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ACS Sustainable Chem. Eng., **Just Accepted Manuscript** • DOI: 10.1021/acssuschemeng.0c01222 • Publication Date (Web): 12 May 2020

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# CO<sub>2</sub>-binding organic liquids comprised of 1,1,3,3-Tetramethylguanidine and alkanol for post combustion CO<sub>2</sub> capture: water inhibitory effect of amine promoters

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## Abstract

CO<sub>2</sub>-binding organic liquids (CO<sub>2</sub>-BOLs) are switchable polarity solvents that can be used as non-aqueous green solvents for energy efficient CO<sub>2</sub> capture. In this study the novel three-component CO<sub>2</sub>-BOLs comprised of 1,1,3,3-Tetramethylguanidine (TMG) as a superbase, an alkanol (methanol, n-butanol, sec-butanol and 1-hexanol) and an amine (EEA, MEA, AMP, DEA, AEEA, PZ, TETA and DETA) were introduced. Screening experiments were performed to find the best combination of solvent components based on CO<sub>2</sub> loading and absorption rate. The TMG/methanol/MEA BOL with a molar ratio of 0.3/0.6/0.1 was selected as the preferred solvent which has an equilibrium absorption ( $\alpha_{eq}$ ) and a CO<sub>2</sub> uptake within 30 min ( $\alpha_R$ ) of 0.396 and 0.283 mol CO<sub>2</sub>/mol solvent, respectively. CO<sub>2</sub>-BOLs were characterized using FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy to specify the produced ionic species, explain the water inhibitory effect of MEA and propose a plausible reaction mechanism for the reaction of CO<sub>2</sub> with the three-component BOLs in the absence and presence of water impurity. It was found that the addition of MEA to the two-component BOLs (base/alcohol) restricts the formation and precipitation of bicarbonate salt that leads to the lower energy consumption for solvent regeneration.

**Keywords:** CO<sub>2</sub> capture; Switchable ionic liquids; Switchable solvents; CO<sub>2</sub>-binding organic liquids.

## Introduction

Carbon dioxide (CO<sub>2</sub>) as a greenhouse gas contributes to the emerging concern of global warming and climate change.<sup>1</sup> Therefore, developing the efficient CO<sub>2</sub> capture and storage technologies has received much attention for effective reduction of CO<sub>2</sub> emission to the atmosphere from various sources.<sup>2</sup> Moreover, the valuable recovered CO<sub>2</sub> can be re-used and utilized for different applications.<sup>3</sup>

Chemical absorption in aqueous amine solvents is the most mature technology for CO<sub>2</sub> capture among different approaches.<sup>4</sup> However, solvent degradation, high energy consumption of absorbent regeneration, limited tolerance for other acid gases, high makeup rate, relatively low absorption efficiency and equipment corrosion in conventional aqueous amine systems have led researchers to develop alternative solvent systems.<sup>5, 6</sup> Conventional ionic liquids as green solvents are attractive for post-combustion CO<sub>2</sub> capture. Some drawbacks of ionic liquids including: high viscosity and cost and difficult synthesis restricted their applications.<sup>7</sup> Moreover, hybrid solvents by integrating ionic liquids and other materials enhanced physical properties of ionic liquids and promoted their industrial application.<sup>8, 9</sup>

Switchable solvents, also known as “smart” solvents are defined as solvents that change properties via reversible chemical transformations when they are exposed to an external stimulus.<sup>10</sup>

Switchable solvents are classified as: (1) switchable polarity solvents (SPSs), (2) switchable hydrophobicity solvents (SHSs), (3) and switchable water (SW).<sup>11</sup>

CO<sub>2</sub>-binding organic liquids (CO<sub>2</sub>-BOLs) or switchable ionic liquids (SILs) are CO<sub>2</sub>-triggered SPSs that their polarity can be switched using carbon dioxide.<sup>12</sup> CO<sub>2</sub>-BOLs were proposed as non-aqueous carbon dioxide capture solvents due to their unique properties including: their ability to switch some properties, selectivity for CO<sub>2</sub>, compatibility with other acid gases, low specific heat

and regeneration energies, high chemical absorption capacity, recyclability, physical CO<sub>2</sub> absorption after the formation of ionic liquid, no need for additional inert solvent, non-corrosive nature, no cumbersome synthesis protocols and low desorption temperature below the boiling point of the solvent.<sup>13</sup> BOLs differ from traditional ionic liquids because the BOLs are non-ionic before the chemical reaction of CO<sub>2</sub> with the BOL.<sup>14</sup>

Generally, SILs are divided into two categories:<sup>15</sup> single-component SILs and two-component SILs which have their own advantages and disadvantages over each other. The most common CO<sub>2</sub>-BOLs are comprised of an amidine or guanidine base in conjunction with an alcohol or amino alcohol to create amidinium or guanidinium alkylcarbonate salts upon reaction with CO<sub>2</sub>.<sup>16</sup>

The two-component CO<sub>2</sub>-BOLs comprised of DBU (1,8-Diazabicyclo(5.4.0)undec-7-ene) and alcohols including: organic primary alcohols,<sup>17</sup> alcohol functionalized ionic liquids,<sup>18</sup> amino-alcohols,<sup>19</sup> saccharides<sup>20</sup> and glycerol<sup>21</sup> have been studied for CO<sub>2</sub> capture. However, there are limited number of researches incorporating TMG as superbase in the two-component BOLs.

Heldebrant et al.<sup>17</sup> studied the thermodynamic of CO<sub>2</sub> capture using TMG and different alcohols (1-Hexanol, 1-Pentanol, 1-Butanol, 1-Propanol and i-Propanol) in acetonitrile. The NMR spectroscopic analysis was implemented to determine the equilibrium constants of reactions. Ozturk et al.<sup>6</sup> investigated the kinetics of CO<sub>2</sub> reaction with TMG/1-Hexanol solvent. The reaction order, reaction rate constant and activation energy of 2.5 wt.% TMG solvent were obtained to be 0.98, 64.10 m<sup>3</sup>kmol<sup>-1</sup>s<sup>-1</sup> and 9.76 kJmol<sup>-1</sup>, respectively at 298 K. Orhan et al.<sup>22</sup> used stopped-flow technique to measure the rate constants and activation energies of CO<sub>2</sub> reaction with TMG (2.5-10 wt.%) /1-Propanol BOL at 298 K. Carrera et al.<sup>20, 23</sup> used highly abundant saccharides (D-Mannose, D-Glucose,  $\beta$ -Cyclodextrin, Alginic Acid and Mannitol) combined with TMG for CO<sub>2</sub> capture. The TMG/Man (10 eq. of TMG per molecule of d-Mannose) was capable to capture 30.78 wt.%

CO<sub>2</sub> at 4 MPa and room temperature. However, there is no published study about evaluation of TMG-based BOLs for equilibrium CO<sub>2</sub> solubility and CO<sub>2</sub> absorption rate. Equilibrium data are necessary for modeling and design of processes utilizing CO<sub>2</sub>-BOLs. CO<sub>2</sub>-BOLs suffer from trace amounts of water in the reaction medium which results in the precipitation of solid bicarbonate salt.<sup>24</sup> In addition to the operational difficulties, bicarbonate salt is more stable than alkyl carbonate and alkyl carbamate salts that leads to the consumption of more energy for solvent regeneration step.

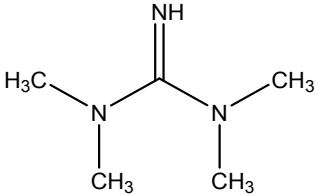
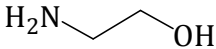
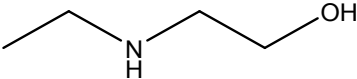
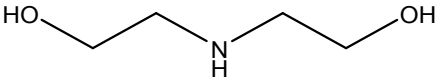
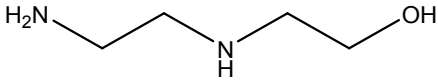
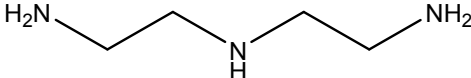
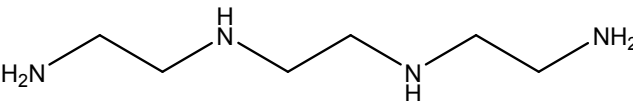
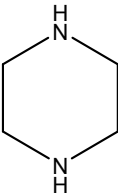
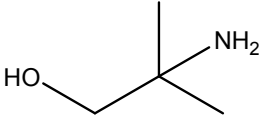
In this study the three-component CO<sub>2</sub>-BOLs comprised of TMG as superbase, an alcohol and an amine were developed for CO<sub>2</sub> capture to overcome the above mentioned drawbacks of two-component systems (base/alcohol) and improve the absorption capacity. The novel three-component BOLs were assessed based on the equilibrium CO<sub>2</sub> solubility and absorption rate. Screening experiments were performed to find the best combination of TMG, alcohol (Methanol, 1-Butanol, 2-Butanol and 1-Hexanol) and amine (ethanolamine (MEA), N-ethylethanolamine (EEA), Diethanolamine (DEA), 2-(2-aminoethylamine)ethanol (AEEA), piperazine (PZ), 2-amino-2-methyl-1-propanol (AMP), Triethylenetetramine (TETA) and Diethylenetriamine (DETA)) in the solvent mixture. The selected systems were further characterized by Fourier-transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy (<sup>1</sup>H and <sup>13</sup>C NMR) to specify the production of ionic species, describe the inhibitory effect of amine promoters and propose a plausible reaction mechanism.

Materials and methods

Chemicals

The chemicals were purchased from Merck. The name, acronym and molecular structures of the base (TMG) and amines are shown in Table 1. The water content of chemicals was brought to less than 20 ppm using distillation and drying over molecular sieve. The CO<sub>2</sub> with high purity from Roham Gas Company (purity>99.9%) was used in absorption experiments.

Table 1: The base and amines used in this study.

Name	acronym	Molecular structure
1,1,3,3-Tetramethylguanidine	TMG	
Ethanolamine	MEA	
N-ethylethanolamine	EEA	
Diethanolamine	DEA	
2-(2-aminoethylamine)ethanol	AEEA	
Diethylenetriamine	DETA	
Triethylenetetramine	TETA	
Piperazine	PZ	
2-amino-2-methyl-1-propanol	AMP	

## CO<sub>2</sub> absorption/desorption: Apparatus and procedure

Fig. 1 shows the employed equipment in the CO<sub>2</sub> absorption experiments. The detailed procedure of absorption process has been described in previous publications.<sup>25-27</sup> Our apparatus consists of: (1) CO<sub>2</sub> cylinder, (2) gas container (stainless steel, 182 ml), (3) reactor (stainless steel, 37 ml) with circulating water jacket, (4) magnetic stirrer, (5) circulating water bath and (6) computer. The gas container and the reactor were equipped with the pressure and temperature sensors with the accuracy of  $\pm 2.5$  kPa and  $\pm 0.1$  K, respectively.

The CO<sub>2</sub> absorption rate ( $\alpha_R$ ) and equilibrium solubility data ( $\alpha_{eq}$ ) which were used in the screening experiments were obtained by the proposed method of Park and Sandall:<sup>28</sup>

$$\alpha_{eq} = \frac{n_{CO_2}^l}{n_{alcohol} + n_{amine} + n_{base}} \quad (1)$$

$$\alpha_R = \frac{n_{CO_2}^l \text{ within 30 min}}{n_{alcohol} + n_{amine} + n_{base}} \quad (2)$$

In the denominator of the above equations  $n$  refers to the number of molecules of the mentioned components in the liquid phase. The number of absorbed CO<sub>2</sub> molecules ( $n_{CO_2}^l$ ) was calculated from Eq. (3):

$$n_{CO_2}^l = n_{CO_2} - n_{CO_2}^g \quad (3)$$

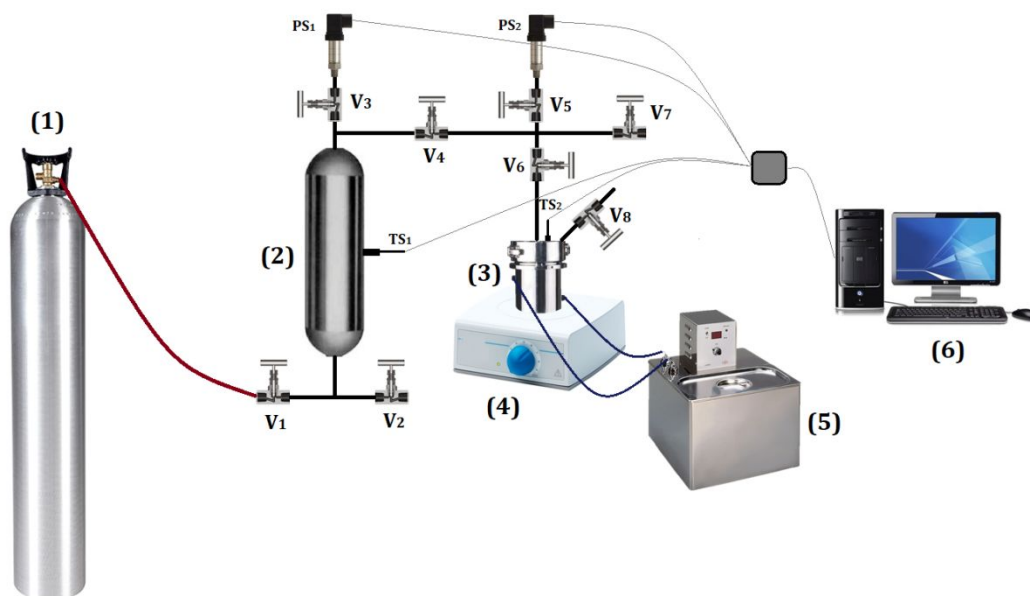
The amount of injected CO<sub>2</sub> into the reactor ( $n_{CO_2}$ ) and the number of unabsorbed CO<sub>2</sub> molecules in the gas phase ( $n_{CO_2}^g$ ) were obtained by Eqs. (4) and (5):

$$n_{CO_2} = \frac{V_{gc}}{R} \left( \frac{P_1}{Z_1 T_1} - \frac{P_2}{Z_2 T_2} \right) \quad (4)$$

where  $Z$ ,  $R$ ,  $V_{gc}$ ,  $P$  and  $T$  are the compressibility factor, the universal gas constant, gas container volume, the pressure and the temperature of gas container, respectively. Subscripts 1 and 2 refer to the conditions before and after CO<sub>2</sub> injection, respectively.

$$n_{CO_2}^g = \frac{(V - V_s)(P_t - P_s^*)}{Z_{CO_2}RT} \quad (5)$$

$P_t$ ,  $P_s^*$ ,  $V$  and  $V_s$  are the total pressure, the vapor pressure of the solvent, the volume of the autoclave and the volume of the injected solvent into the autoclave, respectively. The Peng-Robinson equation of state<sup>29</sup> was implemented for the calculation of the compressibility factors in the gas phase.



**Fig. 1:** Schematic of the experimental setup for CO<sub>2</sub> absorption; (1) CO<sub>2</sub> cylinder, (2) gas container, (3) autoclave reactor, (4) magnetic stirrer, (5) circulating water bath and (6) computer.

The solvent regeneration experiments were carried out at 100 °C. A condensing system was implemented to flow back the evaporated liquids into the flask. The solvents were reused after regeneration and their performance was compared based on CO<sub>2</sub> absorption capacity ( $\alpha_{eq}$ ) at 308.2 K and the initial pressure of 25.00 bar. The solvent regeneration efficiency was obtained as follow:

$$\eta = \frac{\alpha_{eq}^n}{\alpha_{eq}^0} \times 100 \quad (6)$$



Where  $\eta$ ,  $\alpha_{eq}^n$  and  $\alpha_{eq}^0$  are regeneration efficiency (%), CO<sub>2</sub> loading after the n<sup>th</sup> cycle and CO<sub>2</sub> loading of original solvent (mol CO<sub>2</sub>/mol solvent).

## Characterization

The characterization of CO<sub>2</sub>-BOLs before and after the reaction with CO<sub>2</sub> was performed by nuclear magnetic resonance spectroscopy (NMR) using Bruker's Avance 500-MHz instrument. The NMR spectra of samples were referenced to CDCl<sub>3</sub> as internal standard. SpinWorks 4 processing software was implemented for the processing of NMR spectra. Moreover, the Fourier-transform infrared spectroscopy (FTIR) was applied to characterize the solvents and products after CO<sub>2</sub> uptake using Shimadzu-8400S instrument. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were performed using TA-Q600 instrument from room temperature to 473.2 K at a heating rate of 10 K/min under flowing Ar.

## Results and Discussion

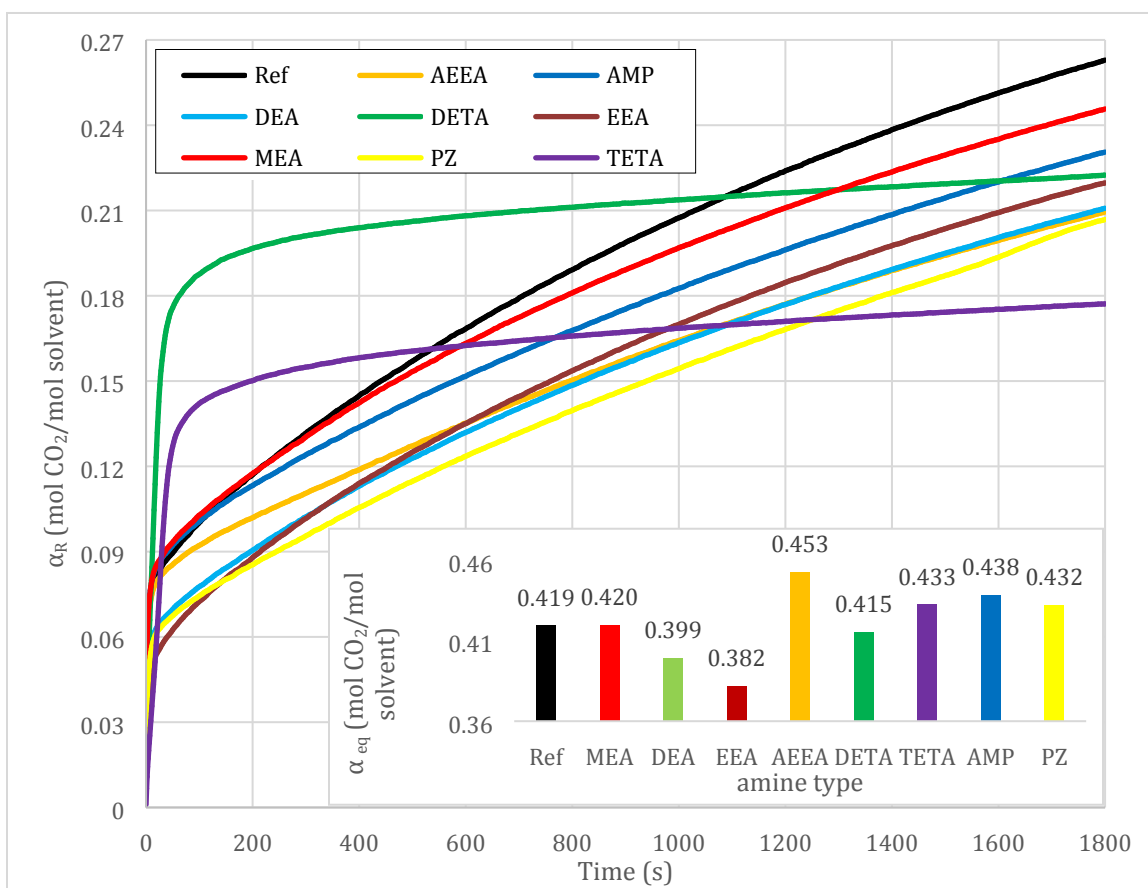
### Screening experiment

Physical and chemical properties of CO<sub>2</sub>-BOLs can be tuned by changing or chemically modifying the mixture components (base, alcohol and amine)<sup>17</sup>. In this study, screening experiments were used to evaluate the solvent components based on the CO<sub>2</sub> absorption rate and equilibrium solubility of CO<sub>2</sub>. All experiments were conducted at the initial reactor pressure of 25.00 bar, constant temperature of 308.2 K and components molar ratio of 0.3/0.6/0.1 (TMG/alcohol/amine). Fig. 2 illustrates the effect of amine type on  $\alpha_R$  using TMG/1-hexanol/amine CO<sub>2</sub>-BOL. The order of amine promoters based on the  $\alpha_R$  is as follows:

$\alpha_R$ : MEA>AMP>DETA>EEA>DEA>AEEA>PZ>TETA

The physicochemical properties of BOLs (e.g. viscosity, CO<sub>2</sub> solubility and diffusivity) and the reaction kinetics affect the CO<sub>2</sub> absorption rate.<sup>30</sup> As depicted in Fig. 2, DETA and TETA have the best performance at the beginning of CO<sub>2</sub> absorption process, but, their application has been restricted by the formation of highly viscous and even solid ionic products that prevents the proper mixing and CO<sub>2</sub> diffusion into the solvent. Moreover, it was observed that the non-modified solvent with the molar ratio of 1/2 (TMG/1-Hexanol) has better performance in term of absorption rate (Ref, Fig. 2). Among the amines examined, MEA had the highest  $\alpha_R$  of 0.246 mol CO<sub>2</sub>/mol solvent. Effect of the type of amine as the promoter on  $\alpha_{eq}$  using TMG/1-Hexanol/amine CO<sub>2</sub>-BOLs is also shown in Fig. 2. AEEA ( $\alpha_{eq}$ =0.453 mol CO<sub>2</sub>/mol solvent) and EEA ( $\alpha_{eq}$ =0.382 mol CO<sub>2</sub>/mol solvent) exhibited the best and worst performance with the following order among other amines:  $\alpha_{eq}$ : AEEA>AMP>TETA>PZ>MEA>DETA>DEA>EEA.

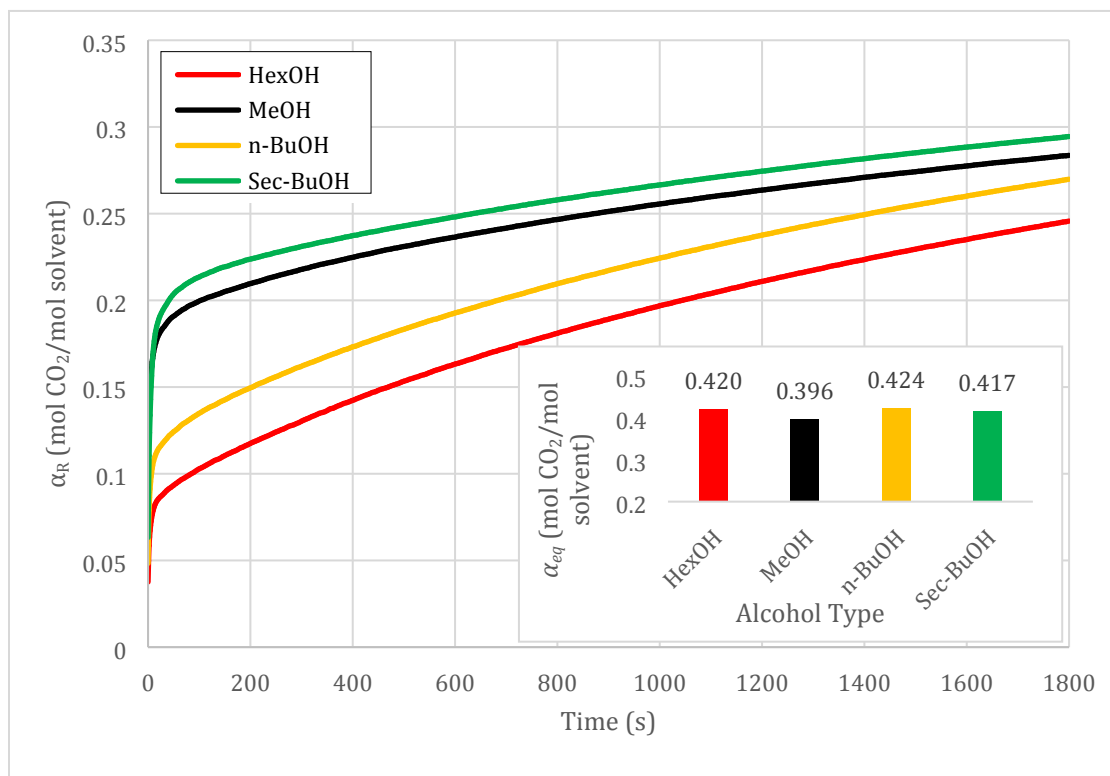
The amine promoters in this study act at the same time as a base in the amine/alcohol system and as an alcohol in the TMG/amine system. Therefore, describing the role of amines on the CO<sub>2</sub> absorption based on the amine properties such as basicity is complicated.<sup>17</sup> It was observed that addition of promoters except DEA, EEA and DETA has positive effect on the equilibrium CO<sub>2</sub> absorption compared to the non-promoted solvent. The molar ratio of TMG/1-Hexanol in both modified and non-modified systems was 1/2.



**Fig. 2:** Effect of amine on the rate and equilibrium CO<sub>2</sub> absorption and CO<sub>2</sub> loading versus reaction time from the initial pressure of 25.00 bar at the constant temperature of 308.2 K using TMG/1-Hexanol/amine (0.3/0.6/0.1) CO<sub>2</sub>-BOL (Ref: TMG/1-Hexanol (1/2)).

As a sterically hindered amine, AMP had higher  $\alpha_{eq}$  and lower  $\alpha_R$  compared to MEA without solid product precipitation. AEEA shows the highest absorption capacity among the amine promoters. However, considering the results of both  $\alpha_R$  and  $\alpha_{eq}$ , since MEA has the highest absorption rate and proper absorption capacity among other amines, we chose MEA as the promoter for the rest of the screening experiments to determine the most appropriate alcohol, and also, for characterization experiments.

Fig. 3 presents the effect of alcohol type (methanol, 1-hexanol, n-butanol, sec-butanol) on  $\alpha_R$  and  $\alpha_{eq}$  from the initial pressure of 25.00 bar at the constant temperature of 308.2 K using TMG/alcohol/MEA (0.3/0.6/0.1) CO<sub>2</sub>-BOL. The studied organic solvents for CO<sub>2</sub> absorption suggest that the solubility parameter of solvent has linear relation against the reaction rate constant.<sup>31</sup> Accordingly, MeOH has the highest  $\alpha_R$  of 0.284 mol CO<sub>2</sub>/mol solvent compared with 1-butanol and 1-hexanol with the  $\alpha_R$  of 0.270 and 0.246 mol CO<sub>2</sub>/mol solvent, respectively. Although sec-butanol exhibited the highest  $\alpha_R$  of 0.294 mol CO<sub>2</sub>/mol solvent, its main drawback is the production of solid ionic species.



**Fig. 3:** Effect of alcohol type on the rate and equilibrium CO<sub>2</sub> absorption and CO<sub>2</sub> loading versus reaction time from the initial pressure of 25.00 bar at the constant temperature of 308.2 K using TMG/alcohol/MEA (0.3/0.6/0.1) CO<sub>2</sub>-BOL.

The choice of alcohol has no significant effect on the  $\alpha_{eq}$  for the studied BOLs. 1-butanol has the highest  $\alpha_{eq}$  equal to 0.424 mol CO<sub>2</sub>/mol solvent and the lowest  $\alpha_{eq}$  of 0.396 mol CO<sub>2</sub>/mol solvent refers for methanol. However, the physical properties of BOLs including viscosity, polarity and melting point depend on the alcohol chain length. Blasucci et al.<sup>32</sup> showed that the shorter alcohol chain length leads to the higher difference between ionic and non-ionic forms. Heldebrant et al.<sup>17</sup> reported that the choice of alcohol has negligible effect on the enthalpy and Gibbs free energy of reactions in the TMG/alcohol BOLs.

Methanol as a shorter and more acidic molecule would be a better choice in the presence of water as impurity which takes part in direct competition with alcohol for the reaction with CO<sub>2</sub>. Consequently, we chose methanol as the alcohol in screening experiments in the three-component BOL solvent. For the sake of comparison, the values of  $\alpha_R$  and  $\alpha_{eq}$  for the tested solvents in the screening experiments are presented in Table 2.

**Table 2:**  $\alpha_R$  and  $\alpha_{eq}$  of tested solvents in the screening experiments from the initial pressure of 25.00 bar at the constant temperature of 308.2 K using TMG/alcohol/amine (0.3/0.6/0.1) CO<sub>2</sub>-BOL based on the molality scale and molar ratio.

Solvent	$\alpha_R$ (mol CO <sub>2</sub> /mol solvent)	$\alpha_R$ (mol CO <sub>2</sub> /Kg solvent)	$\alpha_{eq}$ (mol CO <sub>2</sub> /mol solvent)	$\alpha_{eq}$ (mol CO <sub>2</sub> /Kg solvent)
TMG/1-Hexanol (Ref)	0.263	2.469	0.419	3.934
TMG/1-Hexanol/MEA	0.246	2.412	0.420	4.119
TMG/1-Hexanol/DEA	0.211	1.983	0.399	3.751
TMG/1-Hexanol/EEA	0.219	2.090	0.382	3.646
TMG/1-Hexanol/AEEA	0.209	1.966	0.453	4.262
TMG/1-Hexanol/DETA	0.222	2.091	0.415	3.908
TMG/1-Hexanol/TETA	0.177	1.602	0.433	3.919
TMG/1-Hexanol/AMP	0.230	2.195	0.438	4.180
TMG/1-Hexanol/PZ	0.206	1.971	0.432	4.135
TMG/MeOH /MEA	0.283	4.725	0.396	6.613
TMG/n-BuOH /MEA	0.270	3.171	0.424	4.980
TMG/sec-BuOH /MEA	0.294	3.453	0.417	4.898

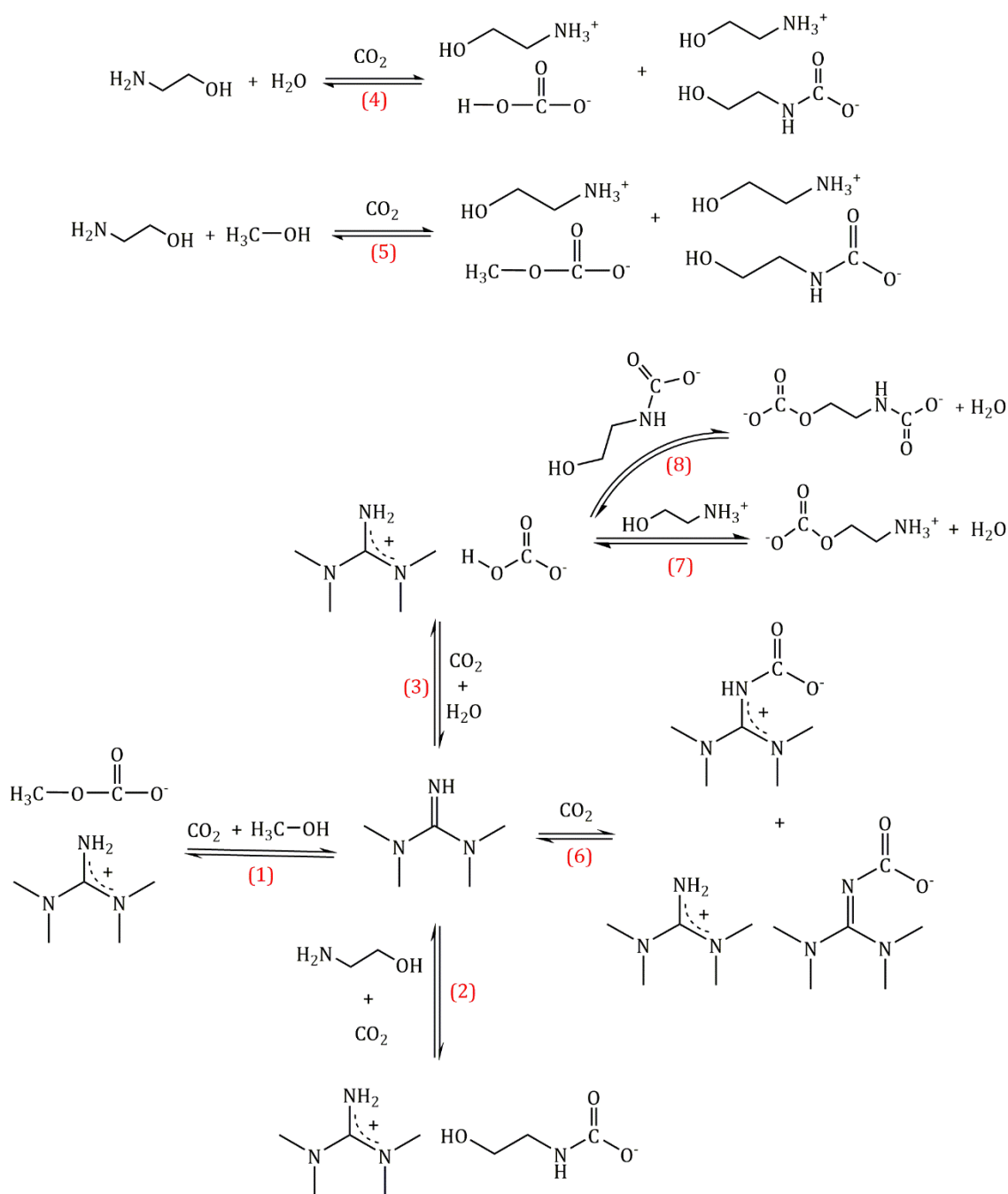
### **TMG/MEA/MeOH ternary system**

The three-component CO<sub>2</sub>-BOLs resulted in the higher equilibrium CO<sub>2</sub> absorption compared with TMG/alcohol BOL. The two-component BOLs suffer from trace amounts of water in the reaction medium which results in the production and precipitation of solid bicarbonate salt. Addition of amine to the system not only increases the weight capacity of BOLs, but also inhibits the formation of solid bicarbonate salt in the presence of water. Screening experiments showed that the three-component TMG/MeOH/MEA CO<sub>2</sub>-BOL had better performance compared with other alcohols and amines based on equilibrium CO<sub>2</sub> absorption and absorption rate, as well as, prevention of solid product formation. The unreacted BOLs and ionic products were characterized to specify the production of ionic species, explain the inhibitory effect of MEA and propose a plausible reaction mechanism for the reaction of CO<sub>2</sub> with the TMG/MeOH/MEA as a three-component BOL in the absence and presence of water impurity. Therefore, the pure TMG, the two-component solvents (TMG/MeOH, TMG/MEA, MEA/MeOH) and the three-component BOL (TMG/MeOH/MEA) were characterized using FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. In all the experiments equimolar mixtures were used for the absorption experiments, while the mole fraction of water was chosen to be 0.3 for the experiments in wet condition.

### **Nuclear magnetic resonance (NMR) spectroscopy**

#### **Two-component TMG/MeOH and TMG/MEA BOLs**

The two-component solvents were characterized using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy before and after reaction with CO<sub>2</sub> to confirm the production of ionic products. The produced ionic species of CO<sub>2</sub> reaction with TMG/MeOH and TMG/MEA BOLs are [TMGH<sup>+</sup>][CH<sub>3</sub>OCOO<sup>-</sup>] (reaction 1, Fig. 4) and [TMGH<sup>+</sup>][MEACOO<sup>-</sup>] (reaction 2, Fig. 4), respectively.



**Fig. 4:** Plausible reaction mechanism for the absorption of CO<sub>2</sub> in the TMG/MeOH BOL modified by MEA.

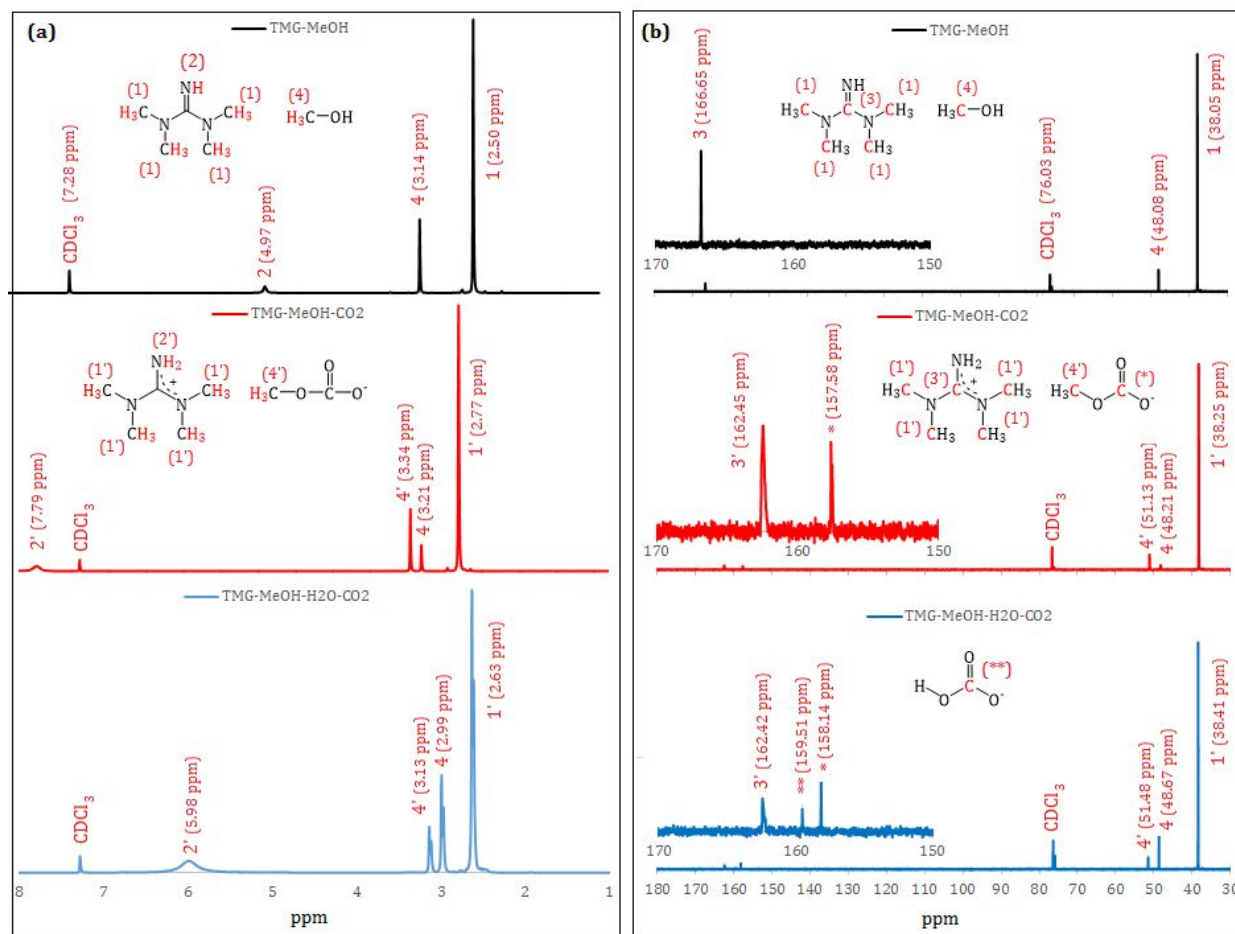
Fig. 5 shows the <sup>1</sup>H and <sup>13</sup>C NMR spectra of unreacted BOL (TMG/MeOH) and the products of BOL reaction with CO<sub>2</sub> in the absence and presence of water (TMG/MeOH/CO<sub>2</sub> and

TMG/MeOH/H<sub>2</sub>O/CO<sub>2</sub>). The <sup>1</sup>H NMR spectrum of TMG/MeOH/CO<sub>2</sub> depicts that the signal at δ=4.97 ppm related to the N-H proton in the unreacted TMG/MeOH was broadened and deshielded to δ=7.79 ppm which supports the formation of [TMGH<sup>+</sup>][CH<sub>3</sub>OCOO<sup>-</sup>] salt and protonation of TMG at position H2 (Fig. 5. a). Moreover, the intensity of hydrogen peak at position H4 of unreacted MeOH decreased at 3.14 ppm and a new peak was appeared at 3.34 ppm (H4') which was attributed to the hydrogens of methyl carbon in MeCO<sub>3</sub><sup>-</sup>.

Further, the formation of ionic compounds was also supported by <sup>13</sup>C NMR spectroscopic studies. The <sup>13</sup>C NMR spectrum of TMG/MeOH mixture after reaction with CO<sub>2</sub> represents a new carbon signal at δ=157.58 ppm (C\*) that was attributed to the carbonyl carbon of methylcarbonate anion (CH<sub>3</sub>OCOO<sup>-</sup>). Furthermore, the peak of carbon near the protonated nitrogen (C3) got shielded from δ=166.65 to 162.45 ppm. Also, the intensity of methyl carbon peak (C4) of unreacted MeOH decreased at 48.08 ppm and a new signal (C4') related to the methyl carbon in CH<sub>3</sub>OCOO<sup>-</sup> was observed at 51.13 ppm. The production of guanidinium methyl carbonate salt was also reported by Heldebrant et al.<sup>17</sup>

Addition of water to the TMG/MeOH BOL resulted in the production and precipitation of solid bicarbonate salt ([TMGH<sup>+</sup>][HOCOO<sup>-</sup>]). According to reaction 3 (Fig. 4), the <sup>13</sup>C NMR spectrum of TMG/MeOH/H<sub>2</sub>O/CO<sub>2</sub> (Fig. 5) shows the characteristic signal for the carbonyl carbon of bicarbonate salt ([TMGH<sup>+</sup>][HOCOO<sup>-</sup>]) at 159.51 ppm (C\*\*). The signal for the carbonyl carbon of guanidinium methylcarbonate salt ([TMGH<sup>+</sup>][CH<sub>3</sub>OCOO<sup>-</sup>]) was appeared at 158.14 ppm as a result of CO<sub>2</sub> reaction with TMG/MeOH mixture (reaction 1, Fig. 4). The peak of carbon in position C3 shielded from 166.54 to 162.42 ppm.

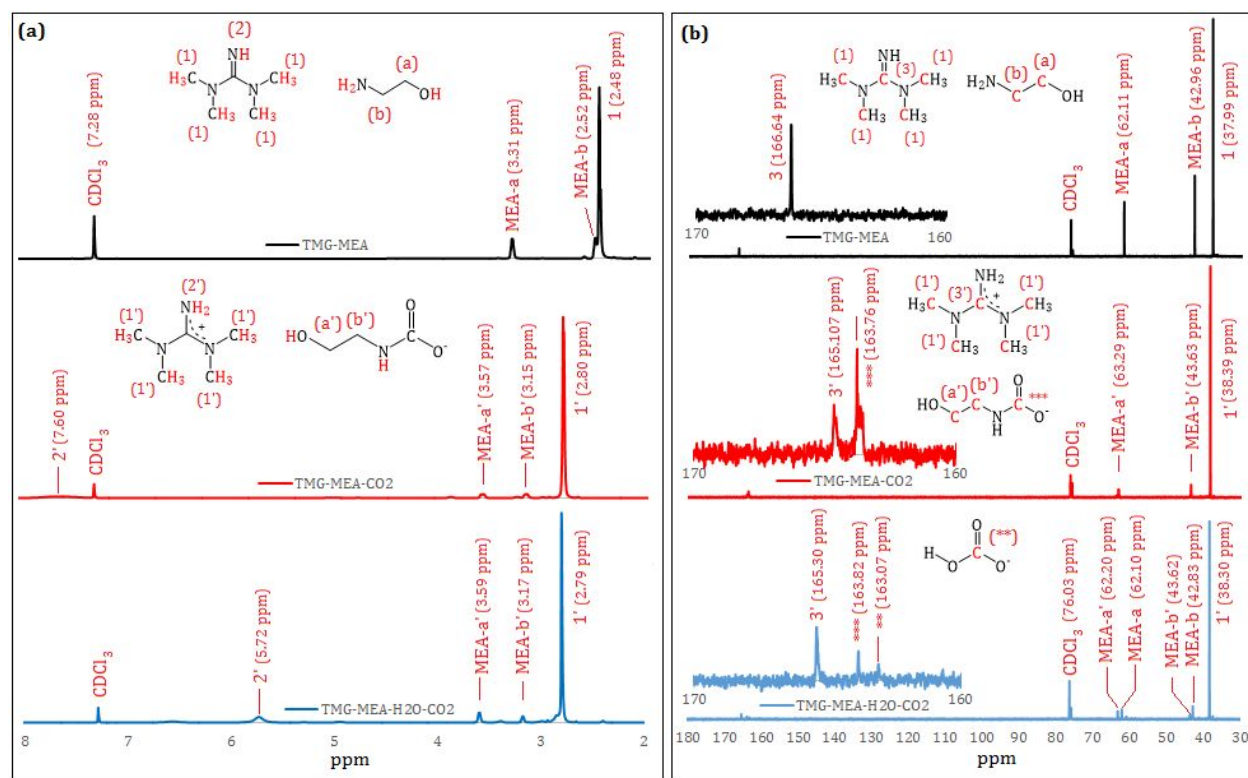




**Fig. 5:** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra for the TMG/MeOH, TMG/MeOH/CO<sub>2</sub> and TMG/MeOH/H<sub>2</sub>O/CO<sub>2</sub> mixtures in CDCl<sub>3</sub>.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of TMG/MEA, TMG/MEA/CO<sub>2</sub> and TMG/MEA/H<sub>2</sub>O/CO<sub>2</sub> are illustrated in Fig. 6. The production of [TMGH<sup>+</sup>][MEACOO<sup>-</sup>] carbamate salt was confirmed by the appearance of a broad peak at  $\delta=7.60$  ppm in the  $^1\text{H}$  NMR spectrum. The chemical shifts in the  $^{13}\text{C}$  NMR spectrum of MEA/TMG/CO<sub>2</sub> shows that the carbon close to the protonated nitrogen in TMG molecule was shifted up-field from 166.64 ppm to 165.10 ppm and a new peak for the carbonyl carbon of carbamate anion was appeared at  $\delta=163.76$  ppm (C<sup>\*\*\*</sup>) which supports the production of [TMGH<sup>+</sup>][MEACOO<sup>-</sup>] salt.

Existence of water in the reaction mixture leads to the formation of [TMGH<sup>+</sup>][HOCOO<sup>-</sup>] as supported by the <sup>13</sup>C NMR spectrum of TMG/MEA/H<sub>2</sub>O/CO<sub>2</sub> where the peak at 163.07 ppm was attributed to the carbonyl carbon of bicarbonate salt. Moreover, bicarbonate salt is also the main product of CO<sub>2</sub> reaction with MEA and water according to (reaction 4, Fig. 4). However, the production of carbamate salt after the CO<sub>2</sub> reaction with TMG/MEA BOL (reaction 2, Fig. 4) makes the solvent more resistant against water impurity compared with TMG/MeOH BOL. Researches showed that the presence of water did not impede the formation of SILs (carbamate salt) upon exposure to CO<sub>2</sub>.<sup>19, 33, 34</sup> Carbamate and zwitterionic carbamate salts are also produced in the reaction of CO<sub>2</sub> with pure TMG (reaction 6, Fig. 4).<sup>35, 36</sup> Reactions 2 and 3 are more favored than reaction 6 due to the steric hindrance of TMG molecule compared to the MEA and water molecules.



**Fig. 6:** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra for the TMG/MEA, TMG/MEA/ $\text{CO}_2$  and TMG/MEA/ $\text{H}_2\text{O}/\text{CO}_2$  mixtures in  $\text{CDCl}_3$ .

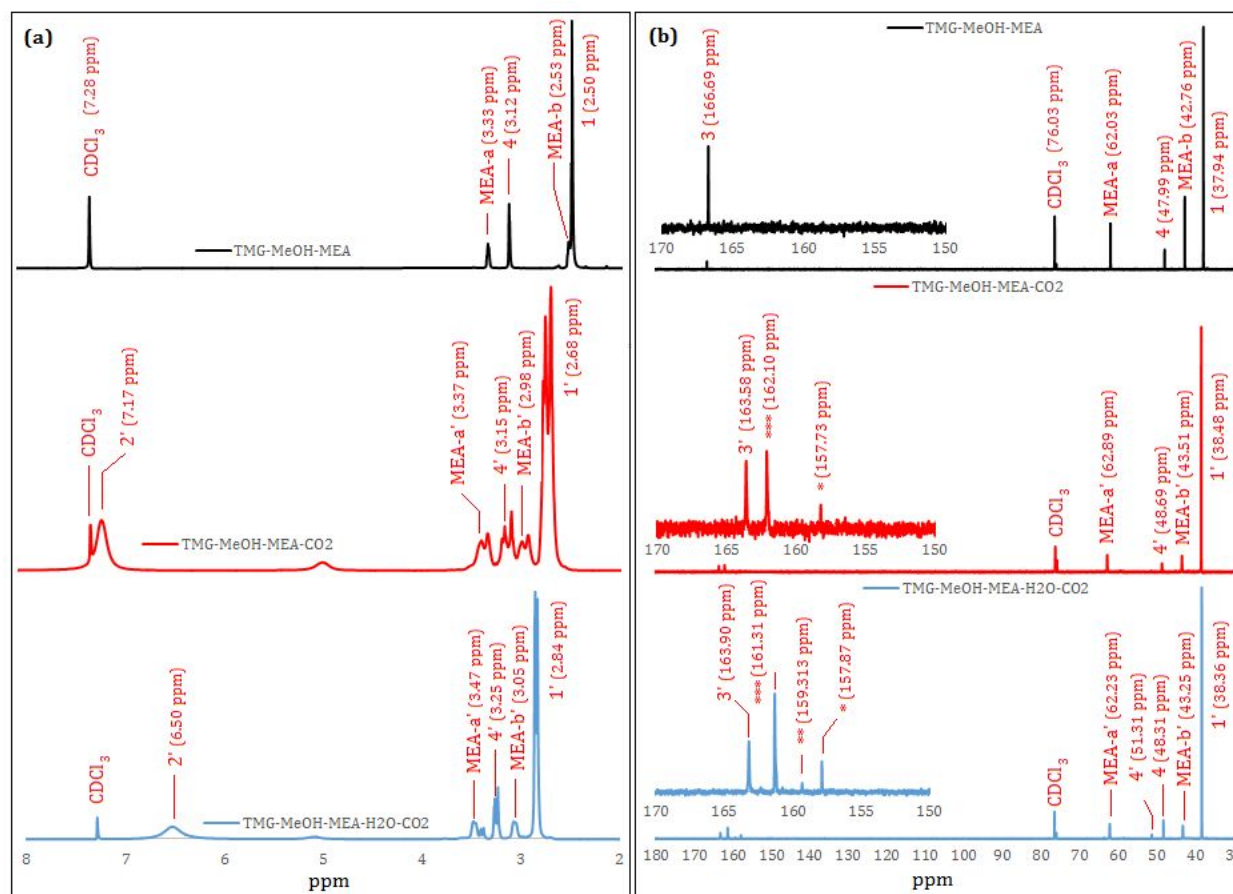
### Three-component TMG/MeOH/MEA

The NMR spectroscopy of the three-component TMG/MeOH/MEA BOL and the products of  $\text{CO}_2$  reaction with the solvent are presented in Fig. 7. The broad band in  $^1\text{H}$  NMR spectrum of TMG/MeOH/MEA/ $\text{CO}_2$  mixture at  $\delta=7.17$  ppm is attributed to the protonation of nitrogen atom in the TMG molecule. The  $^{13}\text{C}$  NMR spectrum of the TMG/MEA/MeOH/ $\text{CO}_2$  shows the signals related to the carbonyl carbons in the anion of ionic products including  $[\text{TMGH}^+][\text{CH}_3\text{OCOO}^-]$  and  $[\text{TMGH}^+][\text{MEACOO}^-]$  at 157.73 ppm ( $\text{C}^*$ ) and 162.10 ppm ( $\text{C}^{***}$ ), respectively. The characteristic peak of carbon close to protonated nitrogen was shifted up-field ( $\delta=163.58$  ppm) compared to unreacted solvent mixture ( $\delta=166.69$  ppm). Moreover, MeOH can take part in the

CO<sub>2</sub> absorption in the presence of MEA yielding amine carbamate ([MEA<sup>+</sup>H<sup>+</sup>][MEACOO<sup>-</sup>]) (reaction 5, Fig. 4) and methyl carbonate ([MEA<sup>+</sup>H<sup>+</sup>][CH<sub>3</sub>OCOO<sup>-</sup>]).<sup>37</sup>

In the three-component TMG/MeOH/MEA BOL, water as a shorter and more acidic molecule reacts more favorably with CO<sub>2</sub> yielding bicarbonate salt (reaction 3, Fig. 4) rather than methyl carbonate (reaction 1) and amine carbamate (reaction 2). Heldebrant et al.<sup>17</sup> calculated the ratio of equilibrium constants,  $K_{H_2O}/K_{MeOH}$ , to be 1.43 in the competitive reactions of CO<sub>2</sub> with water/MeOH/DBU mixture. The signal at 163.07 ppm in the TMG/MeOH/MEA/H<sub>2</sub>O/CO<sub>2</sub> was attributed to the carbonyl carbon of bicarbonate salt. However, addition of MEA as a promoter to the two components TMG/MeOH BOL in the presence of water significantly inhibited the formation and precipitation of solid salts after CO<sub>2</sub> uptake.

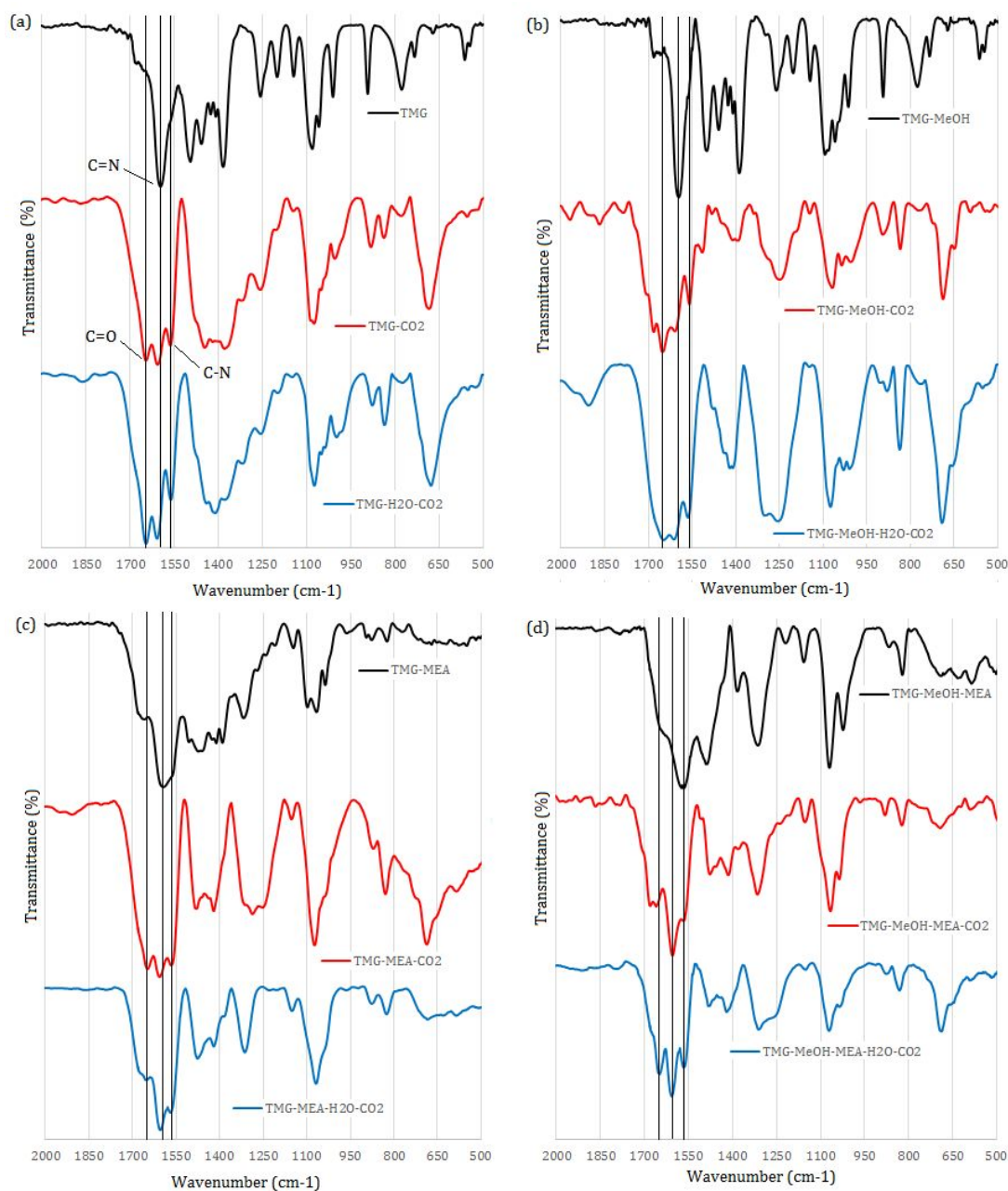
The production of amine carbamate in both reactions 2 and 5, as a more stable salt in comparison to methyl carbonate, causes lower bicarbonate precipitation and leads to a water tolerable solvent system. Additionally, the protonated and non-protonated MEA (depending on the solution basicity) have a hydroxyl group prone to react with HCO<sub>3</sub><sup>-</sup> (reaction 7, Fig. 4) to produce a carbonate salt.<sup>38</sup> According to (reaction 8, Fig. 4), the MEA and its carbamate are also available to react with HCO<sub>3</sub><sup>-</sup>. The equilibrium constant of MEA carbonate formation is 0.66 that was calculated using the peak areas in the NMR spectra.<sup>38</sup>



**Fig. 7:** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra for the TMG/MeOH/MEA, TMG/MeOH/MEA/ $\text{CO}_2$  and TMG/MeOH/MEA/ $\text{H}_2\text{O}/\text{CO}_2$  mixtures in  $\text{CDCl}_3$ .

## FTIR Spectroscopy

Fig. 8 shows the FTIR spectra of two-component and three-component BOLs in the absence and presence of water. The observed peak at  $1597\text{ cm}^{-1}$ , belongs to the  $\text{C}=\text{N}$  ring stretching vibration of unreacted TMG. This peak becomes weaker and shifts to  $1562\text{ cm}^{-1}$  after reaction with  $\text{CO}_2$  that is the evidence of the presence of protonated TMG. The appeared peak at  $1647\text{ cm}^{-1}$  was attributed to the  $\text{C}=\text{O}$  stretching absorption band after  $\text{CO}_2$  uptake related to the bicarbonate, carbonate and carbamate carbonyl group. The bands at  $2939\text{ cm}^{-1}$  and  $2877\text{ cm}^{-1}$  shows the  $\text{C}-\text{H}$  stretching vibrations in TMG, MeOH and MEA molecules.

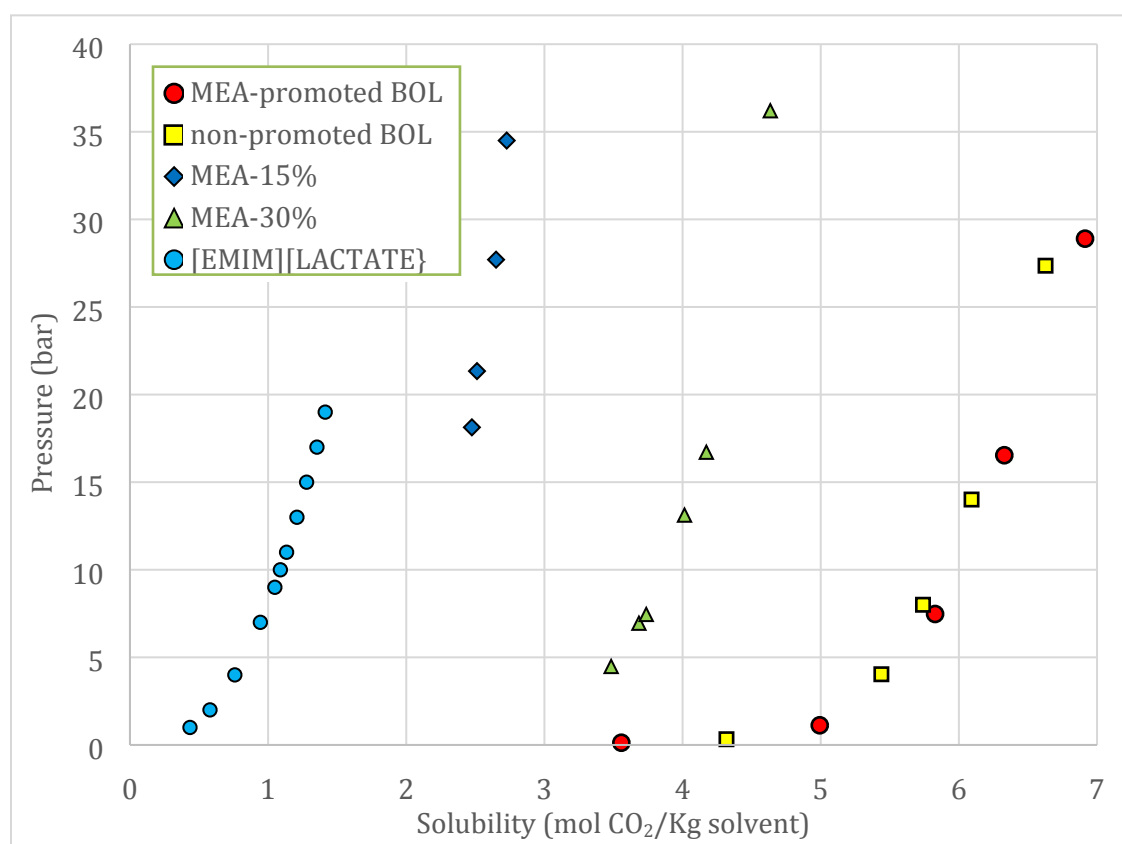


**Fig. 8:** FTIR spectrum of (a) TMG, TMG/CO<sub>2</sub> and TMG/H<sub>2</sub>O/CO<sub>2</sub>; (b) TMG/MeOH, TMG/MeOH/CO<sub>2</sub> and TMG/MeOH/H<sub>2</sub>O/CO<sub>2</sub>; (c) TMG/MEA, TMG/MEA/CO<sub>2</sub> and TMG/MEA/H<sub>2</sub>O/CO<sub>2</sub> (d) TMG/MeOH/MEA, TMG/MeOH/MEA/CO<sub>2</sub> and TMG/MeOH/MEA/H<sub>2</sub>O/CO<sub>2</sub> systems.



## Equilibrium CO<sub>2</sub> Solubility

The equilibrium CO<sub>2</sub> solubility data were obtained for the TMG/MeOH/MEA (0.3/0.6/0.1) and TMG/MeOH (1/2) BOLs at 313.2 K and the pressure range of 0-29 bar (Fig. 9). It was observed that the addition of MEA as a promoter to the two-component TMG/MeOH BOL while keeping their molar ratio constant at 1/2 enhances the CO<sub>2</sub> absorption capacity. There is no published data for the equilibrium solubility of CO<sub>2</sub> in the TMG based SILs. Therefore, for the sake of comparison, the equilibrium CO<sub>2</sub> solubility data in 2.7 and 7 mol MEA/Kg H<sub>2</sub>O solvents<sup>39</sup> and 1-ethyl-3-methylimidazolium L-(+)-lactate ([EMIM][LACTATE]) ionic liquid<sup>40</sup> were also presented in Fig. 9.



**Fig. 9:** The equilibrium CO<sub>2</sub> solubility in TMG/MeOH/MEA (0.3/0.6/0.1) BOL, TMG/MeOH BOL (1/2), 15 wt.% aqueous MEA, 30 wt.% aqueous MEA and [EMIM][LACTATE] IL at 313.2 K.

### Solvent regeneration

The recyclability of TMG/MeOH/MEA (0.3/0.6/0.1), TMG/MeOH/H<sub>2</sub>O (0.3/0.6/0.1) and TMG/MeOH/MEA/H<sub>2</sub>O (0.25/0.5/0.15/0.1) solvent mixtures were evaluated by two absorption-desorption cycles and the obtained results are illustrated in Fig. 10. It should be noted that due to the low number of regeneration cycles examined, these experiments are quite preliminary. The recycling ability of any solvent needs more experiments and about 10 cycles are commonly required. In this work we have been focused on introducing the solvation behavior of the solvents and recycling investigations were beyond our scope. However, one cycle of experiments were performed as follows.

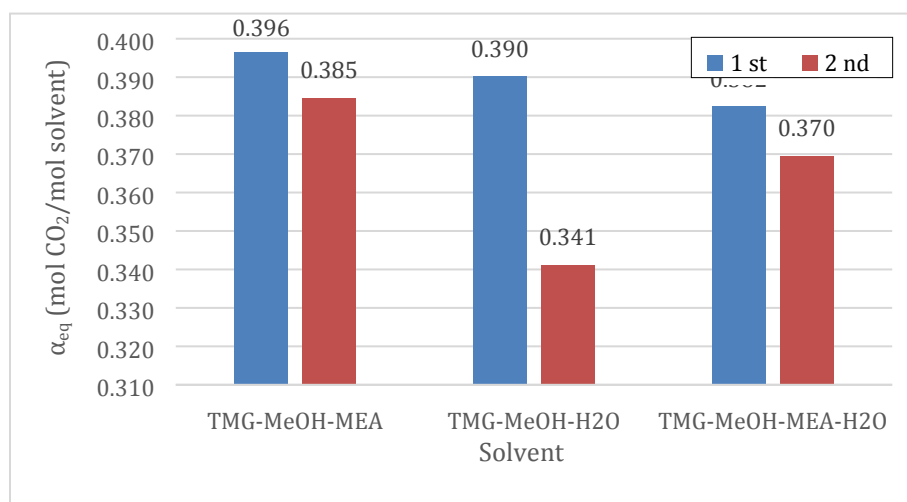
The solvents were regenerated via thermal desorption at 100 °C. It was found that the TMG/MeOH/MEA maintained the high regeneration efficiency after the first cycle ( $\eta = 97.2\%$ ). The TMG/MeOH/H<sub>2</sub>O system has poorer recyclability, such that the regeneration efficiency after the 1<sup>st</sup> cycle was 87.4%. It was observed that the MEA promoted system in the presence of water (TMG/MeOH/MEA/H<sub>2</sub>O) exhibited better regeneration performance than that of non-promoted system (TMG/MeOH/H<sub>2</sub>O). The evaporation loss of BOLs can be reduced using MEA as promoter due to the inhibition of bicarbonate salt formation which has higher thermal stability than carbonate and carbamate species.

The absorption experiments in Fig 10 show that in the 1<sup>st</sup> cycle the equilibrium CO<sub>2</sub> absorption for the tested solvents is in the following order: TMG/MeOH/MEA (0.396 mol CO<sub>2</sub>/mol solvent) > TMG/MeOH/H<sub>2</sub>O (0.390 mol CO<sub>2</sub>/mol solvent) > TMG/MeOH/MEA/H<sub>2</sub>O (0.382 mol CO<sub>2</sub>/mol solvent) for which initial  $\alpha_{eq}$  is almost identical. Moreover, the values of  $\alpha_R$  were also calculated for the TMG/MeOH/MEA, TMG/MeOH/H<sub>2</sub>O and TMG/MeOH/MEA/H<sub>2</sub>O to be 0.246, 0.267 and 0.245 mol CO<sub>2</sub>/mol solvent, respectively. However, the equilibrium condition for the



TMG/MeOH/H<sub>2</sub>O mixture was attained after extremely longer time compared to other solvents (Fig. S1) due to the formation of solid products which restricts proper mixing of solvent.

TGA and DSC were also used to investigate the thermal stability of solvents (Fig. S2). Obviously, using a higher chain length alcohol like hexanol increases the boiling point of solvent which is advantageous in the recyclability point of view such that the regeneration is applicable below the boiling point of solvent.



**Fig. 10:** Absorption/regeneration cycles for the TMG/MeOH/MEA (0.3/0.6/0.1),

TMG/MeOH/H<sub>2</sub>O (0.3/0.6/0.1) and TMG/MeOH/MEA/H<sub>2</sub>O (0.25/0.5/0.15/0.1) solvent mixtures

(absorption condition: 308.2 K and 25.00 bar, desorption condition: 100 °C).

## Conclusions

CO<sub>2</sub>-binding organic liquids or switchable ionic liquids provide advantages over conventional aqueous alkanolamine solutions in terms of CO<sub>2</sub> loading, selectivity and regeneration efficiency. However, two-component ionic liquids suffer from traces amounts of water in the reaction medium that results in the production of solid bicarbonate salt which has negative effect on the regeneration efficiency and applicability of solvent. Addition of primary, secondary and polyamines to the two-component BOLs (superbase/alcohol) enhanced the CO<sub>2</sub> absorption capacity and inhibited the

formation of solid products. Application of some amines led to the formation of solid products which is detrimental for practical applications. Screening experiments showed that the TMG/MeOH/MEA system has the most appropriate performance in terms of absorption rate and equilibrium CO<sub>2</sub> loading. The pure TMG, two-component solvents (TMG/MeOH, TMG/MEA and MEA/MeOH) and three-component solvent system (TMG/MeOH/MEA) were further analyzed by FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy in the wet and dry conditions. It was concluded that the presence of water has negative effect on CO<sub>2</sub> uptake and leads to the formation of solid bicarbonate salt. The TMG/MeOH system is more sensitive to water because bicarbonate salt is more stable than methyl carbonate, but the TMG/MEA system which produces the carbamate salt is more water tolerable. Furthermore, introducing MEA to the TMG/MeOH system inhibited the formation of bicarbonate due to the production of amine carbamate in the reaction of CO<sub>2</sub> with TMG/MEA and MEA/MeOH systems and also the reaction of protonated or non-protonated MEA and its carbamate with HCO<sub>3</sub><sup>-</sup> that produces carbonate salt. The results of characterization experiments were used to evaluate and prove the formation of ionic species and explaining the role of MEA in the solvent system and proposing a reaction mechanism. One regeneration cycle experiments were performed on TMG/MeOH/MEA (0.3/0.6/0.1), TMG/MeOH/H<sub>2</sub>O (0.3/0.6/0.1) and TMG/MeOH/MEA/H<sub>2</sub>O (0.25/0.5/0.15/0.1) solvents in which TMG/MeOH/MEA showed the best performance. Obviously, one cycle is not enough informative and more regeneration experiments are required.

## Acknowledgments

The financial support provided by Iran National Science Foundation (grant number: 97011809) is gratefully acknowledged.

## Supporting Information

**Fig. S1:** Reactor pressure vs absorption time.

**Fig. S2:** TGA and DSC of solvents after CO<sub>2</sub> absorption.

## References

- (1) Lee, J. Y.; Aviso, K. B.; Tan, R. R. Optimal sizing and design of hybrid power systems. *ACS Sustain. Chem. Eng.* 2018, 6 (2), 2482-2490, DOI 10.1021/acssuschemeng.7b03928
- (2) Hassanpouryouzband, A.; Yang, J.; Tohidi, B.; Chuvilin, E.; Istomin, V.; Bukhanov, B. Geological CO<sub>2</sub> capture and storage with flue gas hydrate formation in frozen and unfrozen sediments: method development, real time-scale kinetic characteristics, efficiency, and clathrate structural transition. *ACS Sustain. Chem. Eng.* 2019, 7 (5), 5338-5345, DOI 10.1021/acssuschemeng.8b06374.
- (3) Castro, S.; Albo, J.; & Irabien, A. Photoelectrochemical reactors for CO<sub>2</sub> utilization. *ACS Sustain. Chem. Eng.* 2018, 6 (12), 15877-15894, DOI 10.1021/acssuschemeng.8b03706.
- (4) Karpe, P.; & Aichele, C. P. Amine modeling for CO<sub>2</sub> capture: internals selection. *Environ. Sci. Technol.* 2013, 47 (8), 3926-3932, DOI 10.1021/es3046845.
- (5) Yan, H.; Zhao, L.; Bai, Y.; Li, F.; Dong, H.; Wang, H.; Zhang, X.; Zeng, S. Superbase ionic liquid-based deep eutectic solvents for improving CO<sub>2</sub> absorption. *ACS Sustain. Chem. Eng.* 2020, 8 (6), 2523-2530, DOI 10.1021/acssuschemeng.9b07128.
- (6) Ozturk, M. C.; Orhan, O. Y.; Alper, E. Kinetics of carbon dioxide binding by 1, 1, 3, 3-tetramethylguanidine in 1-hexanol. *Int. J. Greenhouse Gas Control.* 2014, 26, 76-82, DOI 10.1016/j.ijggc.2014.04.023.
- (7) Huang, K.; Chen, F. F.; Tao, D. J.; Dai, S. Ionic liquid-formulated hybrid solvents for CO<sub>2</sub> capture. *Curr. Opin. Green Sustainable Chem.* 2017, 5, 67-73, DOI 10.1016/j.cogsc.2017.03.016.
- (8) Chen, F. F.; Huang, K.; Fan, J. P.; Tao D. J. Chemical solvent in chemical solvent: A class of hybrid materials for effective capture of CO<sub>2</sub>. *AIChE J.* 2018, 64 (2), 632-639, DOI 10.1002/aic.15952.

- (9) Zhang, J. B.; Peng, H.; Liu, Y.; Tao, D. J.; Wu, P.; Fan, J. P.; Huang, K. Highly efficient CO<sub>2</sub> capture by polyethylenimine plus 1-ethyl-3-methylimidazolium acetate mixed absorbents. *ACS Sustain. Chem. Eng.* 2019, 7 (10), 9369-9377, DOI 10.1021/acssuschemeng.9b00530.
- (10) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. Green chemistry: Reversible nonpolar-to-polar solvent. *Nature*. 2005, 436 (7054), 1102-1102, DOI 10.1038/4361102a.
- (11) Herrero, M.; Mendiola, J. A.; Ibanez, E. Gas expanded liquids and switchable solvents. *Curr. Opin. Green Sustainable Chem.* 2017, 5, 24-30, DOI 10.1016/j.cogsc.2017.03.008.
- (12) Clarke, C. J.; Tu, W. C.; Levers, O.; Brohl, A.; Hallett, J. P. Green and sustainable solvents in chemical processes. *Chem. Rev.* 2018, 118 (2), 747-800, DOI 10.1021/acs.chemrev.7b00571.
- (13) Hart, R.; Pollet, P.; Hahne, D. J.; John, E.; Llopis-Mestre, V.; Blasucci, V.; Liotta, C. L. Benign coupling of reactions and separations with reversible ionic liquids. *Tetrahedron*. 2010, 66 (5), 1082-1090, DOI 10.1016/j.tet.2009.11.014.
- (14) Privalova, E.; Nurmi, M.; Marañón, M. S.; Murzina, E. V.; Mäki-Arvela, P.; Eränen, K.; Mikkola, J. P. CO<sub>2</sub> removal with 'switchable' versus 'classical' ionic liquids. *Sep. Purif. Technol.* 2012, 97, 42-50, DOI 10.1016/j.seppur.2012.01.047.
- (15) Jessop, P. G.; Mercer, S. M.; Heldebrant, D. J. CO<sub>2</sub>-triggered switchable solvents, surfactants, and other materials. *Energy Environ. Sci.* 2012, 5 (6), 7240-7253, DOI 10.1039/C2EE02912J.
- (16) Pollet, P.; Davey, E. A.; Ureña-Benavides, E. E.; Eckert, C. A.; Liotta, C. L. Solvents for sustainable chemical processes. *Green Chem.* 2014, 16 (3), 1034-1055, DOI 10.1039/C3GC42302F.
- (17) Heldebrant, D. J.; Yonker, C. R.; Jessop, P. G.; Phan, L. Organic liquid CO<sub>2</sub> capture agents with high gravimetric CO<sub>2</sub> capacity. *Energy Environ. Sci.* 2008, 1 (4), 487-493, DOI 10.1039/B809533G.
- (18) Wang, C.; Mahurin, S. M.; Luo, H.; Baker, G. A.; Li, H.; Dai, S. Reversible and robust CO<sub>2</sub> capture by equimolar task-specific ionic liquid-superbase mixtures. *Green Chem.* 2010, 12 (5), 870-874, DOI 10.1039/B927514B.

- (19) Yu, T.; Yamada, T.; Gaviola, G. C.; Weiss, R. G. Carbon dioxide and molecular nitrogen as switches between ionic and uncharged room-temperature liquids comprised of amidines and chiral amino alcohols. *Chem. Mater.* 2008, 20 (16), 5337-5344, DOI 10.1021/cm801169c.
- (20) Carrera, G. V. S. M.; Jordao, N.; Branco, L. C.; da Ponte, M. N. (2015). CO<sub>2</sub> capture systems based on saccharides and organic superbases. *Faraday Discuss.* 183, 429-444, DOI 10.1039/C5FD00044K.
- (21) Ostonen, A.; Sapei, E.; Uusi-Kyyny, P.; Klemelä, A.; Alopaeus, V. (2014). Measurements and modeling of CO<sub>2</sub> solubility in 1, 8-diazabicyclo-[5.4. 0]-undec-7-ene Glycerol solutions. *Fluid Phase Equilib.* 374, 25-36, DOI 10.1016/j.fluid.2014.04.021.
- (22) YÜKSEL, Ö.; ÖZTÜRK, M. Ç.; ŞEKER, A.; ALPER, E. Kinetics and performance studies of a switchable solvent TMG (1, 1, 3, 3-tetramethylguanidine)/1-propanol/carbon dioxide system. *Turk. J. Chem.* 2015, 39 (1), 13-24.
- (23) Carrera, G. V.; Jordao, N.; Branco, L. C.; da Ponte, M. N. CO<sub>2</sub> capture and reversible release using mono-saccharides and an organic superbase. *J. Supercrit. Fluids.* 2015, 105, 151-157, DOI 10.1016/j.supflu.2015.02.015.
- (24) Heldebrant, D. J.; Jessop, P. G.; Thomas, C. A.; Eckert, C. A.; Liotta, C. L. The reaction of 1, 8-diazabicyclo [5.4. 0] undec-7-ene (DBU) with carbon dioxide. *J. Org. Chem.* 2005, 70 (13), 5335-5338, DOI 10.1021/jo0503759.
- (25) Zoghi, A. T.; Feyzi, F.; Zarrinpashneh, S. Experimental investigation on the effect of addition of amine activators to aqueous solutions of N-methyldiethanolamine on the rate of carbon dioxide absorption. *Int. J. Greenhouse Gas Control.* 2012, 7, 12-19, DOI 10.1016/j.ijggc.2011.12.001.
- (26) Najafloo, A.; Zoghi, A. T.; Feyzi, F. Measuring solubility of carbon dioxide in aqueous blends of N-methyldiethanolamine and 2-((2-aminoethyl) amino) ethanol at low CO<sub>2</sub> loadings and modelling by electrolyte SAFT-HR EoS. *J. Chem. Thermodyn.* 2015, 82, 143-155, DOI 10.1016/j.jct.2014.11.006.
- (27) Zoghi, A. T.; Feyzi, F.; Zarrinpashneh, S. Equilibrium solubility of carbon dioxide in a 30wt.% aqueous solution of 2-((2-aminoethyl) amino) ethanol at pressures between atmospheric and 4400 kPa: an experimental and modelling study. *J. Chem. Thermodyn.* 2012, 44 (1), 66-74, DOI 10.1016/j.jct.2011.08.011.

- (28) Park, M. K.; Sandall, O. C. Solubility of carbon dioxide and nitrous oxide in 50 mass methyldiethanolamine. *J. Chem. Eng. Data.* 2001, 46 (1), 166-168, DOI 10.1021/jc000190t.
- (29) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundamen.* 1976, 15 (1), 59-64, DOI 10.1021/i160057a011.
- (30) Lv, B.; Zhou, X.; Zhou, Z.; Jing, G. Kinetics and Thermodynamics of CO<sub>2</sub> Absorption into a Novel DETA-AMP-PMDETA Biphasic Solvent. *ACS Sustainable Chem. Eng.* 2019, 7 (15), 13400-13410, DOI 10.1021/acssuschemeng.9b02700.
- (31) Sada, E.; Kumazawa, H.; Osawa, Y.; Matsuura, M.; Han, Z. Q. Reaction kinetics of carbon dioxide with amines in non-aqueous solvents. *Chem. Eng. J.* 1986, 33(2), 87-95, DOI 10.1016/0300-9467(86)80038-7.
- (32) Blasucci, V. M.; Hart, R.; Pollet, P.; Liotta, C. L.; Eckert, C. A. Reversible ionic liquids designed for facile separations. *Fluid Phase Equilib.* 2010, 294 (1-2), 1-6, DOI 10.1016/j.fluid.2010.04.005.
- (33) Yamada, T.; Lukac, P. J.; Yu, T.; Weiss, R. G. Reversible, room-temperature, chiral ionic liquids. Amidinium carbamates derived from amidines and amino-acid esters with carbon dioxide. *Chem. Mater.* 2007, 19 (19), 4761-4768, DOI 10.1021/cm0713531.
- (34) Yamada, T.; Lukac, P. J.; George, M.; Weiss, R. G. Reversible, room-temperature ionic liquids. Amidinium carbamates derived from amidines and aliphatic primary amines with carbon dioxide. *Chem. Mater.* 2007, 19 (5), 967-969, DOI 10.1021/cm062622a.
- (35) Pereira, F. S.; deAzevedo, E. R.; da Silva, E. F.; Bonagamba, T. J.; da Silva Agostini, D. L.; Magalhaes, A.; Gonzalez, E. R. P. Study of the carbon dioxide chemical fixation—activation by guanidines. *Tetrahedron*, 2008, 64 (43), 10097-10106, DOI 10.1016/j.tet.2008.08.008.
- (36) Batagarawa, M. S.; Adam, F. The chemical fixation of carbon dioxide by tetramethylguanidine and triazabicyclo dec-5-ene bases. *ChemSearch Journal.* 2016, 7 (1), 25-31.
- (37) Barzagli, F.; Lai, S.; Mani, F. Novel non-aqueous amine solvents for reversible CO<sub>2</sub> capture. *Energy Procedia*, 2014, 63, 1795-1804, DOI 10.1016/j.egypro.2014.11.186.

- (38) Cieslarova, Z.; dos Santos, V. B.; do Lago, C. L. Both carbamates and monoalkyl carbonates are involved in carbon dioxide capture by alkanolamines. *Int. J. Greenhouse Gas Control*. 2018, 76, 142-149, DOI 10.1016/j.ijggc.2018.07.005.
- (39) Wagner, M.; von Harbou, I.; Kim, J.; Ermatchkova, I.; Maurer, G.; Hasse, H. Solubility of carbon dioxide in aqueous solutions of monoethanolamine in the low and high gas loading regions. *J. Chem. Eng. Data*. 2013, 58 (4), 883-895, DOI 10.1021/je301030z.
- (40) Zoubeik, M.; Mohamedali, M.; Henni, A. Experimental solubility and thermodynamic modeling of CO<sub>2</sub> in four new imidazolium and pyridinium-based ionic liquids. *Fluid Phase Equilib*. 2016, 419, 67-74, DOI 10.1016/j.fluid.2016.03.009.

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