



Solubility of CO₂ and CH₄ in sterically hindered amine-based deep eutectic solvents



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ABSTRACT

Decarbonization of methane is essential in many applications such as biogas and natural gas. Solvents with high selectivity towards CO₂ are required for the upgradation of biogas and natural gas. Deep eutectic solvents (DESs) sharing green properties of ionic liquids have shown the ability to capture CO₂ selectively. In this work, we have synthesized four novel secondary amine-based DESs using quaternary ammonium salt as hydrogen bond acceptor. The CO₂ and CH₄ uptake of the synthesized DESs were experimentally investigated. The viscosities of DESs were also evaluated and correlated with the Vogel-Fulcher-Tammann (VFT) and the Arrhenius equation. The modified Lydersen-Joback-Reid method was used for the critical properties estimation of synthesized DESs. All the synthesized DESs have shown high CO₂ absorption and relatively very low CH₄ absorption indicating their high selectivity towards CO₂. The experimental DES-CO₂ and DES-CH₄ vapor-liquid equilibria were successfully correlated with the NRTL model and Peng-Robinson equation of state.

1. Introduction:

Biogas and natural gas are considered to be clean fuel due to the high concentration of methane. However, both natural gas and biogas contain a significant amount of CO₂ which should be removed in order to be transported in pipelines [1]. For the safe transportation of these gases through pipelines, CO₂ must be below 2% [2]. Besides, CO₂ presence lowers the calorific value of biogas and natural gas. Therefore, the CO₂ content of these gases needs to be lower down to make them suitable for vehicular fuel [3]. Conventionally, amine scrubbing is used for biogas and natural gas treatment [4]. The process consists of an absorption column where an amine solution is used for CO₂ absorption and then subsequently, amine solution loaded with CO₂ is sent to the stripper column where CO₂ desorbs at high temperature. Although, amine solvents are useful for gas treatment but they suffer from various problems [5]. The high regeneration energy, corrosiveness, low selectivity for CO₂ and the volatility are the main drawbacks of these

solvents [6,7]. Therefore, researchers have been investigating new solvents for biogas and natural gas treatment having high CO₂ selectivity compared to CH₄.

Ionic liquids (ILs) have gained attention as environment friendly solvents showing the potential for gas separation [8]. The properties such as non-corrosiveness, high thermal stability, low vapor pressure, non-flammability, and low regeneration energy requirement make ILs promising solvent to replace conventional solvents [9,10]. However, high viscosity, poor biodegradability and complex purification of ILs limit their applicability in the industry [9,11].

Considering the problems associated with ILs, Abbott et al. proposed deep eutectic solvents (DESs) sharing green properties of ILs [12]. The synthesis procedure of DESs is relatively easy and inexpensive compared to ILs. DESs are mostly formed by the combination of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in a fixed molar ratio [13]. Due to hydrogen bond interaction, DESs have lower freezing point than the precursor components. DESs properties can be tuned for

Abbreviations: [bmim][BF₄], 1-butyl 3-methylimidazolium tetrafluoroborate; [bmim][DCA], 1-Butyl-3-methylimidazolium dicyanamide; [bmim][PF₆], 1-butyl 3-methylimidazolium hexafluorophosphate; [bmim][Tf₂N], 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; BTEACl, Benzyltriethylammonium Chloride; ChCl, Choline Chloride; [C₈mim][BF₄], 1-Octyl-3-methylimidazolium tetrafluoroborate; [C₆mim][PF₆], 1-Hexyl-3-methylimidazolium hexafluorophosphate; DEA, Diethanolamine; EA, Ethanolamine; EAE, 2-Ethylamino ethanol; [emim][BF₄], 1-Ethyl-3-methylimidazolium tetrafluoroborate; [emim][Tf₂N], 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; GUA, Guanidinium hydrochloride; MAE, 2-Methylamino ethanol; MEA, Monoethanolamine; MTPPhBr, Methyltriphenylphosphonium bromide; [P₆₆₆₁₄][Met], Trihexyl(tetradecyl)phosphonium methioninate; [P₆₆₆₁₄][Pro], Trihexyl(tetradecyl)phosphonium proline; [P₆₆₆₁₄][Pyr], Trihexyl(tetradecyl)phosphonium pyrazole; TBAB, Tetrabutylammonium Bromide; TEA, Triethanolamine; TPAC, Tetrapropylammonium chloride

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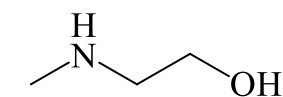
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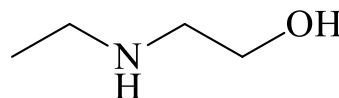
Table 1

List of chemicals used for synthesis of DESs.

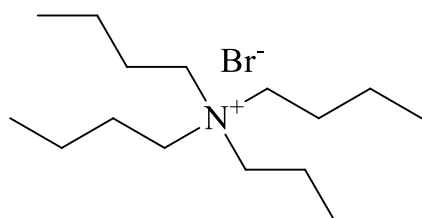
Chemical Name	Source	CAS Registry Number	Purity(%)	Water content(%)
Choline Chloride	SD Fine Chem Ltd	67-48-1	≥ 98	N/A
Tetrabutyl ammonium Bromide	SD Fine Chem Ltd	1643-19-2	≥ 99	N/A
Tetramethyl ammonium Chloride	Spectrochem	75-57-0	≥ 98	N/A
Benzyltriethyl ammonium Chloride	SD Fine Chem Ltd	56-37-1	≥ 98	N/A
2-Methylaminoethanol	Sigma Aldrich	109-83-1	> 98	< 0.20
Carbon Dioxide	Sigma Gases	124-38-9	≥ 99.9	N/A



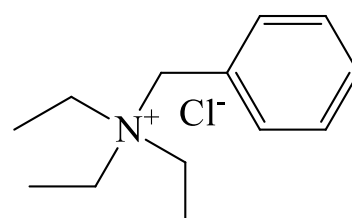
2-Methylamino ethanol



2-Ethylamino ethanol

Hydrogen Bond Donor

Tetrabutylammonium bromide



Benzyltriethylammonium chloride

Hydrogen Bond Acceptor**Fig. 1.** Structures of HBA and HBD.**Table 2**

List of synthesized deep eutectic solvents (DESs).

Hydrogen Bond Donor	Hydrogen Bond Acceptor	Molecular weight(g/mol)	Density(g/ml)	Name
2-Methylaminoethanol(MAE)	Tetrabutyl Ammonium Bromide(TBAB)	124.56	0.9697	DES1
	Benzyltriethyl ammonium Chloride(BTEACl)	105.64	0.9682	DES2
2-Ethylaminoethanol (EAE)	Tetrabutyl Ammonium Bromide(TBAB)	135.78	0.9588	DES3
	Benzyltriethyl ammonium Chloride (BTEACl)	116.87	0.9542	DES4

Table 3

Viscosity of DESs and ionic liquids reported in the literature.

DES	μ (cP)	T(K)	Reference
DES 1	45.00	298.15	This work
DES 2	37.60	298.15	This work
DES 3	34.30	303.15	This work
DES 4	39.00	303.15	This work
GUA/2EA	78.32	298.15	[22]
TPAC/4EA	55.31	298.15	[22]
MTPPhBr/4EG	109.80	298.15	[10]
MTPPhBr/8TFA	136.15	298.15	[10]
ChCl/2urea	447.00	298.15	[42]
[bmim][PF ₆]	382.00	293.15	[43]
[bmim][BF ₄]	132.00	293.15	[43]

various applications depending upon the precursors selected for the HBAs and HBDs [14]. Recently, DESs have found its application in different areas like aliphatic–aromatic separation, gas-separation process, phenol and metal removal from water and oil, extractive distillation and extractive desulfurization [15–18]. CO₂ uptake in DESs follows trends as that of ILs i.e solubility is favored at lower temperature and higher pressure. Factors such as HBA/HBD molar ratio and nature of HBA and HBD significantly affect the CO₂ absorption [19,20]. Addition of the superbase into the DESs, helps in the formation of active alkoxide and enhances the CO₂ uptake [21]. The alkyl chain length of HBA and HBD, the symmetry of the salt and moisture content of the salt also significantly affect the CO₂ absorption [22–24]. Kroon et al. synthesized six decanoic acid-based hydrophobic DESs and showed that CO₂ absorption in the synthesized DESs was comparable to fluorinated

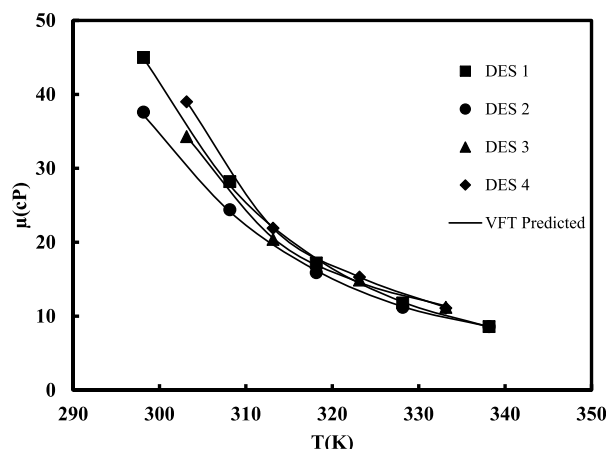
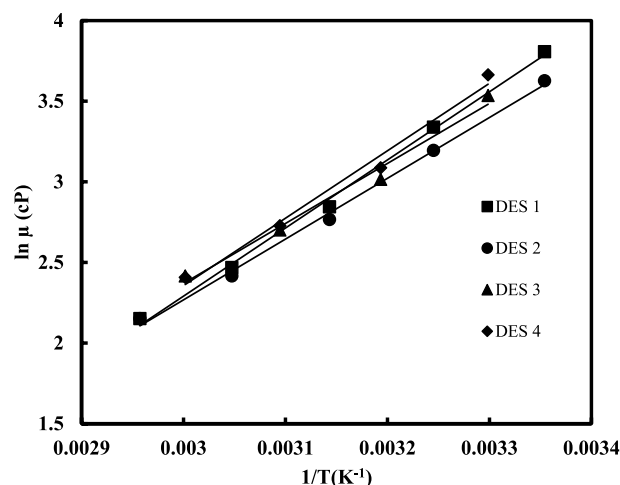


Fig. 2. Viscosity of DESs at different temperatures.

Fig. 3. $\ln \mu$ vs $1/T$ plot for Arrhenius equation.

ILs [25]. Dina et. al. investigated the CO_2 loading in the DESs formed by monoethanolamine and methyltriphenylphosphonium bromide [26]. They found that these DESs have more CO_2 solubility compared to monoethanolamine solvents.

Biogas upgradation requires high solvent selectivity for CO_2 compared to CH_4 to prevent the loss of methane. Therefore, selectivity of CO_2 over CH_4 is an important criteria for designing of a suitable solvent to be utilized in biogas decarbonisation as well as natural gas sweetening [27]. Previous studies have shown that sterically hindered secondary alkanolamines such as ethylaminoethanol possess very high CO_2 solubility compared to conventional monoethanolamine solvents [28–31]. Therefore, CO_2 and CH_4 absorption in the sterically hindered secondary amine-based DESs were investigated in this work. The CO_2 and CH_4 absorption in the synthesized DESs was determined in the temperature range of 303.15–323.15 K and at varied pressure (up to 15 bar). The viscosities and densities of all synthesized DESs were also determined and correlated well with Vogel-Fulcher-Tammann (VFT) and the Arrhenius equation. Further, the Non-Random Two liquids (NRTL) model and Peng-Robinson equation of state were used to predict the experimentally determined DES/ CO_2 and DES/ CH_4 vapor-liquid equilibrium.

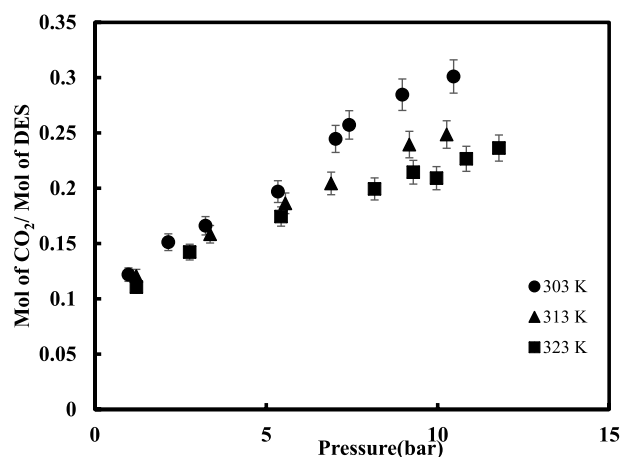
2. Experiment:

2.1. Materials

The list of chemicals along with their purity used in this work, has been given in Table 1. Fig. 1 shows the structures of the chemicals used for the synthesis of various DESs.

2.2. Synthesis of DESs

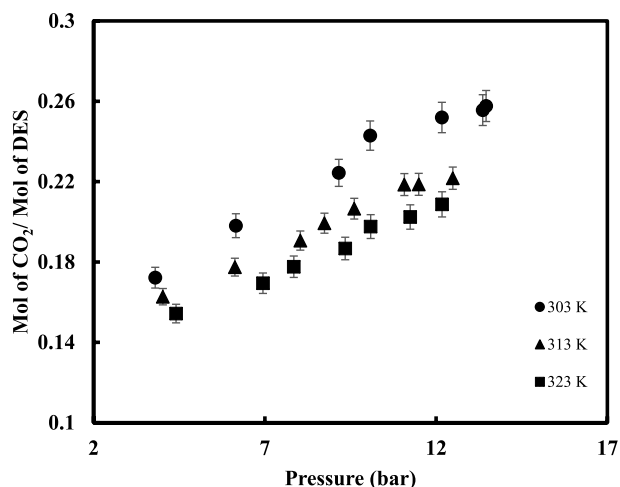
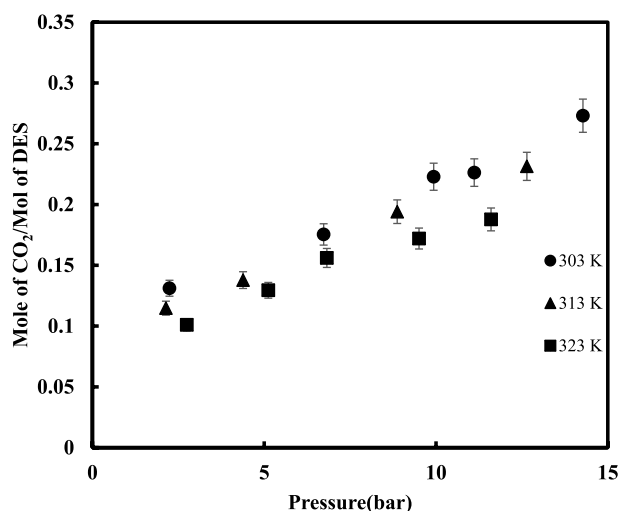
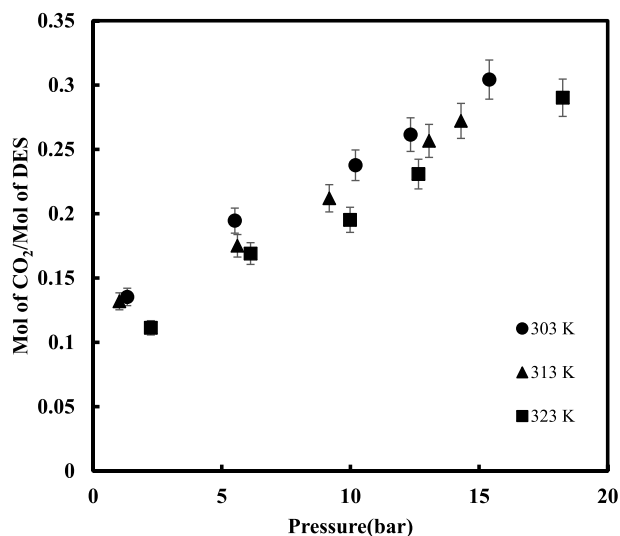
The DESs were synthesized using the method as described by Abbott

Fig. 4. CO_2 solubility in DES 1 at different temperatures.

et.al. [32]. In general, fixed molar ratios of HBA and HBD were thoroughly mixed and heated at 353.15 K. The experiment was continued until a homogenous colorless liquid was formed. Various combinations of HBA and HBD were used for the synthesis of DESs as given in the supplementary information (Table 1). A fixed HBA/HBD molar ratio (i.e. 1:4) was used for the formation of all DESs. All the synthesized DESs showed homogeneous liquid behavior at 303.15 K temperature. The list of synthesized DESs and their molecular weight has been given in Table 2.

Table 4
VFT and Arrhenius parameters of DESs.

DES	VFT Equation μ_0 (m.PaS)	A(K)	T_0 (K)	StandardDeviation	Arrhenius Equation $\mu_\infty(10^{-5}$ m.PaS)	E_a (kJ/mol)	R^2
DES 1	0.0091	1476.51	120.91	0.4025	3.09	35.13	0.9969
DES 2	0.0024	1877.94	106.91	0.2811	0.12	31.34	0.9962
DES 3	2.4943	108.21	261.85	0.2341	0.15	30.94	0.9850
DES 4	3.2924	81.17	270.31	0.0577	3.74	34.78	0.9862

Fig. 5. CO₂ solubility in DES 2 at different temperatures.Fig. 6. CO₂ solubility in DES 3 at different temperatures.Fig. 7. CO₂ solubility in DES 4 at different temperatures.

2.3. Characterization

The sample weight was measured by the Mettler Toledo balance (NewClassic MS). Perkin Elmer Spectrum two spectrometer was used for recording the FTIR spectra of the samples (wavenumber range: 450–4000 cm⁻¹). Before each measurement, background signal quality was checked. Bruker Avance (FT-NMR) spectrometer was used to record ¹H NMR spectra at 400 MHz. CDCl₃ was used as an internal reference in ¹H NMR.

2.4. Viscosity measurement

The viscosities of DESs were measured using Anton Paar make rheometer (MCR-52, Physica). The rheometer was equipped with a thermal jacket that was connected to the heating circulation pump to control the temperature (accuracy ± 0.01 K). In a typical rheological experiment, DESs were placed in the thermally insulated measuring cylinder for sufficient time to maintain the temperature, and then viscosity was measured.

2.5. Gas-solubility measurements

The gas solubility was measured according to the procedure as described in our previously published work [33–35]. In general, the apparatus consists of an equilibrium cell (capacity 25 ml) attached to a gas reservoir. The inside pressure of both the equilibrium cell and gas reservoir was measured using pressure transducers. The temperature of the system was maintained constant using IKA-make chiller and homogeneity of gas in the solvent was maintained using constant stirring of 300 rpm. During the experiment, both gas reservoir & equilibrium cell were degassed and the equilibrium cell was charged with the known amount of DESs. The gas was first introduced into the reservoir to determine the initial moles of gas. Using a valve attached between the equilibrium cell and reservoir, gas was transferred from the reservoir to the equilibrium cell. The system pressure was recorded at a regular interval of time. The pressure of equilibrium cell reduces gradually due to solubility of the gas in the DES until an equilibrium condition is reached (~6 hrs). At equilibrium, system pressure was measured and the moles of gas available in the cell were calculated using equation of state. The amount of gas dissolved in the DESs was determined from the difference of the initial moles of gas fed and final moles of the gas available at equilibrium.

3. Gas absorption modelling

3.1. Estimation of critical properties

All the DESs are composed of two precursors i.e HBAs and HBDs. Therefore, precursor molecule's critical properties were first estimated using "Modified Lydersen – Joback – Reid" (LJR) method [36]. The details of the critical properties estimation method have been given in our previous work [35].

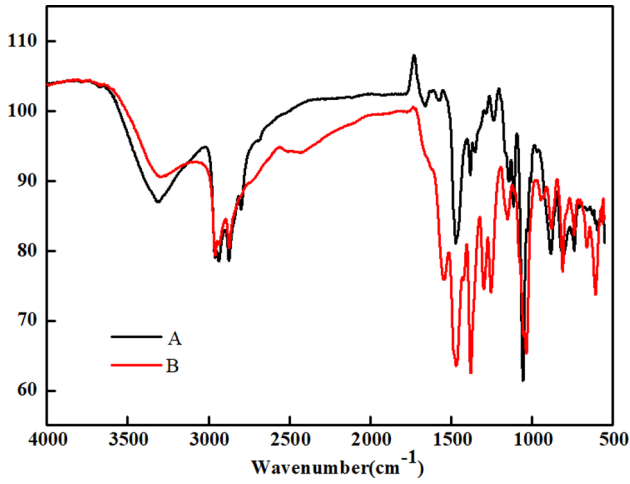
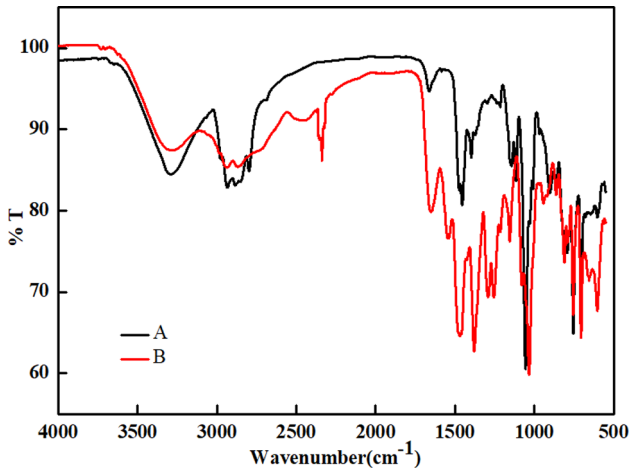
3.2. Thermodynamic models

The solubility of CO₂ and CH₄ in the synthesized DESs were correlated using Non-Random Two Liquid (NRTL) model and Peng-Robinson equation of state. The NRTL model is given by:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \quad (1)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (2)$$

Fig. 8. FTIR spectra of DES 1 (a) before (b) after CO₂ absorption.Fig. 9. FTIR spectra of DES 2 (a) before and (b) after CO₂ absorption.

$$\tau_{ij} = p_{ij} + \frac{q_{ij}}{T} + e_{ij} \ln(T) + f_{ij} T \quad (3)$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15) \quad (4)$$

$$\tau_{ii} = 0 \quad (5)$$

$$G_{ii} = 1 \quad (6)$$

The Peng-Robinson equation of state is given as;

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \quad (7)$$

Where a and b are parameters for attractive interaction and

excluded volume of molecules, respectively.

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (8)$$

where a_i and a_j are the function of critical properties and temperature.

k_{ij} is the binary interaction parameter given by;

$$k_{ij} = k_{Aij} + k_{Bij} T + k_{Cij} / T \quad (9)$$

$$b = \sum_i x_i b_i \quad (10)$$

where b_i is the function of critical properties.

4. Result and discussion

4.1. Viscosity

Solvent transport properties are essential for mass and heat transfer. It is essential to measure the solvent viscosity that affects the design, operation, and economy of the CO₂ capture unit. The viscosities of synthesized DESs were measured and compared with the DESs previously reported, as given in Table 3. It can be observed from the table that all amine based DESs synthesized in the current work have lower viscosity than the DESs reported in the literature. Moreover, viscosities of amine based DESs are almost ten times lower than that of ChCl / 2urea DES and [bmim][PF₆] ionic liquid.

The viscosity dependency on the temperature of synthesized DESs has been shown in Fig. 2. The viscosity of synthesized DESs decreases with an increase in temperature which is a usual trend of the molecular solvents. This can be explained due to the weakening of HBD and HBA interaction at elevated temperature which promote molecular movement and therefore viscosity decreases [37].

Vogel-Fulcher-Tammann (VFT) equation was used to correlate the DESs viscosity dependency on temperature [38,39]. The VFT equation is given by;

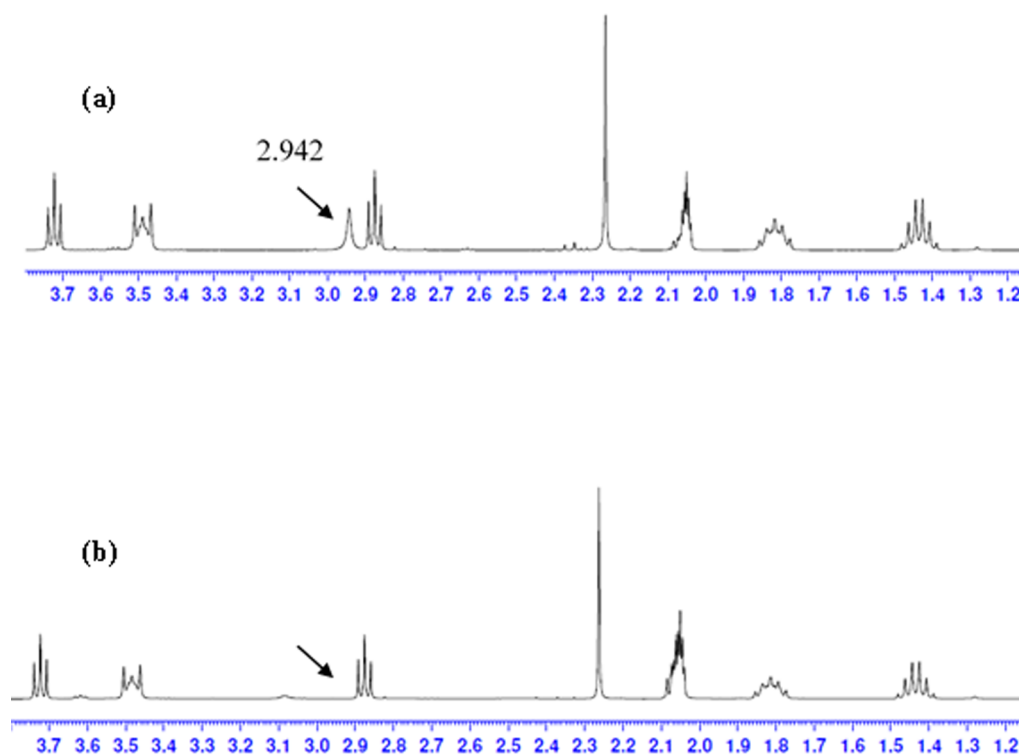
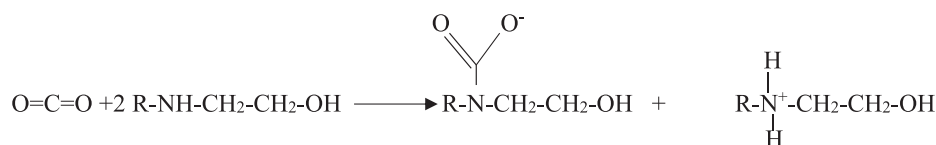
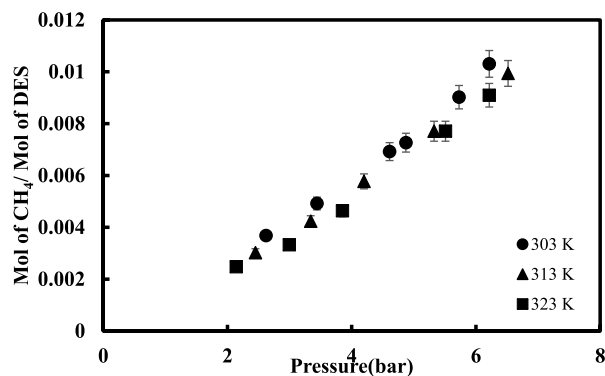
$$\ln(\mu/\mu_0) = \frac{A}{T - T_0} \quad (11)$$

where μ_0 , T_0 and A are empirical constants. The VFT model correlates well the experimental data as shown in Fig. 2. The calculated parameters of the VFT model are given in Table 4.

The Arrhenius equation for viscosity as a function of temperature is given by;

$$\ln(\mu/\mu_\infty) = \frac{E_\mu}{RT} \quad (12)$$

where R is gas constant, E_μ is the viscous flow activation energy, and μ_∞ is the empirical constant. The experimental viscosities of the DESs were also fitted using Arrhenius equation as shown in Fig. 3 and the calculated Arrhenius parameters are given in Table 4.

Fig. 10. HNMR Spectra of DES 1 (a) before and (b) after CO₂ absorption.Fig. 11. Proposed reaction mechanism of DESs and CO₂.Fig. 12. CH₄ solubility in DES 1 at different temperatures.

4.2. Solubility of gases

4.2.1. CO₂ Uptake of DESs

The experimentally measured CO₂ uptakes of DESs 1, 2, 3 and 4

have been shown in Figs. 4, 5, 6 and 7, respectively. It was observed that for fixed temperature and pressure, DES1 has the highest CO₂ solubility and DES4 has the lowest CO₂ solubility among all synthesized DESs. This is due to the higher symmetry of HBA (i.e. TBAB) present in DES1 and lower steric hindrance caused by the shorter alkyl chain length of HBD[40,41]. In general at fixed temperature and pressure the trend of CO₂ uptake of the synthesized DESs follows as; DES1 > DES2 > DES3 > DES4. Also, CO₂ solubility was high at low temperatures and decreases at elevated temperatures. For example, at fixed pressure of 10 bar the CO₂ solubility was 0.301 mol CO₂/mol DES at 303.15 K for DES1 which was reduced to 0.21 mol CO₂/mol DES at 323.15 K. Similar behavior was also observed in case of DES2, where CO₂ absorption capacity was 0.24 mol CO₂/mol DES at 303.15 K and 10 bar, which decreases to 0.19 mol CO₂/mol DES at 323.15 K. Lower CO₂ absorption capacity at higher temperature indicates easy regeneration of DESs. After CO₂ absorption, it was found that the viscosity of the DESs significantly increases which can be attributed to the chemisorption of CO₂ in DESs. To confirm the chemisorption behavior of CO₂ absorption, the DESs were characterized by FTIR before and

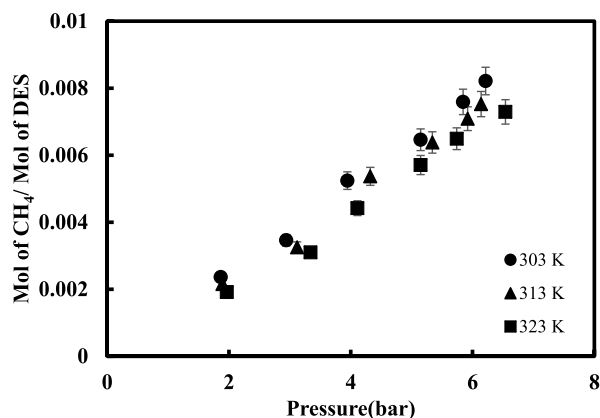
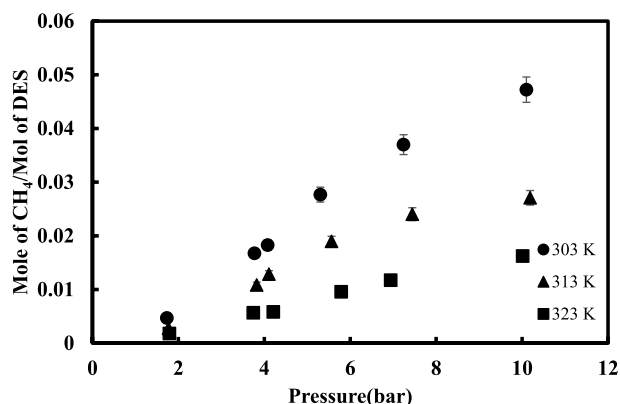
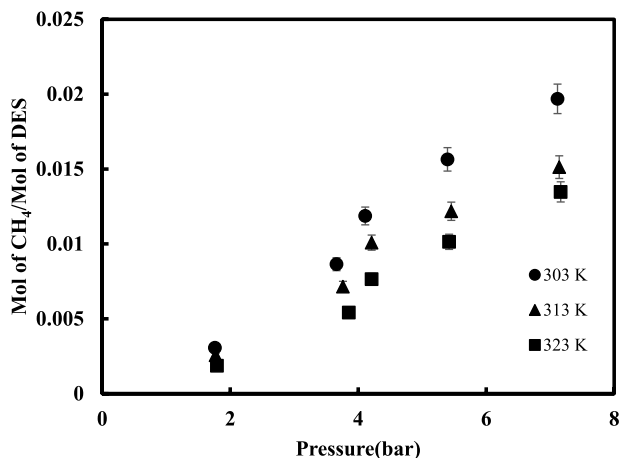
Fig. 13. CH₄ solubility in DES 2 at different temperatures.Fig. 14. CH₄ solubility in DES 3 at different temperatures.Fig. 15. CH₄ solubility in DES 4 at different temperatures.

Table 5
Critical properties of DESs:

DESs	V _c (cm ³ /mol)	T _c (K)	P _c (bar)	Omega(ω)
DES 1	424.94	629.74	28.51	0.7328
DES 2	379.61	623.09	32.11	0.6880
DES 3	475.62	649.88	26.13	0.7491
DES 4	428.62	642.66	29.15	0.7044

V_c: Critical volume, T_c: Critical temperature, P_c: Critical Pressure, Omega(ω): Acentric factor

after CO₂ absorption as shown in Figs. 8 and 9. The weak intensity and broad peak at 3330 cm⁻¹ attributed to hydrogen bond in DESs which changes to high intensity and narrow peak after CO₂ absorption. This is attributed to the hydrogen bond weakening due to CO₂ absorption. In addition, new peaks in the range of 1300–1350 cm⁻¹ and 1500–1600 can be ascribed to the symmetric and asymmetric stretches of –COO⁻, respectively. This was further confirmed by the HNMR spectra of DES1 before and after CO₂ absorption as shown in Fig. 10. It can be observed from the HNMR result that singlet present at 2.94 disappeared after CO₂ absorption. This is due to the formation of the N-COO bond in the DES which confirms the formation of carbamate [29]. Similar behavior was also observed for other DESs. A reaction mechanism of DES and CO₂ has been proposed based on stoichiometry and FTIR, HNMR analysis as shown in Fig. 11. The “R” in the proposed mechanism represents the methyl or ethyl group.

4.2.2. CH₄ Solubility in DESs

The experimentally measured CH₄ solubility in all the synthesized DESs has been shown in Figs. 12, 13, 14 and 15. The CH₄ solubility in the DESs was quite low as compared to CO₂ solubility. It was found that at a temperature of 303.15 K and 10 bar pressure the CO₂ uptake was almost 7 folds higher than the CH₄ uptake of the DESs. At a fixed temperature and pressure, DES3 has shown the highest CH₄ uptake among all the synthesized DESs. In general the trend of CH₄ uptake of the synthesized DESs follows as; DES3 > DES4 > DES1 > DES2. Similar to the CO₂ solubility, CH₄ solubility in DESs decreases with increasing temperature. The experimental results show that the CH₄ uptake in the synthesized DESs increases linearly with an increase in the pressure. This suggests the physisorption behavior of CH₄ in the DESs. This may be the reason for lower CH₄ uptake in synthesized DESs compared to CO₂. From industrial prospects higher CO₂ uptake and lower CH₄ uptake of the synthesized DESs are advantageous for the treatment of biogas and natural gas. These solvents would reduce the loss of CH₄ and selectively absorb the CO₂ from the gases.

4.3. Thermodynamic Modelling:

VLE modeling of the CO₂-DESs and CH₄-DESs systems was done using Aspen plus V8.6. It was assumed that the synthesized DESs are non-volatile. The NRTL thermodynamic model and Peng-Robinson equation of state were used to correlate the experimental solubility of CO₂ and CH₄ in the DESs. The binary parameters for the Peng-Robinson equation of state depend on the property parameters of DESs such as temperature, critical pressure and critical volume. Therefore, the property parameters required were calculated using Modified Lydersen – Joback – Reid” (LJR) method as given in Table 5. The experimental VLE data of CO₂-DESs and CH₄-DESs was fitted with NRTL model and Peng-Robinson equation of state as given in the supplementary information (Figs. 3-9). It was observed that the NRTL model has a better fit compared to the Peng-Robinson equation of state. This depicts higher non-ideal behavior of CO₂-DES and CH₄-DES systems due to hydrogen bonding present in the DESs. The calculated binary parameters for NRTL model and Peng-Robinson equation are given in Tables 6 and 7, respectively.

4.4. Comparison with previous literature:

The CO₂ uptake of the synthesized DESs was also compared with the previously reported work as shown in Table 8. It has been observed that the DESs synthesized in the current work show higher CO₂ solubility compared to other amine-based DESs available in the literature. For instance, the DES 1 has CO₂ uptake of 0.301 at 303 K and 10 bar, which is much higher than TBAB/6DEA (0.114) as well as TBAB/6EA (0.117). Additionally, CO₂ solubility in the synthesized DESs was significantly higher than the ionic liquids reported in the literature. However, the CO₂ uptake in the DESs was significantly lower as compared to

Table 6

Calculated NRTL binary interaction parameters.

Component i	CO ₂	CO ₂	CO ₂	CO ₂	CH ₄	CH ₄	CH ₄	CH ₄
Component j	DES 1	DES 2	DES 3	DES 4	DES 1	DES 2	DES 3	DES 4
ρ_{ij}	720.00	−45.43	−0.84	−1.08	−3.81	90,000	−0.15	13.05
ρ_{ji}	50.29	−18.24	80.00	80.00	9.44	0.69	−92.25	33.52
q_{ij}	−1099.44	8329.65	0.00	0.00	463.47	−880.00	−17160.32	3675.78
q_{ji}	−16135.80	6353.01	10,010	10,010	−1257.89	−1.15	37096.38	−2158.20
α_{ij}	0.30	0.30	0.3	0.3	0.30	0.30	0.30	0.3

Table 7

Calculated Peng-Robinson binary interaction parameters.

Component i	CO ₂	CO ₂	CO ₂	CO ₂	CH ₄	CH ₄	CH ₄	CH ₄
Component j	DES 1	DES 2	DES 3	DES 4	DES 1	DES 2	DES 3	DES 4
k_{aij}	6.01	−107.15	−63.32	−3.07	−9.90	−59.08	−57.28	4.09
k_{bij}	−0.01	0.17	0.1	0.04	0.02	0.09	0.1	0.00
k_{cij}	−1064.50	16845.10	10,000	509.33	1476.08	9107.55	8345.1	−836.35

Table 8CO₂ uptake of the various solvents reported in the literature.

Solvents	T(K)	P(bar)	CO ₂ uptake(mol CO ₂ /mol solvent)	CO ₂ uptake (g CO ₂ / g solvent)	Reference
DES 1	303.15	10.46	0.30	0.106	This work
DES 2	303.15	10.07	0.24	0.100	This work
DES 3	303.15	09.93	0.22	0.071	This work
DES 4	303.15	10.19	0.24	0.090	This work
TBAB/6DEA	303.15	10.11	0.11	0.036	[33]
ChCl/6DEA	303.15	09.71	0.09	0.036	[33]
TBAB/3TEA	298.15	10.00	0.08	0.021	[44]
TBAB/6EA	298.15	10.00	0.12	0.059	[44]
MTPPPhBr/6EA	298.15	10.00	0.14	0.072	[44]
TPAC/4EA	298.15	10.57	0.94(mol/kg)	0.041	[22]
GUA/2EA	298.15	11.29	1.36(mol/kg)	0.060	[22]
[bmim][BF ₄]	303.15	09.96	0.166	0.032	[45]
[bmim][PF ₆]	303.15	10.17	0.186	0.029	[46]
[emim][Tf ₂ N]	298.15	10.07	0.293	0.033	[47]
[emim][BF ₄]	298.15	8.80	0.119	0.026	[48]
[C ₈ mim][BF ₄]	313.15	28.90	0.468	0.073	[49]
[bmim][Tf ₂ N]	313.15	22.00	0.667	0.070	[46]
[bmim][DCA]	313.15	14.20	0.188	0.040	[46]
[C ₆ mim][PF ₆]	313.15	25.70	0.427	0.060	[50]
[P ₆₆₆₁₄][Met]	295.15	1.00	~0.900	0.063	[51]
[P ₆₆₆₁₄][Pro]	295.15	1.00	~0.900	0.066	[51]
[P ₆₆₆₁₄][Pyr]	296.15	1.00	1.020	0.082	[52]
30 wt% aqueous MEA	313.15	12.56	0.763	0.550	[53]
30 wt% aqueous MDEA	313.15	12.41	1.065	0.393	[53]

conventional monoethanolamine solution.

4.5. Proposed separation process for biogas Decarbonization:

A separation process for biogas decarbonization has been proposed as shown in Fig. 16. The process mainly consists of an absorber column and a stripper column. The absorber column is operating at low temperature and high pressure to absorb the maximum of the CO₂ leaving behind essentially almost pure methane from the top. The solvent containing essentially CO₂, leaves from the bottom of the absorber column is termed as CO₂ rich solvent. The CO₂ rich solvent after heating in a heat exchanger is fed to the stripper column. The stripper column operates at high temperature and low pressure to desorb the CO₂ from the top and essentially pure solvent termed as CO₂ lean solvent leaves

from the bottom of the stripper column. The CO₂ lean solvent after exchanging heat with CO₂ rich solvent in a heat exchanger is recycled to the absorber column.

5. Conclusions:

In this work, four novel sterically hindered secondary amine-based DESs were synthesized using 2-methylamino ethanol and 2-ethylaminoethanol as HBDs. All the synthesized DESs in the current study have shown significantly low viscosity as compared to DESs reported in the literature. Moreover, viscosities of amine based DESs are almost ten times lower than that of ChCl / 2urea DES and [bmim][PF₆] ionic liquid. The highest CO₂ uptake was shown by the DES 1 (0.301 mol of CO₂/mol of DES) at 303.15 K and 10 bar among all the synthesized DESs. The FTIR and HNMR spectra showed chemisorption behavior of CO₂ in the amine based DESs. The carbon dioxide solubility in the DESs was quite high compared to the methane solubility, indicating higher selectivity of DESs towards CO₂. On comparison with previous works, it was found that CO₂ uptake of DES 1(0.301) in the current study was much higher than TBAB/6DEA (0.114), TBAB/6EA (0.117) as well as ionic liquids reported in the literature. Thermodynamic modeling of DES-CO₂ and DES-CH₄ systems showed that the NRTL model best fits the VLE data. A separation process flow diagram for biogas decarbonization was also proposed based on the experimental results.

CRediT authorship contribution statement

Mohd Belal Haider: Conceptualization, Methodology, Software, Writing - original draft. **Rakesh Kumar:** Supervision, Visualization, Investigation, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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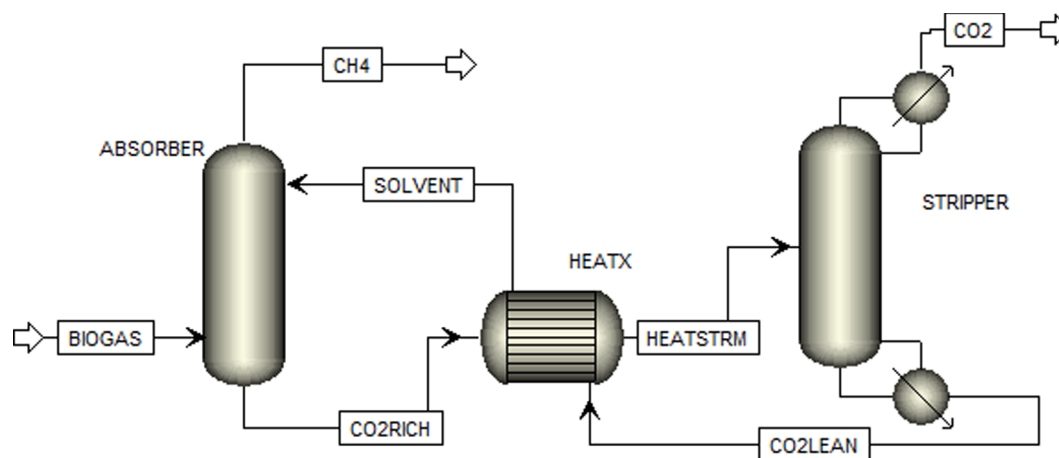


Fig. 16. Proposed flow-diagram for biogas decarbonization using amine-based DESs.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2020.117055>.

References

- ## Appendix A. Supplementary material
- Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2020.117055>.
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