

# Exploring the potential of highly selective alkanolamine containing deep eutectic solvents based supported liquid membranes for CO<sub>2</sub> capture

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## ABSTRACT

Amine based solvents are being used extensively for CO<sub>2</sub> capture for the last several decades owing to their relatively high CO<sub>2</sub> affinity. They are considered as standard solvents for CO<sub>2</sub> separation but still, face limitations of high energy requirement, high volatility, high vapor pressure and toxicity. To overcome these limitations, for the first time in this study, amine based deep eutectic solvents (DES) are incorporated into membranes for CO<sub>2</sub> capture. Three different alkanolamines; monoethanolamine, (MEA), diethanolamine (DEA), triethanolamine (TEA) were selected as HBDs and choline chloride as HBA. The synthesis of the DESs was confirmed by FTIR characterization as well as physicochemical properties of the resulting liquid mixture. Subsequently, the synthesized DESs were impregnated into the porous support to prepare supported liquid membranes (SLMs). The SLMs showed excellent selectivity of CO<sub>2</sub> up to 70.47 and 78.86 for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> respectively. This high selectivity of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> can be attributed to the chemisorption of CO<sub>2</sub> with DES and high basicity of DES. The effect of operating temperature, the HBA: HBD mole ratio, and CO<sub>2</sub> concentration on membrane performance was also investigated. The results of amine DESs were compared with the competing ionic liquids based membranes, and the significant high gas separation was attributed to the low viscosity and the high CO<sub>2</sub> solubility in amines that makes them an appropriate alternative to the conventional ILs.

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## 1. Introduction

World Health Organization (WHO) declared COVID-19 as a pandemic on March 11, 2020 which resulted in global lockdown, hitting the transportation industry for weeks. Despite closure of world economic activity, decline in overall CO<sub>2</sub> emissions in 2020 is estimated to be 4–7% in comparison with emissions in 2019 [1]. 36.7 Gigatons fossil CO<sub>2</sub> emissions were recorded in 2019 which were 62% higher than CO<sub>2</sub> emissions in 1990 [2]. The emissions pathway is not compatible to the goals of Paris agreement which mainly consist of limiting global temperature rise below 2 °C above preindustrial temperature levels [3]. Fossil CO<sub>2</sub> emissions which contributes to 86% of total CO<sub>2</sub> emissions [4] are major contributor to global warming [5,6], and there is need to take measures for CO<sub>2</sub> mitigation. CO<sub>2</sub> capturing and sequestering technolo-

gies such as absorption [7], adsorption [8], and cryogenic methods [9] are thus of great importance [10]. Among all these, amine based absorption is the most common and traditional method as it is being used for the last seven decades due to their high affinity for CO<sub>2</sub>, low cost, low viscosity, and reversible reaction with CO<sub>2</sub> [11,12]. Despite all these benefits, the amine based solvents pose a lot of drawbacks such as high energy requirement for solvent regeneration, high vapor pressure, oxidative and thermal degradation, high volatility, toxicity and corrosiveness [13–15].

In order to overcome these challenges, ionic liquids (ILs) provide a promising alternative as they have low vapor pressure, high thermal and oxidative stability, and flexibility of adjusting properties by the choice of cation and anion [16–18]. Although ILs emerge as a potential solvent for CO<sub>2</sub> capturing but they face a number of limitations too. One of the major issues is their high viscosity that negatively affects the mass flow rate and hence permeability. In addition the synthesis is complex and involves the use of toxic precursors, they are non-biodegradable, and highly expensive that make it unfit for commercial applications [19,20].

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In 2003, a new class of ILs called deep eutectic solvents (DES) emerged as a potential alternative to ILs [21,22]. The DESs are a mixture of two components; one acting as hydrogen bond donor (HBD) and the other as hydrogen bond acceptor (HBA) [22,23]. They can be prepared very easily with no expensive precursors and equipment and no further purification is required. DESs are inexpensive, eco-friendly, have low vapor pressure and can be used in a wide range of applications [24,25].

The first DES (based on choline chloride and urea) was prepared in 2003 by Abbott et al [21]. Since then, they have been widely used in organic synthesis [26], catalysis [27], biodiesel transformation [28], electrochemistry [29], nanotechnology [30], and separation technologies [24,31]. Owing to their advantageous properties such as biocompatibility, biodegradability, low cost and ease of preparation, the potential of DES has been explored for CO<sub>2</sub> capture [22,32–34]. At the early stage of DES application in CO<sub>2</sub> capture, Li et al. investigated the CO<sub>2</sub> solubility parameters in choline chloride/urea DES [35]. The results of this study indicated that the CO<sub>2</sub> solubility increased by both, increasing pressure as well as decreasing temperature [35]. Later, choline chloride/urea/H<sub>2</sub>O based DES at constant pressure and varied temperature was evaluated as medium for CO<sub>2</sub> capture [36]. This study highlighted the effect of water on CO<sub>2</sub> solubility of DES system. The results prove higher solubility of CO<sub>2</sub> in DES system. In another detailed investigation, Sarmad et al. designed 35 DESs with different HBA and HBD combination to investigate CO<sub>2</sub> solubility in DESs [37]. All the reported DESs showed considerable CO<sub>2</sub> solubility values, in the range of 0.18 to 2.035 m<sub>CO2</sub>, under varied operating conditions. The CO<sub>2</sub> solubility of the reported DESs was still found to be lower than the alkanolamine solvents [38,39]. For instance the MEA based DES show CO<sub>2</sub> solubility 265% higher than the 30 wt% aqueous MEA [38]. Keeping this in view, the amine based DESs were also explored for CO<sub>2</sub> capture and the promising results were obtained indicating the potential of the amine based DESs in CO<sub>2</sub> capture technology [4,38,40]. The reported amine based DES utilizes alkanolamines as HBD. These DESs show considerably lower vapor pressure that dramatically lowers the volatility of amines with significantly higher performance than aqueous amines [41]. The IL literature suggests that the amine based DESs show significantly lower viscosity as compared to the amine tethered ILs [37]. In the reported literature, ILs and DESs are extensively explored as membrane liquid due to inherent advantages of membrane technology that includes eco-friendliness, low power consumption, and ease of operation. In particular, DES based supported liquid membranes (SLMs) are broadly investigated in wide applications such as for olefin, paraffin separation, amino acid purification and CO<sub>2</sub> separation [42,43]. In SLMs a highly flexible polymeric support is impregnated with a membrane liquid for CO<sub>2</sub> capture [44,45]. Craveiro et al. [46] fabricated the DES based SLMs for CO<sub>2</sub> capture. ChCl was mixed with different HBDs (urea, ethylene glycol, glycerol, and oxalic acid). This was among the first studies highlighting the feasibility of DES-SLMs for CO<sub>2</sub> separation [46]. Saeed et al [47] investigated the CO<sub>2</sub> separation performance of Betaine based natural DESs (NADESs), when incorporated into SLMs. The study reported significantly higher separation of NADES based SLMs in comparison to imidazolium ionic liquid based SLMs [47]. In another study Saeed et al. [48] synthesized DES based SLMs by mixing organic acids including oxalic acid, malic acid, and tartaric acid as HBD and ChCl as HBA. This study also showed the potential of DES application in CO<sub>2</sub> separation [48].

In our previous work [45] we fabricated the polymerized DES (PDES) based SLMs to explore their CO<sub>2</sub> separation potential. The DES was prepared by mixing ChCl as HBA and polyacrylic acid and polyacrylamide as HBD. The prepared PDES show exceptional permeability and selectivity results [45]. In another study we prepared DES by mixing ChCl and urea in different molar ratios of 1:1,

1: 2, and 2: 1, and incorporated them into SLMs to investigate the effect of molar concentrations on CO<sub>2</sub> gas separation performance of DES-SLMs. The study showed that ChCl/urea DES-SLM with molar ratio 2: 1 outperform the other prepared DES-SLMs in permeability and selectivity viewpoint.

To the best of the authors' knowledge, amine based DESs have never been used in membrane systems for CO<sub>2</sub> capture. The motivation for this work was derived from the theoretical work of Shen et al. followed by our previous study that confirmed the potential of the use of DESs in membrane technology for CO<sub>2</sub> capture as a promising approach [45,49,50]. Shen et al. performed the molecular dynamic simulation to investigate the CO<sub>2</sub> capturing capacity of ethaline (Choline chloride: ethylene glycol) DES in nanoporous materials. The results prove that the DES diffuses faster in pores confined with DES as compared to DES in bulk, which suggested the application of DES based membranes for CO<sub>2</sub> capture. Moreover, the utilization of amine based HBDs, being good CO<sub>2</sub> absorbers, can significantly improve the CO<sub>2</sub> affinity of the DESs. In this study, alkanolamines were used as HBDs and choline chloride as HBA for DES synthesis which was then incorporated into the porous support for the fabrication of SLMs. The selectivity and permeability of the synthesized membrane were tested in ideal and mixed gas conditions. The results were plotted on the well-known Robeson's upper bound to evaluate the effectiveness of DES based membranes. The membrane performance was also investigated under different operating conditions.

## 2. Experimental

### 2.1. Materials

Choline Chloride (ChCl), Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), were used for DES synthesis, whereas Polyvinylidene difluoride (PVDF), and N-Methyl-2-Pyrrolidone (NMP) were used for support synthesis. All the chemicals were obtained from Sigma Aldrich (Germany) with ≥99% purity.

### 2.2. Preparation of amine based DESs

The DESs were prepared by mixing HBA (ChCl) and HBDs (MEA, DEA, and TEA) on a magnetic stirrer in two different HBA:HBD molar ratios of 1:6 and 1:8, respectively. During the process, the temperature was maintained at 80 °C. This stirring and heating process continued for 30 min, until a colorless homogenous solution appeared and the formation of DES is confirmed. The same procedure was adapted to prepare six different samples of DES. The structure and molar ratio of the prepared samples is presented in Table 1.

### 2.3. Membrane fabrication

The DES-SLM was synthesized by using the PVDF porous membrane as support. The phase inversion method was used for support synthesis. The polymer solution was prepared by adding the PVDF solution (15 wt%) into NMP with continuous stirring for 24 h. As a result, a clear homogenous solution was formed. The polymer solution was cast into a film by using an automated casting device (Elcometer, UK). The cast membrane was dipped into the nonsolvent coagulation bath for 10 min to complete the phase inversion process. The resulting membrane was then dried and stored in a desiccator before further use.

Subsequently, the DES-SLM was prepared by the impregnation method using a pressurized cell (Sterlitech HP4750). In a typical

**Table 1**

Composition and nomenclature of the synthesized amine DESs.

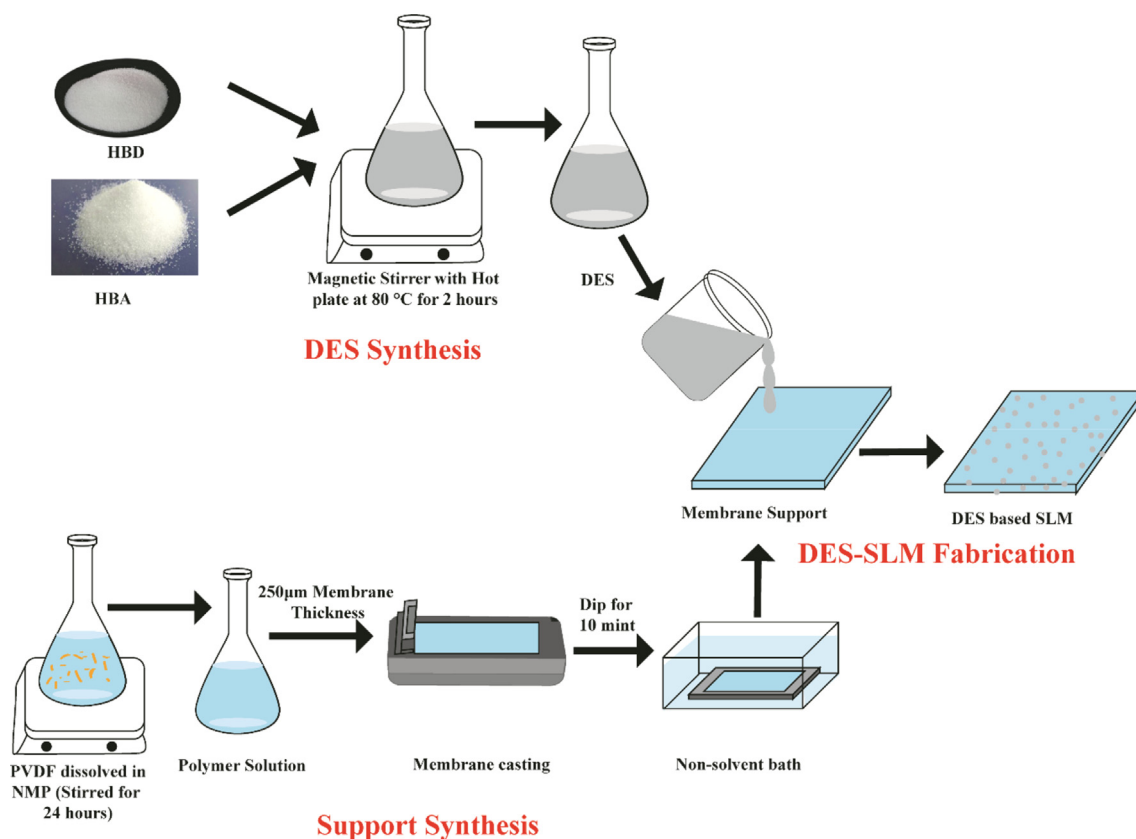
Sample	Molar Ratio	Abbreviation	Chemical Structure
ChCl/MEA	1:6	C1M6	
ChCl/MEA	1:8	C1M8	
ChCl/DEA	1:6	C1D6	
ChCl/DEA	1:8	C1D8	
ChCl/TEA	1:6	C1T6	
ChCl/TEA	1:8	C1T8	

synthesis, 3 mL of the DES liquid was impregnated into the porous structure of the PVDF support by applying 2 bar nitrogen pressure to ensure that the pores are completely filled with the DES. As a result, a thin layer of the liquid was formed under the PVDF support which indicated the complete synthesis of the DES-SLM. The schematic diagram of SLM fabrication is represented in Fig. 1.

### 3. Characterization techniques

#### 3.1. FTIR characterization

The synthesized DESs were characterized by FTIR spectroscopy. The FTIR spectroscopy was performed at room temperature in the

**Fig. 1.** Schematic diagram of amine DESs SLM fabrication.

range of 4000–800  $\text{cm}^{-1}$  with a resolution of 8  $\text{cm}^{-1}$ . For this purpose, Thermo-Nicolet (6700P) FTIR Spectrometer (USA) was used. The density and viscosity measurements were carried out to evaluate the physicochemical properties of DESs. The density was measured by using Krüss DS7800 model vibrating tube densitometer at a pressure of 1 atm, whereas the viscosities were obtained by using Ubbelohde viscometer at room temperature.

### 3.2. Membrane performance testing

A custom-built permeation setup was used to test the performance of the synthesized membrane. The composition of permeate was studied by using gas chromatograph (YL Instruments, South Korea) fitted with two thermal conductivity detectors. The schematic illustration of the gas separation setup is shown in Fig. 2. The working principle and specifications of the setup are reported earlier [51]. The membrane was placed on an airtight metallic porous support and feed gas was introduced at 1 L/min. The experiment was conducted at a temperature range of 298–338 K to analyze the effect of temperature on membrane performance. The measurement was conducted three times for each experiment to get accurate results.

The transport of gases through SLMs is based on solution diffusion mechanism. According to this model

$$J = DS \quad (1)$$

where J refers to permeability, D is the diffusion coefficient and S represents the solubility coefficient. 'D' and 'S' were measured by the time lag method [52,53]. In this method, a high vacuum is

applied at one side of the test cell, and D is calculated by calculating the lag time before the steady-state is achieved. A 50  $\text{cm}^3$  cylinder along with a pressure transducer is attached to the vacuum pump with valve V. The test gas was introduced from one side of the cylinder and vacuum was maintained at the other side until a steady state was achieved. The graph of increasing gas pressure gives the value of time lag intercept  $\theta$  on the vacuum side. 'D' was calculated by using the equation

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

where  $l$  represents membrane thickness. Once the value of D is calculated, the S was calculated using Eq. (1). The selectivity of the gas A over gas component B was calculated using the following equation.

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

## 4. Results and discussion

### 4.1. Characterization of DESs

The FTIR analysis of the individual constituents and the DESs was performed to confirm the DESs formation. The FTIR spectra of pure ChCl, MEA, DEA, TEA, and their corresponding DESs formed are presented in Fig. 3 (A, B, C). The pure ChCl shows characteristic peaks of the hydroxyl group and alkyl group at 3250 and 2900  $\text{cm}^{-1}$  [54]. The C-N and N-H peaks were observed at 1200 and 1550  $\text{cm}^{-1}$  respectively. The peak at 1050  $\text{cm}^{-1}$  refers to the

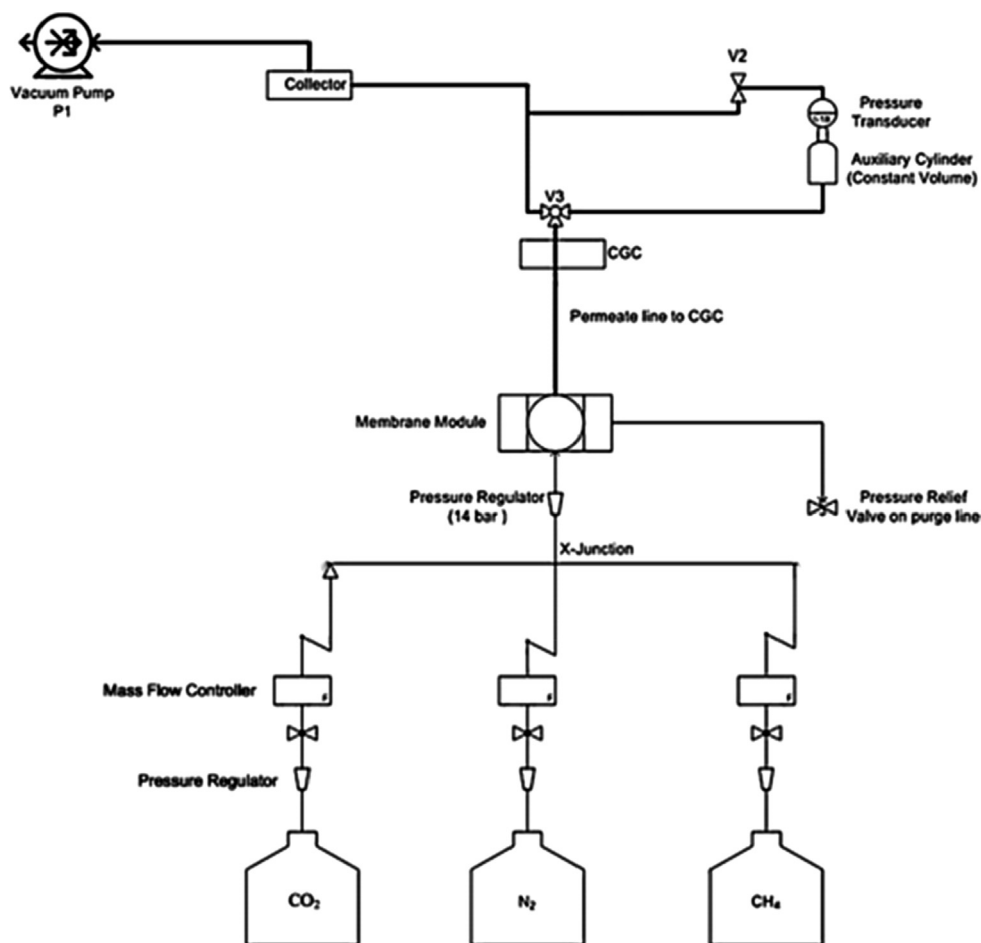


Fig. 2. Gas permeation setup.

carbonyl group [55]. Fig. 3 (A) shows the functional group analysis of ChCl: MEA based DES at different molar ratios and its ingredients. The FTIR spectra of pure MEA showed the presence of OH group and alkyl group at the vibrational band of 3500–3000 and 2850  $\text{cm}^{-1}$  respectively. The peaks at 1650 and 1015  $\text{cm}^{-1}$  attributed to the N-H and C-H group, whereas  $-\text{CH}_2$  group bending appeared at 1450  $\text{cm}^{-1}$  [40]. The IR spectra of DEA based DES is represented in Fig. 3 (B). The broad vibrational band between 3600 and 3500 and 1470  $\text{cm}^{-1}$  exhibit characteristic hydroxyl group and N-H bending of secondary amine peak of DEA respectively. The band at 1500  $\text{cm}^{-1}$  suggested the presence of the  $-\text{CH}_2$  group [4]. IR spectra of TEA represented in Fig. 3 (C) showed the vibrational band of the hydroxyl group at 3000  $\text{cm}^{-1}$ . The peaks at 1465 and 1050  $\text{cm}^{-1}$  exhibit the presence of  $-\text{CH}_2$  and C-N group [56–58]. The formation of MEA-, DEA-, and TEA- DESs was confirmed by their FTIR spectra as it is evident from Fig. 3 that all the functional groups of individual constituents appeared in the DESs FTIR spectra. The hydrogen bonding between the precursors of DES can be confirmed by the redshift of alkyl and amine functional groups. The shifting of peaks towards the lower wavenumber indicates the stronger hydrogen bonding between HBA and HBD [42]. For all the synthesized DESs, the peaks of the amine group become intense by increasing the ratio of alkanolamines in DES. This amplified peak intensity is attributed to the increase of the amine group with alkanolamines addition [59].

The  $\text{CO}_2$  absorption is predominately dependent on the molar volume of the sorbent [60]. To calculate the molar volume, the molar mass was multiplied to the reciprocal of the density, as given in Equation (4).

$$V = \frac{M_{DES}}{\rho} \quad (4)$$

The molar mass of the prepared DESs is calculated by the following equation as proposed by Abbott et al. and Peng et al [61,62].

$$M_{DES} = \frac{X_{HBA}M_{HBA} + X_{HBD}M_{HBD}}{X_{HBA} + X_{HBD}} \quad (5)$$

where

X = Molar ratio M = Molar mass

The physicochemical properties of the DESs are presented in Table 2. All the calculations were repeated thrice to ensure reproducibility of the results. The synthesized amine based DESs show considerably lower viscosity as compared to amine based ILs which show viscosity in the range of 1000–10,000 cP [63,64]. The MEA based DESs shows the lowest viscosity values as compared to DEA and TEA based DESs.

#### 4.2. Gas separation performance of DES-based SLMs

The separation performance of the synthesized membranes was tested by permeating both the pure and mixed gases. In pure gas experiments,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2$  were used and their permeability and selectivity results are presented in Table 3. The selectivity of the synthesized membranes for  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{N}_2$  ranges from 54.00 to 70.47 and 55.23 to 78.86, respectively. The gas transport through the synthesized membrane is governed by the solution diffusion mechanism [65]. The permeating gas absorbs in the DESs from the feed side, diffuses through the thickness of the membrane, and is desorbed at the permeate side. The separation performance thus depends on the solubility and diffusivity of gases through the membrane. The interpretation of the gas permeability and selectivity results requires the data for gas diffusion and solubility coefficients presented in Table 4.

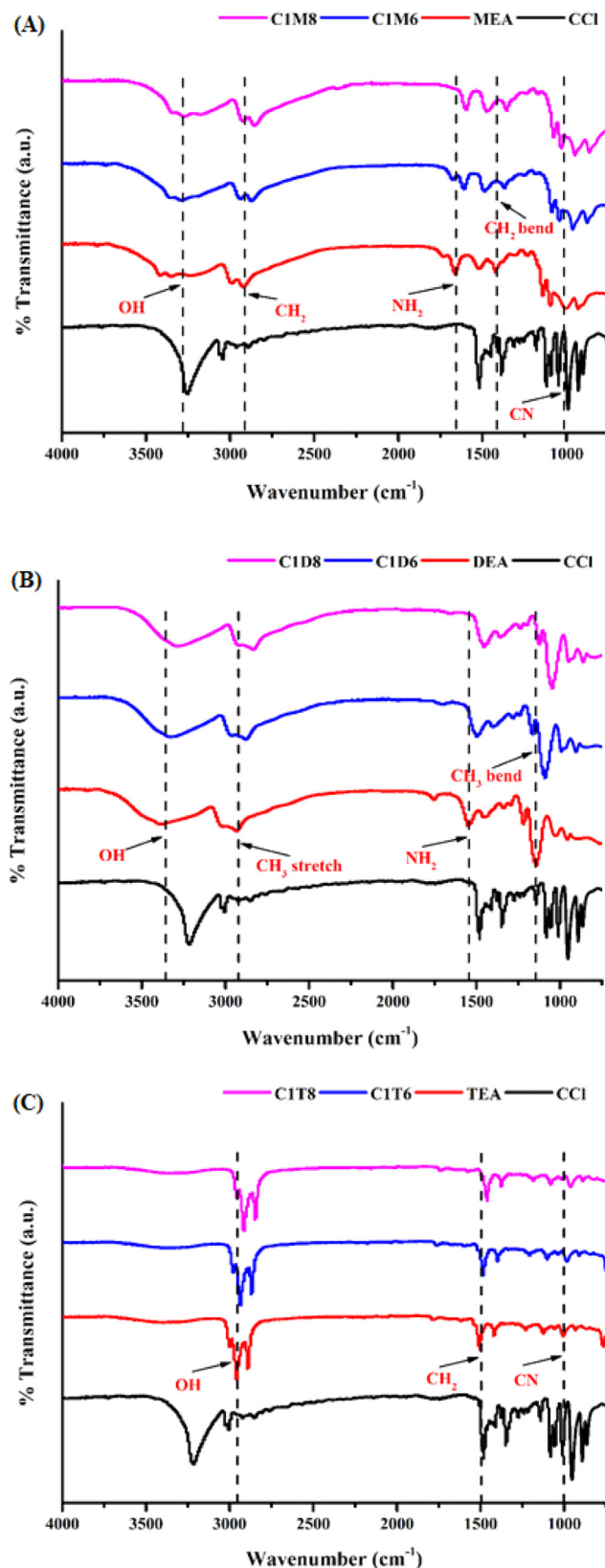


Fig. 3. (A). FTIR spectra of MEA based DES (B). FTIR spectra of DEA based DES (C). FTIR spectra of TEA based DES.

In the case of amine based DESs, along with the physical absorption, chemisorption also plays a dominant role thereby increasing the solubility of  $\text{CO}_2$  synergistically. The physical absorption is



**Table 2**  
Physical properties\* of DESs.

SLM Code	M <sub>DES</sub> (g mol <sup>-1</sup> )	Viscosity (cP)	Density (g cm <sup>-3</sup> )	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )
C1M6	71.3	25.0	1.0617	67.15
C1M8	69.02	22.6	1.0552	65.40
C1D6	109.06	75.1	1.09396	99.69
C1D8	108.19	70.23	1.09232	99.04
C1T6	146.82	83.5	1.12526	130.47
C1T8	147.34	80.46	1.11392	132.27

\* Measurements were made at 298 K.

**Table 3**  
CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> pure gas permeability and selectivity.

SLM Code	Permeability (Barrer)			Selectivity	
	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
C1M6	28.94	0.45	0.40	64.31	72.35
C1M8	33.12	0.47	0.42	70.47	78.86
C1D6	25.88	0.44	0.39	58.82	66.36
C1D8	28.34	0.45	0.41	62.98	69.12
C1T6	24.3	0.45	0.44	54.00	55.23
C1T8	25.67	0.47	0.43	54.62	59.70

**Table 4**  
Solubility and Diffusion of CO<sub>2</sub>.

SLM Code	Diffusion of CO <sub>2</sub> (10 <sup>-8</sup> cm <sup>2</sup> /s)	Solubility of CO <sub>2</sub> (10 <sup>-2</sup> cm <sup>3</sup> (STP)/cm <sup>3</sup> cmHg)	Permeability of CO <sub>2</sub> (Barrer)
C1M6	3.12	9.27564	28.94
C1M8	2.87	11.5401	33.12
C1D6	3.05	8.48525	25.88
C1D8	3.01	9.41528	28.34
C1T6	3.45	7.04348	24.3
C1T8	3.12	8.22756	25.67

associated with the hydrogen bonding between the HBA and HBD, whereas, chemisorption can be attributed to the reaction kinetics [25,38]. The MEA based DESs showed the highest selectivity results because the number of hydrogen atoms on the nitrogen of MEA is more than that of DEA and TEA [66]. As the number of hydrogen atoms increases, the strength of hydrogen bonding and CO<sub>2</sub> solubility also increases. It is well established that the solubility of CO<sub>2</sub> increases by increasing the molar ratio of the amine content in the DES [38] which in turn increases the permeability and selectivity. The highly basic nature of choline chloride and alkanolamines also contributes to the high CO<sub>2</sub> capturing performance of DESs [45,67]. Moving from MEA to DEA and TEA, the permeability decreases due to an increase in viscosity (Table 2) and extensive hydrogen bonding [41]. The lower permeability of TEA can also be attributed to the absence of the N-H bond to directly interact with the CO<sub>2</sub>, which in turn hampers the chemisorption of CO<sub>2</sub> in TEA based DESs [68]. The presence of three hydroxyl groups in TEA also contributes to the extensive hydrogen bonding network that in turn increases the viscosity. This increased viscosity also hinders the permeability of amine DES SLMs [69,70].

The CO<sub>2</sub> permeability can be further explained based on hole theory. According to this theory, hole size is controlled by HBA and HBD interaction [71]. The hole size refers to the free spaces between the individual DES molecules through which permeating gases pass. The larger the hole size, the greater will be the permeability. The MEA based DES shows high permeability values of 28.94 and 33.12 Barrer with a molar ratio of 1.6 and 1.8 respectively. It is a well-known fact that a slight increase in the molar

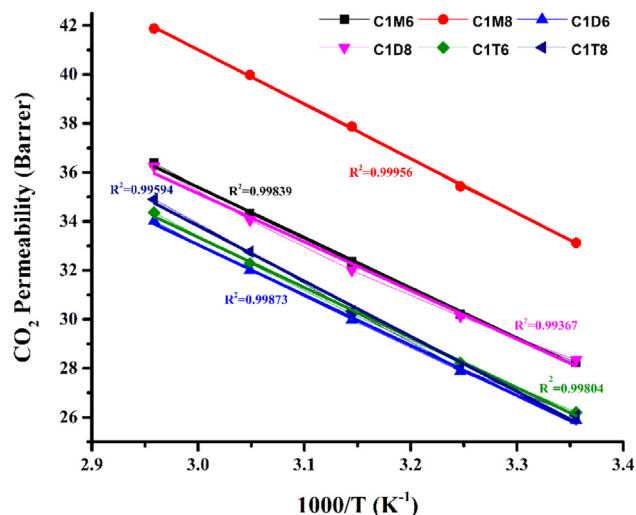
concentration of amine moieties increases the viscosity, consequently, lowering the diffusion coefficient and hence permeability [72]. On the contrary, the synthesized membrane showed higher permeability with an increase in a molar content of amines, because the permeability results are primarily dependent on molecular interactions instead of bulk physicochemical properties and CO<sub>2</sub> has significantly stronger interaction towards the amine DESs [52]. The solubility value of CO<sub>2</sub> is much higher than CH<sub>4</sub> and N<sub>2</sub> in amine based DESs as CH<sub>4</sub> and N<sub>2</sub> only show physical absorption with DES [73].

The membranes were also characterized by binary mixed gas (50:50) permeation and the results are presented in Table 5. In mixed gas permeation, the overall CO<sub>2</sub> permeability and selectivity generally decrease due to the presence of CH<sub>4</sub> and N<sub>2</sub> that competitively hinders the permeability and selectivity of CO<sub>2</sub> [74]. However, from the comparison of Table 3 and Table 5 it can be inferred that the presence of competing gases has no significant effect. This can be ascribed to the large attraction of DES for CO<sub>2</sub> as compared to CH<sub>4</sub> and N<sub>2</sub>. Among all the SLMs, MEA based SLMs show the highest selectivity due to the comparatively lower viscosity values that are consistent with the literature [75]. The highest selectivity results are shown by C1M8 SLMs at a molar ratio of 1:8. This could be attributed to the lower diffusivity of CH<sub>4</sub> and N<sub>2</sub> at an increased concentration of MEA due to an increase in the viscosity.

The gas separation performance of synthesized amine based DES SLMs was compared with the reported amine based IL membrane literature whose selectivity values ranges between 5 and 50 [44,76–80]. The synthesized DES SLMs outperform the amine based IL membranes and show significantly higher selectivity as compared to the reported literature [44,76–80].

**Table 5**  
CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> mixed gas permeability and selectivity.

SLM Code	Permeability (Barrer)			Selectivity	
	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
C1M6	28.30	0.44	0.39	64.31	72.66
C1M8	32.16	0.45	0.41	70.47	78.43
C1D6	25.29	0.43	0.38	58.82	66.55
C1D8	27.71	0.44	0.40	62.98	69.27
C1T6	23.76	0.44	0.44	54.00	54.00
C1T8	25.12	0.46	0.42	54.61	59.80

**Fig. 4.** Arrhenius plot of temperature and CO<sub>2</sub> permeability.

**Table 6**  
Activation energies of DES based SLMs.

SLM Code	Activation energy $E_a$ (KJ/mol)
C1M6	4.12
C1M8	3.87
C1D6	4.34
C1D8	4.21
C1T6	4.95
C1T8	4.78

#### 4.3. Effect of temperature on CO<sub>2</sub> permeability

The CO<sub>2</sub> permeability of amine DES is directly related to the temperature. As evident from Fig. 4, all the DES-SLMs exhibited

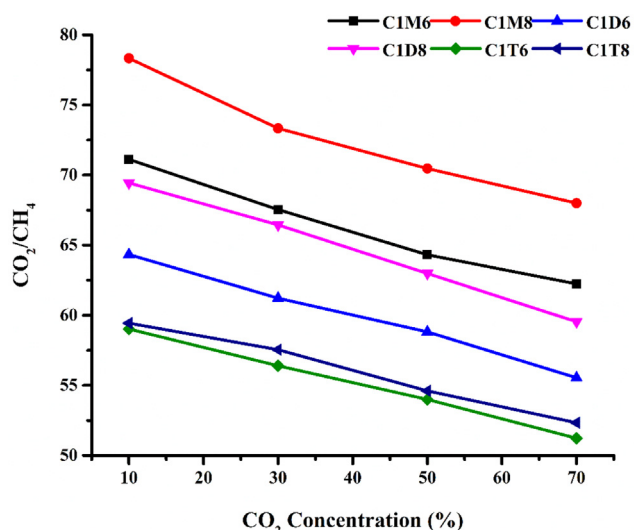


Fig. 5. Effect of CO<sub>2</sub> concentration on CO<sub>2</sub>/CH<sub>4</sub> selectivity.

Arrhenius behavior of CO<sub>2</sub> permeability over a temperature range of 298–338 K with the coefficient of determination ( $R^2$ ) > 0.99. By increasing temperature from 298 to 338 K, the average permeability of the synthesized membranes increases by an order of 9 Barrer. This can be attributed to the fact that the viscosities of the DESs decrease dramatically by increasing temperature [56,75,81]. It can be explained by the Arrhenius equation which states that viscosity is inversely proportional to the temperature [82]. The hydrogen bonding and intermolecular and intramolecular forces become weak by elevating the system temperature that lowers viscosity. At low viscosity, the rate of diffusion escalates due to the increased mobility of free species in DES, which in turn results in higher permeability [37]. The results suggested that the increase in temperature, as in accordance with SILM literature, resulted in an increase in CO<sub>2</sub> permeability for all of the SLMs [83,84]. The CO<sub>2</sub> permeability results investigated at wide temperature indicates the application of synthesized DES-SLMs at different operating temperatures, which suggests applicability of the synthesized membranes at commercial scale.

The relation between temperature and activation energy can be explained by the Arrhenius equation as given below

$$P = P_0 \exp(-E_a/RT) \quad (7)$$

where  $P$  represents the permeability of CO<sub>2</sub>,  $P_0$  is the pre-exponential factor,  $R$  is gas constant and  $T$  refers to the feed temperature. The activation energies of all the synthesized membranes are listed in Table 6. They were found to be in the range from 3.87 to 4.95 KJ/mol. The activation energies of the synthesized membranes are significantly lower than the earlier reported competing SILMs [83,84]. The C1M8-SLM showed the lowest activation energy among all other SLMs. These lower activation energy values are due to the lower viscosity of amine DESs. The increase in temperature also increases the ionic motion and the hole size in the DES. This phenomenon leads to the lowering of resistance to and hence the decreases of the activation energy ( $E_a$ ) for CO<sub>2</sub> permeation. The activation energy results strongly support the practical application of amine DESs based SLMs for CO<sub>2</sub> capture.

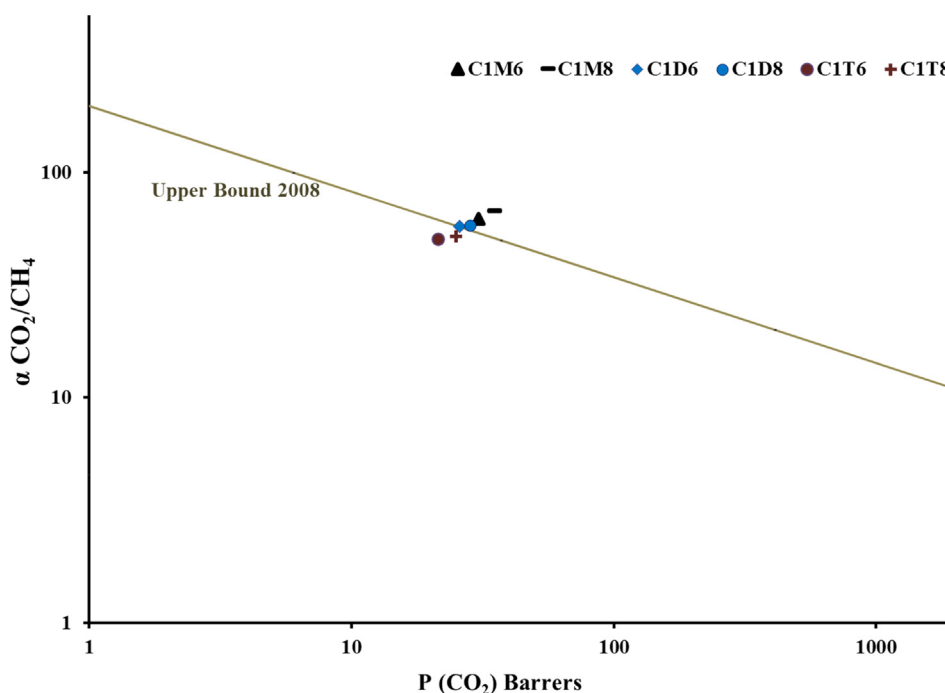


Fig. 6. CO<sub>2</sub> separation performance of the studied SLMs plotted on Robeson upper bound.

#### 4.4. Effect of CO<sub>2</sub> concentration on CO<sub>2</sub>/CH<sub>4</sub> selectivity

The CO<sub>2</sub>/CH<sub>4</sub> selectivity is considerably affected by the change in concentration of CO<sub>2</sub> in the feed gas. As the concentration of CO<sub>2</sub> increases from 10 to 70%, CO<sub>2</sub>/CH<sub>4</sub> selectivity reduced from 78.34 to 68 in case of C1M8-SLM. At a low concentration of CO<sub>2</sub>, DES is unsaturated that facilitates faster diffusion and solubility of CO<sub>2</sub> through the DES-SLMs. At a high concentration of CO<sub>2</sub>, SLMs become saturated, and fewer DES constituents are available for the transport of CO<sub>2</sub> molecules that lower the selectivity of CO<sub>2</sub> and CH<sub>4</sub> [85,86]. The effect of CO<sub>2</sub> concentration on CO<sub>2</sub>/CH<sub>4</sub> selectivity is represented in Fig. 5. The effect of CO<sub>2</sub> concentration on CO<sub>2</sub>/CH<sub>4</sub> selectivity is very small which proves the remarkable performance of DES-SLMs at different conditions of feed concentration. The synthesized DES-SLMs exhibit excellent selectivity even at high CO<sub>2</sub> concentrations that suggests the membrane applicability at commercial scale where feed concentration greatly varied.

#### 5. Comparison with literature

Membrane-based separation is an environmentally friendly and economical method to mitigate the acidic gas (CO<sub>2</sub>) related to environmental concerns. The challenge is to have high selectivity along with permeability of SLM for the CO<sub>2</sub> capture. The comparison with amine-based IL membranes reveals that the amine based DES-SLMs synthesized in this study have considerably higher CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity [44,76–80]. In order to gauge the future application of these membranes, the results were plotted on the well-known Robeson upper bound 2008 (Fig. 6) [87]. This upper bound is considered as the target line for the membrane researchers in evaluating the commercial potential of the membrane materials [87]. The comparison shows that most of the amine based DES-SLMs (C1M6, C1M8, C1D6, and C1D8-SLMs) crossed the upper bound while C1T6 and C1T8-SLMs lie very close to the upper bound.

#### 6. Conclusions

Novel amine based DES SLMs were fabricated and the effect of different alkanolamines and their molar ratio on membrane permeability and selectivity for CO<sub>2</sub> capturing was thoroughly investigated. MEA, DEA, and TEA were chosen as alkanolamines. Among all the fabricated membranes, C1M8-SLM showed the highest permeability and selectivity over CH<sub>4</sub> and N<sub>2</sub> due to high affinity for CO<sub>2</sub> plus, stronger hydrogen bonding and lower molar volume and relatively lower viscosity. The DESs with a high molar ratio of alkanolamines show considerably higher results as compared to DESs with comparatively lower amine content. The effect of temperature and CO<sub>2</sub> concentration in feed on the membrane performance confirmed the absence of facilitated transport and practicability of DES-SLMs at elevated temperatures respectively. This study is the very first milestone in designing the amine based DES-membrane systems for efficient CO<sub>2</sub> capture. The results obtained prove that high performance DES-SLMs can be developed by incorporation of the CO<sub>2</sub>-specific DESs with suitable selection of HBA/HBD to surpass the upper bound outstandingly.

#### CRediT authorship contribution statement

**Manzar Ishaq:** Conceptualization, Data curation, Investigation, Methodology, Writing - original draft. **Mazhar Amjad Gilani:** Validation, Writing - review & editing. **Muhammad Roil Bilad:** . **Ahmad Faizan:** Resources, Funding acquisition, Formal analysis, Writing - review & editing. **Arsalan Ahmad Raja:** Resources, Funding acquisition, Formal analysis, Writing - review & editing. **Zobila**

**Muhammad Afzal:** . **Asim Laeeq Khan:** Supervision, Funding acquisition, Data curation, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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