




Experimental study on the effect of water addition to ChCl-MEA DES towards its performance in CO₂ removal from syngas

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Abstract

ChCl-MEA DES was used to absorb CO₂ from gasification syngas consisting of CO₂, CO, CH₄, and H₂. This study investigated the effect of water addition on CO₂ absorption capabilities of ChCl-MEA DES with different mole ratios of ChCl to MEA, and different absorption temperatures. It was found that water addition had a positive effect on CO₂ solubility of ChCl-MEA DES, with the maximum obtained value of 0.5 mol-CO₂/mol-DES for aqueous ChCl-MEA DES with 75%vol water at absorption temperature of 40 °C and pressure of 9 bar. In general, water addition increases CO₂ solubility and absorption rate of ChCl-MEA DES. ChCl-MEA DES 1:5 mol ratio was able to benefit from water addition up to 75%vol water content. While ChCl-MEA 1:10 had its CO₂ solubility increase with water addition up to 50%vol, after which, it declined. Investigation into water addition at different absorption temperatures revealed that water addition at 40 °C produced the most significant CO₂ solubility enhancement compared to water addition at 20 °C and 60 °C. This might be caused by the tradeoff between the effects of high temperature in decreasing ChCl-MEA DES viscosity and lowering its CO₂ solubility. Highest CO₂/CO selectivity for ChCl-MEA DES 1:5 was found to be around 34.6, CO₂/CH₄ was 26.7, and CO₂/H₂ was 4. Water addition was found to have slight reducing effect on the CO₂ selectivity of ChCl-MEA DES.

Keywords CO₂ · Absorption · Deep eutectic absorbent · Syngas · Water

1 Introduction

Gasification is a thermochemical process to convert solid fuel to gaseous products called syngas. Syngas usually consists of H₂, CO, CO₂, CH₄, and H₂S. Syngas could be used as chemical feedstock in various synthesis process such as methanol, ammonia, and hydrogen fuel [1–3]. However, to be able to be utilized for these applications, syngas needs to be upgraded to meet strict requirements for the respective applications. This upgrading process usually includes the removal of CO₂ and H₂S. CO₂ removal in the industry is most commonly done using absorption process by solvents such as amine, Rectisol, and Selexol [4, 5]. Albeit

performing well, these commercially available absorbents still carry a lot of drawbacks. Some of those weaknesses, such as amine's corrosive nature and absorbent loss [6, 7] or physical absorbents' need of extreme operating condition [8, 9], incur considerable cost to the CO₂ capture process.

Therefore, innovations into more efficient CO₂ capture process are required. One of the potential candidates is deep eutectic solvent (DES). DES has been increasingly studied in the last decade, as it generally offers advantages such as good CO₂ absorption performance in moderate operating conditions and easy regeneration [10]. DES based on choline chloride (ChCl) in particular has been the focus of many studies due to its advantages like compatibility with many compounds to form DES, environmental friendliness, and affordable cost [11–14]. One ChCl-based DES that was found to perform well was DES synthesized from choline chloride and monoethanolamine (ChCl-MEA DES). ChCl-MEA DES has been shown by various studies to have the CO₂ solubility between 0.21 and 0.38 mol-CO₂/mol-DES at moderate operating conditions [15, 16]. While this is still lower than the conventional MEA absorbents that could theoretically reach the capacity of 0.5 mol-CO₂/mol-amine [17],

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the CO₂ solubility of DES could potentially be increased by increasing absorption pressure.

Despite the potential of high CO₂ solubility, ChCl-MEA DES is not ready to be used commercially. One main drawback is the high viscosity of the DES that could reduce absorption performance and making regeneration difficult. A study by Mjalli et al. reported that the viscosity of ChCl-MEA DES is around 49.5 cP at 25 °C [18]. Viscosity of DES decreases with increase in temperature [18], meaning that increasing absorption temperature could alleviate the issue of high viscosity. However, it has also been reported that CO₂ solubility in DES decrease with the increase in absorption temperature. Another simple and affordable method of addressing the high viscosity issue would be by mixing DES with water to form aqueous DES solution. Other than lowering its viscosity significantly, it was found that mixing water into DES provides the additional benefit of increasing its CO₂ solubility as well as absorption rate [15, 19]. However, Hammond et. al. [20, 21] found that there is a maximum threshold of water content that could be tolerated by DES, above which DES dissolve into its components. This threshold varies from one DES to another, necessitating study into the optimum yet safe amount of water that could be mixed with certain DES. This subject is important to study for various safe and efficient application of DES such as with gas streams that might contain water vapor, or DES for treatment of biomass [22, 23].

In this study, the effect of water addition to ChCl-MEA DES was investigated with the goal of maximizing the CO₂ absorption capabilities of aqueous ChCl-MEA DES absorbent. The effect of water addition is examined with batch absorption experiments using ChCl-MEA DES with different mole ratios and at different absorption temperatures. Viscosity measurements were done to quantify the effect of water addition at various temperatures towards lowering the viscosity of aqueous ChCl-MEA DES. FTIR spectra was also conducted on pure DES and aqueous DES, before and after CO₂ absorption to provide information regarding the absorption mechanisms involved. Furthermore, gas chromatography data of the outlet gas was used to determine CO₂ selectivity of ChCl-MEA DES absorbent.

2 Experiment setting

2.1 DES preparation

Materials used in this study include 99.5% purity monoethanolamine (MEA) purchased from Chinese chemical vendor, Aladdin-e, and used without purification. Choline chloride (ChCl) 99% purity from the same vendor was also used in this study. It is oven dried for 24 h at 105 °C before use to

remove water content. The water addition was done using demineralized water.

This study used 2 types of ChCl-MEA DES, 1:5 and 1:10 mol ratio. They would be referred to as DES 1:5 and DES 1:10, respectively. The pure DES were prepared by first weighing appropriate amounts of each material and placing them in a glass beaker. The beaker was then sealed and heated at 70 °C for 3 h while stirred at 300 rpm. The result was a single phase clear viscous DES liquid that would then be stored in sealed containers before use. Aqueous DES was prepared by mixing appropriate volumetric amounts of pure ChCl-MEA DES and demineralized water to create aqueous DES solutions with 0, 25%vol, 50%vol, 75%vol, 80%vol, and 85%vol of water. Aqueous MEA solutions were prepared by mixing MEA with demineralized water using the same method as aqueous DES and with the same water content in them. These aqueous DES and aqueous MEA solutions were kept in sealed containers before use.

2.2 Absorption experiment

CO₂ absorption experiments were conducted in a 100 mL batch reactor with heating and stirring capabilities. The inlet valve to the reactor was connected to a model syngas tank and the outlet valve led to a needle valve for gas sampling into gas bags. The model syngas used in this study was purchased from a chemical vendor in China and consist of 30%vol H₂, 40%vol CO₂, 5%vol CO, 5%vol CH₄, and 20%vol N₂. This choice of syngas was chosen to simulate the composition of syngas from supercritical water gasification (SCWG) and diluted with N₂ to ensure safety during experiment. The complete schematics of the reactor used is depicted in Fig. 1.

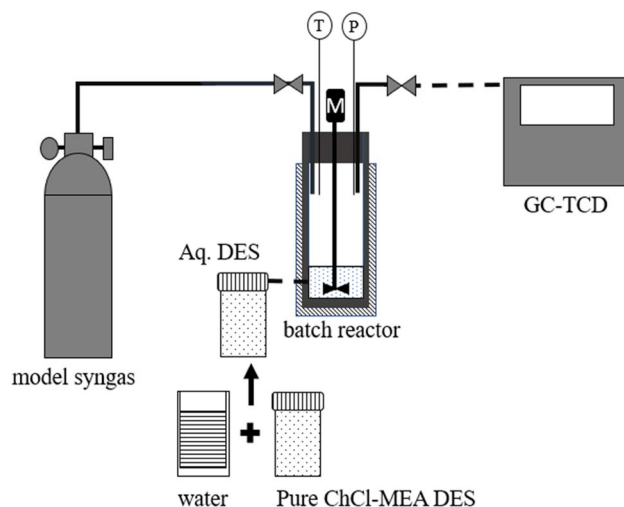


Fig. 1 Batch reactor setting for CO₂ absorption experiments

Batch absorption experiment was conducted by first placing 2 mL of absorbent sample in the reactor, which was then sealed and flushed with N_2 to remove excess air. The reactor was then heated to 40 °C, and once the target temperature was reached, model syngas was injected until the reactor's internal pressure reached 9 bar. In a previous work [15], the authors have investigated the effect of pressure towards CO_2 solubility in ChCl-MEA DES between 1 and 10 bar and found that absorption pressure significantly affected CO_2 solubility in ChCl-MEA DES. Therefore, the effect of pressure is not evaluated in this study and the experiment runs were conducted only on one selected pressure condition at 9 bar to focus on the effect of water addition to ChCl-MEA DES towards its performance in CO_2 removal from syngas.

After the target pressure was reached, the magnetic stirrer was turned on at 300 rpm. Pressure decrease in the reactor was recorded periodically from this point every minute until constant pressure reading was reached, at which point equilibrium was assumed to have been reached and the experiment would be stopped. Gas samples were then collected and the reactor is left to cool before liquid samples were collected for further characterization.

Readings taken from the experiment include pressure decrease within the reactor and outlet gas composition, which was characterized using gas chromatography (GC). It is assumed that the gas compressibility factors of the gas species used are still around 1 and the gases behave as ideal gas at experiment conditions. Using the ideal gas equation, the mole of gas present at the initial and final stages of the experiment runs could be determined based on the pressure inside the reactor as seen in Eq. (1).

$$\Delta n = \frac{\Delta P v}{RT} \quad (1)$$

where Δn is the mole amount of gases absorbed, ΔP is the pressure difference in the reactor before and after the absorption experiment, v is the reactor volume, R is the ideal gas constant, and T is the absorption temperature. Using this mole data with the gas composition data from GC, the mole amount of each gas species in the initial and final stages of the experiment could be determined. The amount of gas absorbed for each species was determined to be the mole difference of each gas species between the initial and final stages.

The mole amount of each gas species absorbed was then converted to mole amount of each gas species absorbed for every mole of DES (mol-gas/mol-DES). This is done by converting the volumetric amount of DES present in the absorbent used in the experiment run to mole amount. First, the volumetric amount of DES in the absorbent was determined. For example, since the total volumetric amount of absorbent used in each run was fixed at 2 mL, the volumetric amount of DES in aqueous DES with 75%vol water would be 0.5 mL.

The value of gases absorbed by water was then calculated for the particular amount of water present in the experiment run and excluded from the calculations. The volumetric amount of DES obtained was then converted to mass by using its density, which was calculated by weighing certain volumetric amount of DES. The density of DES and gas solubility in water used in this study were determined in our previous study [15].

The mass value obtained was then converted to mole amount by multiplying it with the specific DES' molecular weight. The molecular weight of DES was determined with the method suggested by Ghaedi et al. [24], which considered the molecular weight of each DES component as well as their mole ratio in the DES. The formula for molecular weight (g/mol) based on the reference is listed in Eq. (2).

$$M_{DES} = \frac{X_{HBA}M_{HBA} + X_{HBD}M_{HBD}}{X_{HBA} + X_{HBD}} \quad (2)$$

where M_{DES} is the molecular weight of DES. X_{HBA} and X_{HBD} denote the mole fraction of hydrogen bond acceptor (HBA, in this case ChCl) and hydrogen bond donor (HBD, in this case MEA), respectively, while M_{HBA} and M_{HBD} are the molecular weight of HBA and HBD, respectively. This method resulted in the molecular weights of 74.1 g/mol and 68.2 g/mol for DES 1:5 and DES 1:10, respectively. After the mole amount of DES present in a particular experiment run was determined, the mole amount of gas absorbed per mole DES could be determined.

The average CO_2 absorption rate is calculated using CO_2 solubility value divided by the time that it takes for the system to reach equilibrium. The equilibrium condition was assumed to have been reached when the pressure decrease was observed to be less than 0.05 bar, or around 0.5% of the initial pressure, over a time period of 30 min.

The experiments in this study were conducted with mixed model gas. Gas selectivity of CO_2 over other gases was calculated according to the selectivity factor (S_p) as suggested in studies by Mandal et. al. [25] and Lu et. al. [26]. The equation is displayed in Eq. (3).

$$S_p = \frac{(X_{CO_2})Y_i}{(X_i)Y_{CO_2}} \quad (3)$$

where S_p is selectivity factor. X_{CO_2} and X_i are mole fractions of CO_2 and other gas species i (H_2 , CO , or CH_4) absorbed in the DES, respectively, while Y_{CO_2} and Y_i are mole fraction of CO_2 and other gas species i in the initial gas phase, respectively.

2.3 Characterization equipment

Gas analysis in this study was done with GC-9790 gas chromatography from Zhejiang Fuli Analytical Instrument

Co. Ltd. It is equipped with a thermal conductivity detector (TCD) TDX-01 packed column and run with helium as carrier gas at 30 mL/min flow. Fourier transform infrared (FTIR) spectroscopy was conducted using a Nicolet 6700 FTIR spectrometer from Thermo Nicolet Corp., USA. The samples characterized were ChCl-MEA DES 1:5 with 75%vol water content before and after being used for CO₂ absorption in the batch absorption experiment. Viscosity measurement was done with NJD-8S rotary viscometer from Zhengzhou Nanbei Instrument Equipment Co. Ltd. The measured samples were ChCl-MEA 1:5 and 1:10 mol ratio in pure condition (0%v water) and as aqueous DES solutions. A heating jacket was used to regulate the temperature of the sample during viscosity measurements which were conducted at 20 °C and 40 °C.

3 Result and discussion

3.1 Effect of water addition on ChCl-MEA DES viscosity

To quantify the effect of water addition towards the viscosity of ChCl-MEA DES at various temperatures, viscosity measurements were conducted at 20 °C and 40 °C for DES 1:5 and DES 1:10 with various water content. The result of measurement is displayed in Fig. 2, with the viscosity values of aqueous MEA in the same range of temperature and water content reported by Arachchige et al. included as comparison [27].

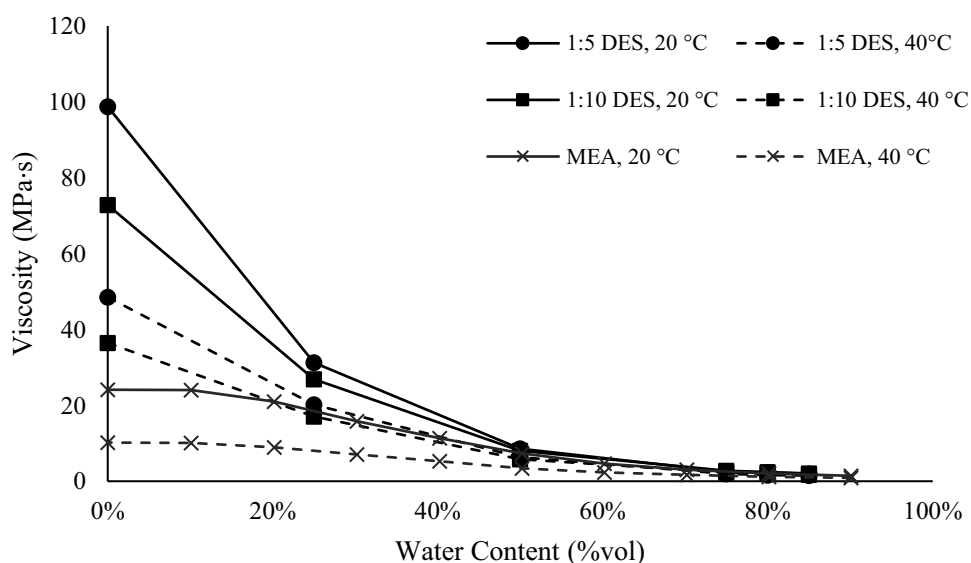
Figure 2 shows that for pure DES (0%vol water), an increase in temperature from 20 to 40 °C lowered DES viscosity significantly. The viscosity of DES 1:5 dropped from 98.74 to 48.53 MPa·s (51% decrease), while the

viscosity of DES 1:10 went from 72.79 to 36.45 MPa·s (50% decrease). From Fig. 2, it could also be observed that DES 1:10 had around 75% of the viscosity of DES 1:5 both in 20 °C and 40 °C. It shows that the viscosities of ChCl-MEA DES with different mole ratios are affected by temperature change similarly. While the higher viscosity of DES 1:5 compared to DES 1:10 might be explained by the higher ratio of ChCl to MEA molecules in DES 1:5, ChCl molecules are larger in size compared to MEA and might be hindering the free movement of molecules, resulting in higher viscosity for DES 1:5.

Water addition to DES was shown to produce significant reductions for all DES in all studied temperatures. Aqueous DES 1:5 at 20 °C with 25%, 50%vol, and 75%vol water content had viscosity values of 32%, 9%, and 3% of the pure DES 1:5; respectively. Similar values were obtained for DES 1:10 at 20 °C. While for viscosity measurements at 40 °C, the reduction of viscosity is smaller compared to 20 °C. Aqueous DES 1:5 with 25%vol, 50%vol, and 75%vol water content had viscosity values of 42%, 13%, and 4% of pure DES 1:5 at 40 °C. These results would be useful for material selection process involving ChCl-MEA DES not only for CO₂ capture, but other applications that utilize aqueous ChCl-MEA DES.

When compared to MEA, the viscosity values of aqueous DES were higher, especially in the lower water contents. However, the difference gradually becomes smaller as water was added. Starting from around 70%vol water, the viscosity values of aqueous DES and aqueous MEA were almost identical. This result shows that at higher water content, the pumping utility load required for circulating aqueous DES would be comparable to that of aqueous MEA.

Fig. 2 Effect of water addition on viscosity of ChCl-MEA DES and aqueous MEA [27]



3.2 Effect of water addition on CO₂ solubility and absorption rate in ChCl-MEA DES with different mole ratios

CO₂ solubility experiments to evaluate the effect of water addition in DES with different mole ratios towards CO₂ solubility in DES were conducted at 40 °C, which is practically easier to achieve compared to 20 °C that might require chilling in some ambient conditions. The result of CO₂ solubility experiments conducted at (40 °C, 9 bar) for DES 1:5, DES 1:10, and aqueous MEA solution as comparison is displayed in Fig. 3.

Figure 3 displays the amount of CO₂ that could be absorbed by aqueous DES 1:5, aqueous DES 1:10, and aqueous MEA solutions with different water contents. It is measured in mol-CO₂/mol-absorbent, which signifies the CO₂ solubility in each molecule of absorbent (DES 1:5, DES 1:10, or MEA). The amount of CO₂ absorbed by water has been excluded from the values displayed in Fig. 3. The CO₂ solubility in water for this experiment was found to be 1.73×10^{-3} mol-CO₂/mol-water, which is in good agreement with the value reported by Lucile et al. for these conditions [28].

The ability of DES to absorb CO₂ has been explained by the free volume, or holes formed between the molecules in a DES structure [29]. The difference in CO₂ solubility in DES 1:5 and DES 1:10 might be explained by the difference in the available free volume in both DES. DES 1:10 with more MEA molecules as hydrogen bond donor (HBD) might be more susceptible to HBD self-interaction, where HBD molecules form hydrogen bond with each other. Haider et al. [30] suggested that this could cause a decrease in free volume, hence producing low CO₂ solubility in the respective DES.

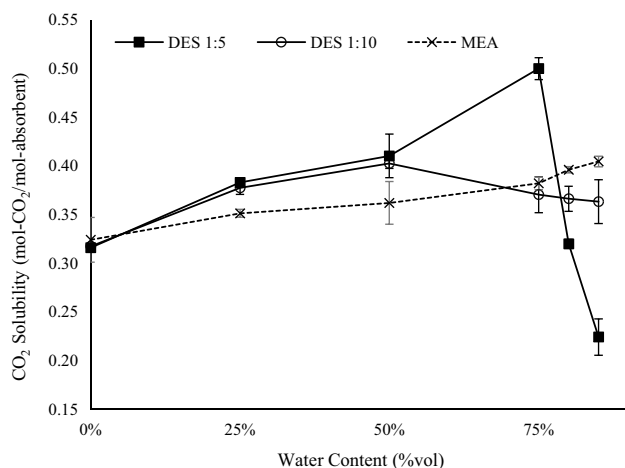


Fig. 3 Effect water addition on CO₂ solubility in ChCl-MEA DES 1:5, DES 1:10, and aqueous MEA at 40 °C, 9 bar

Figure 3 shows that from pure DES up to 50%vol water, DES 1:5 and DES 1:10 had very similar CO₂ solubility values. The CO₂ solubility values of aqueous solution with 50%vol water of both DES were 25% higher compared with their respective pure conditions (with 0%vol water). At pure condition, ChCl-MEA DES had the same CO₂ solubility as MEA. This might be caused by the high viscosity of pure ChCl-MEA DES that made it difficult for CO₂ molecules to enter the bulk DES, resulting in CO₂ mostly only interacting with MEA molecules on the surface of DES. Water addition to DES lowered its viscosity and CO₂ was able to interact with the bulk of the DES, increasing its CO₂ solubility. Water addition also increased the CO₂ solubility in MEA absorbent, but the effect was not as significant. As a result, aqueous DES had 8.7% and 14.4% higher CO₂ solubility compared to aqueous MEA at 25%vol and 50%vol water, respectively.

The increasing CO₂ solubility in DES due to water addition might be explained by the effect of water that assists in the spread of DES. A study by Ullah et al. [31] found that CO₂ molecules reside on the surface of DES for a considerable time before moving into its bulk phase. This would suggest that increasing the spread of DES would provide more surface area for CO₂ to reside. It allows for more contact between DES and CO₂ molecules, which in turn would increase the mass transfer of CO₂ from the gas into the liquid phase. As seen in Fig. 2, water addition also significantly lowers the viscosity of DES. This would also facilitate easier contact between DES and CO₂ molecules.

The benefit of adding water into DES continued up to 75%vol water for DES 1:5, where it reached the maximum CO₂ solubility of 0.5 mol-CO₂/mol-DES. Further addition of water resulted in a drop in CO₂ solubility, to 0.32 mol-CO₂/mol-DES at 80%vol water. For DES 1:10, the maximum CO₂ solubility value obtained was 0.40 mol-CO₂/mol-DES at 50%vol water. Water addition to 75%vol resulted in a drop in CO₂ solubility to 0.37 mol-CO₂/mol-DES. This drop in CO₂ solubility after certain amounts of water was added might be caused by the breaking of DES structure due to the presence of excess water, as suggested by Hammond et al. [20].

From the result of this experiment, it was found that the maximum water content threshold where DES still remain stable was 75%vol for DES 1:5 and 50%vol for DES 1:10. These results suggest that the mole ratio of DES materials affected DES resistance to breaking down due to water addition. This different resistance levels might also be explained using the finding of Hammond et al. [20], who reported that water was seen acting as a second hydrogen bond donor (HBD). It should be mentioned that in ChCl-MEA DES, ChCl acts as hydrogen bond acceptor (HBA) and MEA acts as HBD. This could mean that DES 1:5, which has higher ratio of ChCl/MEA compared to DES

1:10, would have more free HBA active sites. These free active sites could form a bond with water without disrupting the existing DES structure. Therefore, DES 1:5 would be able to “tolerate” more water before breaking down compared to DES 1:10. The lower CO₂ solubility in DES after breakdown when compared to MEA with the same water content, as observed with DES 1:5 above 75%vol water and DES 1:10 above 50%vol water, could be caused by the large molecules of ChCl hindering contact between CO₂ and MEA molecules.

The 56% CO₂ solubility increase in DES 1:5, from 0.32 mol-CO₂/mol-DES in its pure form to 0.50 mol-CO₂/mol-DES in aqueous DES 1:5 with 75%vol water, is on par with other studies on aqueous DES. Comparing the studies by Hsu et al. [32] and Haider et al. [33] showed that adding water to Reline (ChCl-Urea DES) up to around 50%wt water increased its CO₂ solubility from 0.06 to 0.11 mol-CO₂/mol-DES at 8–10 bar and 40 °C, a 83% CO₂ increase from its pure form. Ren et al. reported that the CO₂ solubility of Arginine-Glycerol DES at 10 bar and 30 °C increased from 0.45 in its pure form to 0.55 mol-CO₂/mol-DES in aqueous DES with 50%wt of water (a 22% increase) [34]. It could be seen from these comparisons that ChCl-MEA DES has a relatively high initial CO₂ solubility in its pure form and experience a significant increase in CO₂ solubility with addition of water, making it a potential candidate for CO₂ absorption enhancement by water addition compared to other DES.

From these results, it is apparent that water addition to ChCl-MEA DES improves its CO₂ solubility. Coupled with the fact that it increases the DES’ process friendliness by lowering its viscosity, water addition to DES makes for a simple and affordable process to enhance the CO₂ solubility of ChCl-MEA DES.

Compared to commercially used 30%wt aqueous MEA solution, which was reported by Wagner et al. [35] to have the CO₂ solubility between 0.4 and 0.7 mol-CO₂/mol-MEA at 40 °C and 4 bar, the CO₂ solubility of aqueous ChCl-MEA DES still falls below the commercial MEA absorbent. However, DES potential in the form of the presence of both physical and chemical CO₂ absorption modes in amine-based DES, as suggested by a few researchers [16, 36], could allow for the CO₂ solubility in ChCl-MEA DES to be significantly increased by increasing absorption pressure or by taking advantage of processes which produce syngas at high pressures such as supercritical water gasification (SCWG). Further research is still needed to fully realize DES potential as an energy efficient green solvent.

Another parameter that needs to be evaluated in designing an absorption system would be the absorbent’s CO₂ absorption rate. The effect of water addition on the absorption rate calculated for DES 1:5, DES 1:10, and MEA is displayed in Fig. 4.

Figure 4 shows that CO₂ absorption rate for all studied absorbents increase with the increase in water content. This might be due to the better spread of the absorbent with more water present, allowing for better contact between CO₂ and absorbent molecules. This in turn would result in more CO₂ absorbed per unit time, which shows up as higher absorption rate. From Fig. 4, it could also be seen that DES 1:5, DES 1:10, and MEA had almost identical CO₂ absorption rate. This might be explained by the possibility of chemical absorption of CO₂ by ChCl-MEA DES in addition to physical absorption. While most DES absorbs CO₂ by physical absorption, it has been mentioned that some researchers have suggested that amine-based DES absorbs CO₂ either chemically or with both absorption modes [16, 36]. Since physical absorption usually involves the formation of weak bonds such as the van der Waals bonds, it is quicker than chemical absorption which is governed by reaction kinetics in addition to mass transfer. The CO₂ absorption rate results depicted in Fig. 4 seems to be in good agreement with those references. The lower CO₂ absorption rate for DES compared to MEA after they break down could also be attributed to the presence of ChCl molecules hindering CO₂ absorption by MEA molecules. This would explain why DES 1:5, which has higher ChCl/MEA ratio compared to DES 1:10, had a lower CO₂ absorption rate at 85%vol water compared to DES 1:10.

To confirm the presence of chemical absorption in these experiments, FTIR analysis was conducted on aqueous DES 1:5 with 75%vol water before and after CO₂ absorption. The result is displayed in Fig. 5.

Figure 5 shows the FTIR spectra for aqueous DES 1:5 75%v water before and after it was used for CO₂ absorption experiment. The peak around 3500 cm⁻¹ is thought to be the result of the broadening of O–H and N–H bonds in ChCl and MEA, suggesting formation of hydrogen bond between the

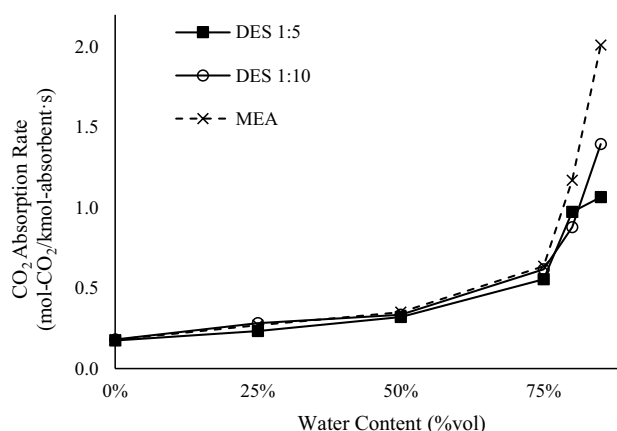


Fig. 4 Effect of water addition on CO₂ absorption rate in DES 1:5, DES 1:10, and aqueous MEA at 9 bar

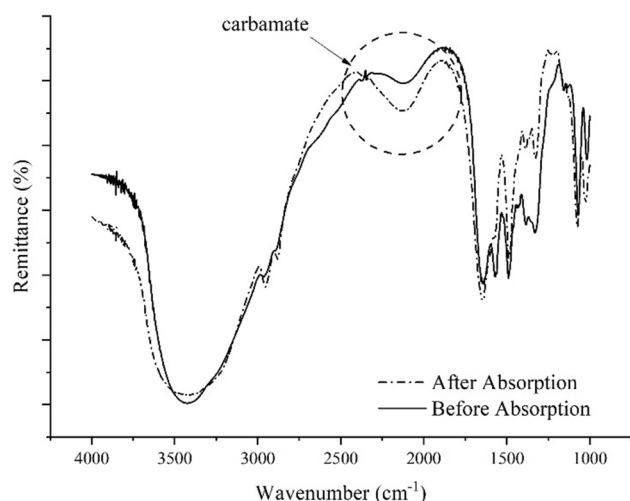


Fig. 5 FTIR result of aqueous ChCl-MEA DES 1:5 with 75%vol water before and after CO₂ absorption

two components [37]. Its presence in the FTIR result could be used as an indication of the formation of DES between ChCl and MEA in the absorbent used in this study. The difference between DES before and after absorption could be seen in the appearance of a peak in the wavelength between 2500 and 2000 cm⁻¹, circled in Fig. 5, which is associated with carbamate [38]. Carbamate is formed from the reaction between MEA and CO₂, and could be taken as an indicator that chemical absorption also played a role in CO₂ capture by ChCl-MEA DES.

As mentioned before, it is possible that chemical absorption of CO₂ in ChCl-MEA DES occurs in addition to physical absorption. The mechanisms might be explained using the finding reported by Altamash et al. [39] who found that CO₂ formed van der Waals bonds with both HBA and HBD in ChCl-malic acid DES. With ChCl-MEA DES, it is possible that physical absorption happens between CO₂ and ChCl while chemical absorption happens between CO₂ and MEA. The presence of both modes of absorption in ChCl-MEA DES might bring benefit to its utilization, such as the ability for deep CO₂ cleaning. But it also could bring some challenges such as in the regeneration of ChCl-MEA DES. Characterization and optimization of ChCl-MEA DES in regard to its absorption modes could be a topic that needs studying in the future. Its regeneration study would also be an issue worth investigating.

FTIR results could also be used to evaluate the effect of water on DES condition by comparing the FTIR results of DES 1:5 in pure form, with 75%vol water (assumed to still be intact but with high water content), and with 85%vol water content (assumed to be a condition where DES 1:5 has broken down) by comparing the appearance of the peak that appears around 3500 cm⁻¹ which, as mentioned in the

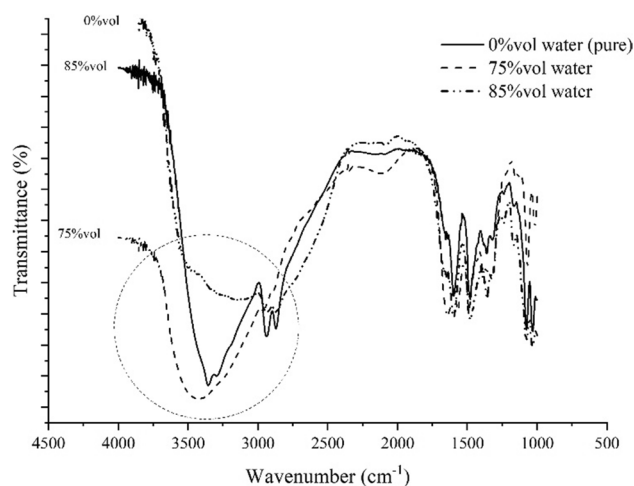


Fig. 6 FTIR results for pure DES 1:5, DES 1:5 with 75%vol water, and DES 1:5 with 85%vol water

discussion on Fig. 5, could be an indicator of DES formation. The comparison is displayed in Fig. 6.

As seen in Fig. 6, the peak at 3500 cm⁻¹ (circled) for pure DES 1:5 is sharp, indicating strong hydrogen bond in the DES. For DES 1:5 with 75%vol water, the peak is still clearly defined, even though there is some broadening of the peak. In a study regarding the effect of water on ChCl-Glycol DES by Gabriele et al., it was suggested that this is caused by the weakening of hydrogen bond in the DES due to presence of water [19]. While the FTIR result for DES 1:5 with 85%vol water did not show any peak in this region, supporting the idea that the excessive water content has broken down the DES structure.

3.3 Effect of water addition on CO₂ solubility and absorption rate in ChCl-MEA DES at various absorption temperature

Figure 2 has shown low temperature result in high DES viscosity, which could be hindering efficient mass transfer between CO₂ and DES molecules. On the other hand, studies have shown that CO₂ solubility is higher at lower temperatures [15]. Therefore, there is a tradeoff in the opposite ways temperature could affect CO₂ absorption by DES. To evaluate whether water addition affects the balance of that tradeoff, the effect of water addition at various temperatures is studied in this section. The temperatures chosen to be studied in this section were 20 °C and 40 °C as studied in the previous section, as well as 60 °C which was added due to the confirmation of carbamate formation in CO₂ absorption in ChCl-MEA DES as discussed in Section 3.2. While the formation of carbamate is an exothermic reaction, its reaction kinetics increase with increase in temperature. Therefore, the effect of higher temperature on CO₂ solubility and

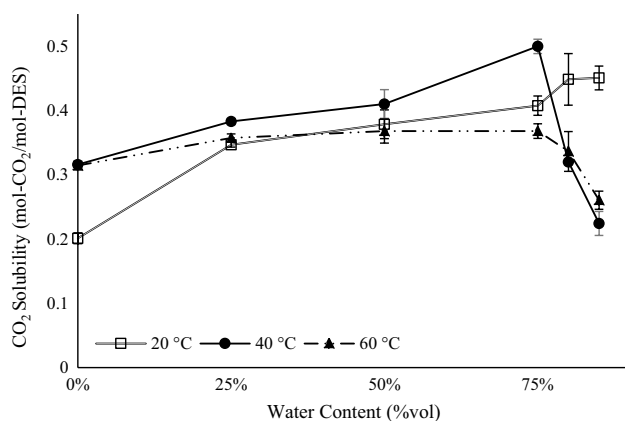


Fig. 7 Effect of water addition on CO₂ solubility in DES 1:5 at 9 bar and various temperatures

absorption rate in ChCl-MEA DES shall be analyzed. The result is shown in Fig. 7.

From the result depicted in Fig. 7, 40 °C seems to be the optimum absorption temperature for CO₂ capture with ChCl-MEA 1:5. For absorption temperature of 20 °C, it could be seen that the CO₂ solubility in aqueous DES 1:5 continues to increase with the increase of water content before leveling off at 80%vol water. This continued increase in CO₂ solubility might be caused by the high DES 1:5 viscosity at 20 °C limiting the penetration of water into the bulk DES, therefore limiting the damage effect of excess water to DES structure.

For 40 °C and 60 °C, the CO₂ solubility of DES 1:5 increased with the addition of water compared to its pure condition (0%vol water). Both also experienced a drop in CO₂ solubility above 75%vol water. The difference is that while at 40 °C water addition caused a constant increase in CO₂ solubility between 0 and 75%vol water, the CO₂ solubility at 60 °C increased a little until 25%vol water before leveling until 75%vol water content. The maximum value of CO₂ solubility at 60 °C is also only around 67% of that at 40 °C. This might be caused by the already lower viscosity of DES 1:5 at 60 °C compared to 40 °C, causing water addition to have lesser impact to viscosity and CO₂ solubility. There is also the possibility of the increase in DES vapor pressure at 60 °C compared to 40 °C causing a drop in CO₂ solubility, something that has been observed for physical absorbents [40, 41].

The effect of absorption temperature towards CO₂ absorption rate in ChCl-MEA DES was also evaluated up to 75%vol water, where DES 1:5 was still expected to be structurally intact. The result is shown in Fig. 8.

Figure 8 shows that CO₂ absorption rate in DES 1:5 increases with water content and absorption temperature. The higher water content might be facilitating better contact between CO₂ and DES molecules. While higher absorption temperature could have double positive effect on CO₂

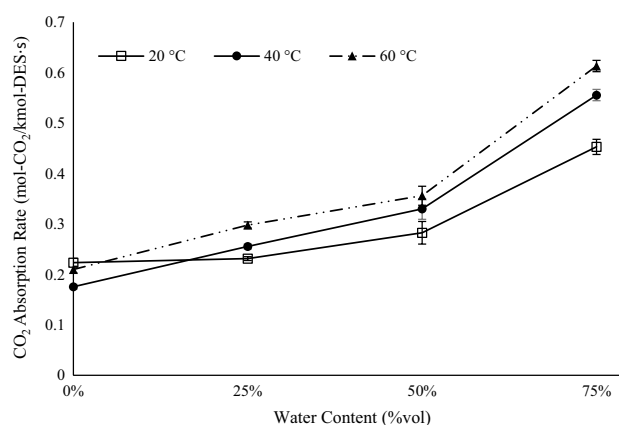


Fig. 8 Effect of water addition on CO₂ absorption rate in DES 1:5 at 9 bar and various absorption temperatures

absorption rate in DES 1:5, it lowers DES viscosity, such as indicated in Section 3.1, and at the same time, it increases the reaction kinetic of carbamate formation. The high CO₂ absorption rate of pure DES 1:5 at 20 °C could be explained by the small CO₂ solubility in DES 1:5 at these conditions, as indicated in Fig. 6, causing it to reach equilibrium in a relatively short time.

The results from Figs. 7 and 8 suggest that the optimum value of CO₂ solubility could be obtained at absorption temperature of 40 °C, while higher temperature, in this case 60 °C, produced the highest CO₂ absorption rate in DES 1:5. These characteristics would be useful when designing and optimizing CO₂ capture process with DES 1:5.

3.4 Effect of water addition to CO₂ selectivity in aqueous ChCl-MEA DES

High selectivity of an absorbent towards CO₂ over other gases is an important factor for CO₂ capture from multi component gas stream such as syngas, natural gas, or flue gas. When utilizing water addition to enhance CO₂ absorption with ChCl-MEA DES, the effect of water addition towards CO₂ selectivity over CH₄, CO, and H₂ in ChCl-MEA DES must also be considered. In this section, the effect of water addition towards CO₂/CH₄ and CO₂/CO selectivity in DES 1:5 is evaluated. Other than providing efficient capture of CO₂ from syngas, these selectivity values are also important parameters in other applications. Good CO₂/CO selectivity would allow for the absorbent to be used for syngas utilization that requires certain amount of CO to be present, such as methanol synthesis [42, 43]. While good CO₂/CH₄ selectivity is required for CO₂ capture from natural gas, which mainly consist of these two gases, CO₂/H₂ value might be useful for CO₂ removal from syngas. CO₂/CH₄, CO₂/CO, and CO₂/H₂ selectivity in ChCl-MEA DES 1:5 at various conditions is displayed in Fig. 9.

Figure 9(a) shows that DES 1:5 has CO_2/CH_4 selectivity between 24.9 and 26.7 at 40 °C. It also shows CO_2/CH_4 selectivity between 13.3–20.3 at 20 °C and 15.6–20.0 at 60 °C depending on water content. In general, higher water content seem to lower CO_2/CH_4 selectivity in DES 1:5. Increase in water content from 0 to 75% vol decreased CO_2/CH_4 selectivity in DES 1:5 by 34.5%, 6.7%, and 22.0% for absorption temperatures of 20 °C, 40 °C, and 60 °C; respectively. Similar trends are observed for Fig. 9(b), with CO_2/CO selectivity at its highest at 40 °C and decreasing with the increase in water content. The highest CO_2/CO value obtained was 36.4 for pure DES 1:5 at 40 °C.

The high CO_2/CH_4 and CO_2/CO selectivity at 40 °C might be due to the high CO_2 solubility in DES at that

temperature, as displayed in Fig. 6, while the decreasing trend of both selectivity when water content was increased might be attributed to the change in free volume that caused increased absorption of CH_4 and CO , thereby lowering CO_2 selectivity over those gases.

The high CO_2 selectivity at 40 °C compared to 20 °C and 60 °C could also be caused by the higher CO_2 solubility at that temperature. It has been shown that above room temperature, gas solubility in amine-based DES drops with the increase in temperature [37]. In this study, the decrease in CO_2 solubility is steeper than that of other gases at higher temperature, leading to a decrease in CO_2 selectivity over other gases at higher temperatures. This phenomenon might be caused by the increase in free volume with the increase in temperature, as suggested by Al-Murshedi et al. [44]. This increase in free volume might be allowing more of the other gases to get absorbed by DES, thereby lowering the CO_2 selectivity over other gases.

The low CO_2 selectivity at 20 °C might be caused by another phenomenon. As seen in Figs. 2 and 6, DES at 20 °C has low CO_2 solubility and high viscosity. It is possible that the high viscosity hindered the effective mass transfer of CO_2 and other gases. This in turn leads to low absorption and selectivity of CO_2 .

The CO_2/H_2 selectivity values shown in Fig. 9(c), which is between 4 and 2, are relatively low compared to the DES' selectivity values of CO_2/CO (36–23) and CO_2/CH_4 (27–13). For upgrading of syngas that is high in H_2 , this would require further research. Increasing the CO_2/H_2 selectivity might be able to be done by incorporating DES with other CO_2 capture technologies such as membrane. CO_2 selective membranes such as polypropylene (PP), polyvinylidene fluoride (PVDF) [45], and poly(vinyltrimethylsilane) (PVTMS) membranes [46] have been reported to be highly selective towards CO_2 and might be used to increase the CO_2/H_2 selectivity of DES.

Compared to conventional CO_2 absorbents, the CO_2/CH_4 selectivity results obtained in this study are relatively high. CO_2/CH_4 selectivity of Rectisol is around 10, for Fluor PC it is 17, for Purisol it is 25, and for Selexol it is 13 [47]. While compared to other DES, it was reported that pure tetrabutylammonium bromide–caprolactam DES had the CO_2/CH_4 and CO_2/CO selectivity of 45 [48], while tetrabutylammonium bromide–MEA DES was reported to have CO_2/CH_4 selectivity of 25, very similar to the result from this study [37]. In its current state, the high CO_2/CH_4 selectivity of ChCl -MEA DES compared to commercial absorbents could make it viable for efficient CO_2 capture from landfill gas or natural gas, which mostly consist of CO_2 and CH_4 .

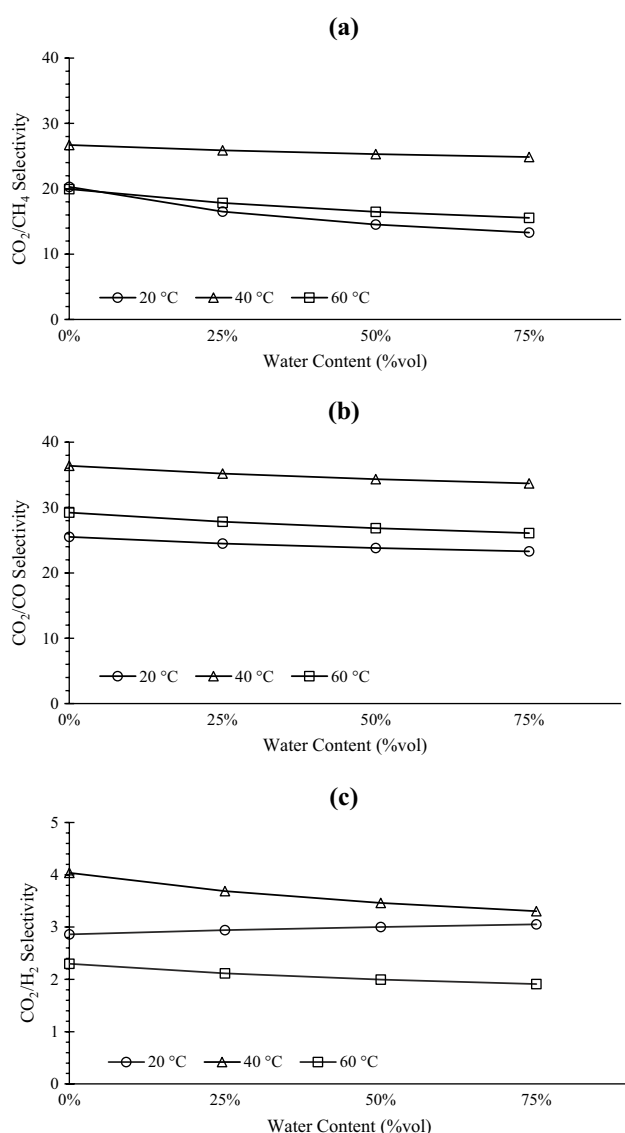


Fig. 9 Effect of water addition on CO_2/CH_4 (a), CO_2/CO (b), and CO_2/H_2 (c) selectivity in DES 1:5 at 9 bar and various absorption temperatures

4 Conclusion

Water addition was investigated as a simple method to improve the CO₂ absorption behavior of ChCl-MEA DES. It was found that aqueous ChCl-MEA DES 1:5 with 75%vol water produced a maximum CO₂ solubility at 0.50 mol-CO₂/mol-DES at 40 °C and 9 bar. Water addition was found to have a positive effect on CO₂ solubility and absorption rate up to certain amount of water, after which the excess water would break down the DES and decrease the CO₂ solubility in DES. ChCl-MEA DES 1:5 was able to benefit from water addition up to 75%vol, while ChCl-MEA DES 1:10 was only able to withstand up to 50%vol water.

In terms of the effect of water addition at various absorption temperatures, it was found that water addition affects CO₂ solubility differently at different temperatures. Water addition at absorption temperature of 40 °C was found to provide the biggest improvement. It produced the highest CO₂ solubility as well as CO₂ selectivity. This might be caused by the temperature effect tradeoff between decreasing DES viscosity and lowering its CO₂ solubility.

The highest obtained CO₂/CH₄ and CO₂/CO selectivity value in ChCl-MEA DES 1:5 were 26.7 and 34.6, respectively. These values were obtained from the use of pure ChCl-MEA DES at 40 °C and are higher than conventional CO₂ absorbents, while its CO₂/H₂ was found to be between 2 and 4. Water addition was found to slightly decrease both selectivity.

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