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Research Article

Gas Permeability and Selectivity of Synthesized Diethanol Amine-Polysulfone/Polyvinylacetate Blend Membranes

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Abstract: The control of anthropogenic carbon dioxide release is one of the most challenging environmental problem faced by developing countries, as the interfering of atmospheric carbon dioxide level and climate revolutionize. An rising technology is the membrane gas separation, which is more dense, energy efficient and possibly more economical than past technologies, such as solvent absorption. Amine has a greater efficiency for removal of carbon dioxide. The blending technique not only provides improved chemical and thermal stability but is also efficient enough to improve the perm-selective properties with economical viability. In this study, research will be carried out to study the gas permeability behavior of glassy Polysulfone and Polyvinyl acetate rubbery polymeric blend membranes with diethanol amine. Polymeric amine blend membranes with different blending ratios were prepared in dimethyl acetamide solvent, flat sheet membrane were developed with enhance properties. We were studied PSU/PVAc blend with DEA amine using a gas permeability application for CO_2 and CH_4 at different feed pressures.

Keywords: Blend membrane, carbon dioxide removal, DEA amine, gas permeability, natural gas, PSU polymer, PVAc polymer, selectivity

INTRODUCTION

The existence of CO_2 in natural gas decreasing its calorific value for incomplete combustion as well as environmental issues occur like its emission to atmosphere is increasing Global Warming and Green House Effects, need to be removed and increases the worth value. A wide study of gas transport properties for PSU has been conducted by Paul and co-workers (Barbari *et al*., 1988). One of the most extensively patented polymeric materials are polysulfones (Chiao, 1988; Bikson *et al*., 1985; Coplan *et al*., 1983; Rose, 1981a, b; Quentin, 1977; Quentin, 1973). They are regarded as amongst the most chemically and thermally robust thermoplastic polymers available; and polysulfones have been extensively applied to gas separation (Chiao, 1989; Bourganel, 1977; Graefe *et al*., 1975; Kawakami *et al*., 1991). Poly Vinyl Acetate (PVAc.) is an important polymer, exhibiting piezoelectric, pyro-electric and ferroelectric properties (Kroschwitz, 1989). The typical advantages of PVAc are flexibility, formability and low density.

Alkanolamines are widely used as the absorbents for CO_2 capture. Amine-containing chemical solvents are usually favored when the partial pressure of CO_2 within the feed gas is comparatively low or if once CO_2 is reduced to a very low concentration within the treated gas. Physical solvents are to be used at high CO_2 pressures within the feed gas and when deep CO_2 removal is not required.

Several researchers have investigated the chemistry of CO_2-amine solutions over the years due to its important industrial application for CO_2 removal from gas streams. Table 1 shows the comparison of amines and membranes for CO_2 removal systems.

The overall reaction between CO_2 and secondary amines is:

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+ + R_1R_2NCO_2^- \quad (1)$$

where, R represents the functional groups for DEA, $R_1 = R_2 = -CH_2CH_2OH$. The Dankwerts' zwitterions mechanism has recently become one of the most widely accepted mechanism for amine reaction with CO_2 (Blauwhoff *et al*., 1984; Versteeg and Van Swaaij, 1988; Versteeg *et al*., 1990; Versteeg and Oyevaar, 1989; Glasscock *et al*., 1991; Littel *et al*., 1992):

$R_1 = R_2 = -CH_2CH_2OH$
$R_1R_2NH + CO_2 \leftrightarrow R_1R_2NH^+COO^-$ (Zwitter ion)
$R_1R_2NH^+COO^- + R_1R_2NH \leftrightarrow R_1R_2NCOO^-$ (Carbamate) $+ R_1R_2NH_2^+$
Overall reaction is:
$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+$

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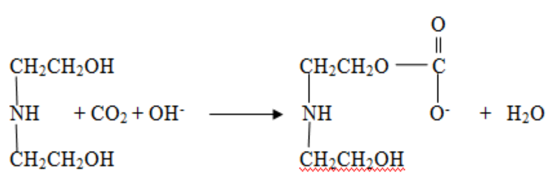
Table 1: Comparison of amines and membranes for CO_2 removal systems (Baker, 2004)

Operating issues	Amines	Membranes
User comfort level	Very familiar	Still considered new technology
Hydrocarbon losses	Very low	Losses depend upon conditions
Meets low CO_2 spec.	Yes (ppm levels)	No (<2% economics are challenging)
Meets low H_2S spec.	Yes (<4 ppm)	Sometimes
Energy consumption	Moderate to high	Low, unless compression used
Operating cost	Moderate	Low to moderate
Maintenance cost	Low to moderate	Low, unless compression used
Ease of operation	Relatively complex	Relatively simple
Environmental impact	Moderate	Low
Dehydration	Product gas saturated	Product gas dehydrated
Capital cost issues		
Delivery time	Long for large systems	Modular construction is faster
On-site installation time	Long	Short for skid-mounted equipment
Pre-treatment costs	Low	Low to moderate
Recycle compression	Not used	Use depends upon conditions

Table 2: Experimental data points close to the present empirical upper bound for CO_2/CH_4 separation

Polymer	P (CO_2)	α (CO_2/CH_4)	References
PVSH doped polyaniline	0.029	2200	Hachisuka *et al*. (1995)
Polypyrrole 6FDA/PMDA (25/75) -TAB	3.130	140	Zimmerman and Koros (1999)
Polyimide TADATO/DSDA (1/1) -DDBT	45	60	Yang *et al*. (2001)
Poly (diphenyl acetylene) 3a	110	47.80	Shida *et al*. (2006)
Poly (diphenyl acetylene) 3e	290	31.50	Shida *et al*. (2006)
Poly (diphenyl acetylene) 3f	330	27.50	Shida *et al*. (2006)
PIM-7	1.100	17.70	Budd *et al*. (2005)
PIM-1	2.300	18.40	Budd *et al*. (2005)
Polyimide 6FDA-TMPDA	555.700	22.70	Wang *et al*. (2007)
Polyimide 6FDA-durene	677.800	20.18	Lin and Chung (2001)
6FDA-based polyimide (8)	958	24	Nagel *et al*. (2002)
PTMSF	19,000	4.42	Mizumoto *et al*. (1993)
PTMSF	29,000	4.46	Mizumoto *et al*. (1993)
Polyimide PI-5	190	33.90	Al-Masri *et al*. (1999)
Polyimide 6FDA-TMPDA/DAT (1:1)	130.200	38.90	Wang *et al*. (2007)
Polyimide 6FDA-TMPDA/DAT (3:1)	187.600	33.90	Wang *et al*. (2007)

Its mean:



The amine solution has the potential to purify the natural gas having acid gas (Kerry, 2007). So, by blending a glassy polymer with different amine solutions, the separation ability is enhanced for CO_2/CH_4 mixture. Amine has a natural attraction for both CO_2 and H_2S, allowing this to be a very well-organized and valuable removal process on the performance of polymeric membrane to study high selectivity and high permeability.

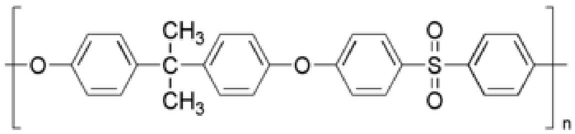
In this study, when the mixture of gases CO_2/CH_4 will pass through the Enhanced Amine Polymeric membrane the amine absorb the maximum carbon dioxide and CO_2 permeation rate will be higher in the membrane and maximum amount of CH_4 will not be absorb in the membrane so the permeation rate of CH_4 in the membrane will be less. Table 2 represents the some experimental data for CO_2/CH_4 separation. So by the following formula the selectivity of membrane will be increase:

$$\alpha\, CO_2/CH_4 = \frac{P_{CO_2}}{P_{CH_4}}$$

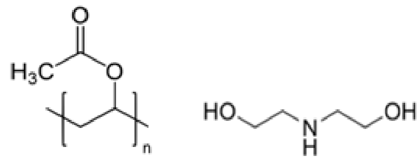
METHODOLOGY

Materials and membrane fabrication: Polysulfone (PSU) Udel® P-1800 having a glass transition Temperature (T_g) of 185°C was acquired from Solvay Advanced Polymers; L.L.C, U.S. PSU was in minced form. Polyvinyl Acetate (PVAc.) average M_w ~100,000 by GPC, beads from Sigma Aldrich having a glass transition Temperature (T_g) 30°C. Diethanol amine and Dimethyl Acetamide (DMAc.) solvent with a purity of 99.99% was purchased from Merck.

In this process, experimentation on blending of glassy and rubbery polymer that was Polysulfone, Polyvinyl acetate and Diethanol amine (Fig. 1) were carried out in solvent Dimethylacetamide (DMAc) (Fig. 2). The blending was 20% weight/weight. The solvent was 80% without amine and 20% polymer of total weight. PSU was pre-heated for one night to remove any moisture content. Initially PVAc. was allow to dissolved in the DMAc. solvent completely. Then glassy polymer and amine was added, continuous



(a) Polysulfone



(b) Polyvinyl acetate (c) Diethanol amine

Fig. 1: Structure of polysulfone, polyvinyl acetate and diethanol amine

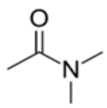


Fig. 2: Structure of Dimethylacetamide (DMAc.)

Table 3: Composition of different polymer blend membranes

Blending 20% W/W	Solvent DMAc. 80%	Polymer 20% PSU (%)	Polymer 20% PVAc. (%)	Amine DEA (%)
	100%	100	0	-
		0	100	
	90%	100	-	10
		95	5	
		90	10	
		85	15	
		80	20	

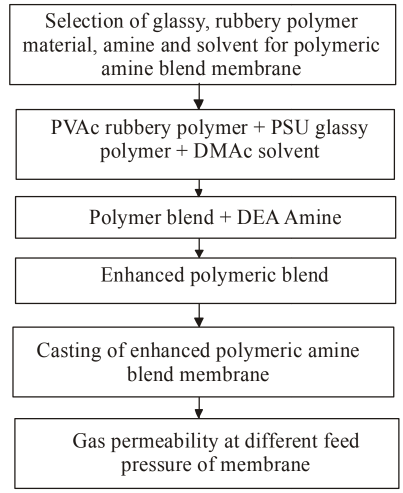


Fig. 3: Research methodology

stirred for 24 h at room temperature to obtain a homogeneous mixture. To obtain a clear solution followed by bath sonication in Transonic Digital S, Elma® for 1 h. for the purpose of degassing. Both polymers were completely dissolved in solvent and there was no indication of settling upon eminence the solution thus we can say that it was a miscible polymer blend. This dope solution was casted on a glass plate by using casting knife with an opening of 200 μm. The casted membranes were placed in a room temperature for 5 days to evaporate the solvent. The developed membranes were peeled off from glass plate for study the industrial application. The different compositions of polymeric blend membrane are shown in Table 3 and methodology defines in Fig. 3.

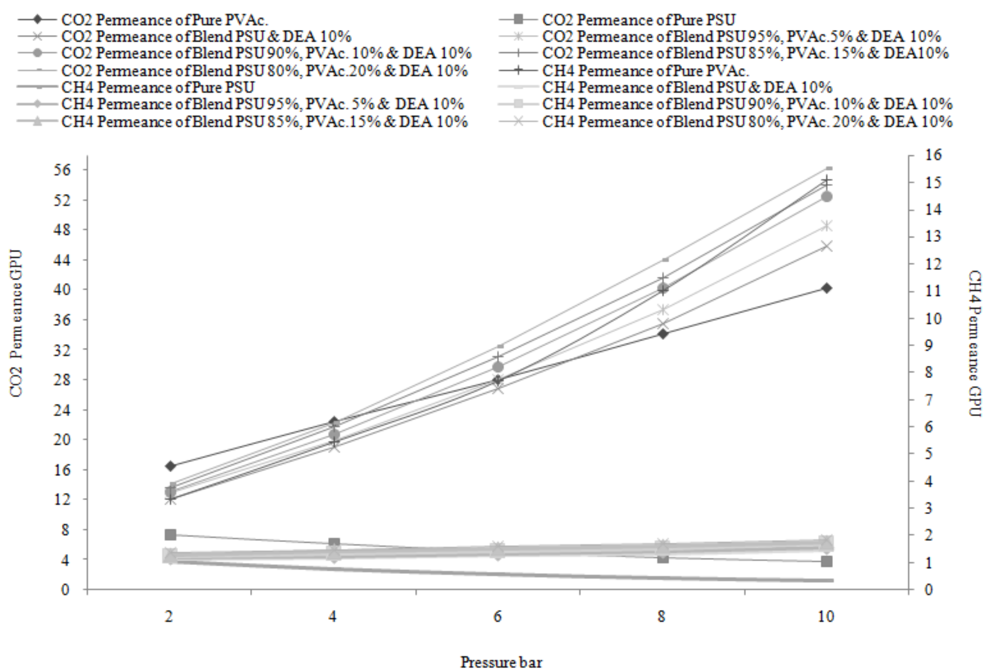


Fig. 4: CO_2 and CH_4 permeance of polymeric DEA amine blend membrane in various feed pressures

RESULTS AND DISCUSSION

Gas permeability: Natural gas purification applications require CO_2 separation from CH_4. We evaluated the feasibility of using PSU/PVAc/DEA amine membranes for this purpose by measuring the permeance of a CO_2/CH_4 mixture under different operating pressures. The apparatus used for the

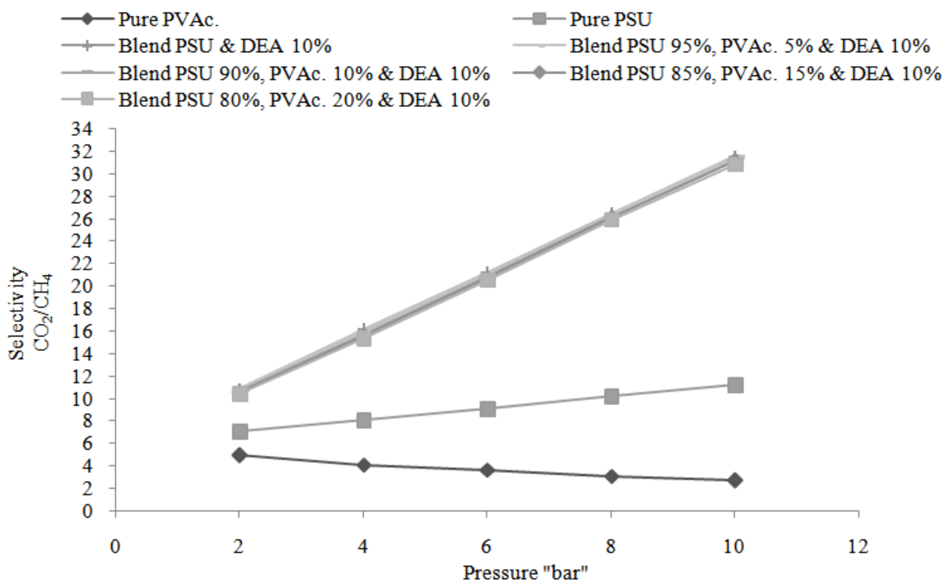


Fig. 5: CO_2/CH_4 selectivity's of polymeric DEA amine blend membrane in various feed pressures

Table 4: CO_2 permeability of polymeric DEA amine blend membranes

	CO_2 permeance 'GPU'						
Pressure 'bar'	Pure PSU	Pure PVAc.	Membrane PSU and DEA 10%	Membrane PSU 95%, PVAc. 5% and DEA	Membrane PSU 90%, PVAc. 10% and DEA	Membrane PSU 85%, PVAc. 15% and DEA	Membrane PSU 80%, PVAc. 20% and DEA
2	7.406534	16.48457	12.0606055	12.8954466	13.0699452	13.561180	14.1415659
4	6.153237	22.42997	19.0131683	19.9369583	20.6858260	21.723696	22.2945603
6	5.090528	28.01494	26.9159622	28.0149406	29.7683650	31.164796	32.5208401
8	4.342335	34.08332	35.4697637	37.4144707	40.1930101	41.577140	44.0881192
10	3.870025	40.24454	45.9096759	48.6678154	52.4271247	54.005576	56.3062617

Table 5: CH_4 permeability of polymeric DEA amine blend membranes

	CH_4 permeance 'GPU'						
Pressure 'bar'	Pure PSU	Pure PVAc.	Membrane PSU and DEA 10%	Membrane PSU 95%, PVAc. 5% and DEA	Membrane PSU 90%, PVAc. 10% and DEA	Membrane PSU 85%, PVAc. 15% and DEA	Membrane PSU 80%, PVAc. 20% and DEA
2	1.05458	3.347096	1.11626407	1.19849727	1.22058660	1.2860841	1.36017249
4	0.76509	5.458785	1.17861869	1.24761992	1.31556686	1.3973487	1.45256893
6	0.56126	7.692395	1.26873568	1.33001752	1.42492497	1.5005852	1.58467065
8	0.42655	11.02978	1.34441479	1.41994576	1.53364964	1.5952201	1.70250249
10	0.34663	15.09170	1.45740774	1.54910818	1.67797626	1.7380160	1.82690184

Table 6: Selectivity CO_2/CH_4 of polymeric DEA amine blend membranes

	Selectivity CO_2/CH_4						
Pressure 'bar'	Pure PSU	Pure PVAc.	Membrane PSU and DEA 10%	Membrane PSU 95%, PVAc. 5% and DEA	Membrane PSU 90%, PVAc. 10% and DEA	Membrane PSU 85%, PVAc. 15% and DEA	Membrane PSU 80%, PVAc. 20% and DEA
2	7.0231820	4.925036	10.8044376	10.7596796	10.7079213	10.544551	10.3968915
4	8.0425370	4.108967	16.1317383	15.9799936	15.7238880	15.546367	15.3483665
6	9.0698130	3.641901	21.2147910	21.0635877	20.8911807	20.768429	20.5221445
8	10.18011	3.090119	26.3830508	26.3492253	26.2074264	26.063576	25.8960674
10	11.16474	2.666667	31.5009141	31.4166667	31.2442589	31.073118	30.8206278

permeation experiment was the CO_2SMU where CO_2/CH_4 flow rate (0.1 m^3/sec) was controlled by a flow meter/controller. These trials were carried out at room temperature (298±2 K) under ambient pressure (101±2 kPa).

Observed gas permeability as well as structural, physical compatibility and properties of PSU, PVAc and DEA amine blends make homogenous blend membranes very attractive. According to Houde *et al*. (1992), pure PSU polymer shows different CO_2 permeation characteristics. Compared to a pure PSU membrane, the blend membranes exhibited improved CO_2 permeability and selectivity due to the presence of the rubbery polymer (PVAc) and DEA amine. Our gas permeability study of PSU/PVAc/DEA amine blended membranes were evaluated by using pure gas (CO_2 and CH_4) under five different feed pressures of 2, 4, 6, 8 and 10 bars, respectively.

Figure 4 relates to Table 4 and 5 and shows that the permeance of CO_2 and CH_4 for a pure PSU membrane was reduced with increased pressure. On the other hand, a pure PVAc membrane's CO_2 and CH_4 permeance rose with increased pressure. We observed that as the 10% DEA amine and percentage of PVAc increased in PSU, the permeability of both CO_2 and CH_4 also rose with pressure increases.

Figure 5 relates to Table 6 showing that pure PSU's selectivity for CO_2/CH_4 rose with increased pressure. On the other hand, pure PVAc membrane's selectivity for CO_2/CH_4 decreased with increasing pressure. As for our synthesized blended membranes, as 10% DEA amine and the percentage of PVAc increased in PSU, the membrane's selectivity also rose with increased feed pressure.

We therefore concluded that a pure PSU glassy polymeric membrane, a pure PVAc rubbery polymeric membrane and a polymeric amine membrane were not only completely miscible but also characteristically increased a blended membrane's permeance for CO_2 as feed pressures rose while also demonstrating increased selectivity.

CONCLUSION

Polymeric Amine Blend Membrane could be an advanced technique for gas separation. Blending of friendly environmental polysulfone, polyvinyl acetate with diethanol amine has proven to be an appropriate tool to produce novel materials with combined characteristics in having each improved application properties and low value benefits in material performance. In addition, as DEA amine was added we also observed remarkable improvement in the membrane's permeability and selectivity of/for CO_2; most likely due to soluble nature of CO_2 in DEA amine, indicating that the presence of amine enhanced carbon dioxide solubility across the membrane. Therefore, PSU/PVAc./DEA polymer blends may be considered a new, economical, high performance raw material suitable for the preparation of gas separation membranes for the separation of CO_2 from CH_4 with enhanced permeation and selectivity. In the future work we have a tendency to conjointly add the inorganic fillers like carbon molecular sieves; zeolites in blend which is further enhanced the polymeric amine blend membrane. Therefore, this will increase the economic process in gas trade.

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