Study on the effect of ZIF-8 nanoparticles on the transport behavior of CH$_4$ and CO$_2$ gases in polysulfone membrane

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Abstract. CO$_2$ capture has been given much attention worldwide in order to minimize the CO$_2$ emission in protecting the harmful impact on climate change. In this study, zeolitic imidazolate framework-8 (ZIF-8) nanoparticles was embedded in polysulfone (PSf) polymer and the changes of the transport behavior of CO$_2$ and CH$_4$ single gases of the resultant membranes were investigated. The solubility of the gases through the membranes were determined by using dual-volume sorption cell at 5 bar and room temperature. Subsequently, the diffusion coefficients were determined from the permeability and solubility values. From the results obtained, the CO$_2$ sorption values for both resultant membranes were higher than that of CH$_4$. Meanwhile, the membrane incorporated with ZIF-8 demonstrated greater CO$_2$ sorption capacity compared to pure PSf membrane. It can be concluded that the improvement of CO$_2$ permeability after the incorporation of ZIF-8 into PSf is mainly due to the enhancement in solubility and diffusivity of the membrane.

1. Introduction

In recent years, membrane-based technology has progressively dominating the gas separation applications as an alternative to the existing extensive technologies such as cryogenic distillation and pressure swing adsorption. Membrane process is preferable due to its distinctive properties of space and weight saving, requires minimum maintenance and costing as well as easy installation onto existing equipment [1, 2]. Polymeric membrane is known to demonstrate trade-off performance between gas permeability and gas pair selectivity [3, 4].Thus, the addition of nanomaterials in forming hybrid membranes is an advancement to increase the gas permeability and gas selectivity performance.

ZIFs is a nano-porous material with distinct pore structures with desirable properties in terms of high porosity and exceptional thermal and chemical stability [5, 6]. ZIF-8 is chosen in this study as it possesses high selective adsorption ability towards CO$_2$ [7]. Thus, the incorporation of ZIF-8 particles into PSF polymer will increase the affinity towards CO$_2$ while increasing the free volume of the polymer structure due to the alteration in the polymer chain packing [8].

It is of interest to focus on varying polymer structure to increase permeability while maintaining its selectivity. In this work, correlation between the polymer structure with its free volume and ZIF-8 particles have been made. It is expected for the ZIF-8 hybrid membrane to reduce the chain mobility which leads to higher selectivity. Besides, the change of molecular structure in the polymer can improve the trade-off performance to a certain extent.

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It is of interest to focus on varying polymer structure to increase permeability while maintaining its selectivity. In this work, correlation between the polymer structure with its free volume and ZIF-8 particles have been made. It is expected for the ZIF-8 hybrid membrane to reduce the chain mobility which leads to higher selectivity. Besides, the change of molecular structure in the polymer can improve the trade-off performance to a certain extent.
This present work involves the synthesis of pure PSf and ZIF-8 incorporated hybrid membrane. The transport properties including permeability, solubility and diffusivity of CO$_2$ and CH$_4$ gases via gas permeation and sorption tests for the hybrid membrane has been investigated and compared with the values obtained for pure PSf. This information is required to gain insights into the effect of incorporating ZIF-8 particles towards changes in gas transport properties of CO$_2$ and CH$_4$ through the PSf polymer. These results will gain a better fundamental understanding of this hybrid nanoparticles and polymer for the ease of their potential implementation in industrial gas separation.

2. Methodology

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O, > 98%, Aldrich), 2-methylimidazole (2-MeIM, > 99%, Aldrich), polysulfone pellets (Mn ~ 35000, Merck), methanol (CH$_3$OH, > 99.9%, Merck) and chloroform (CHCl$_3$ > 99.8%, Merck) were used as received. Carbon dioxide (CO$_2$, 99.95%) and methane (CH$_4$, 99.95%) gases were supplied by Air Product Malaysia Sdn. Bhd.

2.2. Preparation of ZIF-8

Two solutions containing 2-methylimidazole in 200 mL of methanol and zinc nitrate hexahydrate in 200mL of methanol were prepared, respectively. The two solutions were subsequently mixed rapidly and stirred for 1 h. The solution will eventually turn cloudy and it is then proceeded with centrifugation at 7800 rpm for an interval of 5 min to obtain the ZIF-8 particles from the solution mixture. The ZIF-8 particles were then washed with methanol for 3 times and placed in an oven at 85 °C for 24 h. Lastly, the dried ZIF-8 particles were grinded into finer particles.

2.3. Fabrication of membranes

In this work, pure PSf flat sheet membrane was fabricated using solution casting method as reported in the literature [9]. PSf pellets were firstly dried in an oven at 60 °C to remove excessive moisture. Consecutively, PSf pellets was dissolved in chloroform in a sealed glass bottle and left for 8 h under stirring at room temperature. The polymer solution formulation was set at 10% w/v. The resultant PSf solution was left for degassing overnight at room temperature. The PSf solution was subsequently casted onto a petri dish and covered with a glass plate, then left for 24 h to allow slow solvent evaporation at room temperature. Finally, the membrane film was peeled off from petri dish and dried at 60 °C in vacuum oven to remove the remaining solvent.

ZIF-8/PSf hybrid membrane was also fabricated by using solution blending method [9, 10]. 0.981 g of PSF was dissolved in chloroform in a sealed glass bottle. The polymer solution was left stirring for 8 h at room temperature. In the meantime, 0.009 g of ZIF-8 was added into chloroform solvent in a different sealed glass bottle. The filler suspension was alternately stirred and sonicated for 1 h to disperse the particle. Subsequently, priming method was adapted where 10 % of the PSf solution was added into the filler-solvent suspension, followed by alternate stirring and sonication for 1 h. The step was repeated after adding the remaining 90 % of the PSf solution into filler-solvent suspension. The final mixture solutions were vigorously stirred for 1 h before casted onto the petri dish. The mixture solutions were left at room temperature for 24 h to allow solvent evaporation. The hybrid membrane consisting 1 wt% loading of ZIF-8 was labelled as ZIF-8-1.0/PSf.
2.4. Characterization of Membranes

The morphology of the fabricated membranes was observed under Zeiss Supra 55 VP field emission scanning electron microscope (FESEM). The cross-sections membranes were obtained via freeze-fracturing under liquid nitrogen and sputter-coating with Pt using Quorum Q150R S sputter coater. The density of the membrane samples was measured using Mettler Toledo, OHAUS CP224C density kit. The weight of the membrane samples was first measured in air and high purity ethanol, respectively and the results were then used to determine the density of membrane samples. The fractional free volume (FFV) of the membranes was calculated using equations (3-4) as follows [10]:

\[ V = \frac{M}{\rho} \]  \hspace{1cm} (1)

\[ FFV = \frac{V - 1.3V_v}{V} \]  \hspace{1cm} (2)

where \( V \) is the molar volume of the repeating unit of polymer (cm\(^3\)/mol), \( M \) is to the molecular weight of the repeating unit of polymer (g/mol), \( \rho \) is the density of the membrane (g/cm\(^3\)) and \( V_v \) is the van der Waals molar volume (cm\(^3\)/mol) via Bondi method.

2.5 Transport Behavior of Gases

2.5.1 Gas Permeation

Single gas permeation tests were carried out using a custom-built gas test rig described in detailed from our previous reported work [11]. The CO\(_2\) and CH\(_4\) single permeation tests were performed at constant feed pressure of 5 bar and constant flow rate of 300 ml/min at room temperature. The gas permeability was calculated using equation (3) as follows [12]:

\[ P = \frac{QL}{A(\Delta P)} \]  \hspace{1cm} (3)

where \( P \) is the permeability of gases of membrane sample (Barrer), \( Q \) is the volumetric flow rate of gas through the membrane sample (cm\(^3\)/s), \( L \) is the membrane thickness (cm), \( A \) is the membrane area (cm\(^2\)) and \( \Delta P \) is the pressure drop across the membrane (cmHg), respectively.

The CO\(_2)/\text{CH}_4 ideal selectivity of the membrane was determined by calculating the ratio of CO\(_2\) permeability and permeability of CH\(_4\) as follows:

\[ \alpha_p = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \]  \hspace{1cm} (4)

where \( \alpha_p \) specifies the selectivity of CO\(_2)/\text{CH}_4 and \( P \) refers to the permeability (Barrer).

2.5.2 Gas Sorption

The solubilities of CO\(_2\) and CH\(_4\) were measured where pressure decay principle on a dual-chamber setup is applied [13]. The dual-chamber set-up consists of a sample chamber and a reservoir chamber located next to each other interconnected by a valve. The testing was conducted at a pressure of 5 bar at room temperature.

Prior to testing, the mass of the membrane sample was recorded. The membrane sample is then placed into the sample chamber and the whole set-up was vacuumed overnight. Subsequently, the
reservoir chamber was filled with gas of 5 bar. The amount of gas, \( n_1 \) in the reservoir chamber can be calculated using equation (5), as follows [14]:

\[
 n_1 = \frac{5V_{C1}}{Z_1RT} \tag{5}
\]

where \( V_{C1} \) is the volume of the chamber, \( T \) is temperature of the gas, \( Z_1 \) is compressibility factor of the real gas under 5 bar and \( T \) conditions and \( R \) is the ideal gas constant, respectively.

The valve that interconnects both the sample and reservoir chamber was then opened and the gas starts to flow into the sample chamber and the sorption process by the polymer starts to take place. Once equilibrium point is reached, the final pressure, \( P_2 \) remains constant, and the amount of gas remaining in the reservoir and membrane sample chambers, can be calculated using equation (6), as follows [14]:

\[
 n_{1+2} = \frac{P_2(V_{C1} + V_{C2} - V_S)}{Z_2RT} \tag{6}
\]

where \( V_{C2} \) is the volume of the membrane chamber, \( V_i \) is volume of the membrane sample, \( Z_2 \) is the compressibility factor at \( P_2 \) and \( T \).

The amount of gas dissolved into the polymer, \( n_p \), can be calculated using equation (7) as follows [14]:

\[
 n_p = n_1 - n_{1+2} \tag{7}
\]

The concentration of the gas molecule adsorbed into the membrane was calculated using equation (7) as follows [13]:

\[
 C = \frac{n}{V_p} \times 22414 \tag{8}
\]

where 22414 cm\(^3\)/mol is a numerical conversion factor and \( V_p \) is volume of the polymer sample in the membrane chamber (cm\(^3\)).

The solubility of the membrane was calculated using equation (8) as follows [15]:

\[
 S = \frac{C}{P} \tag{9}
\]

where \( S \) is the solubility (cm\(^3\) (STP)/cm\(^3\).bar) and \( P \) is the pressure of the gas (bar), respectively.

The solubility selectivity was calculated using equation (9) as follows:

\[
 \alpha_{S,CO_2/CH_4} = \frac{S_{CO_2}}{S_{CH_4}} \tag{10}
\]

where \( \alpha_s \) specifies the solubility selectivity of CO\(_2\)/CH\(_4\).

2.5.3 Gas Diffusivity

The diffusivity of the membrane was calculated using equation (10) as follows [15]:
\[ D = \frac{P}{S} \]  \hspace{1cm} (11)

where \( D \), \( P \) and \( S \) are the diffusivity (cm²/s), permeability (cm³ (STP).cm/s.cm².cmHg) and solubility (cm³ (STP)/ cm³.cmHg), respectively.

The diffusivity selectivity was calculated using equation (11) as follows:

\[ \alpha_{D,CO_2/CH_4} = \frac{D_{CO_2}}{D_{CH_4}} \]  \hspace{1cm} (12)

where \( \alpha_D \) specifies the diffusivity selectivity of CO₂/CH₄.

3. Results and Discussion

3.1. Characterization of Membranes

Figure 1 demonstrates the morphology of membranes at cross-sectional view of FESEM images. It can be observed that the ZIF-8 particles were well contained in the PSf polymer. There was no significant formation of interfacial voids between the particles and polymer phase. Overall, the incorporation of ZIF-8 particles has exhibited a good dispersion of particles in polymer matrix and is expected to improve the performance of gas permeation in the hybrid membrane.

![Figure 1. Cross section view FESEM images of membranes (a) pure PSf (b) ZIF-8-1.0/PSf](image)

3.2. FFV of Membranes

Table 1 demonstrates the densities and FFVs of the resultant membranes. The density and FFV of 1.26 g/cm³ and 0.14 were obtained for pure PSf membrane whereas 1.28 g/cm³ and 0.16 were obtained for ZIF-8-1.0/PSf membrane. From Table 1, the hybrid membrane demonstrated lower density and higher FFV in comparison to the pure PSf membrane. The results shown demonstrated that the incorporation of ZIF-8 has led to the increment of accessible cavities in the PSf phase, which increases the FFV value.
Table 1. Density and FFV of fabricated pure PSf and ZIF-8/PSf membranes

| Membranes    | Density (g/cm³) | Fractional free volume (FFV) |
|--------------|----------------|-----------------------------|
| Pure PSf     | 1.28           | 0.14                        |
| ZIF-8-1.0/PSf| 1.26           | 0.16                        |

3.3 Gas Permeation Performance

Permeability measurements were carried out for CO₂ and CH₄ gases at room temperature and 5 bar. Pure gas permeation and selectivity results for CO₂ and CH₄ were shown in Table 2 for pure PSf and ZIF-8-1.0/PSf membranes. CO₂ and CH₄ permeabilities of 6.28 Barrer and 0.27 Barrer were obtained for pure PSf membrane. Meanwhile, CO₂ permeability at 33.12 Barrer was obtained for ZIF-8-1.0/PSf hybrid membrane with CO₂/CH₄ selectivity of 38.8. From the results obtained in Table 2, it was found that ZIF-8-1.0/PSf exhibited higher permeability and selectivity compared to pure PSf membrane. In comparison to the pure PSF membrane, an increment of 527% in CO₂ permeability with the highest CO₂/CH₄ ideal selectivity of 38.8 is achieved for ZIF-8-1.0/PSF. Overall, the addition of ZIF-8 into PSf polymer has resulted in the increment of separation performance of the membrane. The increment of permeability is in agreement with the enhancement of FFV values in the hybrid membrane. The significant improvement of CO₂ permeability is related to the transportation of gas molecules through solution-diffusion mechanism/filler pores through the polymer matrix [16]. Therefore, non-selective voids in the hybrid membrane could be reduced and thus, the gas selectivity increases. The membranes are then proceeded with sorption and diffusivity study.

Table 2. Permeabilities of pure PSf and ZIF-8/PSf membranes

| Membranes    | CO₂ (Barrer) | CH₄ (Barrer) | P_{CO₂}/P_{CH₄} |
|--------------|--------------|--------------|-----------------|
| Pure PSf     | 6.28         | 0.27         | 23.3            |
| ZIF-8-1.0/PSf| 33.12        | 0.85         | 38.8            |

3.4 Gas Solubility

Gas solubility of CO₂ and CH₄ for the resultant membranes at pressure of 5 bar at room temperature is shown in Table 3. The CO₂ and CH₄ solubilities of 35.23x10⁻² cm³(STP)/cm³.cmHg and 10.51x10⁻² cm³(STP)/cm³.cmHg were obtained for pure PSf while 71.43x10⁻² cm³(STP)/cm³.cmHg to 16.25 x10⁻² cm³(STP)/cm³.cmHg were obtained for ZIF-8-1.0/PSf, respectively. CO₂/CH₄ solubility selectivity ranging from 3.35 to 4.40 was also attained for the resultant membranes, where ZIF-8-1.0/PSf membrane demonstrates the highest CO₂/CH₄ solubility selectivity.

Table 3. Solubilities of fabricated pure PSf and ZIF-8/PSf membranes

| Membranes    | CO₂ (10⁻² cm³(STP)/cm³.cmHg) | CH₄ (10⁻² cm³(STP)/cm³.cmHg) | S_{CO₂}/S_{CH₄} |
|--------------|-----------------------------|-----------------------------|-----------------|
| Pure PSf     | 35.23                       | 10.51                       | 3.35            |
| ZIF-8-1.0/PSf| 71.43                       | 16.25                       | 4.40            |
From the results obtained, it is shown the inclusion of ZIF-8 particles into PSf membrane has greater CO\textsubscript{2} sorption capability compared to pure PSf membrane. This is correlated with the increase of free volume of polymer structure and the nature of ZIF-8 particles which are more condensable with CO\textsubscript{2} gas and thus increases the gas solubility in the membrane. Besides, it can be observed that the CO\textsubscript{2} sorption for ZIF-8 based membranes is higher as compared to CH\textsubscript{4} sorption, which is in line with the higher condensabilities of CO\textsubscript{2} compared to CH\textsubscript{4}. Furthermore, higher critical temperature of CO\textsubscript{2} and attraction of CO\textsubscript{2} molecules towards ZIF-8 particles than that of CH\textsubscript{4} also contributes to the enhancement of CO\textsubscript{2} solubility in the hybrid membrane [17, 18].

3.5 Gas Diffusivity

Table 4 shows the diffusivity, D of CO\textsubscript{2} and CH\textsubscript{4} in pure PSf and ZIF-8-1.0/PSf membrane at pressure and temperature of 5 bar and room temperature.

| Membranes       | Diffusivity, D (10\textsuperscript{-8} cm\textsuperscript{2}/s) | Selectivity, α | D\textsubscript{CO2}/D\textsubscript{CH4} |
|-----------------|---------------------------------------------------------------|----------------|------------------------------------------|
| Pure PSf        | 1.78              | 0.26            | 6.99                                     |
| ZIF-8-1.0/PSf   | 3.98              | 0.53            | 8.10                                     |

Based on Table 4, CO\textsubscript{2} and CH\textsubscript{4} diffusivities of 1.78x10\textsuperscript{-8} cm\textsuperscript{2}/s and 0.26 x10\textsuperscript{-8} cm\textsuperscript{2}/s were obtained for pure PSf membrane while 3.98x10\textsuperscript{-8} cm\textsuperscript{2}/s and to 0.53 x10\textsuperscript{-8} cm\textsuperscript{2}/s were obtained for ZIF-8-1.0/PSf, respectively. CO\textsubscript{2}/CH\textsubscript{4} diffusivity selectivity ranging from 6.99 to 8.10 are also obtained for the resultant membranes, where ZIF-8-1.0/PSf membranes demonstrates the highest CO\textsubscript{2}/CH\textsubscript{4} diffusivity selectivity.

From the results obtained, it is shown that the diffusivity of CH\textsubscript{4} is lower in comparison to CO\textsubscript{2}, which is consistent with the known kinetic diameter of CH\textsubscript{4} (3.8 Å) > CO\textsubscript{2} (3.4Å). The embedded ZIF-8 particles in PSf polymer has indirectly created a diffusive path for the CO\textsubscript{2} gas molecule to pass through the membrane with ease, subsequently increased the overall diffusivity [19]. Furthermore, the solubility, permeability and diffusivity of the hybrid membrane are higher than pure PSf membrane, which is consistent with the increment of FFV obtained by ZIF-8 incorporated membrane as discussed in the previous section.

3.6 Performance of Membranes via Robeson’s Upper Bound

In this study, the inclusion of ZIF-8 filler into PSF has resulted in the enhancement of gas separation performance. For further verification, Figure 2 shows the comparison of the separation performance of membranes obtain in this work with reported results for PSF-based MMMs through CO\textsubscript{2}/CH\textsubscript{4} Robeson’s upper bound. ZIF-8-1.0/PSf hybrid membrane fabricated in this work demonstrated higher CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} ideal selectivity in comparison to CO\textsubscript{2}/CH\textsubscript{4} gas pair separation performance of CNTs-PSF [20] and CU\textsubscript{3}BTC\textsubscript{2}/PSF [21] membranes.
Figure 2. Performance comparison between membranes fabricated in the present work and PSF based hybrid membranes reported in literature via CO$_2$/CH$_4$ Robeson’s upper bound.

4 Conclusion

Overall, the incorporation of ZIF-8 particles in PSF has led to the improvement of higher permeability, solubility and diffusivity. It is observed that the transportation of gas molecules through the membranes has improved mostly due to increase of free volume and change of polymer structure after ZIF-8 particles was embedded into PSF polymer, which consequently increases the selectively of the hybrid membrane. It can be concluded that the improvement of CO$_2$ permeability in ZIF-8 based membranes is simultaneous with the enhancement in solubility and diffusivity of the membrane, proving a major role played in both solubility and diffusivity.

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