive without exception. Moreover, it is interesting to note that the ideal separation factor increases as the binodal line is shifted more towards the (polymer)–(solvent/non-solvent) axis. As a result, addition of glycerol gives the highest ideal separation factor.

The CO2 permeance has also increased by the addition of the additive. This can be attributed to instantaneous demixing induced by the presence of the non-solvent additive. As an example, the dope containing glycerol has the binodal curve closest to the (polymer)–(solvent/non-solvent) axis and the membrane prepared from this solution exhibits the highest CO2 permeance. The membrane prepared from the dope containing PEG 400 is more permeable than the one containing ethanol and this can be attributed to the pore-forming property of PEG. It also is very interesting to note that PVP is the second in the rank in terms of the vicinity of the binodal curve to the (polymer)–(solvent/non-solvent) axis but the CO2 permeance is the lowest. This phenomenon is due to the polymeric property of PVP. That is, adding PVP to the dope increases the overall polymer content (PSF + PVP) and as a result rapid coalescence of polymer chains in the skin layer can occur during instantaneous demixing. In other words, the two polymers are considered as one and the system can be treated as pseudo-ternary [34].

CH4 permeance is function of surface defects and membrane skin layer thickness. Instantaneous demixing tends to increase the CH4 permeance while addition of additives tends to decrease surface defects. Hence, the trend observed in CH4 permeance can be different from CO2 permeance. In Table 2, in contrast to the CO2 permeance, CH4 permeance of PEG containing membranes is the highest. This can be attributed to pore-forming property PEG and also its surface defects (selectivity of 4.66 in comparison with 33 as intrinsic selectivity of neat polymer). On the other hand, CH4 permeances of ethanol and PVP containing membranes are less than the CH4 permeance of the neat polysulfone membrane and this implies that ethanol and PVP containing membranes are less defective than neat polysulfone membranes. Among these two, PVP containing membranes are less defective than ethanol containing membranes since polymeric property of PVP can increase the coalescence of polymer chains in the skin layer and as a result a less defective skin layer can be obtained.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO2 permeance (GPU)</th>
<th>CH4 permeance (GPU)</th>
<th>CO2/CH4 selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 wt.% PSF in NMP (25% PSF and 75% NMP)</td>
<td>9.64</td>
<td>4.02</td>
<td>2.39</td>
</tr>
<tr>
<td>25 wt.% PSF in 1/6 PEG 400/NMP (25% PSF, 10.7% PEG and 64.3% NMP)</td>
<td>58.70</td>
<td>12.59</td>
<td>4.66</td>
</tr>
<tr>
<td>25 wt.% PSF in 1/6 ethanol/NMP (25% PSF, 10.7% EtOH and 64.3% NMP)</td>
<td>16.95</td>
<td>3.33</td>
<td>5.09</td>
</tr>
<tr>
<td>25 wt.% PSF in 1/6 PVP/NMP (25% PSF, 10.7% PVP and 64.3% NMP)</td>
<td>10.53</td>
<td>1.45</td>
<td>7.26</td>
</tr>
<tr>
<td>25 wt.% PSF in 1/6 glycerol/NMP (25% PSF, 10.7% glycerol and 64.3% NMP)</td>
<td>78.44</td>
<td>7.66</td>
<td>10.24</td>
</tr>
</tbody>
</table>
It is obvious that ideal separation factor is significantly lower than its intrinsic value (33), which can be attributed to the formation of defects at the skin layer of the membrane. In other words, fabricated membranes are not defect-free but the additives may suppress the formation of voids [27,31,34,41].

4.4. Effect of polymer concentration on the gas separation property

Usually, an increase in the polymer concentration of the casting solution results in a denser and thicker skin layer that tends to promote higher selectivity. In contrast, casting a dilute polymer solution produces a thin and porous skin layer leading to high permeability but low degree of selectivity for gas separation [44]. Furthermore, there is a critical polymer concentration, below and above which the entanglement of macromolecular chains changes abruptly. For the determination of such a critical concentration, the dope (comprising polysulfone and NMP) viscosity was measured by the Stokes method. Fig. 4 shows the dope viscometry results.

As shown in Fig. 4, viscosity data implies a dramatic slope change in a range of polymer concentration between 25 wt.% and 30 wt.%. Thus, intersection of the tangents at these two concentrations renders the critical concentration of about 29 wt.%, where a significant change in the degree of chain entanglement occurs [56,57]. Therefore, higher selectivity can be achieved by increasing the polymer concentration from the previous 25 wt.% (see Table 2) to 30 wt.%. Table 3 shows the gas permeation experiments when the membrane was cast from 30 wt.% polymer solution.

As shown in Table 3, increasing the polymer concentration produces more selective membranes. It is very interesting that the order in CO₂ permeance, i.e. without additive < PVP < ethanol < PEG 400 < glycerol found in Table 2, is maintained precisely in Table 3, although the permeance values in Table 3 are lower than those in Table 2.

4.5. Effect of additives on the morphology of fabricated membranes (SEM results)

As mentioned earlier, addition of a suitable non-solvent additive into the membrane casting solution shortens the precipitation path and accelerates the coagulation process and thus membranes with a thinner skin layer and a more uniform structure can be obtained [13,30,36,43]. Therefore one will expect that the membrane comprising the glycerol must have the thinnest skin layer, since the glycerol containing dope has the narrowest miscible region. This is proven by the SEM images of the following three membranes; the first containing 30 wt.% polysulfone in NMP (Fig. 5a and b), the second containing 30% polysulfone in the mixture of 1/6 ethanol/NMP (Fig. 6) and the third containing 30% polysulfone in the mixture of 1/6 glycerol/NMP (Fig. 7).

As shown in the figures (Figs. 5–7), adding non-solvent additives into the dope can alter membrane morphology.

From the figures, the average skin layer thicknesses of the membranes are in the following order: without additive (Fig. 5, 560 nm) > ethanol (Fig. 6, 340 nm) > glycerol (Fig. 7, 240 nm). From Fig. 3, it is found that the distance between the dope composition (triangle given on the polymer–solvent/additive axis) and the binodal line is exactly in the same order. Hence, the thinnest skin results from the casting dope whose composition is closest to the binodal line, thus leading to the highest flux (Table 3).

Fig. 5 shows that the membrane without additive has a finger-like macro-voids. Probably, the finger-like macro-void ends at the top surface of the skin layer, making the surface defective with pin-holes. Fig. 6 shows that the sublayer has a nodular structure when ethanol is added, diminishing the chance of pin-hole formation at the membrane surface. Fig. 7 shows the sponge-like structure of the membrane containing 30 wt.% polysulfone and 10% ethanol in NMP.
Regarding the permeances of CO2 and CH4, the obtained data can be interpreted by assuming the superimposition of the effects of skin layer thickness and the pin-hole formation. It is further assumed that the skin layer thickness has a stronger effect on the CO2 permeance while the pin-hole formation has a stronger effect on the CH4 permeance.

Then, the order in permeances will be
For CO2: without additive < ethanol < glycerol.
For CH4: without additive > ethanol > glycerol.
The results given in Table 3 agree precisely with the above expectation.

A question may further arise why the CO2 permeance is governed by the skin layer thickness and the CH4 permeation by the pin-hole formation. Perhaps, CH4 molecules are too large to permeate through the skin layer and flows mainly through the pin-holes. Hence, the pin-hole formation governs the CH4 permeance. While CO2 molecules are small enough to go through the membrane matrix of the skin layer more than through the pin-holes, and therefore the skin layer thickness governs the CO2 permeance.

It is particularly interesting to note that the membrane of the highest selectivity corresponds to the thinnest skin layer, and thus the largest CO2 flux, violating the trade-off rule. The reason for the above order in the selectivity seems to be found in the morphology of the porous sublayer. It should be emphasized that the membrane of the highest flux and the highest selectivity could be obtained by proper adjustment of the skin layer thickness and the sublayer morphology, which was done by proper choice of an additive.

4.6. Effect of volatile solvent on the gas separation property and morphology

Even though the selectivity was increased by increasing the polysulfone concentration in the casting dope, the highest ideal CO2/CH4 separation factor achieved was 15 (Table 3) which is much lower than the intrinsic value of 33, indicating the presence of defects at the membrane skin layer. Therefore, further improvement of selectivity was attempted by using a mixture of a volatile solvent (THF) and nonvolatile solvent (NMP) instead of one single nonvolatile solvent.

It is very important to note that the volatile solvent, along with being miscible with water (coagulant), must have sufficient volatility to permit ample evaporation from the nascent membrane [16]. THF is one of high volatile solvents that are both miscible with water and a strong solvent for polysulfone.
Table 4
Methane and carbon dioxide permeance (GPU) at 8 bar for membranes prepared from polymer dopes containing 30 wt.% polysulfone, 10 wt.% additive, 45 wt.% NMP and 15 wt.% THF.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ permeance (GPU)</th>
<th>CH₄ permeance (GPU)</th>
<th>CO₂/CH₄ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt.% PSF, 52.5% NMP and 17.5% THF</td>
<td>3.53</td>
<td>0.46</td>
<td>7.67</td>
</tr>
<tr>
<td>30 wt.% PSF, 10% PEG400, 45% NMP and 15% THF</td>
<td>5.36</td>
<td>0.52</td>
<td>10.31</td>
</tr>
<tr>
<td>30 wt.% PSF, 10% EtOH, 45% NMP and 15% THF</td>
<td>4.11</td>
<td>0.33</td>
<td>12.45</td>
</tr>
<tr>
<td>30 wt.% PSF, 10% PVPK15, 45% NMP and 15% THF</td>
<td>7.71</td>
<td>0.47</td>
<td>16.40</td>
</tr>
<tr>
<td>30 wt.% PSF, 10% glycerol, 45% NMP and 15% THF</td>
<td>8.23</td>
<td>0.26</td>
<td>31.65</td>
</tr>
</tbody>
</table>

Therefore, in this study a THF/NMP (1/3) mixture was used as a solvent instead of 100 wt.% NMP. Fig. 8(a) and (b) shows the effect of THF on the morphology of a membrane without any additives.

As shown in Fig. 8(a) the morphology of the membrane is generally very similar to that of the membrane cast from a dope without THF (Fig. 5) except for a thicker skin layer (800 nm as compared to 560 nm of Fig. 5). As well, the formation of finger-like macro-voids diminished and the macro-voids became much shorter. Generally, adding volatile solvent into a dope shifts the binodal location only by about 5 wt.% of the shift caused by adding a non-solvent [16]. Therefore, the effect of volatile solvent on the rate of the phase inversion is small. But a volatile solvent can rapidly evaporate from the outermost surface of the membrane, which causes the polymer-rich phase to undergo rapid vitrification and hence an oriented membrane skin with few pores or defects will be formed [50,51]. On the other hand, the evaporation step prior to immersion in the coagulation bath also influences the thickness of the membrane. A longer evaporation step generally leads to a thicker membrane while a shorter evaporation time results in a thinner skin layer with significantly different separation performances. Therefore, presence of a volatile (e.g. THF) and less volatile solvent (e.g. NMP) in the dope solution can affect solvent evaporation rate as well as skin formation during dry phase inversion [44].

Figs. 9 and 10 show the cross-sectional SEM images of the membranes that were cast from the dopes where THF/NMP mixture was used instead of NMP along with ethanol (Fig. 9) and glycerol (Fig. 10) additive.

From these figures, the average skin layer thicknesses (l) of the resultant membranes are in the following order: without additive (800 nm) > ethanol (500 nm) > glycerol (400 nm). Note that the above order is exactly the same as that found for the membranes made without addition of THF into the dope (Figs. 5–7). Note also that the thickness values are higher than those of the membranes made without addition of THF.

The thicker skin layer together with the less tendency to form finger-like macro-voids in the sublayer enables the fabrication of membranes with less defects and pin-holes.

The thicker skin layer together with the less tendency to form finger-like macro-voids in the sublayer enables the fabrication of membranes with less defects and pin-holes.

Table 4 summarizes the effect of THF on the permeation properties of the membranes from the casting dopes containing 30 wt.% polysulfone in the THF/NMP solvent mixture, where the THF/NMP ratio was maintained at 1/3. Different additives were used.

Table 4 shows that the addition of THF indeed decreases the permeance, due to the thicker skin layer, while increasing the permselectivity due to the relatively defect-free skin layer. The effect of THF addition on the membrane separation properties can be attributed to the following reasons:

1- THF has reduced the macro-void formation [29].
2- THF has induced delayed L–L demixing, and as a result, a denser membrane structure is prepared [30].
3- Selective loss of highly volatile THF from the outermost surface of the membrane during polymer casting causes the polymer-rich phase to undergo rapid vitrification and an oriented membrane skin with few pores or defects is formed [50,51].

Under the studied condition the effect of different additives on the membranes selectivity is obvious. That is, as mentioned above, instantaneous demixing induced by the presence of different additives can prevent macro-void formation during membrane fabrication and as a result, a membrane with high selectivity can be obtained. Among the additives, glycerol brings the binodal curve closest to the (polymer)–(solvent/non-solvent) axis and the resulting membrane exhibits the highest selectivity. Moreover, the permeance of the membrane prepared from the glycerol containing dope is higher than the other membranes. The highest ideal separation factor was nearly equal to the intrinsic value, indicating that the membrane prepared under the...
given condition, i.e. use of THF/NMP solvent mixture together with glycerol additive, has a thin and defect-free skin layer.

5. Conclusions

The effect of different non-solvent and polymer additives on the gas separation property of polysulfone membranes has been investigated. The results revealed that the non-solvent as well as the polymer additives moved the binodal curve and brought it closer to the dope position. The order in the distance between the binodal curve and the dope composition is as follows: PEG400 > ethanol > PVP > glycerol.

The effects of polymer concentration and the addition of a volatile solvent have also been investigated. In general, the additions of non-solvent and polymer additives increase both permeance and permselectivity. The increase in CO2 permeance is attributed to the instantaneous demixing that caused the formation of a thin skin layer, as proven by the scanning electron microscope. The selectivity is, on the other hand, related to the suppression of finger-like macro-void formation.

Furthermore, it was found that using a THF/NMP mixture instead of NMP as the solvent resulted in a more selective membrane. This is attributed to the formation of a thicker skin layer. THF is lost from the outermost surface of the membrane (during the casting) due to its faster evaporation, which causes the polymer-rich phase to undergo rapid vitrification. As a result, macromolecules are better oriented and few pores or defects are formed. Scanning electron microscope observation proved the formation of a thin skin layer, as proven by the scanning electron microscope.

References