



Research Paper

Separation of Carbon Dioxide by Potassium Carbonate based Supported Deep Eutectic Liquid Membranes: Influence of Hydrogen Bond Donor

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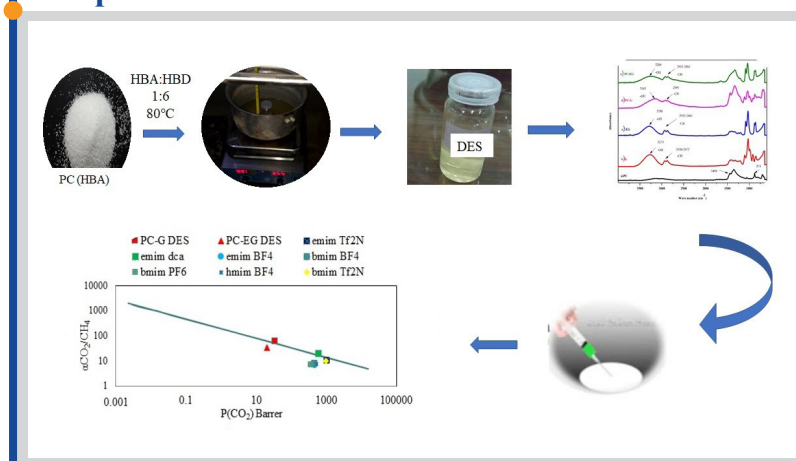
CO₂ separation

Supported liquid membranes

Highlights

- Preparation of highly selective potassium carbonate based Deep Eutectic Solvents
- High CO₂/CH₄ selectivity for a supported DES based liquid membrane
- Supported liquid membranes showed excellent stability under different conditions

Graphical abstract



Abstract

This article focuses on the study of potassium carbonate (PC) based deep eutectic solvents based supported liquid membranes (DES-SLMs) for CO₂ separation. Two types of DESs were synthesized by mixing and subsequently heating PC with glycerol or ethylene glycol separately. The mechanism of interaction was inferred from the spectral analysis (FTIR) whereas thermal study (TGA) was performed to analyze the stability of the membrane. Experiments were carried out to analyze the permeability and separation factor of the membranes. The PC-Glycerol based SLM reported permeability of 34 Barrer and ideal selectivity of 59 while PC-Ethylene Glycol based SLM showed permeability of 20 Barrer and separation factor of 34 under similar operating conditions. Systematic analysis was made for some of the important operating parameters affecting the separation efficacy such as feed composition and temperature. The acquired results were compared with the current state-of-the-art by plotting on the well-known Robeson's upper bound plot. The current efforts of exploitation of PC-DES membrane will lead to new prospective for effective mitigation of CO₂ from the gas mixture.

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1. Introduction

The CO₂ emissions into the environment and atmosphere pose a threat to the human race due to their role in global warming [1]. The extensive use of fossil fuels has resulted in the rise of CO₂ in the environment [2,3]. Moreover, the CO₂ in the biogas, natural gas and syngas decreases the heating value [4]. It is of great importance for the researchers to develop new materials not only for mitigation of CO₂ but also to improve the quality of fuel as well [5]. The conventional technologies for CO₂ separation are absorption [6], adsorption [7] and cryogenic distillation [8]. Among these,

CO₂ absorption using amine-based solvents is the most common industrial technique. However, this technology has its own limitations such as solvent degradation and loss due to evaporation, need for regeneration and corrosion of vessels, that eventually increase the operating cost [9,10].

Polymeric membranes have a promising potential to replace the prevalent techniques for CO₂ removal. Their application has several inherent benefits such as low operating cost, minimal energy requirement, compact size, environment benign process and so on [11]. However, the separation

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efficiency of polymeric membranes is restricted by the trade-off between separation efficacy and permeability presented by the so-called Robeson upper bound curve 2008 [12,13]. The application of porous membrane supports, immobilized with highly selective ionic liquids (ILs), has proved to be promising strategy to fabricate high performance membranes [14,15]. These supported liquid membranes (SLMs) provide a unique feature of combined extraction and stripping steps thereby reducing the regeneration costs [16-18]. With negligible volatility and relatively high thermal stability, ionic liquids are poised to replace the volatile solvents [19,20]. They can be prepared by the suitable selection of cations and anions to achieve high affinity for CO₂ [14,21]. Despite their obvious advantages, ionic liquids face certain challenges in terms of their potential commercial application such as high viscosity leading to lower mass transfer, high toxicity and costs [22].

DESs are the prospective substitute to ILs due to their advantageous attributes like biodegradability, relatively low costs and elevated affinity for CO₂ [23,24]. DESs are the low melting mixture of two or more constituents interacting with each other by hydrogen bonding. They can be designed by the combination of H₂-bond acceptors and H₂-bond donors [25,26]. Choline Chloride-ChCl based DESs were investigated as a material for CO₂ capture by Li et al. Results depicted an increase in solubility of CO₂ with the raise in pressure, and decline in solubility with uptrend of temperature [27]. In another study, DES based on phosphonium and ammonium with different HBDs like 1,4 butanediol, triethylene glycol, glycerol, and ethylene glycol were evaluated. The testified outcomes showed that the kind of salt and HBAs and HBDs mole ratio have noteworthy influence on CO₂ solubility [28]. In recent study, we studied the SLMs prepared with betaine based Natural Deep Eutectic Solvents (NADESSs) for the mitigation of CO₂ from CO₂/CH₄ & CO₂/N₂ mixtures. The results displayed that the permeability of CO₂ was augmented from 25.5-29.3 Barrer while the separation efficacy was also enhance upto 56 on replacement of HBDs from Tart to Ma [29]. The polymerized DES was evaluated by Ishaq et al. for removal of CO₂ from the gas mixture of CO₂/N₂ & CO₂/CH₄. The separation efficacy and permeability were investigated for single and mixed gases. The results revealed that the PDES-SLMs revealed high separation factor of 55 and 60 for (CO₂/CH₄) & (CO₂/N₂) respectively [30].

Alkali metal-based salt has been stated in literature for synthesis of DESs. The potassium carbonate salt is mixed with HBDs such as glycerol and ethylene glycol [31,32]. Potassium carbonate is also used as a promoter for absorption of CO₂ for primary or secondary amines [32,33]. It is well established that aqueous solutions of alkaline materials naturally can absorb CO₂. Based on this property, it acts as HBA and has been proposed to make DES aimed at CO₂ capture.

In the current study, DESs-SLMs were synthesized by mixing potassium carbonate (PC) (HBA) with two different HBDs glycerol and ethylene glycol. This is the first study reporting potassium carbonate based DES-SLMs for CO₂ separation. The prepared DESs were characterized by FTIR to find the interaction mechanism. The DES was then incorporated in the micro porous PVDF membrane support for evaluation of CO₂ capture. The operating parameters effect were also investigated on the performance of immobilized membranes. The separation efficiency of the synthesized membranes was compared with the well-known and much studied competing imidazolium based ionic liquids to determine its potential as an alternative to the conventional ionic liquids.

2. Experimental

2.1. Chemical Reagents

Anhydrous potassium carbonates (PC) having purity 99.995% was procured from Sigma Aldrich. Other chemicals used in this research were glycerol (G) and ethylene glycol (EG) and were procured from MP Bio medicals. N-Methyl-2-Pyrrolidone (NMP) was purchased from Thermo Fisher scientific. Polyvinylidene fluoride with an average molecular weight ~ 180,000 in pellets form was procured from Sigma Aldrich, Germany. Analytical grade chemicals were used in this study and were employed as obtained without any treatment.

2.2. Fabrication of PC-based DES

PC-DESs were synthesized by mixing PC as salt (HBA) with glycerol-(G) (HBD) and ethylene glycol-EG (HBD) in a 1:6 mole ratio [32]. The mole ratio of HBA and HBD were adjusted to obtain homogenous and visibly clear solution. Both the mixtures were transferred in separate glass vials with constant stirring and heated for 2 hours at 80 °C until a colorless liquid

appeared. The homogenous mixtures were then cooled and collected for characterization.

2.3. Preparation of PC-DES-SLMs

Synthesis of PC-DES-supported liquid membranes were carried out by the immobilization of PC-DESs onto microporous polyvinylidene fluoride (PVDF) membranes. The microporous PVDF substrate was synthesized by the technique of phase inversion. Solution (15 wt%) was synthesized in (NMP). The prepared mixture was constantly agitated for duration of 24 hours at ambient temperature. An automatic membrane casting device Electrometer, (UK) was used for casting a homogenous solution. The air gap was adjusted to obtain thickness of 250 micrometer. Coagulation process was completed by phase inversion technique which was carried out by immersing cast film in water for 20 minutes.

The cast film was then desiccated in an oven for a whole day to get rid of any moisture and vaporizable contents. Subsequently, a 2.26 in² (14.58 cm²) coupon of membrane was cut and used for SLM fabrication. DES was layered on upper area of the substrate. It was put into a stainless-steel cell (Sterlitech HP 4750). Nitrogen at 2 bar pressure was introduced into cell on the membrane surface for 1 hour to adequately fill the substrate pores with the DES. The surplus DES was removed from the exterior of membrane support. The membranes were named as PC-G (potassium carbonate-glycerol) and PC-EG (potassium carbonate-ethylene glycol) based DES.

2.4. Characterization techniques

The interaction mechanism of potassium carbonate (PC), G and EG after the synthesis of DESs were investigated by studying FTIR spectra on Thermo-Nicolet 6700 P FTIR Spectrometer (USA). Spectra scan was recorded in the wave number (4000-600) cm⁻¹ at an 8 cm⁻¹ resolution. Thermal analysis was carried out to determine the temperature suitability of DESs. These samples were put in the TGA pan at ambient conditions and the temperature was increased upto 300 °C with a temperature elevation of 10 °C min⁻¹ under the nitrogen atmosphere using TGA instrument (NETZSCH TG 209F3). The separation efficacy of CO₂/CH₄ for DES-SLMs was examined on a gas permeation setup. The separation performance of the pure and mixed gas was investigated by the Gas Chromatography unit (GC) (YL Instruments, South Korea). The gas separation setup is illustrated schematically in Figure 1. The procedure and details of experiment are provided elsewhere [34]. The DES-SLMs were tightly positioned on a porous metallic support. The gas was entered at a flow rate (Q) of (1dm³/min) into the membrane setup with the help of a flow controller (Sierra instrument, USA). The feed in the temperature range of 298K-338K was investigated to determine the temperature's effect on the permeability and separation factor. The permeation test was triplicated for checking the repeatability; average results of three readings are reported in this article. Fick's Law (equation.1) has been used to compute the permeability, 'P' in (Barrer) of DES-SLM

$$P = D S \quad (1)$$

where the coefficient of diffusion is depicted by 'D' and 'S' is the solubility coefficient [35,36].

The diffusion co-efficient (D) was computed by the time lag method by expanding the permeate in a calibrated auxiliary cylinder and plotting the rise in pressure with time. The coefficient was calculated according to the following relation:

$$D = \frac{l^2}{6\theta} \quad (2)$$

where 'l' is the DES-SLM's thickness and θ is the intercept on x-axis of the plot.

Separation factor of the membrane was determined by making the comparison of gas permeabilities (A&B) and is presented by the following expression.

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

3. Results and discussion

3.1. Spectral Study (FTIR) of PC-DESs

The FTIR analysis was recorded to investigate the vibrational bands of potassium carbonate (PC), glycerol (G), ethylene glycol (EG), PC-G DES and PC-EG DES. The frequencies of these compounds were presented by (a-e) spectra as shown in Figure 2. In spectra of PC, the peaks were observed between 874cm^{-1} to 1450cm^{-1} that corresponds to PC [37]. The spectra (b) of glycerol (G) showed the peak at 3273cm^{-1} that lies in the range of $3200\text{-}3600\text{cm}^{-1}$ and is ascribed to -OH group [38]. The CH stretch of alkanes is indicated by the frequency in the range $2937\text{-}2880\text{cm}^{-1}$ [39]. The wave number at $2930\text{-}2872\text{cm}^{-1}$ in the spectra corresponds to CH group in glycerol (G) used in this study. The spectra (c) of ethylene glycol (EG) show the frequencies at 3288

cm^{-1} and $2935\text{-}2861\text{cm}^{-1}$ is for -OH group and CH group stretch, respectively. In the FTIR spectra (d) of PC-G DES shift of characteristic peaks were observed towards a slight lower wave number due to hydrogen bonding as compared to the original FTIR spectrum of glycerol (G). The peaks shift at 3163cm^{-1} of -OH and 2895cm^{-1} of CH group corresponds to PC-G DES. Similarly, in the (e) spectra of PC-EG DES the transition of peaks was also observed towards a slight lower wave number as compared to the original FTIR spectrum of ethylene glycol (EG). The transition of peaks at 3266cm^{-1} of -OH and $2913\text{-}2861\text{cm}^{-1}$ for alkanes corresponds to ethylene glycol (EG) in PC-EG DES. The shift of peaks of ethylene glycol (EG) depicted the interaction between PC and ethylene glycol (EG) in the PC-EG DES. Therefore, the shift of -OH peaks were observed in the spectrum of PC-G and PC-EG revealing the hydrogen bond interaction between HBDs and HBAs in the resulting DESs.

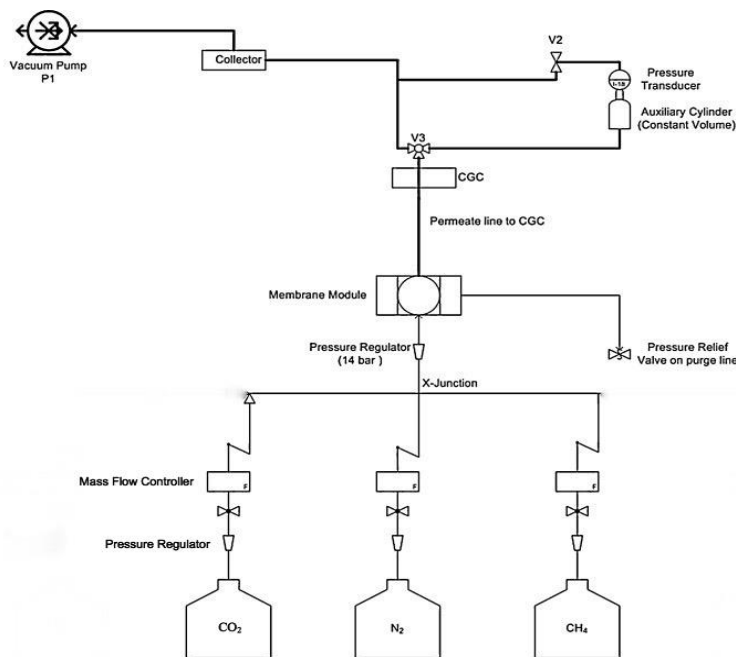


Fig. 1. Gas permeability apparatus schematic.

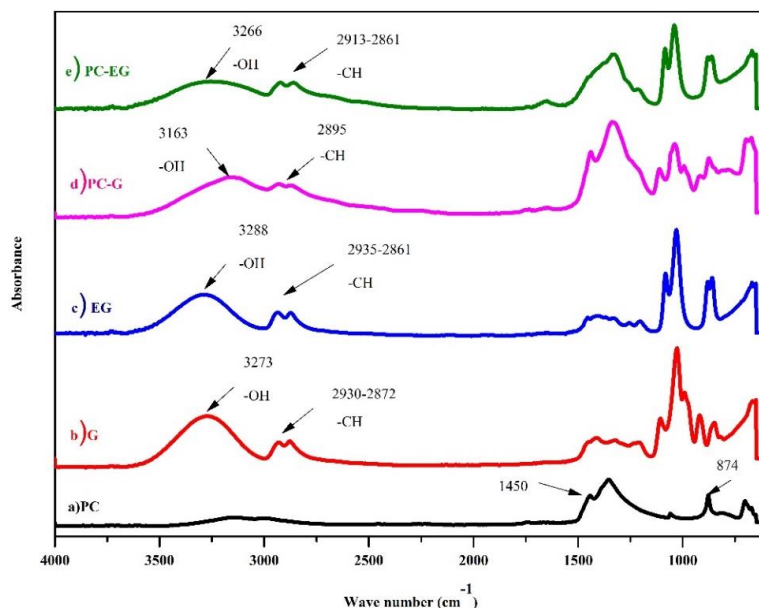


Fig. 2. FTIR Results for Potassium Carbonate (PC), b) Glycerol (G), c) Ethylene Glycol (EG), d) PC-G DES and e) PC-EG DES.

3.2. Thermal Investigation of DESs

To ascertain the thermal efficacy of DES-SLMs at high temperature, the temperature stability of DESs were investigated. The results of TGA are depicted in Figure 3. In the first phase, PC-G and PC-EG DESs exhibited drop in weight below 100 °C that is ascribed to the vaporization of moisture [40]. This weight loss is possibly due to moisture absorbed from the atmosphere as DES samples were transferred into TGA pan and/or during storage. The results revealed that PC-G and PC-EG stability were approximately up to 150 °C. The phase of thermal degradation is observed up to 300 °C with the weight loss for both PC-G and PC-EG DESs. This thermal stability is due to interactions between HBAs and HBDs [18,41] of DESs. The thermal analysis of DESs reveal that the SLMs are suitable for using in the pre and post combustion operating conditions for CO₂ capture.

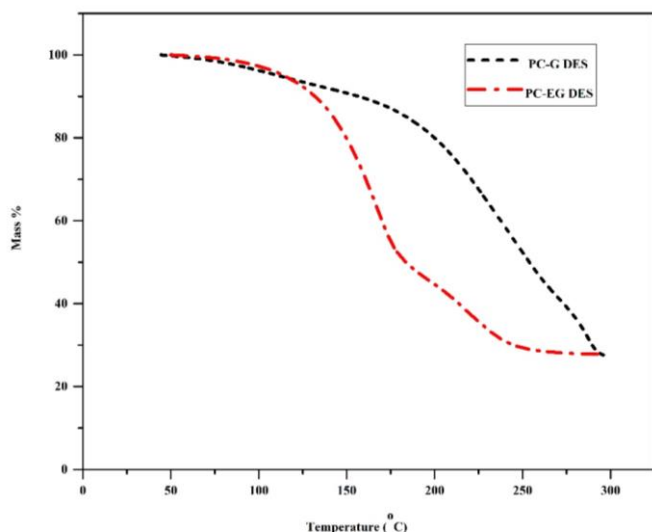


Fig. 3. Thermogravimetric analysis (TGA) of PC-G and PC-EG DES.

3.3. Membrane performance

The performance characteristics of DES-SLMs are presented in Table 1. The SLM exhibits permeability of (20-34) Barrer and ideal selectivity of (34-59) for G to EG respectively. Transport through SLMs are dominated by the model of solution-diffusion. The permeating molecules of gas first dissolve in the liquid of the SLM. It is then transported by the diffusion process and desorbed eventually at low pressure side of the SLM [15,42]. Using the equation-1, the solubility of CO₂ can be calculated. The result of these calculation for the two SLM is displayed in Table 2.

To further ascertain the role of HBA and HBDs on the permeability and separation efficacy of membrane, the solubility and diffusion coefficients are determined. It is found that the CO₂ gas molecules exhibited high solubility because of interaction of acidic gas (CO₂) with the alkaline liquid (PC-DES) on the membrane; hence facilitating the transport of CO₂ gas through the DES-SLM exhibiting high permeability [32]. It has been previously reported that the introduction of -OH groups in the ILs increases the solubility of CO₂ due to the interaction of -OH with CO₂ [43]. Therefore, the enhancement in the permeability and selectivity of CO₂ via PC-G DES-SLM (34 Barrer, 59) as compared to PC-EG DES-SLM (20 Barrer, 34) is possibly due to the existence of one additional -OH in the structure of glycerol (G) than ethylene glycol (EG).

Mixed gas permeability and selectivity was also evaluated in % weight ratio 50(CO₂):50(CH₄) as displayed in Table 3. The results of gas mixture (CO₂ and CH₄) showed that the permeability and selectivity was slightly decreased in comparison to pure gas. The mechanism of competitive sorption of gas molecules between CH₄ and CO₂ resulted in the alleviation of performance of mixture of gases as compared to the pure gas [44]. For SLMs, it has been reported that diffusivity of gas remains the same as it depends upon the viscosity of liquid while gas solubility changes in the liquid due to gas interaction with the solvent [44,45]. Hence, solubility of gases are the

important factors contributing to the decline in the permeability of the mixed gases through DES-SLM as compared to ideal gas [46].

Table 1
Pure gas permeance & selectivity.

Membrane	Pure gas permeability (Barrer)		Pure gas selectivity
	CO ₂	CH ₄	CO ₂ /CH ₄
PC-G DES-SLM	34±1	0.58±0.02	59±1
PC-EG DES-SLM	20±0.6	0.59±0.02	34±1

Table 2
CO₂ solubility and diffusivity.

Membrane	Permeability	CO ₂ Diffusivity	CO ₂ Solubility
	Barrer	10 ⁻² cm ³ (STP)/cm ³ cmHg	10 ⁻⁸ cm ² /s
PC-G DES-SLM	34±1	3.12±0.09	11.07±0.3
PC-EG DES-SLM	20±0.6	3.33±0.09	6.07±0.1

Table 3
Mixed gas permeability and selectivity.

Membrane	Mixed gas permeability (Barrer)		Mixed gas selectivity
	CO ₂	CH ₄	CO ₂ /CH ₄
PC-G DES-SLM	31±0.9	0.55±0.01	56±1
PC-EG DES-SLM	18±0.5	0.58±0.01	31±0.9

3.4. Effect of temperature

DES-SLM permeability was analyzed by elevation in temperature as is shown in Figure 4. The results indicate the permeability of CO₂ increases in the range from 34-40 Barrers for PC-G DES and in the range 20-28 Barrers for PC-EG DES with the increasing of temperature from 298K to 338K. This increasing trend of gas permeability via membrane with the temperature rise can be ascribed to the liquid viscosity [47]. Liquid viscosity decline with the elevation in temperature exhibiting an increase in liquid molar volume. Subsequently, the gas diffusivity would increase attributed to the rise in molar volume and the decline in the DES's viscosity. This outcomes in the increase of gas permeability through the DES-SLMs [18,29,48].

The selectivity of membrane was also studied to evaluate the temperature's effect on the selectivity of DES-SLM. The rise in temperature causes selectivity of membrane to drop. This decreasing trend is due to reduction in solubility of CO₂ in the DESs exploited in the membrane with the elevation in temperature. Moreover, the weaker interaction of CO₂ and DES molecules resulted in the declining trend of CO₂ solubility [29,49,50].

The effect of temperature on permeation of membrane are used to fit into the Arrhenius Equation. Figure 5 confirms that both types of DES based SLMs exhibit Arrhenius relationship with increase in temperature. The trend lines in the figure shows the Arrhenius equation with the Regression coefficient R² of 0.99.

$$P = P_0 e^{-\frac{E_p}{RT}} \quad (4)$$

$$\ln(P) = \ln(P_0) - \frac{E_p}{R} \frac{1}{T} \quad (5)$$

In the above expression (4) and (5), 'T' and 'P' are temperature and permeability of CO₂. Activation energy of CO₂ permeation is given by (E_p) is the sum of activation energy of sorption (E_s) and diffusion (E_D).

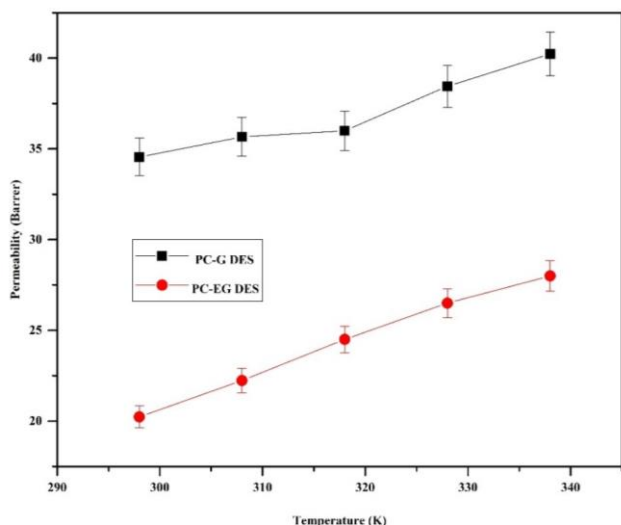


Fig. 4. CO₂ Permeability as function of temperature.

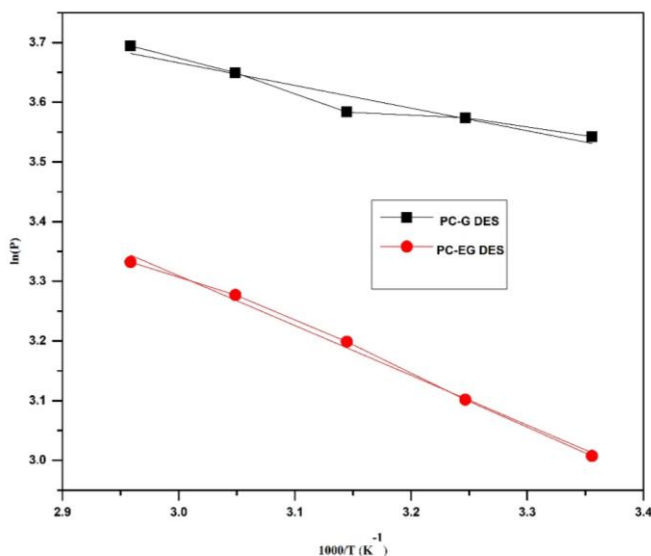


Fig. 5. Arrhenius plot of CO₂ Permeability.

3.5. Concentration of CO₂ in feed mixture

The impact of concentration of CO₂ on the separation factor & permeability of DES-SLM is displayed in Figure 6 and Figure 7. The outcomes depicted that the selectivity of DES-SLMs decreased due to reduction in permeability with rise in CO₂ concentration in the gas mixture. At lower concentration, CO₂ can absorb on the DES-SLMs as the saturation point is not attained and thereby resulting in the rapid transportation of CO₂ via the membrane. In contrast to this, rise in concentration of CO₂ causes its saturation in the DES-SLM consequently causing alleviation in the CO₂ permeability across the membrane [18,29,51,52].

3.6. Comparison of deep eutectic solvent based membrane with other high-performance ILs for CO₂ separation

To highlight the potential of DES-SLM for the upgradation of methane, we made a comparative study of PC-DES-SLMs results with the some of imidazolium IL-membrane for CO₂ separation from methane as displayed in Table 4. Scovazzo et al. reported that imidazolium based SILMs has been attributed to better separation performance than phosphonium and ammonium based SILMs for the removal of CO₂ [53]. Camper et al. studied the

selectivities of SILMs, and concluded that the selectivities increase in the following order: phosphonium > ammonium > imidazolium [46]. Zhang et al reported the [Bmim] [Ac] SILM exhibited selectivity of 40 and high permeability of 2148 Barrer [48]. COSMO approach predicted the trend of increase in solubility with alkyl chain of increasing order of omim > hmim > pmim > bmim > emim. The molecular simulations were used by Cadena et al. to establish the high solubility of CO₂ in imidazolium IL.

In our study, we have synthesized novel NADES-SLMs for mitigation of CO₂. Results revealed the permeability is increased from 25.5-29.3 Barrer while the separation factor is improved upto 56 on substitution of HBD from Tart to Ma [29]. Choline chloride based DES was reported by Ishaq et al. [54] and found the increase in permeability of CO₂ from 20.50-21.30 Barrer and 24.50-27 Barrer on substitution of HBD from PAA and PAM [54]. In our recent study, we have evaluated the membrane comprising of choline chloride and carboxylic acid (Ma, Tart or Oxa) attributed to high separation efficacy on the Robeson Plot 2008 with the separation factor of 51 to 60 and permeability of 30.3 to 37.3 Barrer for CO₂/CH₄ separation [55].

Results of this study and the competing ionic liquids-based membranes were plotted on the well-known Robeson upper bound. The results presented in Figure 8 reflect that the permeability and selectivity of PC-G DES-SLM approached the upper bound while the PC-EG DES-SLM is also not far away from the attractive region of commercial interest. This proves the promising potential of these new types of DES based SLMs having comparable performance to competing ionic liquids along with obvious advantages as low cost, biodegradability, and inherent safety.

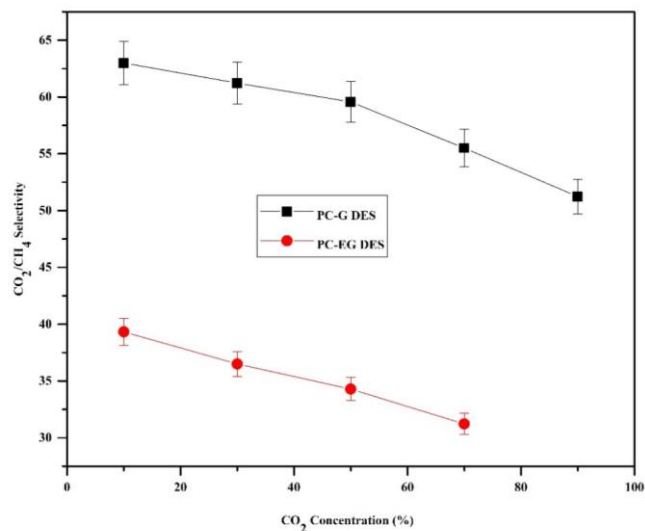


Fig. 6. CO₂ concentration effect on CO₂/CH₄ Selectivity.

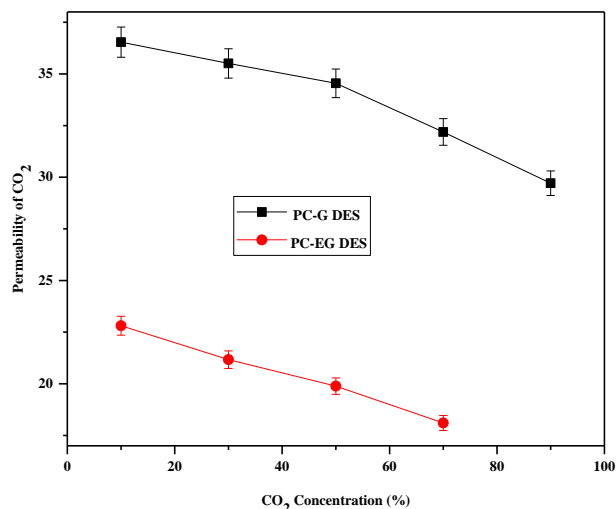


Fig. 7. Concentration of CO₂ vs Permeability of CO₂.

Table 4Comparison of PC-DES-SLMs with DESs-SLMs and imidazolium SILMs for separation of CO₂/CH₄.

Membrane type	CO ₂ Permeability (Barrer)	$\alpha_{(CO_2/CH_4)}$	Ref.
PC-G DES-SLMs	34	59	This work
PC-EG DES-SLMs	20	34	This work
ChCl-Ma DES-SLMs	30.32	51.39	[55]
ChCl-Tart DES-SLMs	34.00	55.74	[55]
ChCl-Oxa DES-SLMs	37.30	60.16	[55]
ChCl-PAM DES-SLMs	25	44.03	[54]
ChCl-PAA DES-SLMs	19.9	49.25	[54]
Be-Ma NADES-SLMs	29.33	56	[29]
Be-Tart NADES-SLMs	25.55	51	[29]
emim Tf2N	1702	12	[16, 56]
emim dca	1237	23	[16, 56]
emim BF ₄	968.5	22	[16, 56]
bmim PF ₆	544	13.3	[16]
bmim Tf2N	1344	-	[16]
Emim TfO	1171	18.5	[16]

4. Conclusions

The novel PC DES-SLMs were synthesized for the mitigation of CO₂ from CO₂/CH₄ mixture by the immobilization process. The FTIR spectra confirmed the presence of H-bond interactions in the prepared DESs. The TGA analysis established the thermal stability of DES that can be exploited into the membrane. Investigation of PC-DES-SLMs exhibited the permeability of CO₂ elevated from 20 to 34 Barrer on changing of HBD from glycerol (G) to ethylene glycol (EG). The separation factor of CO₂/CH₄ increased from 34 to 59 for the replacement of HBD. The fabricated membranes revealed that the permeability of gases increased with the elevation in temperature owing to decrease in solvent's viscosity and increase in diffusivity of gases. On contrary to this, the separation efficacy of membrane was lessened due to reduction in the solubility of CO₂ at elevated temperature. The increment in the concentration of CO₂ in the feed resulted in decline in the selectivity of DES-SLM. The performance of PC-DES-SLM were compared with high performance imidazolium SILM on the upper bound. The results revealed that PC-G DES-SLM exhibited high efficacy in separation factor and permeability for CO₂ separation surpassing the upper bound while the PC-EG was not far off. This low cost and non-toxic solvent exploitation into the PVD membranes has proven to be a potentially unrivalled technology for the mitigation of CO₂ from the industrial gas mixture.

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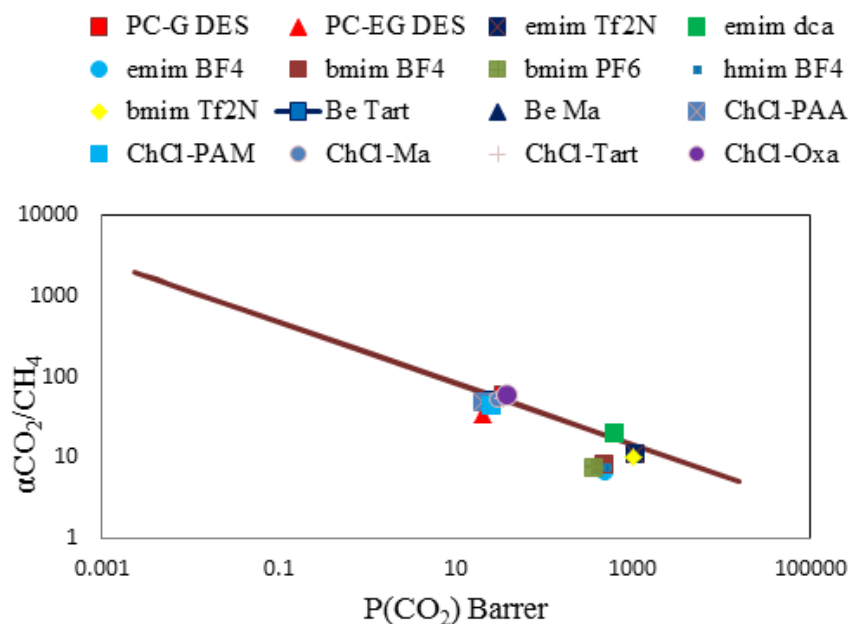


Fig. 8. Robeson plot 2008 for CO₂/CH₄ separation efficacy.

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