



The CO₂ absorption and desorption analysis of tri-solvent MEA + EAE + AMP compared with MEA + BEA + AMP along with “coordination effects” evaluation

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Abstract

The slow kinetics of CO₂ absorption and high energy cost of CO₂ desorption were the main challenges for CO₂ capture technology. To overcome these drawbacks, a novel tri-solvent MEA (monoethanolamine) + EAE (2-(ethylamino)ethanol) + AMP (2-amino-2-methyl-1-propanol) was prepared at different amine concentrations of 0.1 ~ 0.5 + 2 + 2 mol/L. The CO₂ absorption and desorption experiments were conducted on MEA + EAE + AMP and their precursor MEA + EAE to evaluate the absorption–desorption parameters. Results demonstrated that the optimized concentrations of the bi-blend were 0.2 + 2 mol/L for absorption and 0.4 + 2 mol/L for desorption. For the tri-solvent, the optimized concentration was 0.2 + 2 + 2 mol/L, consistently for both abs-desorption sides. Compared with tri-solvent of MEA + BEA + AMP, MEA + EAE + AMP proved better in absorption but poorer in desorption, while its CO₂ loading of operation line was 0.35 ~ 0.70 mol/mol, higher than that of 0.30–0.60 mol/mol MEA + BEA + AMP. These results led to another tri-solvent candidate of amine solvents in an industrial pilot plant.

Keywords CO₂ capture · Tri-solvent · CO₂ absorption and desorption · Absorption–desorption parameter

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Highlights of novelty

1. The tri-solvent MEA+EAE+AMP was developed and compared with MEA+BEA+AMP in terms of absorption and desorption comprehensively.
2. The “coordinative effect” was investigated for bi-solvents of MEA+EAE(RR’NH) and the tri-solvent of MEA+EAE+AMP, and the optimized ratio of MEA/RR’NH was carefully studied for consistency.
3. The structure activity correlation of DEA and EAE as secondary amines were investigated and compared.

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Abbreviations

AMP 2-Amino-2-methyl-1-propanol
BEA Butylethanolamine
DEA Diethanolamine
EAE 2-(Ethylamino) ethanol
MEA Monoethanolamine

Greek Symbols

α Solution CO₂ loading (mol CO₂/mol amine)
 α_{eq} CO₂ loading of solution in equilibrium with PCO₂

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Introduction

The Paris Agreement requires the world to make progress in greenhouse gas control, especially in carbon capture utilization and storage (CCUS) (Rochelle 2009; Shi et al. 2021a; Yan and Zhang, 2019). Among various post-combustion carbon capture (PCCC) technologies such as chemisorption, adsorption, chilled ammonia, and membrane separation, the chemical absorption–desorption with amine solvents turned out to be the most mature technology, which has been adopted in industrial pilot plant (Gelowitz et al. 2013). The main challenge is the slow CO₂ absorption kinetics for secondary–tertiary amine and huge energy costs of MEA (Gelowitz et al. 2013). The energy cost of heat duty contributes 70% of the overall cost of CO₂ capture technology, which is an important issue in the technology development (Liang et al. 2016). Therefore, heat duty reduction has been the main challenge in the research area. Based on previously published researches, the solvent improvement and process intensification have been the main solutions for heat duty reduction (Rochelle 2009).

Since the 1990s, solvent improvement, with 5–6 branches, has been a popular method for energy efficient solutions (Idem et al. 2006). Based on recent publications, a promising and recently developed branch has been developed since 2016, which is a tri-solvent: amine A + B + C including AMP or PZ. Studies at early stages were reported during 2016–2018, such as MEA + AMP + PZ (Chikezie Nwaoha 2018, Nwaoha et al. 2016b, Xiaowen Zhang et al. 2019, Zhang et al. 2018), AMP + MDEA + DETA (Nwaoha et al. 2016a), and MEA + PZ + MDEA (Zhang et al. 2017). Beside these fundamental studies, the tri-solvent MEA + AMP + PZ was also adopted into a pilot plant of cement process, demonstrating lower heat duty and bigger cyclic capacity over MEA (Chikezie Nwaoha 2018). After 2020, the author developed a novel tri-solvent of MEA + BEA + AMP (Shi et al. 2021a, 2021c) and conducted absorption, desorption, and mass transfer analysis (Shi et al. 2021a). Results indicated the super performance of this tri-solvent + catalysts, which lead to a new pathway of preparing amine blends (Shi et al. 2021c). Whether the tri-solvent was better than single or bi-blends required detailed studies of CO₂ absorption or desorption. Thus, it is premature to conclude that the tri-solvent was better than bi-blends.

For the tri-solvent study of A + B + C, one major difficulty is the theoretical and conceptual frameworks of the roles and duties of each amine. For this study, AMP is selected firstly due to its promising performance in CO₂ desorption. The heat duty reduction is the first priority in solvent improvement. From literature study, AMP-based bi-blends or tri-blends exerted the excessive advantage of AMP (higher desorption performance with moderate absorption) (Narku-Tetteh et al. 2017). The carbamate of AMP was unstable, making it easy to be hydrolyzed to bicarbonate under heat (Ciftja et al. 2014;

Hartono et al. 2020). From our previous publications, the energy cost of bicarbonate [HCO₃[−]] regeneration was much lower than that of carbamate breakdown (Shi et al. 2014; Zhang et al. 2018), resulting to extremely low heat duty. Other studies proposed bi-solvents of AMP + PZ (Hairul et al. 2017; Hassankiadeh and Jahangiri, 2018; Jahangiri and Nabipoor Hassankiadeh, 2018; Spietz et al. 2020), AMP + MEA (Nwaoha et al. 2018a), and AMP + DETA (Wai et al. 2018) since 2016. AMP was blended with other amines whose CO₂ absorption kinetics was fast (DETA, PZ, MEA) to offset its absorption disadvantage (Narku-Tetteh et al. 2017).

The EAE was a special secondary amine, which is selected as amine B due to its competitive CO₂ absorption performance. Studies on CO₂ absorption–desorption of EAE has been conducted since 2017 for single amine (El Hadri et al. 2017; Gao et al. 2017; Hwang et al. 2017; Liu et al. 2019; Muchan et al. 2017) and blended amines such as EAE + 1DMA-2P (Gao et al. 2020) and EAE + AEEA (Pandey and Kumar Mondal, 2021; Pandey and Mondal, 2021). The physical and chemical properties of CO₂-EAE, as a single amine, were studied and reported based on viscosity, pKa, and heat of absorption (Liu et al. 2019). Later on, the advantages of blending EAE with other amines were investigated. These results indicated that EAE has fast absorption rates, relative big CO₂ loading, and low heat of absorption (El Hadri et al. 2017; Liu et al. 2019) but unstable carbamate at low CO₂ concentration comparing with MEA (Muchan et al. 2017), and its equilibrium CO₂ loading can reach 0.67–0.68 mol/mol (Liu et al. 2019), higher than that of both MEA and DEA. The pKa of EAE was close to 10.0, bigger than MEA 9.51 and DEA 8.88 (Liu et al. 2019).

Amine C of this study was MEA with small concentration (< 0.5 mol/L) to realize the “coordinative effect” (Liu et al. 2018). Since 2018, this effect was investigated by Liu (Liu et al. 2018; Xiao et al. 2017a, b) and Shi (Shi et al. 2021a, 2020, 2018b) repeatedly and was verified within bi-solvent MEA + RR’NH of MEA + DEA (Shi et al. 2020) and MEA + BEA (Shi et al. 2021b) and tri-solvent of MEA + BEA + AMP (Shi et al. 2021a). The “coordinative effect” appears when blending MEA (< 0.5 mol/L) with secondary amine RR’NH to enhance CO₂ absorption (Liu et al. 2018) and desorption (Shi et al. 2020, 2018b) simultaneously. The mechanisms were published repeatedly (Liu et al. 2018; Shi et al. 2020) with details in Support Information I. Therefore, blending 0.1–0.5 mol/L MEA with EAE and EAE + AMP bi-solvent could enhance CO₂ absorption and desorption at the same time, and the tri-solvents of MEA + EAE + AMP were prepared with amine concentration C_A ranges within 0.1–0.5 + 2 + 2 mol/L in this study. Furthermore, the mechanism of MEA + EAE may be slightly different from that of MEA + DEA. On the other hand,

if blending MEA with concentration higher than 1 mol/L into other amine blends, the CO₂ desorption performance was sabotaged, which was reported on MEA + BEA + AMP at 1 + 2 + 2 mol/L. (Narku-Tetteh et al. 2017).

The first purpose of this study is to develop an energy efficient tri-solvent of MEA + EAE + AMP as similar cases of tri-solvents MEA + PZ + AMP as potential candidate in industrial pilot plant by investigating the optimized solvent concentrations within 0.1 ~ 0.5 + 2 + 2 mol/L. The second purpose is to verify and investigate the coordinative effect of bi-blends MEA + EAE and tri-solvent of MEA + EAE + AMP to extend the database of amine blends with coordinate effects. Previous studies (Shi et al. 2021b) showed that the optimized blending ratio when amines blend for CO₂ absorption may not be the same as that for CO₂ desorption. Whether the optimized ratio was consistent (the same for absorption and desorption areas) determines the competitive amine blend for industrial application (Jahangiri and Nabipoor Hassankiadeh, 2018). Therefore, the consistency was also investigated for the optimized blending ratios of absorption and desorption within MEA + EAE and MEA + EAE + AMP.

Finally, CO₂ absorption–desorption experiments were performed with tri-solvents MEA + EAE + AMP at 0.1 ~ 0.5 + 2 + 2 mol/L and MEA + EAE bi-blends at 0.1 ~ 0.5 + 2 mol/L. The absorption–desorption parameters (Narku-Tetteh et al. 2017) were used to compare MEA + EAE + AMP and MEA + BEA + AMP and MEA + EAE and MEA + BEA under consistent level. This study contained 3 parts: (1) Verify the “coordinative effect” within MEA + EAE, and test the optimum ratio of MEA/EAE by comparing different absorption–desorption performances with MEA + BEA. (2) Compare CO₂ absorption and desorption performances of MEA + EAE + AMP with these of MEA + BEA + AMP and focus on heat duty reduction. The tri-solvents, such as MEA + AMP + PZ, were potential candidates for an industrial amine scrubbing process (Chikezie Nwaoha 2018). (3) Compare the MEA + EAE and MEA + EAE + AMP blends with coordinative effects to analyze the effect of AMP.

Theory

Methodology of tri-solvent preparation

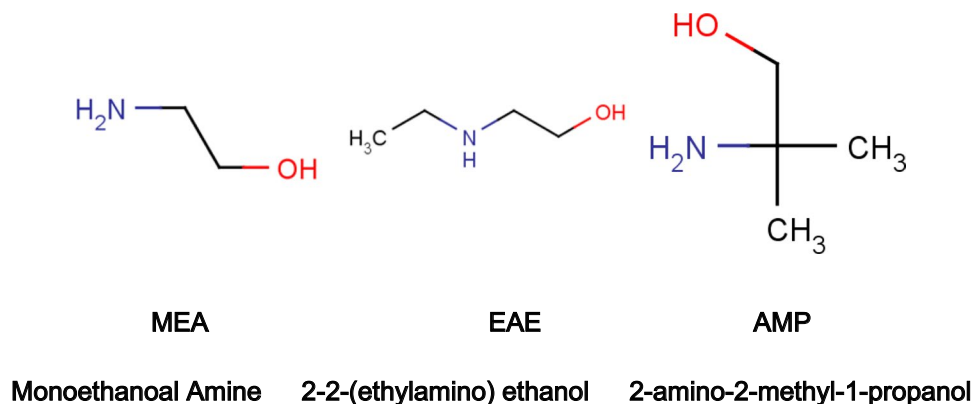
The molecular structures of MEA, EAE, and AMP were plotted in Fig. 1 as amine candidates. All these amines have two common functional groups: (1) only one hydroxyl group (~OH), which is an electron withdrawing (EW) group in the molecules. Reports indicated extra hydroxyl group can decrease absorption rates due to inductive effect of the hydroxyl group to the amino group (Liu et al. 2019). Since the hydroxyl group is an electron-withdrawing (EW) group, it reduced electron cloud density of the molecule if 2 or 3 ~OH groups were introduced. Such effect will reduce the activity of N–C bond generation and carbamate formation. However, three amines with 1 hydroxyl group guaranteed fast absorption rates of tri-solvent. (2) Carbamates generated while reacting with CO₂. All three amines can produce carbamate (R'RNH-COO[−]) when reacting with CO₂, but the AMP has weak carbamate stability due to its stereo hindrance (Ciftja et al. 2014).

For tri-solvents preparation, the selection of amines A, B, and C and their optimized combination ratios were the main difficulties. This study blended MEA with EAE (RR'NH) at 0.1 ~ 0.5 + 2 mol/L to enhance the absorption and desorption performance of EAE simultaneously by means of coordinative effect (Shi et al. 2021b). AMP was blended with MEA + EAE to enhance the CO₂ desorption performance and cyclic capacity simultaneously. AMP was a promising amine candidate with good desorption performance for CO₂ capture industry.

Absorption–desorption parameter analysis

Since 2017, the absorption–desorption parameters have been proposed to evaluate different single or blended amines consistently (Narku-Tetteh et al. 2017). The absorption parameter was calculated in Eq. (1), with initial absorption rates (I_{abs}) presented in Eq. (2); and α_{eq} was calculated using Eq. (3). The absorption parameter was

Fig. 1 The molecular structures of MEA, EAE, and AMP as amines A, B, and C



used to balance the CO₂ absorption rates and α_{eq} , which are usually inconsistent.

$$\text{Absorption parameter} = \text{Initial absorption rate} \times \text{equilibrium loading} \quad (1)$$

5% uncertainty

$$I_{\text{abs_rate}} = \frac{C}{V} \frac{d\alpha}{dt} \text{ (molCO}_2\text{/L.min)} \quad (2)$$

5% uncertainty

$$\text{Estimated Equilibrium loading } \alpha_{eq} = \frac{C_{MEA} \times 0.50 + C_{3A1P} \times 0.58}{C_{MEA} + C_{3A1P}} \quad (3)$$

The desorption parameter was calculated in Eq. (4) (Narku-Tetteh et al. 2017). The I_{des} listed in Eq. (5) and nCO₂ was normalized to 1L. The cyclic capacity was calculated in Eq. (6), and C_A of MEA + 3A1P and MEA + MAE ranged from 2.0 to 2.5 mol/L. The α_{rich} was α_{eq} of bi-blends, and α_{lean} was 0.48–0.50 mol/mol for both blends from desorption curves. The 3A1P and MAE have stable carbamates, and their leans loading at 363 K (90 °C) were difficult to decrease under limited heat input.

$$\text{Desorption parameter} = \frac{\text{Initial desorption rate} \times \text{cyclic capacity}}{\text{heat duty}} \quad (4)$$

10% uncertainty

$$I_{\text{des_rate}} = \frac{dn\text{CO}_2}{dt} = \frac{CVd\alpha}{Vdt} = C \frac{d\alpha}{dt} \text{ (molCO}_2\text{/L.min)} \quad (5)$$

5% uncertainty

$$\text{Cyclic capacity} = (\alpha_{\text{rich}} - \alpha_{\text{lean}})C \text{ (molCO}_2\text{/L.)} \quad (6)$$

The heat duty (H) was calculated with Eqs. (7–8), (Prasongthum et al. 2019) for the first 15 and 30 min of desorption. The nCO₂ was calculated from cyclic capacity and volume, and Q_{input} was tested with electrometer. The amine blends were better candidates with lower heat duty (H).

$$H = \frac{Q_{\text{input}}}{n\text{CO}_2} \frac{\text{kJ/h}}{\text{mol/h}} \quad (7)$$

5% uncertainty

$$n\text{CO}_2 = C \times V \times (\alpha_{\text{rich}} - \alpha_{\text{lean}}) \text{ (molCO}_2\text{)} \quad (8)$$

5% uncertainty

From Eq. (3) of this study specifically, the estimated equilibrium CO₂ loading α_{eq} was close to the weighted average of that of a single amine $\alpha_{eq} = \frac{C_{MEA}\alpha_{eq} + C_{EAE}\alpha_{eq}}{C_{MEA} + C_{EAE}}$. From literature study, the α_{eq} was published as 0.50 mol/mol for MEA, 0.67–0.68 mol/mol for EAE at 15 kPa CO₂ and 313 K, and 0.75 mol/mol for AMP (Support Information I). If blending EAE with MEA, the

equilibrium CO₂ loading α_{eq} of bi-blend will be lower than that of single EAE with MEA introduced, since α_{eq} was only 0.5 mol/mol. However, the exact α_{eq} of bi-solvents or tri-solvents required detailed CO₂ solubility tests (Xiao et al. 2016).

Structure activity analysis of DEA and EAE as secondary amine

Based on literature study, the molecular structure of DEA was similar to EAE, and DEA has hydroxyl group (–CH₂–CH₂–OH) connected to amino group of MEA, while EAE has ethyl group (CH₂–CH₃) connected to amino group instead. The hydroxyl group (OH) has inductive effect which can decrease absorption rates, while ethyl group was electron donating group that favor CO₂ absorption with faster absorption rates (Liu et al. 2019). Therefore, the EAE has better absorption performance than DEA with higher rate of absorption, bigger equilibrium loading, stronger basicity (pKa of 10.0 vs 8.88) (Liu et al. 2019), and lower heat of absorption (El Hadri et al. 2017).

From repeated publication, some important parameters were compared between DEA and EAE, such as the pKa, CO₂ loading, heat of absorption, and rate constant of CO₂ absorption (El Hadri et al. 2017). Comparing with DEA as secondary amine, EAE has bigger CO₂ loading (0.67–0.71 mol/mol) while smaller heat of absorption (–68.95 kJ/mol CO₂) than DEA (0.53–0.58 mol/mol, –74.24 kJ/mol CO₂), indicating its higher absorption capacity and better energy efficiency (CO₂ loading reflect absorption capacity, the bigger the better; while heat of absorption reflect energy efficiency, the smaller the better) (El Hadri et al. 2017; Liu et al. 2019). Furthermore, the absorption rate constants of EAE was quite fast as RR'NH, comparable with MEA (El Hadri et al. 2017). Its activation energy (Ea) was 10 kJ/mol smaller than MEA, and its second order rate constant k_2 was 61–70% of that of MEA under 25–40 °C (El Hadri et al. 2017). Such advantages make EAE as a good candidate of energy efficient amine in industrial application.

The mechanism of coordinative effect of MEA + EAE may be slightly different from MEA + DEA due to different modes of proton transfer (Support Information). The improved mechanism of this special case requires molecular simulation method with exact energy, which await further study.

Experimental apparatus and process

Chemicals

Amines of MEA, EAE, and AMP were commercially available. The CO₂ gas was 99% in purity. A Chittick apparatus was built for CO₂ loading tests of amine samples, up to the code of Association of Official Analytical Chemists (AOAC) (Horwitz 1975). The HCl as standard and methyl orange as indicator were also purchased from Sigma-Aldrich.

The CO₂ loading tests required acid–base titration with HCl vs amine to confirm C_A , and the apparatus collected CO₂ released out of the solution. The volume of CO₂ was recorded, and CO₂ loading were calculated with C_A and $n\text{CO}_2$.

Experiments for CO₂ absorption

The batch process with different operation conditions was the same compared with other studies (Shi et al. 2020). This study adopted 0.3 L MEA + EAE solvents at 0.1 ~ 0.5 + 2 mol/L and 0.3 L MEA + EAE + AMP tri-solvents at 0.1 ~ 0.5 + 2 + 2 mol/L at 313 ± 2 K. This temperate was adjusted to simulate operation conditions in an industrial CO₂ absorber (Natewong et al. 2019). The cooling water bath was used to maintain the temperature since the reaction is exothermic for CO₂ absorption. Then CO₂ (99%) at a fixed gas flow rate of 0.5 L/min was induced into the amine blend with continuous stirring. The pipette process of sampling was similar to that in our previous studies. The absorption profiles were plotted for CO₂ loading α (mol/mol) vs t (min) at a range between 0 and α_{eq} . The CO₂ loadings of the samples were tested twice to maintain the AAD < = 5%. The I_{abs} were calculated at intervals of 0.0–0.3 mol/mol.

Experiments for CO₂ desorption

This recirculation process was similar to other studies. Both MEA + EAE and MEA + EAE + AMP were prepared for 500 mL and heated at 363 K. The temperature was similar to catalytic CO₂ desorption process (Liang et al. 2016). Each sample was pipetted for 2 mL and cooled down to room temperature, ready for CO₂ loading tests. The CO₂ desorption profiles were plotted with CO₂ loading (α) vs time (t) from initial α_{eq} (weighted average of 0.50 mol/mol for MEA, 0.67 ~ 0.68 mol/mol for EAE, and 0.75 mol/mol for AMP). Both MEA and EAE had stable carbamates, and lean loading α_{lean} were observed from the CO₂ desorption profile at 363 K for calculation of cyclic capacity.

The I_{des} were calculated with Eq. (12) based on C_A and slopes ($d\alpha/dt$) of CO₂ desorption curves. Finally, the heat duty (H) was calculated for 0 ~ 30 min from Eq. (14). The desorption parameters derived from heat duty were indicative to comparing bi-solvents MEA + EAE with MEA + BEA and tri-solvents MEA + EAE + AMP with MEA + BEA + AMP consistently.

Results and discussions

Briefly, this study consisted of 3 parts: (1) the coordinative effects within MEA + EAE and compared MEA + EAE with MEA + BEA in abs-desorption parameters; (2) the coordinative effects of tri-solvent of MEA + EAE + AMP and compared with MEA + BEA + AMP in abs-des parameters; and

(3) comparing MEA + EAE with MEA + EAE + AMP to analyze the merit of AMP.

The coordinative effect of MEA + RR'NH has been studied intensively, with cases of MEA + DEA (Liu et al. 2018; Shi et al. 2020; Xiao et al. 2017a, b), MEA + BEA (Shi et al. 2021b), MEA + BEA + AMP (Shi et al. 2021a), etc. The reaction scheme and reaction mechanism were provided in Supporting Information I: mechanism.

The coordinative effect of MEA + EAE bi-blends and compare with MEA + BEA

The criteria of coordinative effects were the I_{abs} and I_{des} of MEA + EAE were better than a EAE single amine alone, while their heat duties (H) were lower. Hence, the absorption and desorption performance were both conducted comprehensively. It was reported repeatedly that the coordinative effects exist within MEA + RR'NH, such as MEA + DEA (Shi et al. 2020, 2018b) and MEA + BEA (Shi et al. 2021b). The MEA + EAE should contain similar effects as well. The optimized ratios of absorption and desorption were analyzed to verify the consistency. The absorption–desorption performances were compared with MEA + BEA comprehensively.

CO₂ absorption of MEA + EAE and compared with MEA + BEA bi-blends

The absorption results were plotted in Fig. 2 with I_{abs} plotted in bar graph (Fig. 3). The order absorption curve did not directly reflect the I_{abs} , since the C_A of MEA + EAE bi-blends varies from 2.0 to 0.5 mol/L. From these curves, it is clear that the MEA + EAE has high α_{eq} among 0.64 ~ 0.68 mol/mol since EAE has higher α_{eq} of 0.67–0.68 mol/mol (Liu et al. 2019; Narku-Tetteh

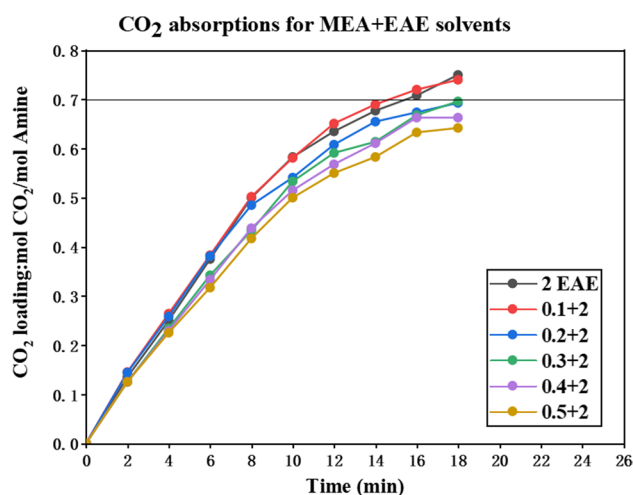


Fig. 2 The CO₂ absorption curves of MEA + EAE bi-blends at 0.1 ~ 0.5 + 2 mol/L

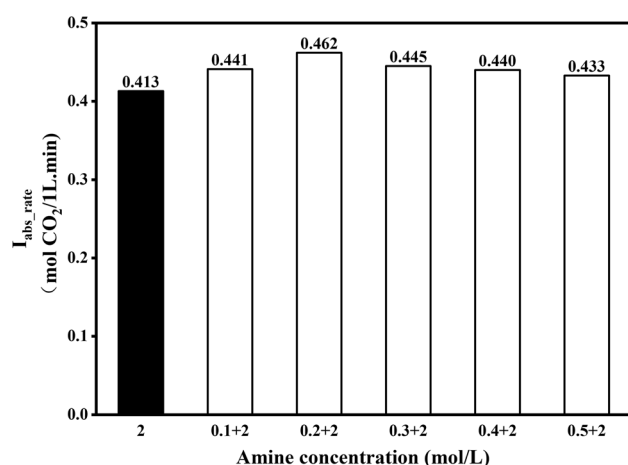


Fig. 3 The initial absorption rates (I_{abs}) of MEA + EAE bi-blends at 0.1 ~ 0.5 + 2 mol/L

et al. 2017) than BEA of 0.60 mol/mol (Narku-Tetteh et al. 2017). The α_{eq} of MEA + EAE were systematically higher than that of MEA + BEA (Shi et al. 2021b) under the same operation conditions, indicating both EAE and MEA + EAE solvents possessed higher CO₂ absorption capacity than BEA and MEA + BEA.

From Fig. 3, the I_{abs} of MEA + EAE has similar trends to that of MEA + BEA (Shi et al. 2021b). It increased first and reached an optimum value at 0.2 + 2 mol/L and started to decrease at 0.3 ~ 0.5 + 2 mol/L. The I_{abs} of the whole sets of MEA + EAE bi-blends were higher than that of 2 mol/L EAE. This phenomenon is a strong sign of “coordinative effect,” which was published repeatedly in MEA + BEA (Shi et al. 2021b), MEA + DEA (Liu et al. 2018; Shi et al. 2020; Xiao et al. 2017a, b), etc. The mechanism was provided in Support Information I: free EAE molecules accept protons from Zwitterion of MEA “MEA-COO⁻” directly, and then, extra free MEA molecules were released to enhance CO₂ absorption (Liu et al. 2018). The order of pK_a was DEA (8.91) (Shi et al. 2018b) < MEA (9.51) (Xiao et al. 2017a, b) < EAE (10.0) (Liu et al. 2019). The bigger value reflects stronger basicity (Bernhardsen and Knuutila, 2017). DEA tended to release free MEA out of “carbamate ammonium salt” due to weaker basicity according to Support Information I (Liu et al. 2018), while BEA and EAE tended to accept protons directly from Zwitterion of MEAH⁺-COO⁻ such as “competition effect” (Shi et al. 2021b). However, at 0.3 ~ 0.5 mol/L, MEA with most EAE converted to EAEH⁺, and extra MEA accepted protons from Zwitterion directly. With increased viscosity of the amine solvents, the I_{abs} reduced from optimum value. Similar effects were observed at MEA + BEA bi-solvent where the optimized ratio was 0.3 + 2 mol/L (Shi et al. 2021b).

Coordinative effect of absorption for MEA + DEA (weaker basicity) at 298–323 K (Liu et al. 2018):

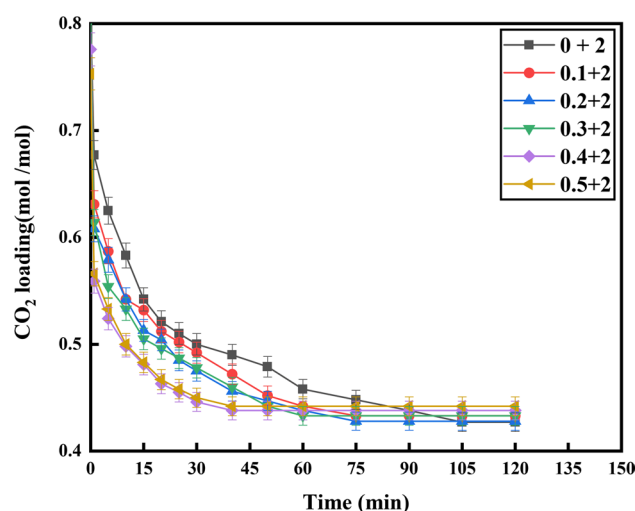
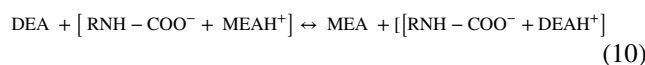
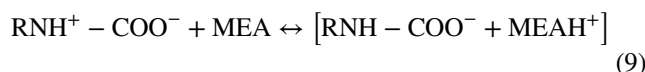
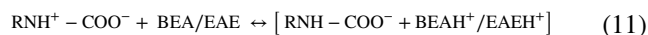


Fig. 4 The CO₂ desorption curves of MEA + EAE bi-blends at 0.1 ~ 0.5 + 2 mol/L



Coordinative effect of absorption for MEA + BEA (strong basicity) at 298–323 K:



The exact values of I_{abs} of MEA + EAE were slightly higher than that of MEA + BEA (Shi et al. 2021b) at similar operation conditions from Support Information II. After comparison, the I_{abs} of BEA and MEA + BEA ranges 0.409–0.442 mol CO₂/L.min (Shi et al. 2021b), while I_{abs} of MEA + EAE ranged 0.413–0.462 mol CO₂/L.min, which was 4.5% higher. This is another proof of better absorption performance of EAE than BEA, even their pK_a were comparable to 10.0 (Bernhardsen and Knuutila, 2017).

CO₂ desorption of MEA + EAE and compared with MEA + BEA bi-blends

The CO₂ desorption curves were demonstrated on Fig. 4 with initial desorption rates (I_{des}) plotted in the bar graph of Fig. 5. In Fig. 4, the α_{eq} was around 0.67–0.68 mol/mol (Liu et al. 2019; Muchan et al. 2017), while the extra CO₂ loading around 0.7–0.8 mol/mol was the CO₂ absorption to water. The α_{lean} was located at 0.43–0.44 mol/mol. Compared to MEA + BEA desorption curves under the same operation conditions, the α_{lean} is around 0.30–0.35 mol/mol (Shi et al. 2021b). Hence, the EAE possesses poorer desorption performance than BEA, probably due to the more stable carbamate produced.

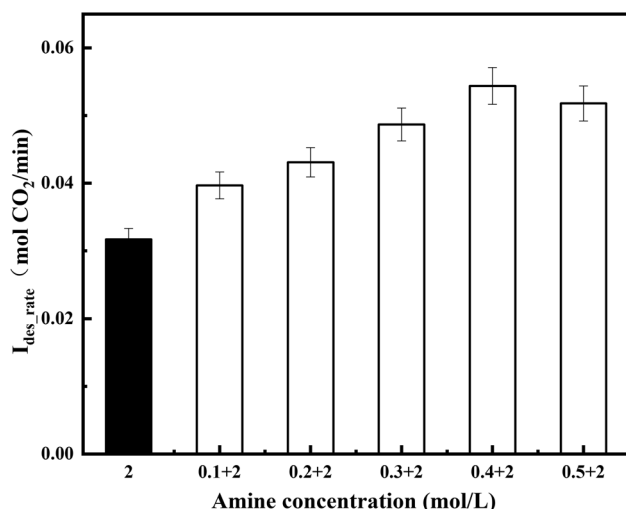
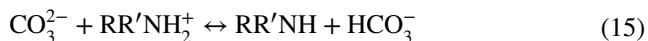
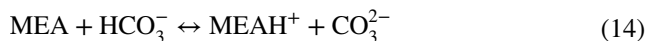


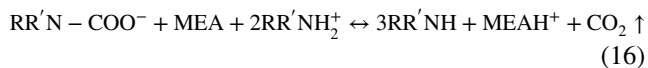
Fig. 5 The initial desorption rates (I_{des}) of MEA+EAE bi-blends at 0.1~0.5+2 mol/L

From Fig. 5, the I_{des} followed similar trends: the I_{des} of MEA+EAE were higher than EAE alone systematically, and it increased first to an optimized ratio of 0.4+2 mol/L and decreased to 0.5+2 mol/L. The similar effects were published within other MEA+RR'NH such as MEA+DEA (Shi et al. 2020) and MEA+BEA (Shi et al. 2021b). The reason for the higher I_{des} of MEA+EAE than EAE alone was the coordinative effect (Shi et al. 2021a). The increased nCO₂ production was taking into effect while blending small concentration of MEA at 0–0.5 mol/L. The mechanism was published repeatedly (Shi et al. 2021a, 2021b), with main reactions written below:

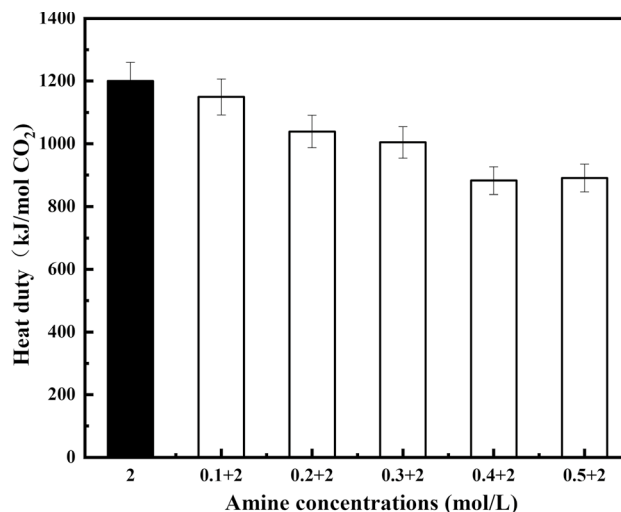
Desorption at 363–378 K with lean CO₂ loadings (negligible HCO₃[−]) (Shi et al. 2021a):



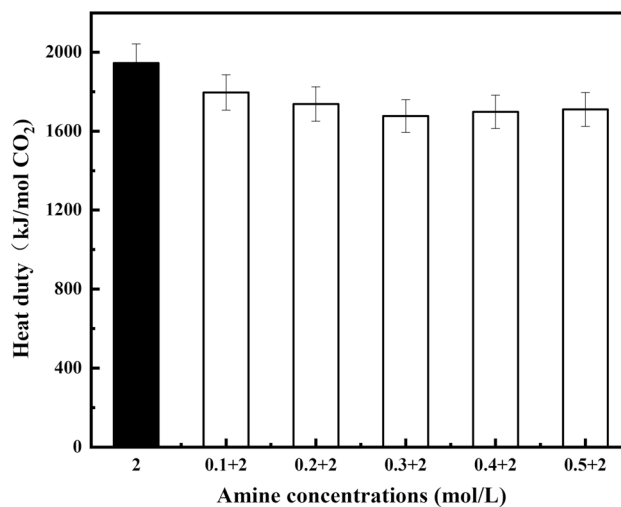
The desorption reactions of MEA+RR'NH at 0.1~0.5/2 as sum of (12–15) (Shi et al. 2021b):



As published repeatedly, the MEA in small concentration facilitates amine H⁺ deprotonation and carbamate hydrolysis of secondary amine RR'N-COO[−], resulting in extra nCO₂ production (Shi et al. 2018a). Extra CO₂ production leads to higher initial absorption rates.



(a) 30 minutes



(b) 60 min

Fig. 6 The heat duties of MEA+EAE bi-blends at 0.1~0.5+2 mol/L at **a** 30 min and **b** 60 min

The heat duties of MEA+EAE bi-blends were plotted in Fig. 6a and b for 30 and 60 min. It is clear that H decreased first with increased C_A of MEA and reached the minimum value at 0.4+2 mol/L for 30 min, while 0.3~0.4+2 mol/L for 60 min and then started to increase. The overall bi-blends of MEA+EAE exhibited lower heat duties than the single EAE alone, reflecting strong coordination. The reason was reported repeatedly (Shi et al. 2020, 2018a) that blending MEA resulted in 10–20% increase of CO₂ production, while Q_{input} only increased 5–10% (Shi et al. 2018a). Then the heat duties decreased until it reached the minimum value. With extra MEA introduced, the increase of CO₂ cannot offset that of Q_{input} , and H increased again (Shi et al. 2018a). Based on the Eq. (17), the increased C_A of MEA at 0.5~1 mol/L leads

to the increase of Q_{input} and $n\text{CO}_2$ as well. However, since it was beyond the optimized ratio of 0.4/2, the increased $n\text{CO}_2$ cannot offset the ΔQ_{input} in the system. The extra CO_2 production was small but extra heat input is big, resulting in poor desorption performance.

$$H = Q/n\text{CO}_2; H' = \frac{Q + \Delta Q}{n\text{CO}_2 + \Delta n\text{CO}_2} \quad (17)$$

The relative heat duty H of MEA + EAE were listed at 30 min with EAE (100%) as benchmark: $0.1 + 2$ (95.8%) > $0.2 + 2$ (86.6%) > $0.3 + 2$ (83.7%) > $0.5 + 2$ (74.2%) > $0.4 + 2$ (73.5%), the smaller the better. The relative heat duty H of MEA + EAE at 60 min were $0.1 + 2$ (92.3%) > $0.2 + 2$ (89.3%) > $0.5 + 2$ (87.9%) > $0.4 + 2$ (87.3%) > $0.3 + 2$ (86.2%), the smaller the better. The overall heat duty reduction was 26.5% for 30 min and 13.8% for 60 min at optimized concentration of 0.3 ~ 0.4 + 2 mol/L. This ratio was around 15–25%, exhibiting strong coordinative effects.

Furthermore, the heat duties of MEA + EAE bi-blends were compared with H of MEA + BEA bi-blends (Shi et al. 2021b) at the same operation conditions. At 30 min, 2.0 mol/L EAE has much higher heat duty (1200 kJ/mol) than BEA (668.7 kJ/mol) (Shi et al. 2021b), since EAE has better CO_2 absorption performance thanks to its more stable carbamate. The stable carbamate results in higher α_{lean} and bigger heat duty H than BEA, so that CO_2 desorption performance of EAE is worse than that of BEA. However, with MEA introduced, the H was reduced for all MEA + EAE blends, with optimized ratio of 0.4/2. This indicated wide range of coordinative effect of MEA + EAE at 0 ~ 0.5 + 2 mol/L, with even wider if 0.6 ~ 0.7 + 2 mol/L were tested, while H of MEA + BEA started to decrease and reached an optimum of 0.2 + 2 mol/L with optimized H of 94.7%. The H of 0.3 + 2 ~ 0.5 + 2 mol/L started to increase and get bigger than BEA alone, which indicated a narrow range (0 ~ 0.3/2) of coordinative effect within MEA + BEA. The intrinsic reason of different blended ratio/ranges awaited further study.

Similarly, for 60-min plot, the heat duty H of EAE has the H of 1945.9 kJ/mol, higher than 1391.3 kJ/mol, the H of BEA. (Shi et al. 2021b) With MEA introduced, the H decreased for all MEA + EAE blends, with optimized H reached 86.2% at 0.3 + 2 mol/L. The H of BEA at 60 min showed a similar trend to 30 min, with optimum concentration of 0.2 + 2 mol/L with minimized relative H of 84.1% (Shi et al. 2021b). The H of 0.3 + 2 ~ 0.5 + 2 mol/L were also higher than BEA alone. This difference is another proof of good CO_2 desorption performance of BEA since H of BEA alone was quite low.

After comparison, it is clear that optimized concentration was 0.3 ~ 0.4 + 2 mol/L of MEA + EAE and 0.2 + 2 mol/L

for MEA + BEA. The absolute heat duty of BEA was much smaller than that of EAE, resulting in the MEA + EAE bi-blends being poorer desorption than MEA + BEA bi-blends. Since MEA + EAE bi-blends have better CO_2 absorption performance than MEA + BEA, their desorption were poorer.

The absorption–desorption parameters of EAE & MEA + EAE were categorized into Table 1. From Table 1, it is clear the optimized ratio of CO_2 absorption was 0.2 + 2 mol/L, while optimized ratio of desorption was 0.4 + 2 mol/L. These two ratios were inconsistent, resulting in difficulties in amine blend preparation of MEA + EAE solvents. In industrial application, the desorption and heat duty reduction were more important than absorption (Idem et al. 2015). Therefore, the optimized ratio was 0.4 + 2 mol/L.

Meanwhile, the Table 1 was compared with that of MEA + BEA (Shi et al. 2021b) under the same conditions. After comparison, the absorption performance of MEA + EAE was better than that of MEA + BEA from I_{abs} and α_{eq} , while the CO_2 desorption of MEA + EAE was poorer mainly due to its lower I_{des} but bigger H . The cyclic capacity was comparable for both bi-blends since the ($\alpha_{\text{rich}} - \alpha_{\text{lean}}$) were close to each other, but the H of MEA + EAE was much higher than the H of MEA + BEA, resulting in poor desorption parameters.

The CO_2 absorption and desorption performance of MEA + EAE + AMP solvents

To overcome the drawbacks of CO_2 desorption performance of MEA + EAE, AMP was introduced for heat duty reduction. The amine blends with AMP has been published repeatedly for the same reason: enhancing CO_2 production and heat duty reduction (Hairul et al. 2017). Similar to MEA + BEA + AMP (Shi et al. 2021a,

Table 1 The absorption–desorption parameters of MEA + EAE (0.1 ~ 0.5 + 2 mol/L) and compared with EAE as benchmark

MEA + EAE solvents	Absorption parameter 5% uncertainty	Desorption parameter ^a (30 min) 10% uncertainty	Desorption parameter (60 min)
(mol/L)	(mol CO_2) ² /L min mol amine	(*10 ⁻³ mol CO_2) ³ /L ² kJ min	(*10 ⁻³ mol CO_2) ³ /L ² kJ min
0 + 2	0.281	0.013	0.008
0.1 + 2	0.296	0.017	0.011
0.2 + 2	0.307	0.022	0.013
0.3 + 2	0.292	0.025	0.015
0.4 + 2	0.286	0.031	0.016
0.5 + 2	0.279	0.029	0.015

The bold demonstrate the best value among each column.

2021c), MEA+EAE+AMP tri-solvents were prepared at 0.1~0.5+2+2 mol/L. Both tri-solvents MEA+BEA and EAE+AMP were developed by the author's group with similar amine concentrations and experimental conditions. The coordinative effects of tri-solvents MEA+EAE+AMP, as the 2nd example of MEA+RR'NH+AMP, were studied, and their absorption-desorption performance were also compared with that of MEA+BEA+AMP comprehensively.

The CO₂ absorption of MEA + EAE + AMP and compared with MEA + BEA + AMP

The CO₂ absorption profile of MEA+EAE+AMP was plotted in Fig. 7 and the I_{abs} were plotted with a bar graph in Fig. 8. The slopes of Fig. 7 did not reflect the order of absorption directly due to different C_A . The exact I_{abs} in Fig. 8 reflected an increasing trend with increased C_A from 0.1~0.2+2+2 mol/L. It dropped a little at 0.3~0.5+2+2 mol/L. The I_{des} of tri-solvent series were higher than the I_{des} of EAE+AMP alone again. This trend was similar to MEA+EAE bi-solvents in absorption. Based on “competition effect” (Liu et al. 2018) in Support Information II, the pKa of EAE was 10.0 (Liu et al. 2019), higher than 9.51 of MEA (Bernhardsen and Knuutila, 2017), which was capable of accepting protons from Zwitterion of MEA “RNH₂⁺-CO₂⁻” directly. The optimized concentration was 0.2+2+2 mol/L, with the same ratio of 0.2/2 to MEA+EAE. With MEA blended into the tri-solvent, the increase of I_{des} was within 21 to 30% for 0.1+2+2 mol/L to 0.2+2+2 mol/L. The rest 3 samples were comparable to each other, which was around 23~24%.

Compared with MEA+BEA+AMP (Shi et al. 2021a), whose optimized ratio was 0.4+2+2 mol/L with ratio of 0.4/2/2, the exact values of I_{abs} of tri-solvent

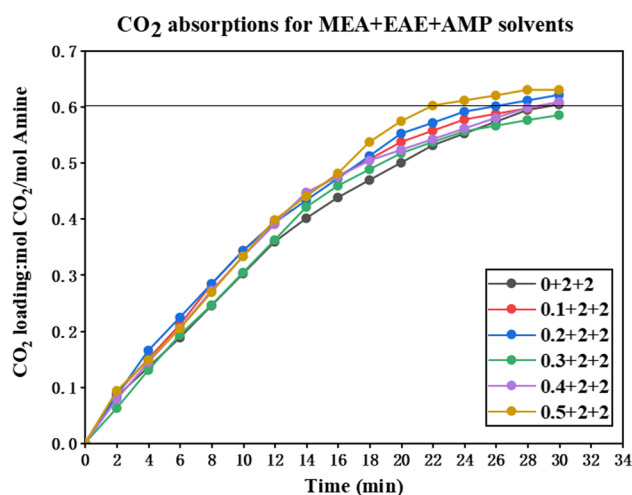


Fig. 7 CO₂ absorption curves of MEA+MAE+AMP at 0.1~0.5+2+2 mol/L. $F_G=1.0$ mol/L

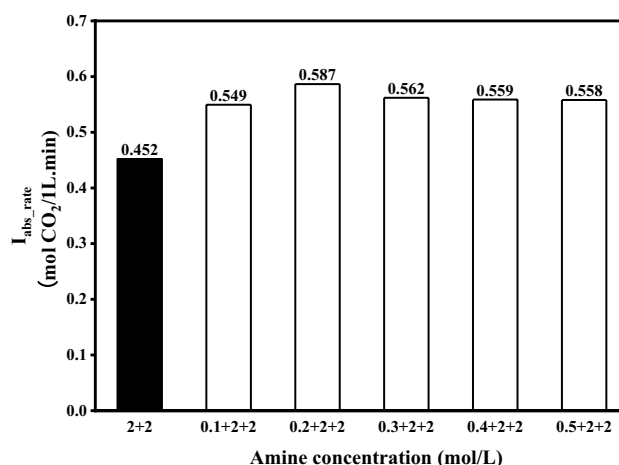


Fig. 8 The initial absorption rates of MEA + MAE + AMP bi-blends at 0.1~0.5+2+2 mol/L

of MEA+EAE+AMP cannot be compared to that of MEA+BEA+AMP due to different volume of amine blends. Different volumes affect different slopes $d\alpha/dt$, making them not comparable (Shi et al. 2020). However, the trends for both tri-solvents were similar, as the I_{abs} increased with the increase of C_A of MEA and reached an apex and then decreased a little. The I_{abs} of MEA-blended tri-solvent were higher than EAE+AMP or BEA+AMP alone due to the reservation of extra free MEA molecules with fast absorption rates.

The CO₂ desorption of MEA + EAE + AMP and compared with MEA + BEA + AMP

The CO₂ desorption curves of tri-solvent were demonstrated in Fig. 9 with bar graph of I_{des} plotted in Fig. 10. From Fig. 9, the curves of tri-solvent were lower than that of EAE+AMP bi-blends. From Fig. 10, the manifested coordinative effect was that I_{des} increased with increased C_A of MEA and the optimized ratio was 0.2+2+2 mol/L. This was because the coordinative effect has already existed within MEA+EAE(RR'NH), while there is negligible effect within MEA+AMP (Shi et al. 2021b). Consequently, the coordinative effect existed within tri-solvent of MEA+EAE(RR'NH)+AMP, which were not affected by AMP. From Fig. 9, the α_{lean} reached 0.35 mol/mol. If compared with desorption curves of MEA+BEA+AMP (Shi et al. 2021a), the α_{lean} reached 0.25 mol/mol. The higher α_{lean} reflected more stable carbamate of EAE than BEA.

From Fig. 10, the I_{des} increased first and reached an optimized value at concentration of 0.2+2+2 mol/L and then started to decrease. I_{des} of 0.1~0.5+2+2 mol/L MEA+EAE+AMP were also higher than EAE+AMP bi-blends as a whole set. This phenomenon was also similar

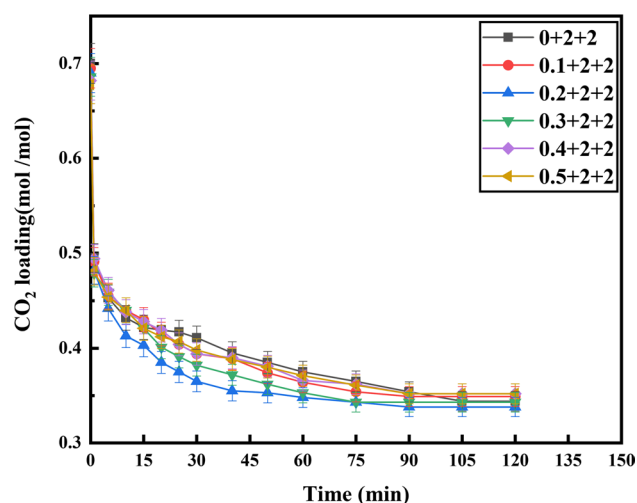


Fig. 9 The CO_2 desorption curves of MEA + EAE + AMP tri-blends at 0.1 ~ 0.5 + 2 + 2 mol/L

to MEA + BEA + AMP (Shi et al. 2021a). However, the I_{des} increased by 11.8% at optimum concentration of 0.2 + 2 + 2 mol/L, while I_{des} increased 5.3% by at 0.3 + 2 + 2 mol/L for MEA + BEA + AMP.

The heat duty H of MEA + EAE + AMP were plotted in Fig. 11a and b at 30 and 60 min. Similar to MEA + EAE bi-solvents, the H decreased first with increased C_A of MEA and reached the minimum at 0.2 + 2 + 2 mol/L at both 30 min and 60 min. The H increased at 0.3 ~ 0.5 + 2 + 2 mol/L, and the H of MEA + EAE + AMP were lower than that of EAE + AMP systematically. The order of heat duty was 0 + 2 + 2 (100%) > 0.1 + 2 + 2 (93.7%) > 0.5 + 2 + 2 (91.8%)

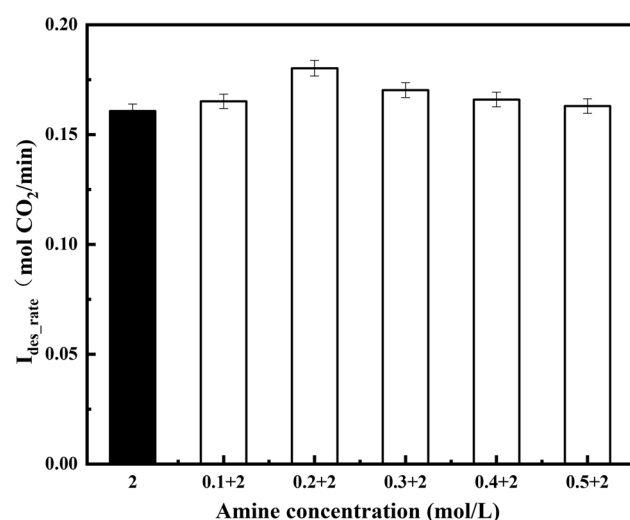
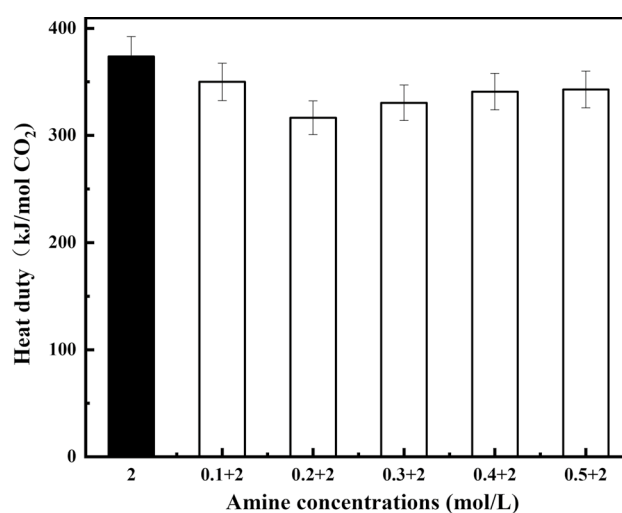


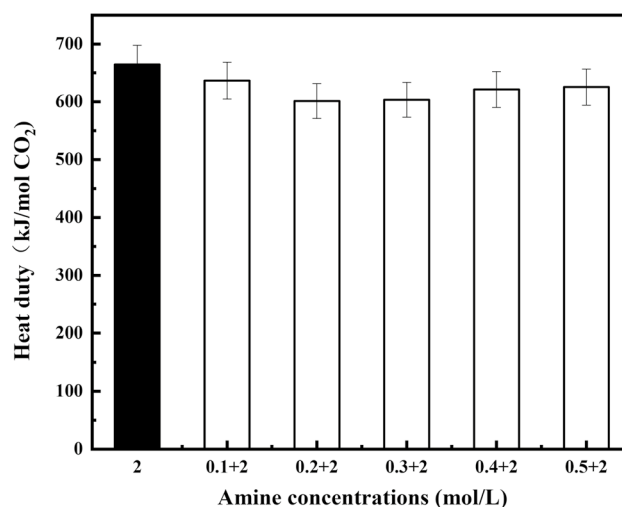
Fig. 10 The initial desorption rates (I_{des}) of MEA + EAE + AMP tri-blends at 0.1 ~ 0.5 + 2 + 2 mol/L

$\approx 0.4 + 2 + 2$ (91.2%) > $0.3 + 2 + 2$ (88.4%) > $0.2 + 2 + 2$ (84.7%) at 30 min, the smaller the better. The order of heat duty was $0 + 2 + 2$ (100%) > $0.1 + 2 + 2$ (95.8%) > $0.5 + 2 + 2$ (94.1%) $\approx 0.4 + 2 + 2$ (93.5%) > $0.3 + 2 + 2$ (90.8%) > $0.2 + 2 + 2$ (90.5%) at 60 min, the smaller the better. The order was the same for both time periods except that the reduction was strong at first 30 min because of massive CO_2 production rich loading region (0–30 min) over lean loading region (30–60 min). (Bairq et al. 2019).

These results were another typical example of “coordinative effect” that blending small amount of MEA can enhance amine regeneration as well as CO_2 desorption of amine blends. Similar samples were published for MEA + RR’NH + AMP/R₃N and MEA + BEA(RR’NH) + AMP (Shi et al. 2021a). Blending



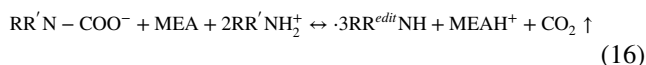
(a) 30 min



(b) 60 min

Fig. 11 The heat duties of MEA + EAE + AMP tri-blends at 0.1 ~ 0.5 + 2 mol/L at **a** 30 min and **b** 60 min

small amount of MEA can enhance CO₂ desorption from Eq. (16). Based on the equation of heat duty calculation, $H = Q_{\text{input}}/n\text{CO}_2$, if $n\text{CO}_2$ increased 20% while Q_{input} increased only 10% with increased C_A of MEA. The overall H reduced (Shi et al. 2018a). On the other hand, with extra MEA added, the increase of CO₂ production cannot offset that of Q_{input} , making the H increased again. (Shi et al. 2018a)



Comparing Fig. 11 with heat duty of MEA + BEA + AMP (Shi et al. 2021a), the H of tri-solvent MEA + EAE + AMP were higher than MEA + BEA + AMP. H ranges 203.8–256.1 kJ/mol CO₂ for MEA + BEA + AMP (Shi et al. 2021a), while H ranges 316.5–373.7 kJ/mol CO₂ for MEA + EAE + AMP at 30 min. H ranges 401.4–522.2 kJ/mol CO₂ for MEA + BEA + AMP (Shi et al. 2021a), while H ranges 601.5–664.6 kJ/mol CO₂ for MEA + EAE + AMP at 60 min. The ratio of heat duty reduction of MEA + EAE was stronger than that of MEA + BEA in desorption, so that the heat duty reduction MEA + EAE + AMP vs EAE + AMP was stronger than MEA + BEA + AMP vs BEA + AMP. Such difference was resulted from the more stable carbamate of EAE than BEA; extra energy was required to complete carbamate hydrolysis or breakdown.

Finally, the absorption–desorption parameters of tri-solvent MEA + EAE + AMP were categorized into Table 2. From Table 2, the optimized concentration is 0.2 + 2 + 2 mol/L for both absorption and desorption. While for MEA + BEA + AMP (Shi et al. 2021a), the optimized concentration is 0.3 + 2 + 2 mol/L. The absorption parameter is not comparable for both solvents due to different volumes of amine used, while the desorption parameter of MEA + EAE + AMP was smaller than that of MEA + BEA + AMP due to their higher heat duty and smaller I_{des} , with comparable cyclic capacity.

Comparison of MEA + EAE + AMP with EAE bi-blends and other published tri-solvents

Amine concentration of MEA has limited dose into the tri-solvent, and the majority of amines were fixed of EAE + AMP (2 + 2 mol/L). The CO₂ absorption–desorption performance of tri-solvents were compared to EAE + 1DMA2P (Gao et al. 2020) and EAE + AEEA (Pandey and Kumar Mondal, 2021; Pandey and Mondal, 2021). After literature study, our experimental results were difficult to compare with those publication due to different experimental apparatus and operation procedures. However, their concept of amine blend was similar to that of the author's group.

For instance, the advantage of EAE were well acknowledged, and it can blend tertiary amine (R₃N) such as 1DMA2P (Gao et al. 2020) or DMAE and MDEA (El Hadri et al. 2017) to boost CO₂ absorption. EAE provides relative larger α_{eq} and lower heat of absorption than MEA, and an improvement concept was established to blend EAE + R₃N over MEA + R₃N. The authors admitted this concept and blend EAE with stereo hindrance amine AMP to enhance desorption as well. Other study adopted EAE + AEEA (Pandey and Kumar Mondal, 2021) for CO₂ absorption–desorption analysis, and find out that 30 wt% EAE + 0.30 wt% AEEA solution was better than 30 wt% MEA solution with bigger initial desorption rates, α_{eq} , and cyclic capacity and less heat of absorption. This concept of using other amine blends to replace MEA was similar to this study of “convert MEA as major amine to activator.”

This second part included a brief comparison of this tri-solvent with several recently published tri-solvents, such as AMP + MDEA + DETA (Nwaoha et al. 2016a), MEA + MDEA + PZ (Xiaowen Zhang et al. 2019, Zhang et al. 2017), MEA + AMP + PZ (Chikezie Nwaoha 2018, Nwaoha et al. 2017, Nwaoha et al. 2016b, Zhang et al. 2018), and MEA + BEA + AMP (Shi et al. 2021a, 2021c).

Table 2 The absorption and desorption parameters of MEA + AMP + EAE (0.1 ~ 0.5 + 2 + 2 mol/L) comparing to 2 mol/L EAE + AMP

MEA + AMP + EAE solvents	Absorption parameter 5% uncertainty	Desorption parameter ^a (30 min) 10% uncertainty	Desorption parameter (60 min) 10% uncertainty
(mol/L)	(mol CO ₂) ² /L min mol amine	(*10 ⁻³ mol CO ₂) ³ /L ² kJ min	(*10 ⁻³ mol CO ₂) ³ /L ² kJ min
0 + 2 + 2	0.316	0.306	0.172
0.1 + 2 + 2	0.382	0.335	0.184
0.2 + 2 + 2	0.405	0.421	0.221
0.3 + 2 + 2	0.385	0.380	0.208
0.4 + 2 + 2	0.381	0.353	0.194
0.5 + 2 + 2	0.378	0.349	0.191

The bolde demonstrate the best value among each column.

The early samples were AMP+MDEA+DETA (Nwaoha et al. 2016a), and results indicated the optimized ratio was 2+1+1.5 mol/L AMP+MDEA+DETA for both absorption and desorption. After 2017, Zhang et al. studied MEA+MDEA+PZ (Xiaowen Zhang et al. 2019, Zhang et al. 2017), and it reported that 3+1.5+1.5 mol/L MEA+MDEA+PZ has the best absorption performance, while 3+2.5+0.5 mol/L MEA+MDEA+PZ has the best desorption performance among various ratios. It was reasonable that increasing the ratio of PZ certainly enhances CO₂ absorption, while increasing the ratio of MDEA will enhance CO₂ desorption (Zhang et al. 2017).

The MEA+PZ+AMP was a typical tri-solvent which has been studied reportedly (Nwaoha et al. 2017, 2016b; Zhang et al. 2018). From repeated publications, the MEA+AMP+PZ with 3+2.5+0.5 mol/L has the best desorption performance with (Zhang et al. 2018) and without catalysts (Nwaoha et al. 2017, 2016b; Zhang et al. 2018). This ratio was same (3MEA/2.5AMP/0.5PZ) as that of MEA+MDEA+PZ since AMP replaced the role of MDEA as bicarbonate donor (Nwaoha et al. 2017, 2016b; Zhang et al. 2018). All the results indicated max ratio of MDEA/AMP to PZ as 2.5/0.5 facilitates CO₂ desorption and significantly reduces heat duty, which is the preferred mixing ratio. However, the consistency was not achieved yet. Later on MEA+AMP+PZ 2+2+1 mol/L (Chikezie Nwaoha 2018) was studied on a pilot plant with techno-economic analysis of CO₂ capture from a 1.2 million MTPA cement plant, indicating the potential of tri-solvent in industrial CO₂ capture pilot plant with reduced heat duty and operation costs.

After analysis and comparison, the most similarity of MEA+EAE+AMP with several published tri-solvents is that AMP is included for all the tri-solvents to enhance CO₂ desorption which most study uses 2.5 mol/L AMP, and we prepared 2.0 mol/L. Several studies adopted MEA to fully make the most advantage for its absorption. The difference is that the MEA was majority for other tri-solvents with C_A of 3.0 mol/L (Nwaoha et al. 2017, Xiaowen Zhang et al. 2019, Zhang et al. 2018), while our study only used 0.1~0.5 mol/L MEA. The other difference is the consistent optimized mixing ratio for abs-desorption sides. The MEA+EAE+AMP has consistent optimized ratio of 0.2+2+2 mol/L, while MEA+AMP+PZ has optimized absorption C_A of 3+1.5+1.5 mol/L and optimized desorption C_A of 3+2.5+0.5 mol/L. The consistent optimized ratio on both sides was another advantage of MEA+EAE+AMP and MEA+BEA+AMP (Shi et al. 2021a). The comparison of heat duty of different tri-solvents under same operation conditions awaited further investigation.

The bi-solvents and tri-solvents with coordination effects

Based on the analysis, both MEA+EAE and MEA+EAE+AMP contained coordinative effects since

EAE was another secondary amine. Blending MEA into EAE can enhance both CO₂ absorption and desorption simultaneously. Besides the similarity, some indexes need to be compared such as the optimized ratio, the lean loading α_{lean} , and the heat duty H reduction. The differences were compared with the introduction of AMP below:

- (1) The optimized ratios of MEA+EAE bi-solvents were inconsistent, which is 0.2+2 mol/L for absorption and 0.4+2 mol/L for desorption. Such inconsistency made the amine preparation difficult to fulfill both requirements in absorber and desorber. However, with AMP added, the optimized ratios of MEA+EAE+AMP tri-solvents were consistent, which is 0.2+2+2 mol/L for both absorption and desorption. Such consistency could facilitate amine preparation for industrial applications. Adding AMP did not affect absorption since MEA+EAE was a good absorbent. However, adding AMP can improve desorption significantly and shift the optimized concentration from 0.4+2 to 0.2+2+2 mol/L.
- (2) The α_{lean} of MEA+EAE blends were 0.43~0.44 mol/mol, while α_{lean} of MEA+EAE+AMP were 0.33~0.35 mol/mol. With AMP introduced, the CO₂ desorption was enhanced, and α_{lean} was decreased, due to unstable carbamate of AMP and small α_{lean} of AMP.
- (3) The cyclic capacity of tri-solvent is better than that of bi-solvents due to multiple factors: C_A increased from 2.5 to 4.5 mol/L, and AMP has larger α_{eq} of 0.75 mol/mol compared with MEA (0.50 mol/mol) and EAE (0.67–0.68 mol/mol), reflecting stronger absorption capacity. The α_{lean} was also reduced due to small α_{lean} of AMP. With repeated cycling, the cyclic capacity may decrease due to amine degradation with decreased C_A .
- (4) The heat duties of MEA+EAE+AMP tri-solvent were much smaller than those of MEA+EAE bi-solvents, because of the advantages of AMP in CO₂ desorption. The CO₂ desorption of EAE is poorer due to its stable carbamate. However, with AMP introduced with weak carbamate stability, a large amount of bicarbonate (HCO₃[−]) was introduced into the amine solvent (Shi et al. 2014), and then overall heat duty was greatly reduced because of massive CO₂ production and much less energy requirement for HCO₃[−] regeneration (Shi et al. 2014) rather than carbamate breakdown/hydrolysis of MEA and EAE.

Last but not least, blending AMP with amine blends MEA+RR'NH, such as MEA+BEA or MEA+EAE, turned out to be an energy efficient solution to enhance CO₂ desorption ability and reduce heat duty for solvent improvement, which is quite applicable in industry. Further studies may be (a) tri-solvent MEA+EAE+AMP with various EAE/AMP ratios (1/3, 1.5/2.5), meaning less

EAE more AMP to enhance desorption and (b) tri-solvent MEA + EAE + AMP with catalysts.

Conclusion

This study focused on the tri-solvent MEA + EAE + AMP, which fully adopted the advantages of AMP in CO₂ desorption, EAE in CO₂ absorption, and coordinative effect of MEA to enhance absorption and desorption simultaneously. Selection of EAE enlarge CO₂ loading and reduce heat of absorption over DEA, and blending AMP into bi-solvents significantly reduced the overall heat duty and enhanced cyclic capacity by increasing α_{rich} and reducing α_{lean} simultaneously, besides increasing C_A . After comprehensive investigations, the tri-solvent MEA + EAE + AMP turned out to be another good candidate for amine blends in a bench-scale pilot plant, comparable to MEA + AMP + PZ (Chikezie Nwaoha 2018).

- (1) The coordinative effect did exist within MEA + EAE(RR'NH) as another example after published MEA + RRNH: MEA + DEA (Shi et al. 2020) and MEA + BEA (Shi et al. 2021b). The optimized ratio was inconsistent for CO₂ absorption at 0.2/2 and CO₂ desorption at 0.4/2. Such difference made the preparation of bi-blend difficult in an industrial pilot plant. Relatively speaking, the 0.4 + 2 was preferred because heat duty reduction was more important than quick absorption.
- (2) The tri-solvent of MEA + EAE + AMP exhibited good absorption and desorption, and the optimized ratio was 0.2/2/2 for both absorption and desorption. Such consistency is convenient for amine blend preparation in a pilot plant. Compared with MEA + BEA + AMP, MEA + EAE + AMP exhibited better adsorption but worse desorption because of the stable carbamate of EAE.
- (3) The cyclic capacity of MEA + EAE + AMP was slightly higher than that of MEA + BEA + AMP due to different ($\alpha_{\text{lean}} \sim \alpha_{\text{rich}}$) ranging between 0.35 and 0.70 mol/mol, wider than 0.30 ~ 0.60 mol/mol of MEA + BEA + AMP. Such difference was favorable in industrial pilot plants. The further studies concerned tri-solvent MEA + EAE + AEMP with various ratios of EAE/AMP and catalytic CO₂ desorption.

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