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# Research of novel polyamine-based biphasic absorbents for CO<sub>2</sub> capture using alkanolamine to regulate the viscosity and mechanism analysis

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# ABSTRACT

Biphasic solvent has attracted widespread attention in CO<sub>2</sub> chemical absorption technology due to its significant potential for reducing capture energy consumption. However, the high viscosity of CO<sub>2</sub>-rich phase after phase split could lead to issues such as high flow resistance, low heat transfer efficiency, and phase separation instability in application. To address these limitations, a strategy of using alkanolamine as a viscosity regulator for biphasic solvents was proposed. Diethanolamine(DEA), an alkanolamine regulator, was introduced to a system of polyamine/amide absorbent, and then a novel biphasic solvent of diethylenetriamine (DETA)/diethanolamine (DEA)/N, N-Dimethylacetamide(DMAC)/water(H2O) was developed. The viscosity of the CO2-rich phase solvent was reduced to 19.02 mPa s, a significant decrease compared to the solution without DEA regulation. The novel solvent exhibited a high cyclic capacity of 2.08 mol/kg, which was 43.4 % higher than that of the solution without DEA, and a desorption rate twice as high as 30 wt% monoethanolamine(MEA). Quantitative <sup>13</sup>C Nuclear Magnetic Resonance (NMR) and Molecular Dynamics (MD) simulations revealed the phase split and viscosity regulation mechanisms. It was proved that DETA species, especially carbamates, tend to self-aggregate with each other due to intermolecular hydrogen bonding with the CO<sub>2</sub> loading increases, which leads to phase split and high viscosity of the saturated solution. Through DEA regulation, the protonation of carbamates and the generation of  $HCO_3^-/CO_3^{--}$  were promoted, which weakened the self-aggregation of carbamates species, decreasing the viscosity and the regeneration energy of saturated CO<sub>2</sub>-rich phase solution. The regeneration energy reached 2.19 GJ/ton CO2, which exhibited a 42.4 % reduction compared with that of 30 wt% MEA.

# 1. Introduction

CO<sub>2</sub> capture, utilization and storage technology (CCUS) is considered one of the most promising techniques for decarbonizing the power and industrial sectors. Among them, the chemical absorption method has emerged as one of the most matured carbon capture technologies due to its wide suitability of different flue gases, easy sale up, and high level of safety and reliability. Typically, amine solutions have found the widest industrial application in chemical absorption processes. However, its large-scale industrial application is impeded by low CO<sub>2</sub> capacity and the substantial energy required for regeneration [1,2]. Consequently, there is an urgent need for the development of efficient absorbents [3].

Recently, a range of alternative amine solvents represented by

blended amine solutions [4,5], ionic liquids [6,7], non-aqueous solvents [8,9], and biphasic solvents [10] have been developed. Among them, biphasic solvent is one of the most promising candidates for significant regeneration energy reduction [11]. Biphasic solvents typically contain a phase separation agent, reactive amines, and water. The solutions experience phase separation triggered by specific conditions, such as alterations in temperature or variations in  $CO_2$  loading.

Currently, phase separation agents used in most biphasic solvents can be divided into two groups, including lipophilic amines such as 2-(diethylamino)-ethanol(DEEA) and N, N-dimethylcyclohexylamine (DMCA) and organic solvents such as ether, alcohol, and amide. The typical biphasic solvents are 4 M(mol/L) DEEA/1M TETA [12], 5 M DEEA/2M MAPA [13], 3 M DMCA/1M MCA [14], 4 M DEEA/2M BDA

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Received 6 October 2023; Received in revised form 13 November 2023; Accepted 23 November 2023 Available online 29 November 2023 1383-5866/© 2023 Published by Elsevier B.V. [15], MEA/1-propane/H<sub>2</sub>O [16] and MAE/3DMA1P /DGM [17] et al. Research has shown that compared to a typical 30 wt% MEA solution, it can reduce energy consumption by 39–58 % and exhibits better absorption performance.

However, Shen et al. [18] discovered that as  $CO_2$  was absorbed into the biphasic solvents, the viscosity of solutions experienced a remarkable surge, which could reach as high as several hundred centipoises, significantly higher than that of 30 wt% MEA. Zhou et al. [19] developed a biphasic solvent of 0.5D1.5A3P which showed better absorption and desorption performance than that of 30 wt% MEA. But the viscosity of the  $CO_2$ -rich phase reached 152 mPa·s, 61 times that of 30 wt% MEA [20]. Liu et al. [10] developed a DAH solvent with low energy consumption which was 32 % lower than the MEA solvent. However, the viscosity of the  $CO_2$ -rich phase reached 114.3 mPa·s. It indicated that the viscosity of various biphasic solvents, especially those utilizing lipophilic amines as phase separation agents, tends to be high. The high viscosity of the  $CO_2$ -rich phase in biphasic solvents can lead to high flow resistance, low heat transfer efficiency, and possible deposition within the absorption tower and reboiler [21,22].

To address this limitation, Zhou et al. [19] attempted to reduce the viscosity of diethylenetriamine and pentamethyldiethylenetriamine (DETA-PMDETA) biphasic solvent by adding 2-amino-2-methyl-1-propanol (AMP), which obtained a remarkable 72 % reduction in the viscosity of the CO2-rich phase. Ma et al. [23] screened seven alkanolamines as viscosity regulators to decrease the viscosity of 1,5diamino-2-methyl-pentane (DA2MP)/n-propanol (PrOH) non-aqueous absorbent. Moreover, they applied quantum calculations from the perspective of chemical reactions to investigate the viscosity regulation mechanism. According to the reported studies, introducing alkanolamine and sterically hindered amines as regulators could reduce the viscosity of amine solutions. However, for various solvents, different regulators exhibit distinct regulatory effects. The research on the method of screening the optimal viscosity regulator as well as the systemic viscosity regulation mechanism, especially for biphasic solvents with high viscosity, is still lacking. It could impede the development of highly efficient biphasic absorbents.

In the previous research, our group screened various reactive amines and phase separation agents [24]. A biphasic solvent composed of polyamine/amide /H<sub>2</sub>O was developed for CO<sub>2</sub> capture. The diethylenetriamine (DETA), which contains three amine groups, was chosen as the reactive amine to achieve an outstanding absorption performance. The organic solvent N, N-Dimethylacet- amide (DMAC), which has lower volatility than DEEA/DMCA, was selected as a phase-separation solvent. The energy consumption of DETA/DMAC/H<sub>2</sub>O can reach 2.3 GJ/ton CO<sub>2</sub>, which exhibits a 39 % reduction compared with that of 30 wt% MEA. However, the viscosity of DETA/DMAC/H<sub>2</sub>O was significant as high as 114.23 mPa·s.

In this work, Diethanolamine (DEA), an alkanolamine with high CO<sub>2</sub> cyclic capacity and regeneration rate, and low volatility, was selected as the optimal viscosity regulator through screening alkanolamines and sterically hindered amines to decrease the viscosity of DETA/DMAC/ H<sub>2</sub>O. And then a novel biphasic solvent DETA/DEA/DMAC/H<sub>2</sub>O was proposed. The absorption and desorption performance of absorbent was analyzed. Moreover, the absorption product distribution at different CO<sub>2</sub> loading in the biphasic system with and without DEA was identified by <sup>13</sup>C Nuclear Magnetic Resonance (<sup>13</sup>C NMR) spectroscopy and the viscosity regulation mechanism of DEA was investigated. Furthermore, this study focused on the close relationship between the viscosity of solution and intermolecular forces within the system [25,26] rather than chemical reactions, utilizing Material Studio to construct the molecular model in Molecular Dynamics (MD) simulations. After the validation of the model, the intermolecular interactions between absorption products within different systems were analyzed. The conclusion obtained from NMR analysis was verified. The molecular-scale understanding of the viscosity regulation mechanism of DEA was comprehensively elucidated.

To our best knowledge, the experimental and simulation researches in this study first provided a detailed method of searching for the alkanolamine viscosity regulators of biphasic absorbents with high viscosity as well as getting a molecular-scale understanding of the viscosity regulation mechanism for biphasic solvents. Finally, we aim to promote the development of efficient biphasic absorbents for  $CO_2$  capture.

# 2. Experiments

#### 2.1. Chemicals

Phase-separation agents: N, N-Dimethylacetamide (DMAC,  $\geq$ 99 %), N-Methylpyrrolidone (NMP,  $\geq$ 99 %), Dimethyl sulfoxide(DMSO,  $\geq$ 99 %), N,N-Dimethylformamide(DMF,  $\geq$ 99 %). Reactive amine: diethylenetriamine(DETA, 99 %). Alkanolamine regulators: primary alkanolamines (Ethanolamine (MEA,  $\geq$ 99 %), 2-amino-2-methyl-1-propanol (AMP,  $\geq$ 99 %)), secondary alkanolamines (diethanolamine (DEA,  $\geq$ 99 %)), 2-(methylamino)ethanol (MAE,  $\geq$ 99 %)), and tertiary alkanolamines (triethanolamine (TEA, 99 %), diethylethanolamine(DEEA,  $\geq$ 99 %), methyldiethanolamine (MDEA, 99 %)). 1,4-dioxane ( $\geq$ 99.5 %), and deuterated water (D<sub>2</sub>O,  $\geq$ 99.9 %). Chemicals were all purchased from Merck. CO<sub>2</sub> and N<sub>2</sub> (both with 99.999 % purity) gases were purchased from Hangzhou Jingong GAS Co., Ltd, Hangzhou, China.

# 2.2. Experimental

# 2.2.1. Regulator screening experiments

A bubble reactor was employed in the preliminary screening experiment to search for the optimal regulator. The unit diagram has been simplified to Fig. S1. Pure CO<sub>2</sub> was supplied at a flow rate of 600 ml/ min. Polyamine/regulator/DMAC/H<sub>2</sub>O blends were prepared with a total mass of 100 g. The mass ratio of polyamine: regulator: DMAC: H<sub>2</sub>O in the blends was maintained at 15 %: 5 %: 40 %: 40 %. Absorption temperature was maintained at 313.15 K by using a water bath. Absorption time was controlled at 20 min. The upper and lower phases were separated using a separating funnel, and properties including CO<sub>2</sub> loading, phase split ratio, and viscosity were obtained for both phases. A digital rotational viscometer (Brookfield Viscometer, DV-II + Pro, accuracy of 1 %) was employed to determine the viscosities of the saturated CO<sub>2</sub>-rich phase solutions at 313.15 K. The vapor pressure of each regulator amine was provided by CAS SciFinder<sup>n</sup> (listed in Table S1).

#### 2.2.2. CO<sub>2</sub> absorption and desorption experiments

A bubble column reactor was employed for CO<sub>2</sub> absorption after preliminary screening. The absorption unit diagram has been simplified to Fig. S2(a). The inlet gas composed of CO2 and N2 contained 12 vol% CO<sub>2</sub>, and it was supplied at a rate of 1000 ml/min. Mass flow controllers (CS200-A, Beijing Sevenstar Company, China, accuracy 1 %) were used to regulate the flow rates. A CO2 infrared gas analyzer (GHX-3010F, Beijing Huayun Company, China, accuracy 1 %) was employed to analyze the concentration of CO<sub>2</sub> in the outlet gas. The absorption temperature was kept at 313.15 K with a water bath. The system was deemed to be equilibrium once the outlet CO2 concentration reached 12 vol%. The density of the CO2 saturated solution was measured using a portable digital density deter (Kyoto Electronics Manufacturing DA-130 N, density accuracy 0.001 g/cm<sup>3</sup>). The upper and lower phases were separated using a separating funnel, and properties including CO<sub>2</sub> loading, phase split ratio, and viscosity were obtained for both phases. A digital rotational viscometer (Brookfield Viscometer, DV-II + Pro, accuracy of 1 %) was employed to determine the viscosities of the saturated CO<sub>2</sub>-rich phase solutions at various temperatures.

After the absorption, as shown in Fig. S2(b), the CO<sub>2</sub>-rich phase of 44.5 g was employed for the CO<sub>2</sub> desorption experiments in a 100 ml three-necked flask. The desorption temperature was uniformly maintained at 110  $^{\circ}$ C using an oil bath and a magnetic rotor. Desorption time was set to 35 min to minimize the impact of water evaporation(by

choosing the 30 wt% MEA for comparison, the flow rates of desorbed  $CO_2$  of absorbents were all approximately 10 ml/min at the endpoint.). An electronic soap film flowmeter (BL-1000, range 1–1000 ml/min, accuracy 1 %) was employed to determine the volume of  $CO_2$  desorbed during the desorption. The water vapor was condensed via ice-water tower.

# 2.2.3. NMR experiments

1, 4-Dioxane ( $\geq 99.5$ %) served as an internal reference standard. Deuterated water (D<sub>2</sub>O,  $\geq 99.9$ %) was introduced into the sample to enable signal locking. The  $^{13}C$  spectra of the unsaturated and saturated solvents were acquired via an Agilent DD2 500 MHz NMR spectrometer. The parameters used in the  $^{13}C$  NMR experiment: delay time, D1 = 60 s ( $\geq 5T1$ ), number of scans, NS = 300. Data processing was performed using MestReNova software.

# 2.2.4. MD simulation details

MD simulations were carried out using Materials Studio (Accelrys) to investigate the molecular interactions involving DETA-carbamates, DETA (including DETA molecules and protonated DETA), DEAcarbamates, DEA (including DEA molecules and protonated DEA), and H<sub>2</sub>O. The ab initio COMPASS III force field was employed to establish the appropriate force field parameters. Amorphous cell modules were used to construct the configurations of the simulation systems of CO<sub>2</sub>saturated solution (containing DETA, DETA-carbamates, DEA-carbamates, DEA, H<sub>2</sub>O, and DMAC, detailed in Table S3). The smart minimizer algorithm was applied for energy minimization to eliminate inappropriate contacts. In the dynamics process, the time step was set at 1 fs. An NVT ensemble equilibrium simulation was conducted for 600 ps to raise the system temperature to match experimental conditions. Subsequently, the systems underwent further equilibration under an NPT ensemble for 3 ns to match their simulation density and pressure with the experiment. Finally, an NVT ensemble was performed for another 2 ns, and the atomic trajectory was noted.

#### 2.2.5. Absorbent regeneration energy

Absorbent regeneration energy ( $Q_{reg}$ , GJ/ton CO<sub>2</sub>) consists of three parts: reaction heat ( $Q_{reac}$ ), sensible heat ( $Q_{sens}$ ) and latent heat ( $Q_{latent}$ ), as depicted in Eq. (1). The specific energy terms can be calculated through Eq. (2) [10,27,28].

$$Q_{reg} = Q_{reac} + Q_{sens} + Q_{latent} \tag{1}$$

$$Q_{reg} = \frac{-H_{abs}}{Mr_{CO_2}} + \frac{c_p m_{sol} \Delta T}{Mr_{CO_2} \bullet n_{CO_2}} + \frac{n_w}{Mr_{CO_2} \bullet n_{CO_2}} \Delta H_w^{vap}$$
(2)

where H<sub>abs</sub> (kJ/mol) is the reaction heat of CO<sub>2</sub> absorption,  $Mr_{CO_2}$  refers to the molar mass of CO<sub>2</sub>, 44 g/mol, C<sub>p</sub> (kJ/(kg·K)) is the heat capacity, m<sub>sol</sub> (kg) is the weight of the lower phase,  $\Delta T$  is the difference between the rich and lean solution temperatures, assumed to be 10 K,  $n_{CO_2}$  (mol) is the amount of desorbed CO<sub>2</sub>, n<sub>w</sub> (mol) is the amount of water evaporated, and  $\Delta H_w^{ap}$  (kJ/mol) is the evaporation heat of H<sub>2</sub>O.

#### 3. Results and discussion

#### 3.1. Absorbent for viscosity regulation

In the previous study, our group screened four aqueous systems containing DETA including 20 %DETA-40 %DMAC, 20 %DETA-40 % NMP, 20 %DETA-40 %DMSO, and 20 %DETA-40 %DMF, which showed distinct phase separation interfaces after absorbing CO<sub>2</sub>. Through assessments of absorption and desorption performance, phase separation behaviors, and regeneration energy of various systems, 20 %DETA/40 % DMAC/40 %H<sub>2</sub>O was identified as the optimal absorbent.

At this ratio, the CO<sub>2</sub>-rich phase loading of the absorbent was maximized, and cyclic loading was also at its peak. Furthermore, the relatively higher mass ratio of water in the biphasic solvent ensures that its phase separation stability is less affected by changes in water content during industrial operations. The energy consumption of the absorbent was 2.3 GJ/ton  $CO_2$ , which exhibits a 39 % reduction compared with that of 30 wt% MEA. However, the viscosity of the solvent was as high as 114.23 mPa·s, which would significantly affect the stability of system operation.

#### 3.2. Regulators preliminary screening

To reduce the viscosity of the solvent, seven typical alkanolamines involving primary alkanolamines (MEA, AMP), secondary alkanolamines (DEA, MAE), and tertiary alkanolamines (TEA, DEEA, MDEA) were selected as regulators in the preliminary screening. The structure and vapor pressure of each alkanolamine are listed in Table S1. According to the previous study, the total amine concentration was kept at 20 %, DMAC concentration at 40 %, and H<sub>2</sub>O concentration at 40 %, to ensure the highly efficient absorption, desorption, and phase split performance of the absorbent. The mass ratio of polyamine: regulator: DMAC: H<sub>2</sub>O in the blends was kept at 15 %: 5 %: 40 %: 40 % for preliminary screening. The results are presented in Table 1. After CO<sub>2</sub> absorption, as shown in Table S2, the phase separation performance of the absorbents after absorption was not affected by the incorporation of all regulators.

Relatively, although all alkanolamines regulators reduced the viscosity of CO<sub>2</sub>-rich solvents compared with the original DETA/DMAC/ $H_2O$  solution in 40 °C, the viscosity of each solution varied considerably, from 39.30 to 82.86 mPa·s. Among them, MEA, DEA, and MAE exhibited the most outstanding regulation effects on viscosity, which reduced the viscosity of CO<sub>2</sub>-rich solvents by 51–66 %. To screen the optimal regulator, absorption loading of the lower and upper phase were investigated. As indicated in Table 1, the variation in absorption loading among the solutions was relatively small (4.07–4.95 mol/kg), superior to 30 wt% MEA (2.50 mol/kg).

In comparison to MAE, MEA, and DEA demonstrate advantages with higher absorption loading and lower volatility [29,30]. Furthermore, due to the superior regenerability, lower phase split ratio, and lower reaction heat of DEA [31,32], DEA was chosen as the optimal regulator. As a result, the DETA/DEA/DMAC/H<sub>2</sub>O biphasic solvent was successfully developed for subsequent analysis.

# 3.3. Viscosity and CO<sub>2</sub> absorption and desorption performance

After determining DEA as the optimal regulator, the mass ratio of the total amine: DMAC:  $H_2O$  in the blends was maintained at 20 %: 40 %: 40 %. Various mass ratios of DETA: DEA, specifically 1:0 (referred to as DEAC), 2:1 (referred to as 2DE1AC), and 3:1 (referred to as 3DE1AC), were chosen for study to explore how the content of DEA affected the viscosity, as well as the absorption and desorption performance of the biphasic solvent.

In the absorption process, as seen in Fig. 1, the absorption loading of absorbents is lower than that of 30 wt% MEA due to the higher initial mass ratio of DMAC and water. Specifically, the  $CO_2$  loading of the DEAC absorbent was 8 % lower compared to that of the 30 wt% MEA. Moreover, due to the lower absorption capacity of DEA compared to DETA, with an increase in DEA content, the total loading of the absorbent gradually decreases. The  $CO_2$  loading of the 2DE1AC solvent was 22 % lower compared to that of the 30 wt% MEA.

Fig. 2 shows the absorption rates of various absorbents. It is worth noting that all the absorption rates in DETA/DEA/DMAC/H<sub>2</sub>O solutions exhibited a significant decrease at various  $CO_2$  loadings, corresponding to the phase separation loading, as depicted in Fig. 1. It indicated that the absorption reaction production of absorbents may transfer and accumulate in the lower phase during phase split, leading to a significantly high viscosity of the lower phase. Consequently, it lowers the mass transfer efficiency between the absorbent and  $CO_2$ , causing a reduction in the absorption rate. Consistent with the reason for the

#### Table 1

Regulators preliminary screening experiment.

Regulator	Phase change	Phase split ratio	Lower phase loading (mol/kg)	Upper phase loading (mol/kg)	Viscosity of the lower phase (mPa·s)
No regulator	Y	0.49	4.91	0.54	114.23
AMP	Y	0.43	4.64	0.54	69.37
MEA	Y	0.45	4.81	0.43	39.30
DEA	Y	0.43	4.79	0.36	55.52
MAE	Y	0.45	4.64	0.57	43.99
DEEA	Y	0.38	5.07	0.49	82.59
TEA	Y	0.39	5.25	0.21	82.86
MDEA	Y	0.40	4.27	0.25	60.65



Fig. 1.  $CO_2$  absorption loading in DETA/DEA/DMAC/H<sub>2</sub>O solutions with different mass ratios of DETA to DEA for 135 min.



Fig. 2. CO<sub>2</sub> absorption rate in DETA/DEA/DMAC/H<sub>2</sub>O solutions.

absorbent  $CO_2$  loading being lower than that of 30 wt% MEA, due to the lower amine content in the absorbent, its overall  $CO_2$  absorption rate is slightly lower than that of 30 wt% MEA.

After CO<sub>2</sub> absorption, the viscosity of the CO<sub>2</sub>-rich phase was measured at various temperatures. As seen in Fig. 3, the higher the ratio of DEA, the lower the absorbent viscosity. The viscosity of 2DE1AC is the lowest, reaching as low as 19.02 mPa·s at 60 °C, which represents a significant reduction of 74.3 % compared to DEAC at the same



Fig. 3. The lower phase viscosities of different absorbents at various temperatures.

temperature.

Regarding the desorption process, as seen in Fig. 4, introducing DEA as a regulator significantly improves the desorption performance of the absorbent. Firstly, the addition of DEA shortened the time for the desorption rate to peak, and the desorption rate of the absorbent continuously increased with the increase in DEA content. For the DEAC absorbent, it takes 11 min to get the peak desorption rate, with a  $CO_2$  desorption loading of 0.338 mol/kg. However, for the same cyclic



Fig. 4. CO<sub>2</sub> regeneration performance.

loading, 2DE1AC only requires 5 min, reducing the time by 54.5 %. Moreover, the time to reach the phase-separation loading is the lowest for 2DE1AC. It means that when the absorbent flow rate is the same, under the same residence time in the stripper, DEA as the regulator dramatically decreases the loading of the CO<sub>2</sub>-lean solution, which can improve the absorption performance of the outlet lean solution in the absorber, ensuring the stable operation of the system [33]. At the same time, in comparison to a 30 wt% MEA solution with a CO<sub>2</sub> loading of 2.47 mol/kg, 2DE1AC requires the same time (5 min) to reach the peak desorption rate, while the desorption rate at the peak point of 2DE1AC is 93.8 % higher than that of 30 wt% MEA. It demonstrates that 2DE1AC significantly outperforms MEA in terms of desorption efficiency. Additionally, since the lean loadings of all solvents exceed that of MEA, the CO<sub>2</sub>-rich phase loading variations during the desorption process in Fig. 4 were not included for the 30 wt% MEA solution.

Moreover, to ensure the regeneration performance of absorbents, the cyclic capacity, defined as the difference in the lower phase loading between absorption and regeneration (since only the lower phase of absorbent was sent to regenerate in the stripper), was evaluated. It can be indicated from Fig. 5 that the regeneration performance of absorbents was enhanced with the introduction of the DEA regulator. The cyclic capacity of 2DE1AC solvent was 2.08 mol/kg, which was 43.4 % higher than that of DEAC.

# 3.4. Phase separation behavior

As depicted in Fig. 6, phase separation resulted in a significant disparity in  $CO_2$  phase loading between the upper and lower phases of DEAC, 2DE1AC, and 3DE1AC solutions. The lower phase occupied over 95 % of absorbed  $CO_2$  of all absorbents. Owing to phase separation, the  $CO_2$ -rich phase loading far exceeds the total  $CO_2$  loading. Specifically, the  $CO_2$ -rich phase loading of 2DE1AC reaches 4.63 mol/kg, surpassing values reported for other biphasic solvents like 4D2B [15], DAH [10], sulfolane/MAE solution [34], and 30 wt% MEA solution, which endows it with excellent regenerability.

#### 3.5. Phase separation and viscosity regulation mechanism

# 3.5.1. NMR analysis

To clarify the phase separation and viscosity regulation mechanism of DEA in the DETA/DEA/DMAC/H<sub>2</sub>O system, <sup>13</sup>C NMR spectra were employed to analyze the absorption reaction production distribution in the upper and lower phase of DEAC and 2DE1AC solutions in various



Fig. 5.  $CO_2$  absorption loading and cyclic capacity of the  $CO_2$ -rich phase at various mass ratios of DETA/DEA.

CO<sub>2</sub> loading.

The <sup>13</sup>C NMR spectra of various samples of DEAC and 2DE1AC solvents during absorption are shown in Figs. 7 and 8, respectively. The carbon atom assignments of each species and their corresponding chemical shift ranges are detailed in Table 2.

As seen in Figs. 7 and 8, the peak signal intensities of DMAC, assigned as carbon 8, 9, 10, and 11, decreased in the lower phase with increased  $CO_2$  loading. Conversely, the upper phase displayed a contrasting pattern. The peak signal intensities of DETA species, assigned as carbon 1–7, raised in the lower phase with increased  $CO_2$  loading, while they exhibited the opposite trend in the upper phase. DEA amine, assigned as carbon 12 and 13, showed an upward trend in both the upper and lower phases with increased  $CO_2$  loading, while the DEA carbamates, assigned as carbon 14, decreased in the lower phase and showed the opposite trend in the upper phase. It indicates that the transport rate of DEA amine was slower than that of DEA carbamates and DETA species. Moreover, there were no significant signals of DMAC molecular in the lower phase.

The results demonstrate that in the DEAC and 2DE1AC biphasic solvent, only DETA and DEA reacted with CO<sub>2</sub>, while DMAC plays the roles of both physical solvent and phase separation agent.

Additionally, the amine protonation and carbamate formation, as well as pH discrepancies under different  $CO_2$  loadings, could lead to minor differences in chemical shifts among carbons bearing the same labels [35,36]. For example, notable variations in chemical shifts were detected among carbons with identical assignments, such as carbon 1' and 1" for assigned carbon 1, and carbon 12 and 12' for assigned carbon 12. The peaks corresponding to 1, 1', and 1'', as well as 12 and 12', exhibited shifts with increased  $CO_2$  loading, which is attributed to the presence of protonated amine and carbamate species [36,37]. Moreover, the peak signal intensities of carbamate corresponding to carbon 6 were observed a decline with increased  $CO_2$  loading in Fig. 7 which was attributed to the pH drop of the solution.

Quantitative analysis of various species distribution in the homogeneous, lower, and upper phases at various  $CO_2$  loadings of DEAC and 2DE1AC systems were further conducted, and the results are presented in Tables 3 and 4.

The average absolute relative deviation (AARD) is 3.68 %.

$$AARD = \frac{1}{n} \sum_{i=1}^{n} (\frac{NMR - chromatography}{chromatography})$$

a DETA species, including molecular and protonated DETA.

b DETA species obtained from ion chromatography, including molecular, protonated and carbamate DETA.

# 3.5.2. Phase separation and viscosity regulation mechanism

Based on the NMR analysis of DEAC and 2DE1AC solutions, it can be inferred that, for the DEAC system, carbamates are the primary reaction products in the absorption process and dominate in the lower phase while bicarbonate and carbonate appear in tiny amounts during phase separation at  $CO_2$  loading of 1.688–1.925 mol/kg. The phase separation could be elucidated through the salting-out mechanism [38].

Before the reaction started, DETA and DEA were miscible with DMAC, and they were connected to both  $H_2O$  and DMAC through hydrogen bonding and intermolecular forces. However, due to the higher polarity of DETA and DEA amines(including molecular and protonated DETA and DEA) compared to DETA and DEA carbamates, DMAC molecules are preferentially captured by amines before being attracted to carbamates, which led to a lower dissolution of carbamates in the DEAC and 2DE1AC systems. As the reaction progressed, the DETA and DEA amine gradually transformed into carbamate species, and DETA and DEA carbamates no longer formed hydrogen bonds with DMAC molecules but instead underwent self-aggregation with each other. When  $CO_2$  loading reached the phase separation loading, the self-aggregation of DETA and DEA species led to the formation of a new



Fig. 6. Phase loading at various CO<sub>2</sub> loading for different solvents at 40 °C. (The data for 4D2B was generated under the same CO<sub>2</sub> absorption conditions compared with other solvents [15]).



Fig. 7. <sup>13</sup>C NMR spectra of the homogeneous, upper, and lower phases of the DEAC solution at various CO<sub>2</sub> loadings.

phase, resulting in phase separation.

According to the NMR analysis, the transport rate of DEA amine from the upper phase to the lower phase was slower than that of DEA carbamate and DETA species including DETA amine and carbamate. This could be attributed to the higher polarity of DEA amine and protonated amine compared to DETA species [39]. It gave them a stronger ability to capture DMAC, H<sub>2</sub>O, and H<sub>3</sub>O<sup>+</sup> and made them more soluble in the upper phase(as seen in Table 5 at CO<sub>2</sub> loading of 1.393–1.728 mol/ kg in the 2DE1AC solution). Consequently, the self-aggregation of DETA species was enhanced in the unsaturated solution (CO<sub>2</sub> loading < 1.393 mol/kg), which also explains why the phase separation loading decreased with the introduction of DEA in Fig. 1. On the other hand, DEA carbamates in the upper phase underwent protonation reactions, as depicted in Eq. (3), leading to the gradual accumulation of HCO<sub>3</sub> in the upper phase with the rise of CO<sub>2</sub> loading [37].

Moreover, from Table 5, the viscosity of the  $CO_2$ -rich phase rose significantly with the increased lower phase loading, especially when approaching saturation (the lower phase loading of 4.01–4.64 mol/kg).



Fig. 8. <sup>13</sup>C NMR spectra of the homogeneous, upper, and lower phase of the 2DE1AC solution at various CO<sub>2</sub> loadings.

 Table 2

 Carbon atom assignments of each species and their corresponding chemical shift ranges in the loaded DEAC and 2DE1AC solution.



This confirms that the transition and self-aggregation of carbamate species in the lower phase during phase separation was the main reason for the high viscosity of the CO<sub>2</sub>-rich solution of DEAC absorbent.

With increased CO<sub>2</sub> loading, the highly polar DEA amine along with the associated hydrogen-bonded  $H_2O$  and  $H_3O^+$  gradually transited in the lower phase. Consequently, the concentration of  $H_3O^+$  and  $H_2O$  increased in the lower phase, which promoted the forward progression of the protonation reaction of DETACOO<sup>-</sup> and DEACOO<sup>-</sup>, as shown in Eq. (3) and Eq. (4) [35,40]. Finally, as seen in Table 3 and 4, the

concentration of carbamate species including DETA and DEA carbamates in the lower phase of 2DE1AC solution was lower than that of DEAC, while the concentration of amines including DETA and DEA, and  $HCO_3/CO_3^{2-}$  in the lower phase increased. As shown in Table 5, the viscosity of the CO<sub>2</sub>-rich phase of 2DE1AC solution showed a significant reduction compared with the DEAC system at the same lower phase loading, especially when approaching saturation. It indicated that the self-aggregation effect of DETA and DEA species ions especially carbamate species in the lower phase was weakened by introducing DEA to the system [41,42].

Indeed,  $HCO_3^-/CO_3^{2-}$  species are more easily regenerated compared to carbamates. This explains why both the absorbent cyclic loading and the regeneration rate improve when the DEA content in the system increases. Moreover, it could contribute to the reduction of energy consumption during regeneration.

$$DEACOO^{-} + H^{+} + H_2O \leftrightarrow HCO_3^{-} + DETAH^{+}$$
(3)

$$DETA(CO_2^-)_n + H^+ + nH_2O \leftrightarrow nHCO_3^- + DETAH^+$$
(4)

Where n = 1,2 or 3.

To further investigate the molecular interactions, viscosity regulation mechanisms in the  $CO_2$ -saturated DEAC and 2DE1AC systems, and to validate the experimental analysis, Molecular Dynamics (MD) simulations were conducted by Materials Studio.

#### 3.5.3. MD simulation

In the molecular dynamic simulation, it is reliable to verify the accuracy of force field parameters and simulation method by comparing the simulated density of amines with experimental values [43]. Guided by this research method, we first calculated the density of various pure amines and amide at 313.15 K and 1 atm in the MD simulation, the results were listed in Table S4. The NPT ensemble was conducted for 3 ns. Frame output every 2000 steps. As seen in Table S4, the deviations were within 2.5 %. Furthermore, we calculated the simulated densities of CO<sub>2</sub>-satured DEAC and 2DE1AC systems at 313.15 K and 1 atm, and compared the data with experimental values. As shown in Table S5, the deviations were within 3 %. Table 3

Species distribution in the homogeneous, lower and upper phases of DEAC solution at various  $CO_2$  loading, as determined using NMR spectroscopy and ion chromatography.

Total CO <sub>2</sub> loading	Liquid phase	DETA <sup>a</sup>	DMAC (mol/kg)	Carbamates	$HCO_3^-/CO_3^{2-}$	ion chromatography (mol/kg)
(IIIOI/Kg)		(IIIOI/Kg)	(IIIOI/ Kg)	(IIIOI/ Kg)	(11101/ Kg)	DETA <sup>b</sup>
1.57	Homogeneous	0.887	4.086	0.895	_	1.673
1.688	Upper	0.218	6.340	0.198	-	0.392
	Lower	0.758	1.715	1.258	0.01	1.991
1.925	Upper	0.275	6.587	0.155	-	0.417
	Lower	1.056	1.017	1.556	0.02	2.578

# Table 4

Species distribution in the homogeneous, lower and upper phases of 2DE1AC solution at various CO<sub>2</sub> loading, as determined using NMR spectroscopy and ion chromatography.

Total CO <sub>2</sub> loading (mol/kg)	Liquid phase	DETA <sup>a</sup> (mol/kg)	DMAC (mol/kg)	DEA <sup>c</sup>	Carbamates <sup>d</sup>	HCO <sub>3</sub> /CO <sub>3</sub> <sup>2-</sup> (mol/kg)	ion chromatography (mol/kg)	
				(mol/kg)	(mol/kg)		DETA <sup>b</sup>	DEA <sup>e</sup>
1.47	Homogeneous	0.418	3.932	0.454	0.374	0.074	0.758	0.427
1.393	Upper	0.301	4.191	0.102	0.35	0.116	0.539	0.181
	Lower	0.741	2.528	0.436	0.941	0.289	1.392	0.645
1.728	Upper	0.078	6.328	0.396	0.137	0.180	0.138	0.451
	Lower	0.856	1.693	0.635	1.416	0.418	1.843	1.030

The AARD is 3.89%.

c DEA species, including molecular and protonated DEA.

d Carbamates species including DETA and DEA carbamates.

e DEA species obtained from ion chromatography, including molecular, protonated and carbamate DEA.

#### Table 5

The viscosity of the CO<sub>2</sub>-rich phase of DEAC and 2DE1AC system under different lower phase loading at 40  $^{\circ}$ C.

Lower phase loading (mol/kg)	Total CO <sub>2</sub> loading (mol/kg)		Viscosity of the CO <sub>2</sub> -rich phase (mPa·s)		
	DEAC	2DE1AC	DEAC	2DE1AC	
3.53	1.688	1.393	26.17	17.11	
4.01	1.925	1.728	35.13	22.08	
4.64	2.25	1.97	108.23	38.59	

Thus, it was indicated that the force field pattern as well as the simulation method used in our study can be reliably matched to the experiment and predict the properties of solvents correctly.

To investigate the viscosity regulation mechanism attributed to the DEA regulator, the intermolecular interactions within the saturated DEAC and 2DE1AC systems were analyzed via MD simulations. The temperature was maintained at 313.15 K to match the absorption experiment condition. The Radial Distribution Functions (RDFs), g(r), was employed for analysis. As seen in Eq. (5), it quantifies the likelihood of locating atom B at a distance r from the reference atom A, averaged over the molecular trajectory [44].

$$g_{A-B}(r) = \frac{n_B/4\pi r^2 \Delta r}{N_B/V}$$
(5)

Where  $n_B$  represents the quantity of atoms B situated within a spherical shell of thickness  $\Delta r$  surrounding atom A,  $N_B$  stands for the total count of atoms B in the cell, and V stands for the cell volume.

As shown in Fig. S3, N and O denote nitrogen and oxygen atoms, respectively. To distinguish whether N and O come from DETA-related components or DEA-related components in the simulation, we assigned distinct atom sets to the nitrogen and oxygen atoms from DETA amine(including DETA molecular and protonated amine), DETA carbamates, DEA amine(including DEA molecular and protonated amine) and DEA carbamates, during the construction of the amorphous cell. These sets are denoted by the subscripts "p1", "c1", "p2", and "c2" respectively. Moreover, the subscript "w" refers to the H<sub>2</sub>O molecules.

From the NMR analysis, the self-aggregation of DETA species

especially carbamates led to the high viscosity in the DEAC system, and the forward progression of the protonation reaction between DETA carbamates and H<sub>2</sub>O could be the main reason for the reduction of viscosity in the 2DE1AC system. Thus, to investigate the hydrogen bond formation within DETA/DEA species and H<sub>2</sub>O molecules in the DEAC and 2DE1AC saturated solution systems, the RDF curves between N<sub>p1</sub>,  $N_{c1},\,O_{p1},\,O_{c1},\,N_{p2},\,N_{c2},\,O_{p2},$  and  $O_{c2}$  with  $O_w$  was analyzed firstly. As shown in Fig. 9, the RDF curves displayed prominent peaks at an r interval of 2.51-2.90 Å, revealing a high probability of hydrogen bond formation within DETA/DEA species and H<sub>2</sub>O in various systems. The position and intensity of these peaks reflect the intensity of hydrogen bond formation in various atomic pairs. The peak position of different atomic pairs follows the order:  $O_c$ - $O_w$  (2.51 Å)  $< N_p$ - $O_w$  (2.72 Å)  $< N_c$ - $O_w$  (2.90 Å), and the peak intensity follows the order:  $O_c-O_w > N_p-O_w >$ Nc-Ow, indicating that the Oc-Ow pair had the most remarkable propensity for forming hydrogen bonds. For the O<sub>c</sub>-O<sub>w</sub> pair, as shown in Fig. 9, the peak intensity follows the order:  $O_{c2}$ - $O_w$  (2DE1AC) >  $O_{c1}$ - $O_w$  $(2DE1AC) > O_{c1}-O_{w}$  (DEAC). Additionally, it can be indicated from Fig. 9 that the atomic pairs related to DETA species in the 2DE1AC system exhibited stronger peaks for all three types of RDF curves between N<sub>c1</sub>, N<sub>p1</sub>, and O<sub>c1</sub> with O<sub>w</sub>, compared to that of atomic pairs related to DETA species in DEAC system, which signified that DEA enhanced the interactions between the DETA carbamates and amines with H<sub>2</sub>O in the saturated solution. The atomic pairs related to DEA species in the 2DE1AC system showed the strongest peaks for all three types of RDF curves, which should be attributed to the high polarity of DEA.

Furthermore, to investigate the self-aggregation effects in the systems with and without DEA regulation, the hydrogen bond formation within DETA species and DEA species in the DEAC and 2DE1AC saturated solution systems was analyzed. However, from the molecular trajectory in the dynamic process, it became evident that self-aggregation not only occurred among DETA species, but also between DETA and DEA species in the 2DE1AC system, as shown in Fig. 10. Thus, in our RDF analysis of the 2DE1AC system, we did not differentiate whether N and O originated from DETA-related components or DEA-related components, but adopt an inclusive approach which considered them as a whole (for example,  $N_c$  included  $N_{c1}$  and  $N_{c2}$ ), to gauge



Fig. 9. (a–c) RDFs of  $O_c\text{-}O_w,\,N_c\text{-}O_w,\,N_p\text{-}O_w$  pairs for DEAC and 2DE1AC systems.



Fig. 10. Self-aggregation of DETA and DEA species in the molecular dynamic process.

the overall strength of self-aggregation effects within the systems.

As shown in Fig. 11, the RDF curves displayed prominent peaks at an r interval of 2.16–3.86 Å, revealing a high probability of hydrogen bond formation in the DETA/DEA carbamates and amine species, which proved the self-aggregation of DETA and DEA species in the saturated solution. The peak position of different atomic pairs follows the order:  $O_c-O_c (2.16 \text{ Å}) < N_c-O_c (2.31 \text{ Å}) < N_p-O_c (2.53 \text{ Å}) < N_p-N_p (2.70 \text{ Å}) < N_c (3.13 \text{ Å}) < N_c-N_p (3.86 \text{ Å})$ , and the peak level of  $N_c-O_c$  was the highest among various atomic pairs, indicating that hydrogen bonds are most

likely to form between the  $N_c$  and  $O_c$  atoms. For the  $N_c\text{-}O_c$  pair, as shown in Fig. 11, the peak intensity follows the order: 2DE1AC < DEAC. Furthermore, in the 2DE1AC system, all of the RDF curves displayed weaker peaks compared to the DEAC solution, indicating a weakening of the hydrogen bonds formed among carbamates and amine species in the 2DE1AC system.

In conclusion, it implied that DEA, as a viscosity regulator, can enhance the interactions between the carbamates and protonated amines with  $H_2O$ , which would prompt the forward protonation



Fig. 11. (a-f) RDFs of Oc-Oc, Nc-Oc, Np-Oc, Np-Np, Nc-Nc, Nc-Np pairs for DEAC and 2DE1AC systems.

reaction of DETA carbamates and weaken the self-aggregation of carbamate and amine species within solutions. As a result, the intensity of intermolecular interaction within the solution was weakened, and the viscosity of the system was reduced [25], which is consistent with the conclusions drawn from NMR analysis.

#### 3.6. Regeneration energy

To evaluate the regeneration energy of the novel absorbent, refer to Table S6 for the relevant calculation parameters.

As shown in Fig. 12, the regeneration energy of 2DE1AC absorbent reached 2.19 GJ/ton CO2, which exhibits about 42.37 % reduction compared with that of 30 wt% MEA and 25.26 % reduction compared with that of the DEAC solution. Furthermore, Fig. 12 illustrates a significant reduction in both sensible heat and latent heat for DEAC, 3DE1AC, and 2DE1AC solutions compared with 30 wt% MEA, which was the main reason for the substantial decrease in the regeneration energy. This phenomenon could be attributed to the lower mass of the regenerating solution and the water content in the lower phase solution of all absorbents. Moreover, due to the higher concentration of carbamates formed from the reaction of DETA with CO<sub>2</sub> and their relatively difficult decomposition, the reaction heat of DEAC is higher than that of MEA. However, as shown in Fig. 12, as the DEA content increases, the reaction heat of the solution gradually decreases. It was attributed to the promotion of the protonation reaction of carbamate species and the formation of  $HCO_3^-/CO_3^{2-}$  species which were easier to decompose in the system with the introduction of DEA. Additionally, DEA has a lower specific heat capacity compared to DETA, contributing to the reduction in Qsens during regeneration.

Thus, as shown in Table 6, besides decreasing viscosity, the addition of DEA regulator further enhanced the regenerability and reduced the regeneration energy of the biphasic absorbent. But the  $CO_2$  absorption capacity of the absorbent was influenced due to the relatively lower absorption capacity of DEA compared to DETA.

All in all, it indicated that using alkanolamine as a viscosity regulator was a promising strategy for optimizing the overall performance of biphasic absorbents. Furthermore, the 2DE1AC absorbent demonstrates higher phase loading, enhanced regeneration efficiency, and reduced energy consumption, solidifying its potential as an energy-efficient alternative for  $CO_2$  capture.

# 4. Conclusion

To address limitations of high viscosity in the biphasic absorbent and develop an optimization strategy for efficient absorbents, a polyamine/ amide biphasic solvent was optimized by the strategy of using alkanolamine as a viscosity regulator, and then a novel biphasic solvent DETA/ DEA/DMAC/H<sub>2</sub>O was proposed with the introduction of DEA. The viscosity of the CO<sub>2</sub>-rich phase reached as low as 19.02 mPa·s, representing a significant reduction of 74.3 % compared to the solution without DEA regulation. Furthermore, the DEA regulator significantly enhanced the regeneration performance of the absorbent. The cyclic capacity of DETA/DEA/DMAC/H2O was 43.4 % higher than that of the solution without DEA and the desorption rate was twice that of 30 wt% MEA. The lower phase loading of the novel absorbent is 4.63 mol/kg, which was significantly higher than that reported for other biphasic solvents. Based on the <sup>13</sup>C NMR analysis and MD simulation, the transition and selfaggregation of DETA species, especially carbamates with increased CO<sub>2</sub> loading in the lower phase, was proved to be the main reason for the high viscosity of the CO<sub>2</sub>-rich phase of the saturated solution. Through DEA regulation, the protonation of carbamates and the generation of  $HCO_3^-/CO_3^{2-}$  were promoted, which achieved a weakening of the selfaggregation of carbamates species, decreasing the viscosity and the regeneration energy of saturated CO2-rich phase solution. The regeneration energy reached 2.19 GJ/ton CO2, which exhibited a 42.37 % reduction compared with that of 30 wt% MEA.



Fig. 12. Regeneration heat of DEAC, 2DE1AC, and 30 wt% MEA solutions.

# Table 6

The performance of various biphasic absorbents with and without DEA regulation.

Biphasicabsorbent	CO <sub>2</sub> absorption capacity(mol/kg)	The viscosity of the lower phase at 60 °C (mPa·s)	Regeneration heat (GJ/ t CO <sub>2</sub> )
DEAC	2.31	73.94	2.93
3DE1AC	2.04	25.15	2.5
2DE1AC	1.91	19.02	2.19

#### CRediT authorship contribution statement

**Zhipeng Chen:** Conceptualization, Methodology, Software, Investigation, Formal analysis, Writing – original draft. **Chao li:** Methodology, Supervision. **Mengxiang Fang:** Resources, Supervision, Writing – review & editing. **Wei Zhang:** Funding acquisition. **Ii Zhang:** Funding acquisition. **Wenyang Fan:** Funding acquisition. **Hangtian Hu:** Methodology, Writing – review & editing. **Fei Liu:** Methodology, Writing – review & editing. **Feng Zhang:** Funding acquisition. **Tao Wang:** Resources, Supervision.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

I would like to submit my data/code if necessary.

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#### Appendix A. Supplementary material

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