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Experimental investigation of novel ternary amine-based deep eutectic solvents for CO_2 capture

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Abstract

This study investigates the effect of using water as a low-viscosity component in ternary amine-based deep eutectic solvents (DESs) on the physicochemical properties, thermal stability, and CO_2 absorption capacity of the resulting DESs. It should be emphasized that water is a component of the ternary DES. The effect of water content in the DES, type of hydrogen bond acceptors (HBAs), hydrogen bond donors (HBDs), and HBA:HBD ratio on the above parameters was investigated. Moreover, the effect of temperature and pressure on the CO_2 absorption capacity of DESs was predicted using the predictive model COSMO-RS. This model was also used to predict the CO_2 solubility in the DESs and the results were compared with the experimental values. The results showed that the addition of small amounts of water, e.g., 5 and 10 wt% during preparation, can significantly decrease the viscosity of the resulting DESs, up to 25% at room temperature, while maintaining the high CO_2 absorption capacity and high thermal stability. The ternary DESs based on MEA exhibited a high CO_2 absorption capacity of 0.155–0.170 g CO_2 / g DES. The ternary DESs were found to be thermally stable with a decomposition temperature of 125°C, which promotes the use of such solvents in post-combustion capture processes. Finally, COSMO-RS proved to be a suitable tool for qualitative prediction of CO_2 solubility in DESs and demonstration of trends related to the effects of temperature, pressure, molar ratio, water content, HBD and HBA on CO_2 solubility.

Introduction

The increase in global energy consumption due to economic growth and urbanization relies heavily on the use of fossil fuels such as oil, coal, and natural gas, releasing enormous amounts of carbon dioxide (CO_2) into the atmosphere. Assuming that greenhouse gas emissions continue to increase at the current rate, global warming is projected to reach 1.5°C between 2030 and 2052 [1]. Given the status of CO_2 as a pollutant and greenhouse gas, intergovernmental regulations impose penalties on countries and factories to reduce and control their CO_2

emissions. One mature and promising technology to reduce anthropogenic CO_2 emissions is post-combustion carbon capture technology [2]. This technology is more often based on chemical or physical absorption processes. However, the predominant technique for CO_2 capture is chemical absorption by aqueous solutions of amine-based solvents, such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), piperazine (PZ), and 2-amino-2-methyl-1-propanol (AMP) [3].

Several research groups have studied the absorption of CO_2 in these solvents (MEA, DEA and MDEA) to determine the absorption capacity, regeneration energy and reaction kinetics [4]. In general, a good solvent must have high CO_2 absorption capacity, fast reaction kinetics, low regeneration energy, and negligible environmental impact. However, Zhao et al. [5] found that the degradation of MEA solution accounts for nearly 10% of the total cost of CO_2 capture. Moreover, MEA requires high regeneration energy. In contrast, MDEA has a low regeneration energy, however, it has much lower reaction kinetics. To overcome these disadvantages, there have been several attempts to use amine mixtures to find a compromise between the different performance parameters. Indeed, Zhang et al. [6] developed a kinetic model of CO_2 absorption in aqueous solutions of MDEA mixed with DEA based on a homogeneous activation mechanism. Glasscock et al. investigated CO_2 absorption and desorption in aqueous solutions containing MDEA/MEA and MDEA/DEA. They concluded that the combined mass transfer/equilibrium model based on the zwitterion mechanism can successfully represent the CO_2 mass transfer rate in the temperature range of the experiments [7]. Also, in a study conducted by Bruder et al. [8], it was found that a mixture of AMP and PZ had a higher loading capacity than AMP alone; however, undesirable precipitation can occur when high concentrations of PZ are added. In general, processes using aqueous amines have some limitations, such as high energy demand, corrosiveness, and degradation of some amines, which leads to foaming, fouling, performance degradation, and production of harmful gasses, resulting in environmental problems [9]. Therefore, in recent years, many research groups have investigated the use of new green solvents to replace aqueous amines in carbon capture processes. Examples of these potentially green solvents include ionic liquids (ILs) and deep eutectic solvent (DESs).

ILs have several interesting properties, including their wide liquid range, non-flammability, non-volatility, and thermal stability, which promote their use as greener solvents in many chemical and industrial processes [10], especially for CO_2 absorption. Many research groups have investigated the use of different types of ILs for CO_2 capture, e.g., Raeissi et al. [11] and Kumełan et al. [12]. It was found that some ILs have excellent absorption capacity for CO_2 with low regeneration energy. Nevertheless, ILs have critical drawbacks that hinder their industrial application, including their high cost, toxicity in some cases, and the complex synthesis process that requires purification steps to remove impurities that could affect the properties of IL.

A new class of green solvents, called deep eutectic solvents (DESs), has shown promise for various applications [13]. These solvents share many similarities with ILs, e.g. low volatility, etc. However, based on the proper selection of their components, DESs have advantages over ILs, such as low cost, nontoxicity, ease of preparation, and biodegradability. In addition, DESs can be used for a variety of applications, including CO_2 capture, due to their ability to be tuned by changing their constituents and the ratio of HBA:HBD [14, 15].

Several researchers have investigated the possibility of using DESs for absorbing CO_2. For example, Lu et al. [16] reported the CO_2 solubility in levulinic acid (LV) and furfuryl alcohol (FA) based DESs with different molar ratios and at different temperatures, where the HBA was fixed as choline chloride (ChCl). In general, it was found that ChCl: LV DESs exhibited better CO_2 absorption capacity than ChCl: FA DESs. It was also found that as the molar ratio of LV or FA increased, the CO_2 solubility increased. As expected, CO_2 solubility increased with the

increase of pressure and decrease of temperature. Li et al. [17] investigated CO_2 solubility in choline chloride with urea DES (ChCl:urea) at 3 different molar ratios, namely 1:1.5, 1:2, and 1:2.5 at temperatures ranging from 313.15 K to 333.15 K. The results showed that ChCl:urea (1:2) had the highest CO_2 solubility, while the other two molar ratios showed similar results. Moreover, the same trend reported by Lu et al. [16] regarding the effect of pressure and temperature on CO_2 solubility was reported by Li et al. [17]. Sze et al. [18] studied the solubility of CO_2 in ternary DESs. The prepared DESs consisted of choline chloride as HBA, glycerol as HBD, and 3 superbases, namely 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), and 1,8-diazabicyclo[5.4.0]undec7-ene (DBU). It was found that ChCl:Gly:DBN with 1:2:6 molar ratio had the best overall performance with a CO_2 absorption capacity of 103 mg CO_2/g DES. However, this system has a very high viscosity, ranging from 5450 to 34,613 mPa.s for the neat DES at 298.15 K. In a recent publication, Adeyemi et al. [19] investigated the solubility of CO_2 in 3 different amine-based DESs at molar ratios of 1:6, 1:8 and 1:10. In all DESs, the HBA was choline chloride, while MEA, DEA and MDEA were used as HBDs. The solvent screening setup (SSS) and total organic carbon (TOC) analyzer were used to measure the CO_2 absorption capacity in all DESs. The results showed that ChCl:MEA at a molar ratio of 1:10 had the highest CO_2 absorption capacity among all the DESs tested. In all cases, as the molar ratio of amines increased, CO_2 solubility increased. The results were compared with those obtained by using conventional DESs such as ChCl:glycerol. It was found that the amine-based DESs have much higher CO_2 absorption capacity. Moreover, the performance of the amine-based DESs was compared with that of 30% wt aqueous amines. For ChCl:MEA DESs, the CO_2 solubility was higher than that achieved by the respective 30 wt% amine aqueous solutions. However, CO_2 solubility in MDEA 30 wt% aqueous solution was higher than that of ChCl: MDEA DES for all 3 molar ratios.

Wu et al. [20] used 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) + imidazole DESs to selectively remove H_2S from gas mixtures containing CO_2 for applications in the natural gas industry. The authors compared the results with other liquid solvents and reported that [Emim]Cl + imidazole DES showed extremely high efficiency in H_2S absorption and great selectivity over CO_2.

Sarmad et al. [21] prepared five new three-component DES by functionalization of choline chloride-ethanolamine (1:7) DES using different types of amines: DEA, MDEA, piperazine and 1-(2-aminoethyl)piperazine. The solubility of CO_2 in the studied DESs was measured at pressures up to 2 MPa and 298.15 K. The Redlich-Kwong equation of state was used to correlate the experimental data and determine the Henry's law constant. The authors applied an analytical method to prove that all studied DESs exhibited chemical absorption of CO_2. Haghbakhsh et al. [22] reported the use of a new alcoholic DES (choline chloride: Butane-1,2-diol (molar ratio 1:4)) for CO_2 absorption in a temperature range from 303.2 to 333.2 K and at pressures up to 3.4 MPa. The authors reported the values of Henry's constants at very dilute CO_2 concentrations, in addition to the calculated values of standard enthalpies, entropies, and Gibbs free energies of dissolution.

Wang et al. [23] reported the use of amino acid DESs modified by the addition of triethanolamine (TEA) to the HBD to mask the protons and protect the amino groups. The authors investigated the effects of HBD modification of L-Arg DESs and L-Lys DESs on CO_2 binding. The experimental data showed that CO_2 loading reached 1.194 mol/mol when L-Arg:glycerol: TEA was in the ratio of 1:3:3, and 1.378 mol/mol when L-Lys: glycerol: TEA was in the ratio of 1:3:3, and both showed good regenerative ability. Al-Bodour et al. [24] studied the solubility of CO_2 in four natural hydrophobic DESs based on carvone, cineole, thymol, and menthol at different temperatures and pressures. The results showed that the solubility reached that in aqueous amine solution at a pressure of about 30 bar. The physical absorption behavior was

confirmed by analytical methods. This has a significant effect on the regeneration energy. Nagulapati et al. [25] used experimental solubility data from the literature for CO$_2$, CO, CH4, H$_2$, and N$_2$ in ChCl/Urea DES to develop machine learning models for predicting the solubilities of various gases in ChCl/Urea DES. The hybrid model developed by the authors exhibited excellent prediction accuracy with low root mean square error values. Moreover, the predicted solubility data were regressed in Aspen Plus V11 to design the process for the separation of H$_2$ from a gaseous feed mixture. Qian et al. [26] reported the use of DESs prepared with glycerol (Gly) and proline (Pro) as HBAs and MEA and MDEA as HBDs. It was found that the DESs based on MEA had better CO$_2$ absorption capacity than the DESs based on MDEA. The authors used ethylene glycol to form ternary DESs. The authors found that the absorption kinetics and regeneration capacity were improved by the addition of EG. Gly: MEA:EG showed better CO$_2$ capture performance than Pro: MEA:EG, reaching up to 0.25 g-CO$_2$/g-DES at room temperature. In addition, Gly: MEA:EG showed excellent tolerance to water content and CO$_2$ concentration, and there was no significant solvent loss after 10 cycles. The analytical methods showed that CO$_2$ formed carbamate by reacting with the amine group in MEA and amino acids. In addition, CO$_2$ was found to react with the–OH group in EG to form CO$_3^{2-}$/HCO$_3^-$. Pasha et al. [27] investigated the CO$_2$ absorption performance of five novel diamine functionalized DESs in microstructured reactors with metal foams as fillers. It was found that the N-methyl-1,3-propanediamine (MAPA) functionalized DES showed remarkable absorption performance without significant increase in viscosity. The CO$_2$ capacity and CO$_2$ absorption of this DES reached 0.78 mol CO$_2$/mol diamine and 98% at gas-liquid flow ratios of 640 and 240, respectively. Moreover, the results showed that the MAPA-functionalized DES exhibited low heat of absorption and remarkable regeneration ability. The authors reported that the overall rate constant and absorption flux of this DES were higher than most amine-functionalized DESs used previously. They concluded that the use of this DES in microreactors has great potential for process intensification in CO$_2$ absorption. In a recent study, Cheng et al. [28] reported the mechanism of CO$_2$ absorption by DESs based on ethylene glycol and protic IL, namely protonated MEA imidazolium ([MEAH][Im]). Analytical techniques showed that the interactions between CO$_2$ and DESs [MEAH][Im]- EG (1:3) and that CO$_2$ reacted not only with the amine group of MEA, but also with the deprotonated EG to form carbamate and carbonate, respectively. The authors proposed two mechanisms for the reaction between CO$_2$ and DESs. It was concluded that the absorption mechanism found in this work was different from that of other DESs formed by protic ILs and EG.

Another important parameter that negatively affects the performance and use of a solvent in many applications is its viscosity. Since DESs share several common properties with ILs, including high viscosity, it is imperative to reduce the viscosity of DESs to reduce operating costs in the industry and improve mass transfer. Most of the above DESs used for CO$_2$ capture have high viscosity, including the amine-based binary DESs studied by Adeyemi et al. [19]. Therefore, the aim of this work is to find novel amine-based ternary DESs with viscosity significantly lower than that of amine-based binary DESs. The proposed amine-based ternary DESs use low viscosity solvents such as water, which acts as the ternary component.

Materials and methods

Materials and sample preparation

The ternary DESs were prepared by a procedure similar to that described by Abbott et al. [13]. The source and purity of the chemicals used are summarized in Table 1.

Based on the molar ratio of HBA:HBD and the required weight percentage of water, the correct amounts of all 3 components were added to a properly sealed vial. The vial was then

Table 1. Source and purity of the chemicals used in this work.

Chemical	CAS number	Purity (*wt*%)	Source
Choline Chloride	67-48-1	$\geq$ 99.0	Sigma- Aldrich
Ethanolamine	141-43-5	$\geq$ 98.0	Sigma- Aldrich
Diethanolamine	111-42-2	$\geq$ 98.0	Sigma- Aldrich
Methyl Diethanolamine	105-59-9	$\geq$ 99.0	Sigma- Aldrich
Tetrabutylammonium Bromide	1643-19-2	$\geq$ 98.0	Sigma- Aldrich
Tetrabutylphosphonium Bromide	3115-68-2	$\geq$ 98.0	Sigma- Aldrich

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heated to about 353 K and stirred for several hours until the mixture became homogeneous and clear. Table 2 shows the main DESs prepared in this work.

Characterization

The melting points of the DESs investigated in this work were measured by differential scanning calorimetry (DSC 131 evo, SETARAM, Switzerland) with a temperature accuracy of +/- 0.1˚C and a precision of +/- 0.05˚C. Water content was measured using a Karl Fischer titrator (GRS Scientific/Aquamax KF Coulometric). The viscosity and density of all prepared DESs were measured as a function of temperature using Anton Paar SVM 3001 viscosity and density meter. Viscosities were measured in the range of 0.2 mPa.s to 30,000 mPa.s with a repeatability of 0.1% and densities in the range of 0.6 to 3 g/cm^3 with a repeatability of 5x10^{-3} g/cm^3. Thermal stability of the samples was determined using the Perkin Elmer Thermogravimetric Analyzer (TGA 4000) with a temperature accuracy of +/- 1˚C and a balance accuracy of +/- 0.02%.

CO_2 absorption capacity

The CO_2 absorption capacity and heat of absorption of the DESs were measured using the Thermal Hazard Technology micro-reaction calorimeter (μRC). The schematic diagram of the experimental setup is shown in Fig 1. The setup consists of a nitrogen gas cylinder and a CO_2 gas cylinder. The gas supply can be easily switched between the two cylinders via the supply switch. The gas flow is controlled by a flow meter connected to the calorimeter and the μRC control and analysis software on the computer. A pressure transducer connected to a pressure regulator is used to measure and display the pressure of the gas during the process.

Table 2. List of DESs prepared in this work.

		DES	Molar Ratio + Solvent Content
	1	ChCl-MEA + Water	1:6 + (2.5 wt% water)
	2	ChCl-MEA + Water	1:6 + (5 wt% water)
	3	ChCl-MEA + Water	1:6 + (7.5 wt% water)
	4	ChCl-MEA + Water	1:6 + (10 wt% water)
	5	ChCl-MEA + Water	1:6 + (12.5 wt% water)
	6	ChCl-MEA + Water	1:8 + (5 wt% water)
	7	ChCl-MEA + Water	1:10 + (5 wt% water)
	8	ChCl-DEA + Water	1:6 + (5 wt% water)
	9	ChCl-MDEA + Water	1:6 + (5 wt% water)
	10	TBAB-MEA + Water	1:6 + (5 wt% water)
	11	TBPB-MEA + Water	1:6 + (5 wt% water)

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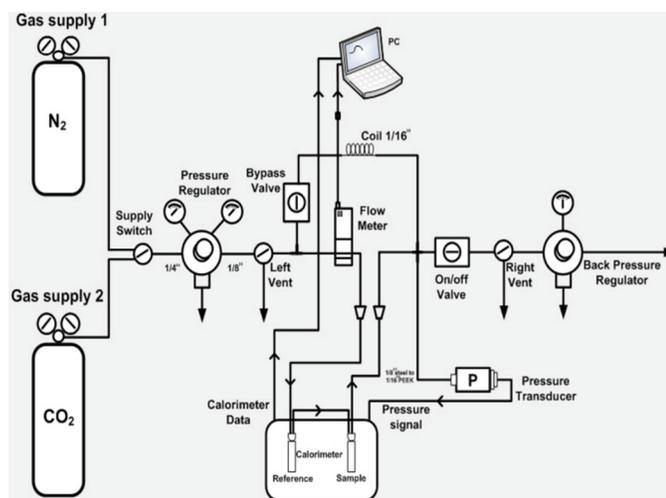
Fig 1. Schematic diagram of the micro-reaction calorimeter [21].

For each experiment, 0.5 g of the sample is injected into the vial using a syringe. The vial is properly sealed with its lid and then placed in the calorimeter with the appropriate tweezers. The μRC control and analysis software was then turned on and the process parameters were entered. The process temperature was set to 40˚C and the pressure to 1 atm. The experiment was then started and a plot of power versus time was displayed in the software. More details about the experimental protocol are appended at the end of this manuscript.

COSMO-RS calculation methodology

The Conductor like Screening Model for Real Solvents (COSMO-RS) was used to determine the effects of temperature and pressure changes on the CO_2 absorption of DESs [29–32]. Two steps were required in order to proceed with the COSMO-RS simulation. First, all involved components were created on the TURBOMOLE program using TmoleX software and a geometry optimization of each component was performed at the DFT energy level with the def-TZVP basis set. At the end of this first step, a single point calculation was conducted and the. *cosmo* files were generated. In the Second step, the COSMOthermX was used for the prediction of the CO_2 solubility of the DESs using the parameterization file BP_TZVP_19.ctd [33].

Furthermore, there are 3 different ways of representing DESs in COSMOtherm: (i) the electroneutral method, (ii) the ion pair method and (iii) the meta file method. In this work, the electroneutral approach was adopted in which each DES' component is treated as a distinct individual species. This means that when the molar ratio of the components of the DES is considered, the cation and the anion of the salt would be considered as individual components. For example, if the molar ratio of ChCl:Urea is 1:2, that would be entered in COSMOthermX as 1:1:2 for chlorine cation, chloride anion and urea, respectively.

The original expressions for the chemical potential and activity coefficient were derived by Klamt and Eckert [30], and they were also reported elsewhere [34].

Results and discussion

Melting point

The DSC thermograms of ChCl-MEA (1:6) and ChCl-MEA (1:6)-water DESs are shown in Fig 2. The melting point of each sample was determined from the peak of the respective melting
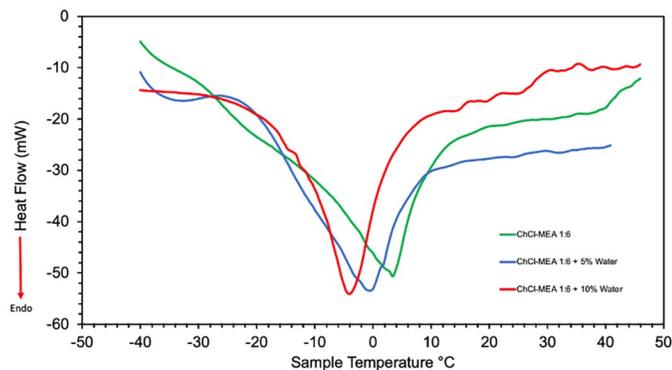
Fig 2. DSC Thermogram of neat ChCl-MEA (1:6) DES and with 5% and 10% water content.

curve. The results were first validated by measuring the melting point of ChCl- MEA (1:6) DES and comparing it with the value reported by Mjalli et al. [35]. There was an excellent agreement between the two values, about 4°C in this study while that reported by Mjalli et al. was 3.84°C. Subsequently, the melting points of ChCl- MEA (1:6) with 5% water and 10% water were determined to be -0.5°C and -4°C, respectively.

The melting points of the 3 DESs are below room temperature, which is desirable for the applications of such solvents. It is also observed that the melting point decreases with increasing water content in DES. It is well known that the formation of hydrogen bonds between the components of DES, in addition to charge delocalization, leads to a significant decrease in the melting point of the mixture compared to that of the individual components [13]. Thus, as the water content in the prepared ternary DESs increases, more hydrogen bonds are formed and further charge delocalization occurs and subsequently lowering the melting point.

Viscosity and density

The viscosities and densities of the prepared DESs were measured as a function of temperature, from 293 K to 353 K, using the Anton Paar SVM 3001. The obtained experimental measurements are provided as supporting Information (S1 and S2 Tables). Fig 3 shows the effects of changing the water content in the ternary DESs on the viscosity and density. It should be noted that the viscosity of the solvent for CO$_2$ absorption is very important not only to overcome mass transfer limitations and increase the solubility of CO$_2$ but also because the viscosity of the solvent increases dramatically with the increase of the solubility of CO$_2$ to the degree that it might cause technical problems in industrial application [36]. By lowering the viscosity
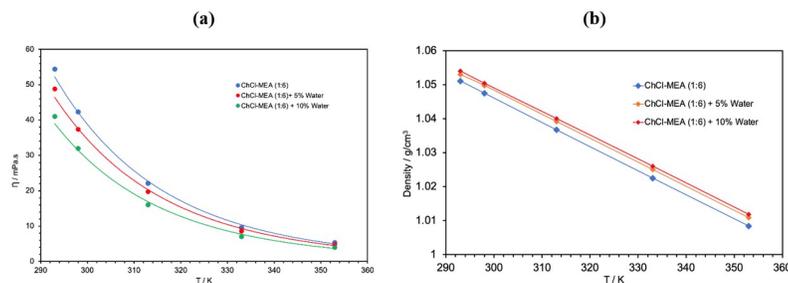
Fig 3. Effect of water content on the viscosity and density of the ChCl-MEA (1:6) DESs.

Table 3. Viscosity of different amine based DESs at room temperature.

	ChCl-MEA (1:6)	ChCl-MEA (1:6) + 5% Water	ChCl-DEA (1:6)	ChCl-DEA (1:6) + 5% Water	ChCl-MDEA (1:6)	ChCl-MDEA (1:6) + 5% Water
Viscosity (mPa. s)	51.71	48.8	567	434.14	139.8	123.16
Reference	Adeyemi et al. [36]	This work	Adeyemi et al. [36]	This work	Adeyemi et al. [36]	This work

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of the DES, the viscosity of the CO_2 saturated DES will be much lower than that for CO_2 in the binary amine DES.

As expected, the viscosity and density of all DESs decrease as the temperature increases. It is also observed that the viscosity of the ternary DESs decreases with increasing water content. This shows that the effect of the presence of a low viscosity component such as water will over-weigh the effect of the increase in the hydrogen bonding and eventually will lead to the decrease in the viscosity of the DESs compared to the binary DESs. This is in agreement with that reported in the literature by other groups [37]. The decrease in viscosity by introducing water as a component in the DES can be seen in other types of amine-based DESs. Table 3 illustrates the decrease in viscosity at room temperature when adding 5% water to each binary amine-based DES.

In fact, it can be noticed that the decrease in viscosity is about 5.6%, 23.4% and 12%, respectively, for MEA, DEA and MDEA based DESs. It is worth noting that the percentage decrease of the viscosity of the ternary DES is larger for high viscosity binary DES. On the other hand, it is observed that the density increases with the increase of water content. However, the increase is much higher at 5% than at 10% for the same DES. The complex hydrogen bonds formed between the water and the other constituents of the DES lead to a contraction of the volume and consequently to an increase in density [38].

The effect of changing the HBD:HBA molar ratio on the viscosity and density of the ternary DESs was also investigated. For this purpose, 3 different molar ratios (1:6, 1:8 and 1:10) were tested for ChCl- MEA- water (5%) DESs. Fig 4 shows that as the molar ratio of MEA in the DES increases, the viscosity and density decrease. The same behavior was reported for the binary DES ChCl- MEA. For example, at 298 K, the viscosity and density decreased by about 22.5% and 2%, respectively, when the molar ratio increased from 1:6 to 1:10. This could be due to the lower viscosity and density of MEA compared to ChCl. Therefore, it is expected that the viscosity and density of the resulting DES will decrease when more MEA is added. As shown in Fig 4, the viscosity and density of all 3 DESs showed inverse proportionality with temperature.
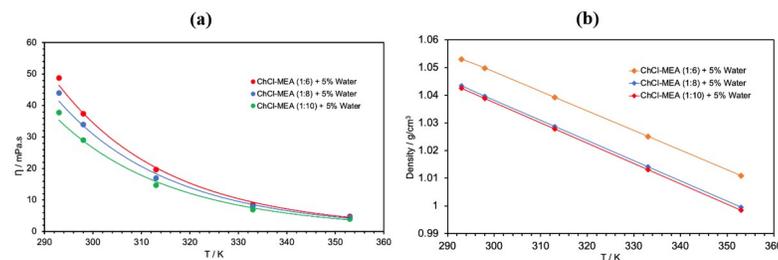
Fig 4. Effect of (HBA:HBD) molar ratio on viscosity and density of ChCl-MEA- 5% water DESs.

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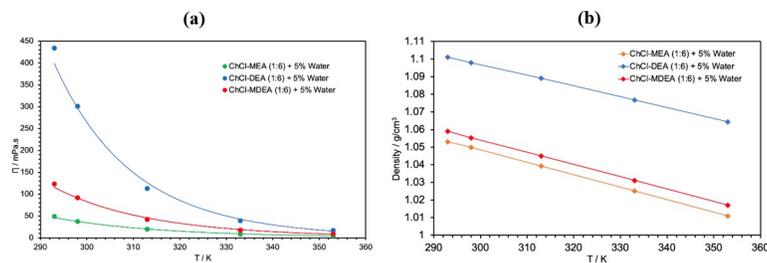
Fig 5. Effect of HBD type on the viscosity and density of ChCl-based DESs + 5% water.

Fig 5 shows the effect of the type of amine (MEA, DEA or MDEA) on the viscosity of the DESs as a function of temperature. DEA based DES has the highest viscosity and density over the whole temperature range with the values 301.2 mPa.s and 1.0979 g/cm^3 at 298 K, while MEA based DES has the lowest viscosity and density with the values 37.4 mPa.s and 1.0388 g/cm^3 at the same temperature. This may be attributed to the high viscosity and density of DEA compared to MEA and MDEA. Another explanation could be related to the hole theory [39]. MDEA and DEA based DESs have higher viscosity and density than MEA due to their larger molecules. This also means that they have a larger ionic radius, resulting in a smaller free volume and thus higher viscosity and density due to the limited mobility of the molecules [40]. These results support the use of MEA as HBD over DEA and MDEA in the CCS applications.

The viscosity and density experimental values of all prepared DESs at different temperatures can be found in the supplementary materials.

CO$_2$ absorption

Capacity results using the microreaction calorimeter used for measuring CO$_2$ absorption was first tested by measuring the absorption capacity of 30 wt% aqueous MEA and compared it with values reported in the literature. The obtained result, 0.12 g CO$_2$ / g solvent, is in excellent agreement with that reported by Ali et al. [41], 0.1195 g CO$_2$ / g solvent. Then, the CO$_2$ absorption capacity of the prepared DESs was measured and compared with that of the corresponding binary DESs and 30 wt.% MEA aqueous solution. Each experiment has been repeated at least twice, the average value was considered and the standard deviation indicated by the error bars in each plot (see Figs 6–9 below).

Effect of the water content. Fig 6 illustrates the effect of water content in the ternary DESs on CO$_2$ absorption capacity. Binary ChCl- MEA (1:6) DES showed a CO$_2$ absorption capacity of 0.17 g/g.
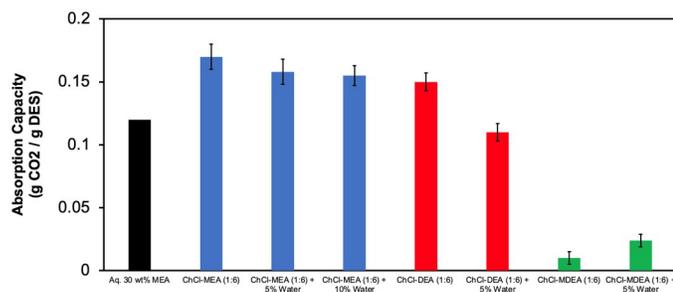
Fig 6. Effect of water content on CO$_2$ absorption compared to 30 wt% aqueous MEA.
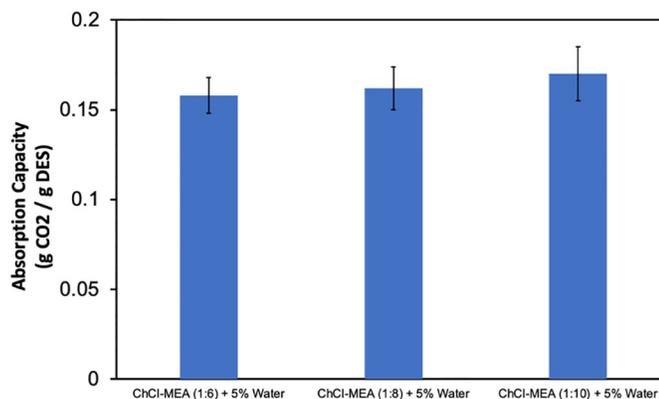
Fig 7. Effect of (HBA:HBD) molar ratio on CO_2 absorption capacity of the ChCl-MEA-5% water DESs.
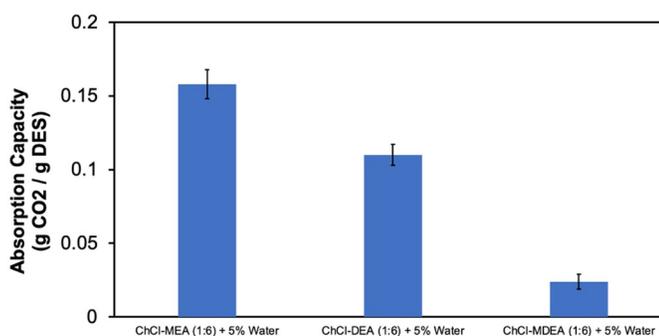
Fig 8. Effect of HBD type on CO_2 absorption capacity of the ChCl-based DESs + 5% water.
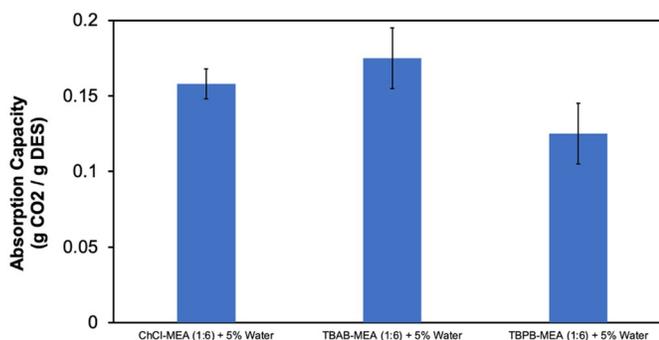
Fig 9. Effect of HBA type on CO_2 absorption capacity of the MEA-based DESs + 5% water.

The absorption capacity of the other two DESs decreased slightly: 0.158 g/g for the ChCl-MEA (1–6)—water (5%) and 0.155 g/g for the ChCl- MEA (1–6)—water (10%). The slight decrease in CO_2 absorption with the increase of water concentration could be due to the decrease in the weight fraction of MEA, which has a high affinity for CO_2. However, the decrease is comparatively small compared to the decrease in the viscosity and consequently

there is a faster mass transfer of CO_2 in the ternary DESs. Compared to the significant decrease in viscosity due to the inclusion of water in the DES, this slight decrease in absorption capacity can be considered insignificant. Consequently, these novel amine-based ternary DESs show great potential for industrial use due to their high CO_2 absorption capacity in addition to their relatively low viscosity.

The effect of water concentration on ChCl- DEA (1:6)-water (5%) was similar to that of ChCl- MEA. However, the decrease of absorption capacity with the increase of water was relatively significant. It can also be seen from Fig 6 that the CO_2 absorption capacity of the DESs based on MEA and DEA was higher than that of the 30 wt% aqueous MEA. This is because the CO_2 absorption by the 30 wt% aqueous MEA is achieved by chemical absorption only, while the CO_2 absorption by the DESs is achieved by chemical and physical absorption [42].

On the other hand, the results for ChCl-MDEA (1:6) DES and ChCl-MDEA (1–6)—water (5%) showed an opposite effect to that of the two aforementioned DESs. In this case, ChCl-MDEA (1:6) DES had an absorption capacity of 0.01 g/g, while ChCl-MDEA (1–6)-water (5%) had an absorption capacity of 0.024 g/g. This increase in CO_2 absorption capacity is due to the fact that the absorption of CO_2 by tertiary amines in the absence of water occurs only by a physical mechanism. However, when water is present, the reaction CO_2 with the tertiary amine to form carbamate becomes possible, and accordingly the CO_2 absorption capacity increases due to the additional chemical absorption [43].

Effect of the HBA:HBD molar ratio.   The effect of HBA:HBD molar ratio on CO_2 absorption capacity is shown in Fig 7. It can be observed that the absorption capacity increases from 0.158 g/g to 0.162 g/g and 0.17 g/g, respectively, when the molar ratio for ChCl- MEA- water (5%) decreased from 1:6 to 1:8 to 1:10. This trend is expected since the availability of MEA for reaction with CO_2 increases with the decrease of the molar ratio in DES, as mentioned earlier. In addition, the viscosity, and thus the mass transfer rate, decreases as the ratio of MEA in DES increases.

Effect of the type of HBA and HBD.   The CO_2 absorption capacity when changing the HBD, namely MEA, DEA and MDEA with ChCl as HBA, and fixing the molar ratio to 1:6 and 5 wt.% water is shown in Fig 8.

It can be seen that ChCl- MEA (1:6)-water (5%) has the highest absorption capacity, while ChCl-MDEA (1:6)-water (5%) has the lowest absorption capacity. This can be explained by the fact that MEA has the highest CO_2 solubility among the 3 amines due to its lower viscosity, which improves mass transfer in the absorption process. On the other hand, as mentioned earlier, MDEA requires water for the chemical absorption of CO_2. However, as water was added during the preparation of DES, it formed complex hydrogen bonds with the components of DES. Therefore, not all of the water is available for reaction with CO_2, so the CO_2 absorption capacity is not as high as that of MEA and DEA based DESs.

In addition, the effect of HBA on the CO_2 absorption capacity was investigated. Three different HBAs, namely ChCl, TBAB, and TBPB, were used with MEA as HBD, a molar ratio of 1:6, and 5 wt% water. It can be seen from Fig 9 that TBAB-MEA (1:6)- water (5%) had the highest absorption capacity and TBPB-MEA (1:6)- water (5%) had the lowest absorption capacity. According to the results reported in the literature, there is no clear trend in the difference of CO_2 absorption between ammonium-based and phosphonium based DESs [41, 44–48]. The solubility depends on many factors including the strength of hydrogen bonding within the DES structure, molar ratio, molar volume, free volume, molecular weight and alkyl chain length [44]. More work is needed to reach a solid conclusion.

Prediction of CO_2 solubility using COSMO-RS.   COSMO-RS was used to determine the effects of temperature and pressure changes on the CO_2 absorption of DESs. In addition, the effects of the molar ratio of HBA:HBD and the nature of HBD and HBA were investigated and

compared with the corresponding experimental results. CO$_2$ solubility was predicted and compared with experimental values to determine the ability of COSMO-RS is in quantitatively predicting CO$_2$ solubility. To proceed with the COSMO-RS simulations, the components involved were first created in the TURBOMOLE program using TmoleX software. Then, COSMOthermX was used to predict the CO$_2$ solubility of the DESs [33].

The effect of temperature change in the range between 293 K and 353 K on CO$_2$ solubility is shown in Fig 10. It is clear that the CO$_2$ solubility of all DESs decreases with increasing temperature.

This trend is due to the fact that as the temperature increases, the molecules gain more kinetic energy and can move more freely, which makes the CO$_2$ molecules more likely to escape into the gas phase. Moreover, ChCl- MEA (1:10)-water (5%) showed the highest CO$_2$ solubility among the tested DESs with ChCl as HBA, while ChCl-MDEA (1:6)- water (5%) showed the lowest CO$_2$ solubility. Moreover, the solubility increases when the molar ratio of MEA:ChCl increases from 1:6 to 1:10. When comparing ChCl- MEA (1:6)- water (5%), ChCl-MEA (1:6)- water (10%) and ChCl- MEA (1:6), it is also found that the solubility of CO$_2$ decreases with increasing water content. All these results are in agreement with the experimental results and reflect the accuracy of this software in qualitatively predicting such factors [49]. Moreover, the effect of pressure changes in the range between 1 bar and 5 bar on CO$_2$ solubility is illustrated in Fig 11. As expected, the CO$_2$ solubility increases with increasing pressure. This relationship is consistent with Henry's law [50].

Fig 12 shows a comparison of the CO$_2$ solubility values predicted by COSMO-RS with the corresponding experimental values at 40˚C for selected DESs.

From Fig 12, it can be seen that the experimental values were higher than those predicted by COSMO-RS for all DESs tested. However, both the experimental and predicted data show the same trend in terms of changes in water content and molar ratio. The relative deviation, $(x^{exp} - x^{COSMO\ RS})/x^{exp}) \times 100\%$, between experimental and predicted values is significant. For example, in the case of ChCl- MEA (1:6), the relative deviation is about 52.7%. This indicates that COSMO-RS can be used qualitatively but not quantitatively to predict CO$_2$ solubility. Most likely, this is due to the fact that COSMO-RS takes into account the physical absorption of CO$_2$ only, but not the chemisorption of CO$_2$ in the amines.
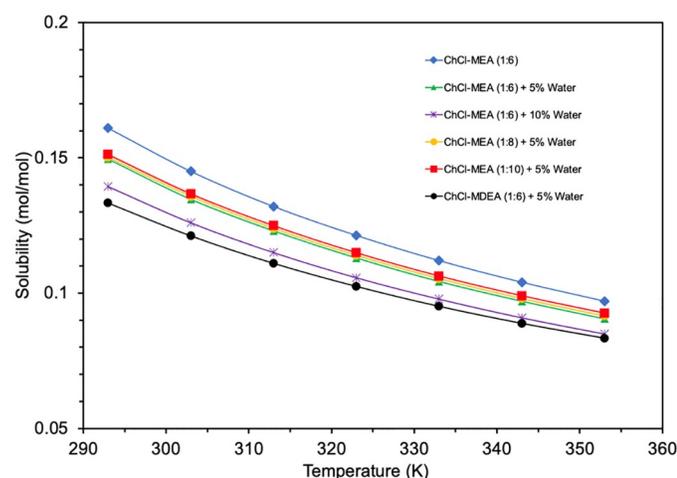
Fig 10. Effect of temperature on CO$_2$ solubility of amine-based DESs predicted by COSMO-RS.
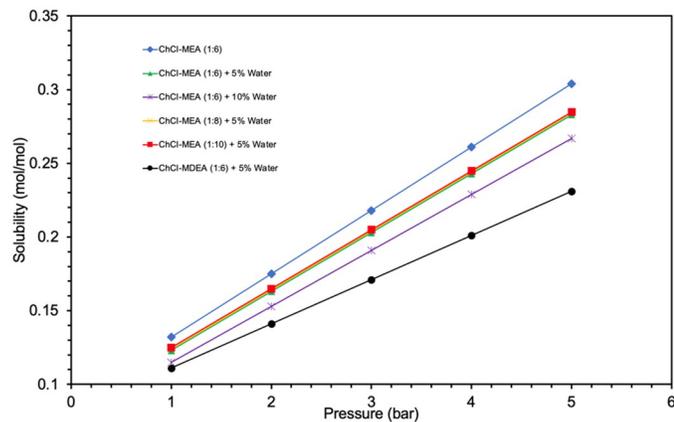
Fig 11. COSMO-RS prediction for pressure effect on CO$_2$ solubility of amine-based DESs.

https://doi.org/10.1371/journal.pone.0286960.g011
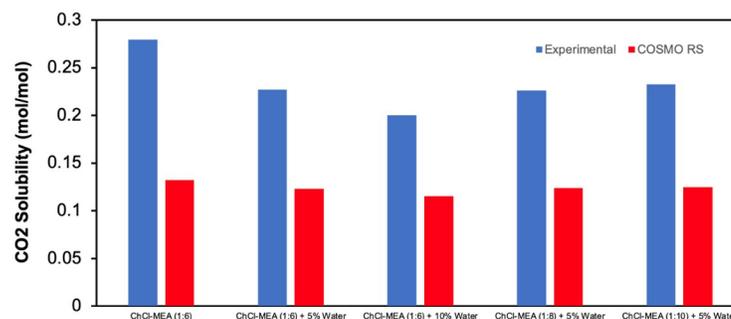
Fig 12. Experimental vs COSMO-RS values for the CO$_2$ solubility of the studied DESs.

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Modeling the DESs viscosity using the Vogel-Fulcher-Tammann (VFT) model

There are several models that describe the effect of temperature on the viscosity of liquids. In this study, the temperature-dependent viscosity data for the different selected DESs were fitted according to the Vogel-Fulcher-Tammann-Hesse (VFTH) equation (Eq 1) [51–53]:

$$\eta = A \cdot exp\left[\frac{B}{T - T_0}\right] \tag{1}$$

This three-parameter model has been shown to be the most accurate equation for estimating the viscosity of fluids, especially in the low temperature range [54].

The fitting results were obtained using MATLAB Fitting Toolbox. The fitting parameters A, B, and T_0, as well as the regression coefficient R^2 and the average absolute relative deviation (AARD) are shown in Table 4. With a correlation coefficient R^2 that is close to 1, an excellent fit is achieved. Moreover, the AARD does not exceed 3.2%, indicating excellent agreement between the experimental data and the VFTH equation.

Table 4. Parameters of the VFTH equation for temperature dependence of viscosity (mPa.s), together with the correlation coefficients and relative deviation.

DES type	A (mPa.s)	B (K)	T_0 (K)	R^2	AARD (%)
ChCl-MEA (1:6)	0.03494	948.1	164.4	1	0.32
ChCl-MEA (1:6) + 2.5% Water	0.02718	1012	158.8	1	0.45
ChCl-MEA (1:6) + 5% Water	0.0181	1138	148.9	1	0.71
ChCl-MEA (1:6) + 7.5% Water	0.01589	1206	140.9	0.9998	2.00
ChCl-MEA (1:6) + 10% Water	0.005001	1518	124.6	0.9999	2.17
ChCl-MEA (1:6) + 12.5% Water	0.07434	657.3	187.8	0.9998	1.07
ChCl-MEA (1:8) + 5% Water	0.04552	852.6	169	0.9997	2.47
ChCl-MEA (1:10) + 5% Water	0.06876	720.2	178.9	0.9998	2.21
ChCl-DEA (1:6) + 5% Water	0.005101	1699	143.4	1	0.87
ChCl-MDEA (1:6) + 5% Water	0.01278	1380	142.6	1	0.54
TBAB-MEA (1:6) + 5% Water	0.04316	792.2	187.1	0.9991	2.04
TBPB-MEA (1:6) + 5% Water	0.0837	691.8	184.8	0.9996	3.22

Thermal stability of DESs

Thermal degradation of alkanolamines in general and MEA in particular leads to significant solvent loss in the stripping section of CCS plants during the regeneration step, where the temperature is usually around 120°C, contributing to an increase in operating costs. At such temperature, amines tend to react irreversibly with acid gasses such as CO_2, H_2S, SO_x, and NO_x, leading to solvent decomposition [55, 56]. Thermal degradation of amines also leads to the formation of undesirable pollutants such as nitrosamines and nitramines, which cause serious environmental and health problems [57, 58]. Moreover, the degradation of amines can lead to other problems such as corrosion, foaming, and fouling of the stripping columns, in addition to the decrease in the absorption capacity of the solvents [59–61].

In this study, the thermal stability of selected DESs was measured using the Perkin Elmer Thermogravimetric Analyzer (TGA) 4000 by plotting the weight fraction of DES against temperature, as shown in Fig 13.

The main objective is to evaluate the effect of water content on the thermal stability of amine-based ternary DESs. It was found that the degradation temperature of ChCl- MEA (1:8) is about 125°C, which is much higher than that of MEA with a degradation temperature of
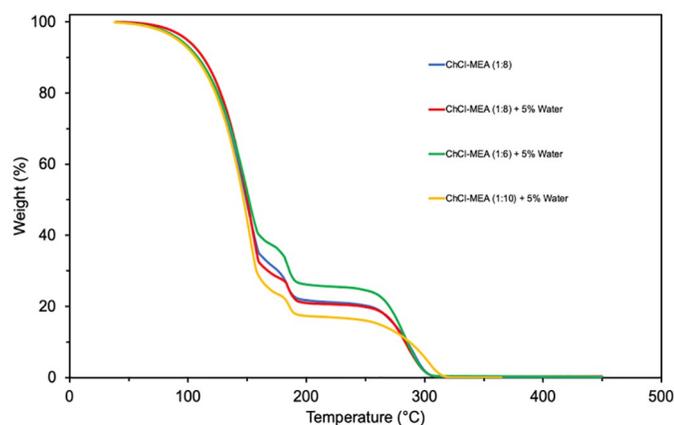
Fig 13. Effect of water content (5%) on the thermal stability of ChCl-MEA DESs.

about 65˚C as reported by Adeyemi et al. [36]. This confirms the clear advantage that amine-based DESs have over stand-alone amines in terms of thermal stability. Moreover, the degradation temperature of the water-containing DESs, namely ChCl- MEA (1:6)-water (5%), ChCl-MEA (1:8)- water (5%), and ChCl- MEA (1:10)- water (5%), was similar. These results indicate that the water did not evaporate at its normal boiling point. This is because the water, when added during the preparation of DES, becomes part of the structure of DES by forming hydrogen bonds with the other constituents of the DES. Such behavior is extremely advantageous for post-combustion process, where the regeneration temperature is around 120˚C [62]. Moreover, the degradation temperature of all DESs is higher than that of 30 wt% aqueous MEA, which has a thermal degradation temperature of about 105˚C according to Kang et al. [63]. This is due to the complex and strong hydrogen bonds between the constituents of DESs, in addition to their negligible vapor pressure, which reduces the solvent loss due to degradation [64].

Conclusion

Novel amine-based ternary DESs having water as a constituent were prepared for the potential use for CO$_2$ absorption. The physicochemical properties such as melting point, viscosity and density of the DESs were measured. It was found that the viscosity of the ternary DESs decreased up to 25% which is highly favorable for CO$_2$ absorption. The thermal stability of these ternary DESs, determined by TGA analysis, was found to be similar to that of binary DESs, with an initial degradation temperature of about 125˚C compared to 105˚C of 30 wt. % MEA aqueous solution. This indicates that the water in these DESs is not free and that it is combined with the HBA and HBD with strong hydrogen bonding. The measured CO$_2$ absorption capacity for the ternary DESs were found to be between 0.155 and 0.17 (g CO$_2$ / g DES) for MEA based DESs, which is higher than that of 30 wt. % aqueous MEA (0.12 g CO$_2$ / g solvent). CO$_2$ solubility in the DESs was predicted using COSMO-RS and compared with the experimental values. It was found that COSMO-RS is a suitable tool for qualitative prediction of CO$_2$ solubility in DESs, since it correctly represents the trend resulting from the effects of changing different factors on CO$_2$ solubility compared to experimental results.

In addition, the influence of water content, molar ratio of HBA to HBD, and type of HBD and HBA on the physiochemical properties and CO$_2$ absorption of the ternary DESs were investigated. The results showed that ChCl- MEA (1:6), (1:8) and (1:10)- water (5 and 10%) were the best candidates for CO$_2$ capture in terms of their CO$_2$ absorption capacity and thermal stability.

In summary, the use of water as constituent in the amine based ternary DESs reduced the viscosity and did not affect the CO$_2$ absorption capacity or the thermal stability compared to binary amine based DESs. This makes the novel ternary DESs a potential solvent for CO$_2$ capture. However, more work is needed to measure the heat needed for regeneration.

Supporting information

S1 Table. Viscosities of the prepared DESs at different temperatures.
(DOCX)

S2 Table. Densities of the prepared DESs at different temperatures.
(DOCX)

S1 Appendix. Experimental protocol.
(DOCX)

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References

1. U.S. Energy Information Administration, Office of Energy Analysis, U.S. Department of Energy. International energy outlook 2019 with projections to 2050. Washington, DC, 2019 Sept.

2. Luis P, Van Gerven T, Van der Bruggen B. Recent developments in membrane-based technologies for CO_2 capture. Prog Energ Combust. 2012; 38(3):419–48.

3. Lv B, Guo B, Zhou Z, Jing G. Mechanisms of CO_2 capture into monoethanolamine solution with different CO_2 loading during the absorption/desorption processes. Environ Sci Technol. 2015; 49(17):10728–35.

4. El Hadri N, Quang DV, Goetheer EL, Zahra MRA. Aqueous amine solution characterization for post-combustion CO_2 capture process. Appl Energ. 2017; 185:1433–49.

5. Zhao Z, Dong H, Huang Y, Cao L, Gao J, Zhang X, et al. Ionic degradation inhibitors and kinetic models for CO_2 capture with aqueous monoethanolamine. Int J Greenh Gas Con. 2015; 39:119–28.

6. Zhang X, Zhang C-F, Liu Y. Kinetics of absorption of CO_2 into aqueous solution of MDEA blended with DEA. Ind Eng Chem Res. 2002; 41(5):1135–41.

7. Glasscock DA, Critchfield JE, Rochelle GT. CO_2 absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine. Chem Eng Sci. 1991; 46(11):2829–45.

8. Brúder P, Grimstvedt A, Mejdell T, Svendsen HF. CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. Chem Eng Sci. 2011; 66(23):6193–8.

9. Lu J-G, Lu C-T, Chen Y, Gao L, Zhao X, Zhang H, et al. CO_2 capture by membrane absorption coupling process: application of ionic liquids. Appl Energ. 2014; 115:573–81.

10. Aghaie M, Rezaei N, Zendehboudi S. A systematic review on CO_2 capture with ionic liquids: Current status and future prospects. Renew Sust Energ Rev. 2018; 96:502–25.

11. Raeissi S, Peters CJ. Carbon dioxide solubility in the homologous 1-alkyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide family. J Chem Eng Data. 2009; 54(2):382–6.

12. Kumełan J, Tuma D, Pérez-Salado Kamps AI, Maurer G. Solubility of the single gases carbon dioxide and hydrogen in the ionic liquid [bmpy][Tf2N]. J Chem Eng Data. 2010; 55(1):165–72.

13. Abbott AP, Capper G, Davies DL, Rasheed RK, Tambyrajah V. Novel solvent properties of choline chloride/urea mixtures. Chem Commun. 2003;(1):70–1. https://doi.org/10.1039/b210714g PMID: 12610970

14. Aissaoui T, AlNashef IM, Qureshi UA, Benguerba Y. Potential applications of deep eutectic solvents in natural gas sweetening for CO_2 capture. Rev Chem Eng. 2017; 33(6):523–50.

15. Aldawsari JN, Adeyemi IA, Bessadok-Jemai A, Ali E, AlNashef IM, Hadj-Kali MK. Polyethylene glycol-based deep eutectic solvents as a novel agent for natural gas sweetening. Plos One. 2020; 15(9): e0239493. https://doi.org/10.1371/journal.pone.0239493 PMID: 32956424

16. Lu M, Han G, Jiang Y, Zhang X, Deng D, Ai N. Solubilities of carbon dioxide in the eutectic mixture of levulinic acid (or furfuryl alcohol) and choline chloride. J Chem Thermodyn. 2015; 88:72–7.

17. Li X, Hou M, Han B, Wang X, Zou L. Solubility of CO_2 in a choline chloride+ urea eutectic mixture. J Chem Eng Data. 2008; 53(2):548–50.

18. Sze LL, Pandey S, Ravula S, Pandey S, Zhao H, Baker GA, et al. Ternary deep eutectic solvents tasked for carbon dioxide capture. Acs Sustain Chem Eng. 2014; 2(9):2117–23.

19. Adeyemi I, Abu-Zahra MR, Alnashef I. Experimental study of the solubility of CO_2 in novel amine based deep eutectic solvents. Enrgy Proced. 2017; 105:1394–400.

20. Wu X, Cheng N-N, Jiang H, Zheng W-T, Chen Y, Huang K, et al. 1-ethyl-3-methylimidazolium chloride plus imidazole deep eutectic solvents as physical solvents for remarkable separation of H_2S from CO_2. Sep Purif Technol. 2021; 276:119313.

21. Sarmad S, Nikjoo D, Mikkola J-P. Amine functionalized deep eutectic solvent for CO_2 capture: Measurements and modeling. J Mol Liq. 2020; 309:113159.

22. Haghbakhsh R, Keshtkar M, Shariati A, Raeissi S. A comprehensive experimental and modeling study on CO_2 solubilities in the deep eutectic solvent based on choline chloride and butane-1, 2-diol. Fluid Phase Equilibr. 2022; 561:113535.

23. Wang X, Zheng K, Peng Z, Liu B, Jia X, Tian J. Exploiting proton masking to protect amino achieve efficient capture CO_2 by amino-acids deep eutectic solvents. Sep Purif Technol. 2022; 299:121787.

24. Al-Bodour A, Alomari N, Gutiérrez A, Aparicio S, Atilhan M. High-pressure carbon dioxide solubility in terpene based deep eutectic solvents. J Environ Chem Eng. 2022; 10(5):108237.

25. Nagulapati VM, Rehman HMRU, Haider J, Qyyum MA, Choi GS, Lim H. Hybrid machine learning-based model for solubilities prediction of various gases in deep eutectic solvent for rigorous process design of hydrogen purification. Sep Purif Technol. 2022; 298:121651.

26. Qian W, Hao J, Zhu M, Sun P, Zhang K, Wang X, et al. Development of green solvents for efficient post-combustion CO_2 capture with good regeneration performance. J CO₂ Util. 2022; 59:101955.

27. Pasha M, Zhang H, Shang M, Li G, Su Y. CO_2 absorption with diamine functionalized deep eutectic solvents in microstructured reactors. Process Saf Environ. 2022; 159:106–19.

28. Cheng J, Wu C, Gao W, Li H, Ma Y, Liu S, et al. CO_2 Absorption Mechanism by the Deep Eutectic Solvents Formed by Monoethanolamine-Based Protic Ionic Liquid and Ethylene Glycol. Int J Mol Sci. 2022; 23(3):1893.

29. Klamt A. Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena. The J Phys Chem-US. 1995; 99(7):2224–35.

30. Klamt A, Eckert F. COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids. Fluid Phase Equilibr. 2000; 172(1):43–72.

31. Hardacre C, Jacquemin J, Manan NA, Rooney DW, Youngs TG. Prediction of gas solubility using COSMOthermX. Plechkova Natalia V., Rogers Robin D., Seddon Kenneth R., Editors. ACS Publications; 2010. p. 359–383.

32. Alioui O, Benguerba Y, Alnashef IM. Investigation of the CO_2-solubility in deep eutectic solvents using COSMO-RS and molecular dynamics methods. J Mol Liq. 2020; 307:113005.

33. Eckert F, Klamt A. A Graphical User Interface to the COSMOtherm Program. no COSMOlogic GmbH & Co KG, Leverkusen, Germany. 2013:1–77.

34. Ali E, Hadj-Kali MK, Alnashef I. Modeling of CO_2 solubility in selected imidazolium-based ionic liquids. Chem Eng Commun. 2017; 204(2):205–15.

35. Mjalli FS, Murshid G, Al-Zakwani S, Hayyan A. Monoethanolamine-based deep eutectic solvents, their synthesis and characterization. Fluid Phase Equilibr. 2017; 448:30–40.

36. Adeyemi I, Abu-Zahra MR, AlNashef IM. Physicochemical properties of alkanolamine-choline chloride deep eutectic solvents: Measurements, group contribution and artificial intelligence prediction techniques. J Mol Liq. 2018; 256:581–90.

37. Dai Y, Witkamp G-J, Verpoorte R, Choi YH. Tailoring properties of natural deep eutectic solvents with water to facilitate their applications. Food Chem. 2015; 187:14–9. https://doi.org/10.1016/j.foodchem.2015.03.123 PMID: 25976992

38. Xie Y, Dong H, Zhang S, Lu X, Ji X. Effect of water on the density, viscosity, and CO_2 solubility in choline chloride/urea. J Chen Eng Data. 2014; 59(11):3344–52.

39. Abbott AP, Harris RC, Ryder KS. Application of hole theory to define ionic liquids by their transport properties. J Phys Chem. B. 2007; 111(18):4910–3. https://doi.org/10.1021/jp0671998 PMID: 17388488

40. Sarmad S, Xie Y, Mikkola J-P, Ji X. Screening of deep eutectic solvents (DESs) as green CO 2 sorbents: from solubility to viscosity. New J Chem. 2017; 41(1):290–301.

41. Ali E, Hadj-Kali MK, Mulyono S, Alnashef I, Fakeeha A, Mjalli F, et al. Solubility of CO$_2$ in deep eutectic solvents: experiments and modelling using the Peng–Robinson equation of state. Chem Eng Res Des. 2014; 92(10):1898–906.

42. Mazari SA, Ghalib L, Sattar A, Bozdar MM, Qayoom A, Ahmed I, et al. Review of modelling and simulation strategies for evaluating corrosive behavior of aqueous amine systems for CO$_2$ capture. Int J Greenh Gas Con. 2020; 96:103010.

43. Versteeg G, van Swaaij WPM. On the kinetics between CO$_2$ and alkanolamines both in aqueous and non-aqueous solutions—II. Tertiary amines. Chem Eng Sci. 1988; 43(3):587–91.

44. Ghaedi H, Ayoub M, Sufian S, Lal B, Shariff AM. Measurement and correlation of physicochemical properties of phosphonium-based deep eutectic solvents at several temperatures (293.15 K–343.15 K) for CO$_2$ capture. J Chem Thermodyn. 2017; 113:41–51.

45. Wang J, Cheng H, Song Z, Chen L, Deng L, Qi Z. Carbon dioxide solubility in phosphonium-based deep eutectic solvents: an experimental and molecular dynamics study. Ind Eng Chem Res. 2019; 58 (37):17514–23.

46. Wazeer I, AlNashef IM, Al-Zahrani AA, Hadj-Kali MK. The subtle but substantial distinction between ammonium-and phosphonium-based deep eutectic solvents. J Mol Liq. 2021; 332:115838.

47. Naik PK, Paul S, Banerjee T. Physiochemical properties and molecular dynamics simulations of phosphonium and ammonium based deep eutectic solvents. J Solution Chem. 2019; 48:1046–65.

48. Luo F, Liu X, Chen S, Song Y, Yi X, Xue C, et al. Comprehensive evaluation of a deep eutectic solvent based CO$_2$ capture process through experiment and simulation. ACS Sustain Chem Eng. 2021; 9 (30):10250–65.

49. Sumon KZ, Henni A. Ionic liquids for CO2 capture using COSMO-RS: Effect of structure, properties and molecular interactions on solubility and selectivity. Fluid Phase Equilibr. 2011; 310(1–2):39–55.

50. Ghaedi H, Ayoub M, Sufian S, Shariff AM, Hailegiorgis SM, Khan SN. CO$_2$ capture with the help of Phosphonium-based deep eutectic solvents. J Mol Liq. 2017; 243:564–71.

51. Vogel H. Das temperaturabhängigkeitsgesetz der viskosität von flüssigkeiten. Phys Z. 1921; 22:645–6. German.

52. Fulcher GS. Analysis of recent measurements of the viscosity of glasses. J Am Ceram Soc. 1925; 8 (6):339–55.

53. Tammann G, Hesse W. Die Abhängigkeit der Viscosität von der Temperatur bie unterkühlten Flüssigkeiten. Zeitschrift für anorganische und allgemeine Chemie. 1926; 156(1):245–57. German.

54. Garca-Coln L, Del Castillo L, Goldstein P. Theoretical basis for the Vogel-Fulcher-Tammann equation. Phys Rev B. 1989; 40(10):7040. https://doi.org/10.1103/physrevb.40.7040 PMID: 9991086

55. Mazari SA, Ali BS, Jan BM, Saeed IM. Degradation study of piperazine, its blends and structural analogs for CO$_2$ capture: a review. Int J Greenh Gas Con. 2014; 31:214–28.

56. Mazari SA, Ali BS, Jan BM, Saeed IM, Nizamuddin S. An overview of solvent management and emissions of amine-based CO$_2$ capture technology. Int J Greenh Gas Con. 2015; 34:129–40.

57. Låg M, Andreassen ÅK, Instanes C, Lindeman B. Health effects of different amines and possible degradation products relevant for CO$_2$ capture. Norvegian Institute of Public Health. 2009. rapport Nasjonalt folkehelseinstitutt, ISBN: 978-82-8082-322-9.

58. Bartsch H, Montesano R. Relevance of nitrosamines to human cancer. Carcinogenesis. 1984; 5 (11):1381–93. https://doi.org/10.1093/carcin/5.11.1381 PMID: 6386215

59. Fytianos G, Ucar S, Grimstvedt A, Hyldbakk A, Svendsen HF, Knuutila HK. Corrosion and degradation in MEA based post-combustion CO$_2$ capture. Int J Greenh Gas Con. 2016; 46:48–56.

60. Zoannou K-S, Sapsford DJ, Griffiths AJ. Thermal degradation of monoethanolamine and its effect on CO$_2$ capture capacity. Int J Greenh Gas Con. 2013; 17:423–30.

61. Rey A, Gouedard C, Ledirac N, Cohen M, Dugay J, Vial J, et al. Amine degradation in CO$_2$ capture. 2. New degradation products of MEA. Pyrazine and alkylpyrazines: analysis, mechanism of formation and toxicity. Int J Greenh Gas Con. 2013; 19:576–83.

62. Song H-J, Lee S, Park K, Lee J, Chand Spah D, Park J-W, et al. Simplified estimation of regeneration energy of 30 wt% sodium glycinate solution for carbon dioxide absorption. Ind Eng Chem Res. 2008; 47 (24):9925–30.

63. Kang M-K, Jeon S-B, Cho J-H, Kim J-S, Oh K-J. Characterization and comparison of the CO$_2$ absorption performance into aqueous, quasi-aqueous and non-aqueous MEA solutions. Int J Greenh Gas Con. 2017; 63:281–8.

64. Helgesen LI, Gjernes E. A way of qualifying Amine Based Capture Technologies with respect to Health and Environmental Properties. Enrgy Proced. 2016; 86:239–51.