Performance Enhancement of Polymeric Blend Membranes Incorporation of Methyl Diethanol amine for CO_2/CH_4 Separation

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Summary: For efficient gas separation the membrane technology is rapidly growing day by day and it is more economical and effectual than past technologies. The main objective of this study is to synthesis polymer blend membranes (PBM) using glassy polysulfone (PSU) and rubbery polyvinyl acetate (PVAc) with the addition of methyl diethanol amine for removal of CO_2 from CH_4. The PBM were developed by varying the composition of PVAc ranging from 5 to 20 wt% with 80 to 100 wt% PSU in DMAc solvent. The amine composition was added to the blend and kept at 10 wt%. The present of MDEA in the PBM had increased the CO_2 permeance as compare with the based polymer membranes. However as the operating pressure increased from 2 to 10 bar, the PBM (PSU95%/PVAc5%) with MDEA was found to increase significantly the permeance of CO_2, hence increasing the separation factor from 9.98±0.02 to 30.19±0.49. EPBM was found a very promising to be used for CO_2/CH_4 separation.

Keywords: Gas permeability; Selectivity; Enhanced blend membrane; Methane; Carbon dioxide.

Introduction

Since CO_2 is regarded as a greenhouse gas enhancing the global warming of the earth, its strong absorption in infrared and atmospheric concentration will influence heat balance of the planet. However, a considerable interest has been developed for its capture by different techniques, such as absorption, adsorption, membrane, cryogenic, high gravitational separation and hybrid system [1, 2]. The membrane process has various points of interest over different techniques, easiness of operation, less operational and capital costs, fewer energy requisites, modular configuration, compact size, and environmental compatibility [3]. Pure glassy and rubbery polymer membranes are problematic in natural gas purification due to its physicochemical characteristics. High-temperature gases for example carbon dioxide are known to collaborate vigorously with glassy polymers and exhibit high solubility. Thus plasticization is particularly challenging in natural gas purification. Polysulfone has good chemical, thermal and mechanical stability plus suitable gas performance [4-6]. Considering also its comparatively low price, PSU is suitable for the fabrication of membranes [7].

The soft and flexible polyvinyl acetate polymer operates above T_g with high permeability but low selectivity [8]. Due to macroscopic membrane plasticization, T_g is reduced while considerably increasing softness and ductility [9-12]. Methyl diethanolamine which belong to tertiary amine is widely used for removing of CO_2 from natural gas. It is a relatively strong base having high reactivity with CO_2, low cost of solvent, thermal stability, low corrosive behavior, low energy requirements, higher loading capacity of 1 mole of CO_2 per mole of amine and high stability [13-15]. The chemistry of CO_2-amine solutions has investigated by numerous researchers over many years because of its significant industrial use for CO_2 removal. The collation of membranes and amines for CO_2 removal systems as shown in Table-1 [16].

The general reaction between CO_2 and tertiary amines is;

$$CO_2 + R_3N + H_2O \xleftrightarrow{k_{2,MDEA}\ ,\ K_1} R_3NH^+ + HCO_3^- \quad (1)$$

where R is the functional groups for MDEA $R_3 = CH_2CH_2OH$. The Dankwerts' zwitterions mechanism has earned a significant importance for amine reaction with CO_2 [17-19].

$$R_3N + H^+ \overset{K_2}{\leftrightarrow} R_3NH^+ \quad (2)$$

$$CO_2 + H_2O \overset{K_3}{\leftrightarrow} HCO_3^- + H^+ \quad (3)$$

$$HCO_3^- \overset{K_4}{\leftrightarrow} H^+ + CO_3^{2-} \quad (4)$$

$$CO_2 + OH^- \xleftrightarrow{K_{OH}, K_5} HCO_3^- \quad (5)$$

$$H_2O \overset{K_6}{\leftrightarrow} H^+ + OH^- \quad (6)$$

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Table-1: Collation of membranes and amines for carbon dioxide removal systems.

Operating Issues	Amines	Membranes
User comfort level	Familiar	Still, consider as new technology
Hydrocarbon loss	Low	Losses depend on conditions
Meet low carbon dioxide specification	In ppm levels	Less than 2% economics are challenging
Meet low H_2S specification	Less than 4 ppm	Occasionally
Energy intake	Medium to high	Low and unless compression utilized
Operating price	Average	Low to medium
Maintenance budget	Low to medium	Low and unless compression utilized
Ease of operation	Quite complex	Comparatively simple
Environmental impact	Moderate	Low
Dehydration	Saturated gas product	Dehydrated gas product
	Capital Cost Issue	
Delivery time	Long for vast systems	Construction of modular is faster
On-site installation time	Time-consuming	Short for skid-mounted equipment
Pre-treatment cost	Less	Low to medium
Recycle compression	Unused	Use relies on conditions

Thus, by blending glassy and rubbery polymers using amine solution, the separation ability is improved for the CO_2/CH_4. Alkanolamine has an attraction toward CO_2 and H_2S, permitting this to efficient removal technique for polymeric blend membrane performance. In this study, once the gasses CO_2/CH_4 will go through the EPBM. The amine ingests the most extreme CO_2 penetration rate as compared to CH_4 due to the maximum amount of CH_4 will not be absorbed in the membrane.

Experimental

Materials and Membrane Fabrication

Glassy, rubbery polymers and amine were used in this study for the synthesis of polymeric blend membranes. PSU (polysulfone) Udel® P-1800 was a powdered grade have a glass transition temperature (T_g) of 185ºC was purchased from Solvay Advanced Polymers; L.L.C, U.S. Polysulfone was selected mainly due to its ease of fabrication, good properties like high strength and good thermal stability associated with low cost and ease of availability. This material also offers very good control of pore size, pore size distribution, and good film-forming properties.

PVAc (polyvinyl acetate) average M_w ~100,000, beads were purchased from Sigma-Aldrich, Germany with glass transition temperature (T_g) of 28ºC. PVAc was selected due to its quite flexible strong bonding and non-acidic nature. The chemical structures of the both polymers are shown in Fig 1 [20-22]. The membrane structure and its performance are largely affected by the selection of suitable solvent. After reviewing the literature on the solubility of PSU and PVAc polymers, dimethylacetamide (DMAc) solvent was selected on the basis of its properties. A dimethylacetamide (DMAc) solvent and methyl diethanolamine (MDEA) 99.99% pure was acquired from Merck, Germany. Addition of amine at 10 wt. % is more suitable for the blend because further addition of amine into polymer blend matrix makes membrane brittle. The chemical structures are shown in Fig 1 [21, 23-25].

The polymer blend membrane was synthesized with different composition of PVAc and PSU in DMAc solvent. Firstly, PVAc was allowed to completely dissolve in the DMAc solvent. After that PSU and MDEA was added, for 24 hours continuous stirring. Polymers and amine were dissolving in a solvent under unremitting stirring at room temperature to obtain a homogeneous blend, commonly referred as the casting solution. To remove air bubbles form during blending the solution was allowed to bath sonication in Transonic Digital S, Elma® for 3 hours.

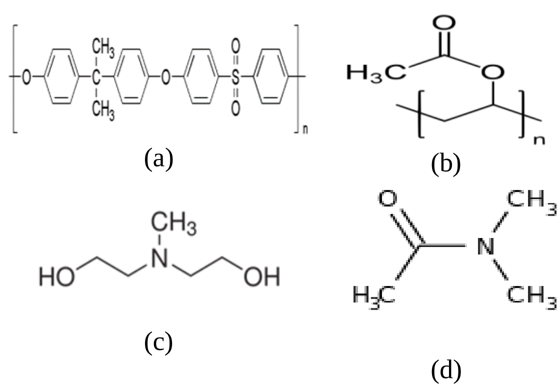

Fig. 1:The structure of (a) Polysulfone, (b) Polyvinyl acetate, (c) Methyl diethanolamine, (d) Dimethylacetamide.

Each polymer was wholly dissolved in the solvent, no indication of agglomeration upon standing the dope solution. Hence, it is a miscible polymer blend. By using casting knife with an opening of 200μm this dope solution was then cast on a glass plate. These cast membranes were placed for 5 days to evaporate the solvent at a room temperature. Then peeled off the membrane from the glass plate for the performance test. The different compositions of polymers and amine of blend membranes are shown in Table-2 and methodology is summarized in Fig. 2.

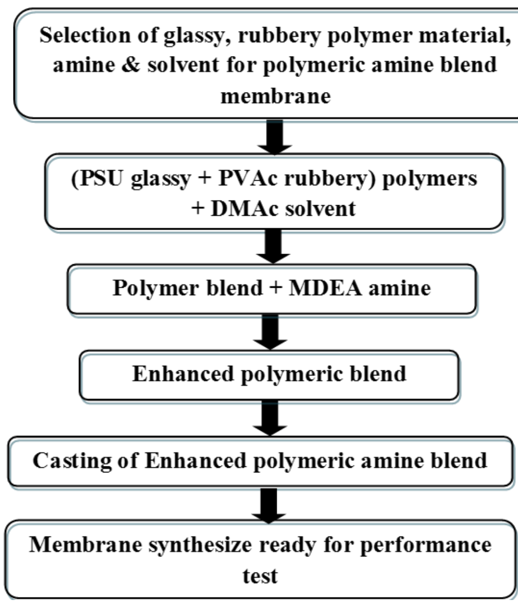

Fig. 2: Research Methodology.

Table-2: Composition of different polymer blend membranes in DMAc solvent.

Membrane	Polymer wt. %		Amine MDEA wt. %
	PSU	PVAc	
01	100%	0%	-
02	0%	100%	
03	95%	5%	10%
04	90%	10%	
05	85%	15%	
06	80%	20%	

Gas Permeance Evaluation

The permeation experiments for pure CO_2 and CH_4 gasses were conducted using gas permeation testing unit CO2SMU (Fig 3) by varying operating pressure from 2 to 10 bar. All tests were carried out at room temperature condition. The CO_2/CH_4 flow rate (0.1cm^3/sec) was controlled by a mass flow controller.

The testing unit contained a stainless steel paired disk with an effective membrane area of 9.60cm^2. It tightened up by O-rings and flanges to reduce the probabilities of a gas leak. Beneath the membrane sample was placed a polypropylene perforated circular sheet and a mesh for sample support. This dead-end membrane module allowed the feed gas streams to enter perpendicularly into the membrane sample. The top half of the membrane module was attached to the upstream of the system for collection of permeate feed and the lower half was attached to the downstream. The retentate wall was close during the test. The upper half and bottom half was coupled together by using five bolts and nuts.

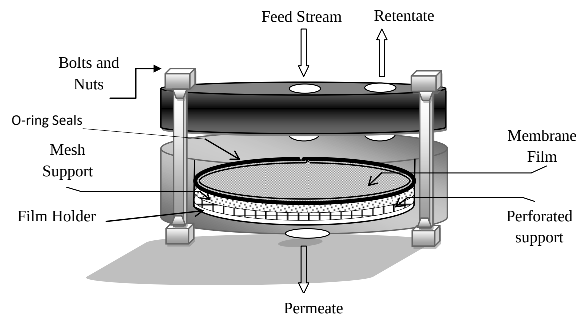

Fig. 3: Schematic illustration of the membrane module.

Bubble flow meter was used to measure the permeate gas flow rate because of its ability to measure accurately at low flow rates of permeate. The testing unit was totally vacuumed to remove any impurities and residual gases at a pressure of ≥ 0.1 bars, before performing the test

Bubble flow meter was used to measure the permeate gas flow rate because of its ability to measure accurately at low flow rates of permeate. The testing unit was totally vacuumed to remove any impurities and residual gases at a pressure of ≥ 0.1 bars, before performing the test. The feed gas was supplied from the gas cylinder equipped with a pressure gauge. A three-way valve was attached as the entry point of the system allowing only one pure gas stream could enter the system at a time. The permeance of the CO_2 and CH_4 gases was calculated by the equation (7) [26]:

$$\frac{P_i}{l} = \frac{J_i}{\Delta P} \quad (7)$$

where i is the gas species, J is the flux of gas, ΔP is the difference partial pressure of gases across the membrane and l denotes the membrane thickness. Hence, the gas selectivity was calculated by the ratios of the CO_2 and CH_4 permeance [27].

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (8)$$

Result and Discussion

Figs 4 and 5 show the permeance of CO_2 and CH_4 against operating pressure across based PSU and PVAc membranes. Figs 4 and 5 show that within the pressure range, pure PSU membrane presented a decreasing trend of permeance with increasing feed pressure. Here in the Fig, the CO_2 and CH_4 permeance decreased from 7.40±0.12 to 3.87±0.2 GPU and 1.05±0.05 to 0.34±0.1 GPU with an increase in the pressure from 2 to 10 bar for pure PSU membrane. The trend for slight permeance decreases with increased operating pressures indicated the absence of PSU plasticization [28, 29]. As the glassy polymer is a combination of crystalline and amorphous phases, the crystallites effort as an effective cross-linking and decreases the available area for permeation, thus permeance of PSU decreases [29, 30].

Figs 4 and 5, pure PVAc membrane shows high permeance, caused by the paucity of polar groups, a low degree of crosslinking and absence of crystallinity. On the other hand pure PVAc membrane, the permeance of CO_2 (14.48±0.01 to 40.24±0.08 GPU) and CH_4 (3.34±0.1 to 15.09±0.08 GPU) increases with the increase of pressure (2-10 bar). Due to PVAc membrane that exists above T_g possess a large intersegmental polymer chain motion [31, 32]. Polyvinyl acetate (PVAc) appears to be one of the most interesting compounds for blending because of its polarity and CO_2 affinity amongst the other proposed polar structures.

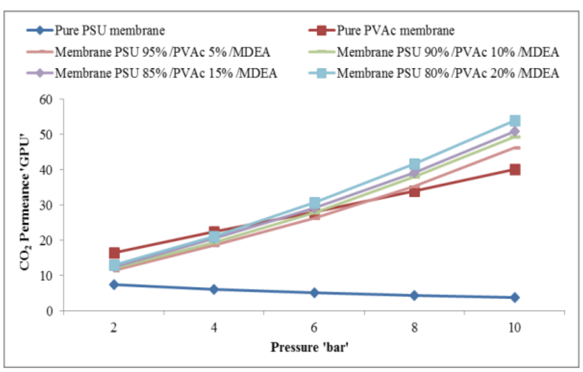

Fig. 4: Effect of CO_2 permeance on various composition of PVAc in PSU membrane with MDEA amine at different feed pressures.

Fig 4 and 5 shows that the polymeric blend membrane illustrated different permeation behavior with the addition of MDEA. With the addition of the MDEA 10 wt% in the PSU/PVAc (95%/5% to 80%/20%) membranes, the CO_2 permeance increased from 11.02±0.11 GPU (48.85%) to 13.05±0.15 GPU (76.24%), respectively at the 2 bar feed pressure. High CO_2 permeance with increasing PVAc composition was due to the rising affinity of CO_2 towards the blended membrane and because CO_2 acquires a non-polar, linear structure with a comparatively smaller kinetic diameter (3.3 Å) compared to the slow moving CH_4 molecule's tetrahedral structure and kinetic diameter of 3.8 Å [33-35].

Similarly, for the slow moving CH_4 gas, the permeance also increased. The CH_4 permeance slightly increased in various compositions of PSU/PVAc with MDEA amine membrane, PSU 95%/PVAc5%/MDEA, from 1.13±0.01 GPU to 1.51±0.01 GPU respectively with pressure increases from 2 to 10 bar as shown in Fig 5. This increased permeance was due to the addition of MDEA and disruption in the polymer's chain packing [36, 37]. This incorporation of MDEA blend in the polymeric membrane caused an enhanced gas permeance. The pressure difference across the membrane increases the volume of CO_2 gas across the membrane's surface, increasing the formation rate of CO_2–amine complexes. Hence, most amine molecules became involved in CO_2–amine interactions as the amine carrier concentration gently reached a state of saturation. Transporter saturation with a gradual reduction in gas flux under increased pressure generally describes the behavior of facilitated transport membranes [38-41]. Morphology of homogenous polymer blend, the amine molecules that occupy the micropores will increase the CO_2 adsorption of these materials due to the well-known interaction between CO_2 and $–NH_2$ groups [42].

Fig 6 shows the selectivity CO_2/CH_4 of based PSU and PVAc membrane at various feed pressures. The CO_2/CH_4 selectivity of pure PSU membrane increased with rising pressure due to small inter-segmental gaps representing higher T_g and resistance to plasticization [43-45]. Chain motion is limited due to bond vibrations in a glassy state. Density-wise, the glassy state deceits between the crystalline state parallel to maximum possible density and the rubbery state. Glassy polymers have high perm-selectivity and therefore, suitable for gas separation [46-48]. Furthermore pure PVAc membrane, the selectivity of CO_2/CH_4 decreases with increasing the pressure caused by the paucity of polar groups, low crosslinking, and the absence of crystallinity [32].

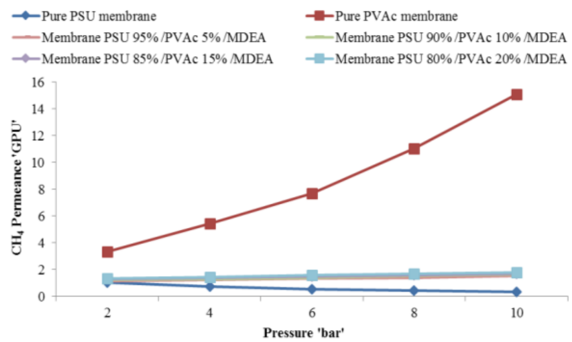

Fig. 5: Effect of CH_4 permeance on various composition of PVAc in PSU membrane with MDEA amine at different feed pressures.

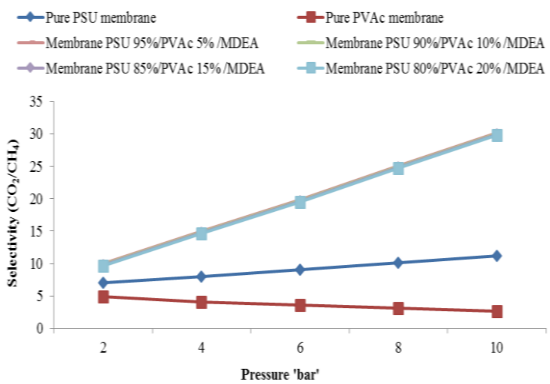

Fig. 6: Effect of selectivity CO_2/CH_4 on various composition of PVAc in PSU membrane with MDEA amine at different feed pressures.

Fig 6 also shows the ideal selectivity for the polymeric amine blend membranes at 2-10 bar feed pressure. All blend membrane showed an increasing trend in the selectivity with the feed pressure increase up to 10 bars. The maximum selectivity for PSU95%/PVAc5%/MDEA (9.98±0.02–30.19±0.49) with increased pressure from 2 to 10 bars under the operating conditions.

With the addition of MDEA in the PSU/PVAc blend with different compositions, increase the permeance and selectivity. Pressure, carrier concentration, and 'cross-linking agent content' are main factors that significantly affected the properties of CO_2 across these membranes.

Robenson Plot Comparison between Present work and Previous Studies in terms of CO_2 Permeability and Selectivity CO_2/CH_4

Various polymers have been researched for gas separation applications yet few have found commercial achievement. These comprise of rubbery polymers such as polyvinyl acetate, and glassy polymers such as polysulfone, polyphenylene oxide, polyimides and cellulose acetate. Suitable membrane materials must show good selectivity for certain species in a mixture to attain efficient separation and permeability while minimizing the required membrane area. Generally, polymer membranes offer a trade-off between permeability and selectivity. Rubbery polymer membranes have low selectivity and high permeability and vice versa for glassy polymer membranes. Even with their mechanical strength, reproducibility and efficient processing capacity, dense membranes are not very attractive because of the upper bound trade-off between selectivity and permeability.

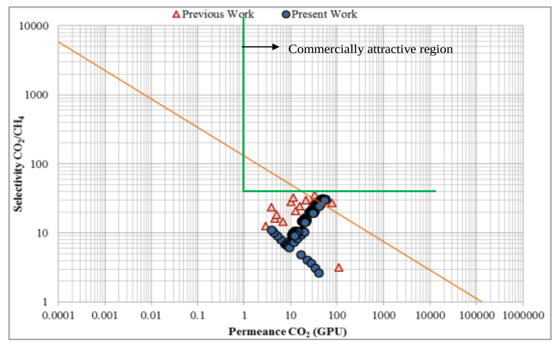

Fig. 7: Log-Log Plot, CO_2/CH_4 selectivity versus CO_2 permeance of previous work and present work.

Robeson posited upper bound trade off in 1991. It was revisited in 2007, which shows the graph of permeability vs. selectivity [49, 50]. These trade-off plots discuss ideal behavior and do not responsible for plasticization or other effects [51-53]. Fig. 7 shows the selectivity for CO_2/CH_4 achieved from the ratio of pure gas permeance plotted between CO_2 permeance for all the PSU, PVAc and blends membrane then report of previous [29, 54-64] and present work. Robeson plot demonstrates the today's commercial membrane performance when natural gas used with high-pressure. The correlation of the log-log CO_2/CH_4 selectivity versus permeability of CO_2. The values obtained for the pressure of 10 bar shows a positive response in reading the prior upper bound values. This enhancement in the properties has been achieved due to the addition of amines viz mono, di, tertiary amines (MEA, DEA, MDEA) respectively. Mostly, industrial membranes in use offer half the selectivity held by the best upper bound materials.

Conclusion

The enhanced polymeric blend membrane has been successfully developed. The performance was evaluated by gas permeation behavior, which is an effective performance measure for evaluating the quality of membrane. Compared to pure PSU membrane, the polymeric blend membranes exhibit improve in CO_2 permeance due to the presence of PVAc/MDEA. As compared to pure PVAc membrane, exhibit improved selectivity because of the presence of PSU/MDEA in the blend. The values obtained for the pressure of 10 bar shows a positive response in reading the prior upper bound values. This enhancement in the properties has been achieved due to the addition of MDEA amine.

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