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## HIGHLIGHTS

• Novel alkanolamine-based biphasic solvent with low regeneration energy and viscosity is proposed for CO<sub>2</sub> capture.

• Tertiary amine 3-(dimethylamino)propan-1-ol(3DMA1P) is firstly introduced to decrease regeneration energy.

• Phase separation mechanism is revealed by NMR and LogP analysis.

• Molecular dynamics simulation is applied to study liquid structure and monitor the phase separation process.

### ARTICLE INFO

Keywords: Carbon dioxide Biphasic solvent NMR analysis Phase separation mechanism Regeneration energy Molecular dynamics simulation ABSTRACT

Biphasic solvents for CO<sub>2</sub> capture have received significant attention due to their potential for energy conservation. However, traditional biphasic solvents result in highly viscous CO<sub>2</sub> rich-phases and high amine losses. To overcome these drawbacks, we have developed a novel alkanolamine-based biphasic solvent by blending 2-(methylamino) ethanol (MAE), 3-(dimethylamino)propan-1-ol (3DMA1P), diethylene glycol dimethyl ether (DGM), and water. The aqueous MAE/3DMA1P/DGM solvent showed a cyclic capacity of 0.45 mol CO<sub>2</sub>/mol amine, which is 1.8 times that of monoethanolamine (MEA), and a desorption rate and regeneration efficiency twice those of MEA. The viscosity of the biphasic solvents can be reduced to 13.12 mPa-s at 313 K, which is lower than that of reported biphasic solvents. The evaluated regeneration energy was 2.33 GJ/ton CO<sub>2</sub>. Cation chromatography measurements revealed the tendency of MAE to accumulate in the CO<sub>2</sub>-rich phase with increasing CO<sub>2</sub> absorption loading. Quantitative <sup>13</sup>C NMR analyses were performed to investigate the species distribution in both phases, and DGM was found to be the major component of the CO<sub>2</sub>-lean phase. Different solubilities of the MAE molecules and MAE carbamate in DGM resulted in phase separation. Molecular dynamics (MD) simulations on the CO<sub>2</sub>-unloaded and CO<sub>2</sub>-loaded solutions verified the phase separation mechanism. MAE molecules tended to cluster, and the interactions between MAE and DGM dropped significantly, with increasing DGM concentration.

### 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is increasingly gaining prominence as a greenhouse gas, and CO<sub>2</sub> emissions from anthropogenic activities and fossil-fuel combustion cause a serious greenhouse effect [1,2]. Chemical absorption with aqueous amines is one of the most efficient and widely used methods for carbon sequestration [3,4]. However, the technology has the drawback of high energy consumption for the regeneration

process, which accounts for 60–80% of the total energy required [5,6]. For the benchmark solvent, 30 wt% monoethanolamine (MEA), the regeneration energy is approximately 4.0 GJ/ton  $CO_2$  [7,8].

Recently, alternative amino solvents have been proposed, such as blended amino solutions [9,10], ionic liquids [11,12], non-aqueous solvents [13], and biphasic solvents [14]. Among these, biphasic solvents are the most promising candidates for  $CO_2$  capture due to their low energy consumption. Biphasic solvents are characterized by their

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tendency to split into two immiscible phases after absorbing CO<sub>2</sub>. Only the CO<sub>2</sub>-rich phase needs to be sent to a stripper tower, thus reducing the sensible and latent heat [15]. Biphasic solvents usually consist of a phase-separation solvent, a reactive amine, and water. Most biphasic solvents are based on two common phase-separation solvents: 2-(diethylamino)-ethanol (DEEA) and N,N-dimethylcyclohexylamine (DMCA). For instance, triethylenetetramine (TETA)/DMCA [16], Nmethylcyclohexylamine (MCA)/DMCA [17], 1,3-propanediamine (MAPA)/DEEA [18], and 1,4-butanediamine (BDA)/DEEA [19] have been investigated for CO2 capture. However, the volatilities and degradation rates of DEEA and DMCA are much higher than those of MEA [20], which aggravates solvent loss and the environmental pollution. Moreover, the viscosities of the CO2-rich phases are too high for industrial applications. For example, the viscosities of 0.5D1.5A3P [5] and DAH [14] are 152 and 114.3 mPa·s, respectively, at 40 °C, almost fifty times that of 30% MEA.

To solve the high-volatility problem, physical solvents have been proposed as alternative phase-separation solvents. Zhang et al. [4] studied a MEA/1-propane/H<sub>2</sub>O biphasic solvent which showed a good phase-separation ability. The sulfolane proposed by Wang et al. [21] could facilitate CO2 absorption, and the heat duty of MEA/sulfolane/ H<sub>2</sub>O was 2.67 GJ/ton CO<sub>2</sub>. Luo et al. [22] reported biphasic solvents consisting of (diethylenetriamine) DETA/sulfolane/H2O that have a cyclic loading 35% higher than that of 30 wt% MEA. Through screening experiments, Xu et al. [23] selected diethylene glycol dimethyl ether (DGM), sulfolane, n-propanol, and dimethyl sulfoxide (DMSO) as the physical solvents; among these, DGM demonstrated the highest potential to reduce the heat duty. In this study, DGM was chosen as the physical solvent for developing a novel biphasic solvent. The secondary amine MAE showed good phase-separation performance and was chosen as the reactive amine because it also has an absorption rate higher than that of MEA [24,25], and the carbamates of secondary amines are more easily desorbed. Furthermore, MAE has a lower reaction heat than MEA [26], thus decreasing the energy consumption [27,28]. The tertiary amine 3DMA1P has lower thermal and oxidative degradations than those of 30 wt% MEA [29], and the absorption capacities (at a low  $CO_2$ partial pressure) and second-order reaction rate constants of 3DMA1P solutions are higher than those of methyldiethanolamine (MDEA) solutions [30,31]. Moreover, the product of the reaction between 3DMA1P and CO<sub>2</sub> was a bicarbonate, which is easier to regenerate than a carbamate. Consequently, 3DMA1P was added to the biphasic solvents to reduce the regeneration heat. Molecular dynamics (MD) simulations were applied to evaluate the thermodynamics, liquid structure, and dynamics of the aqueous amines [32-35]. Xu et al. [36] studied the gas-liquid interfacial characteristics of various physical solvents to elucidate the mechanism for improving the overall mass transfer. Gao et al. [37] proposed weak interactions between the products as one way to trigger phase separation. In this study, we investigated the liquid structure and the dynamic properties of MAE/DGM/H2O solutions to understand their phase-change behavior at the molecular level. In addition, quantitative <sup>13</sup>C nuclear magnetic resonance (NMR) and ion chromatography analyzes were used to determine the species distribution in both the upper and lower phases.

## 2. Experiments

#### 2.1. Chemicals

Diethylene glycol dimethyl ether (DGM,  $\geq$ 99.5%), 2-((2-aminoethyl) amino) ethanol (AEEA, 99%), MEA ( $\geq$ 99%), 2-(methylamino) ethanol (MAE,  $\geq$ 99%), 2-(ethylamino)ethanol (EAE, 99%), 2-(butylamino) ethanol (BAE,  $\geq$ 98%), methyldiethanolamine (MDEA, 99%), 3-(dimethylamino)propan-1-ol (3DMA1P, 99%), 1-dimethylamino-2-propanol (1DMA2P,  $\geq$ 98%), 2-(dimethylamino)ethanol (2DMAE, 99%), 2-amino-2-methyl-1-propanol (AMP,  $\geq$ 95%), 1,4-dioxane ( $\geq$ 99%), and deuterated water (D<sub>2</sub>O,  $\geq$ 99.9%) were purchased from Aladdin. Carbon

dioxide (99.999% pure) and nitrogen (99.999% pure) gases were purchased from Hangzhou Jingong GAS Co., Ltd, Hangzhou, China. Deionized water was used throughout the experiment.

### 2.2. Experimental methods

The absorption apparatus setup is shown in Fig. S1. The inlet gas contained 12 vol% CO<sub>2</sub>, with balance N<sub>2</sub>, and had a flow rate of 1000 mL/min. The flow rates were controlled by mass flow controllers (CS200-A, Beijing Sevenstar Company, China, accuracy 1%). The gas was first saturated with water and then bubbled into a CO<sub>2</sub> absorber. The CO<sub>2</sub> concentration was analyzed using a CO<sub>2</sub> infrared gas analyzer (GHX-3010E1, Beijing Huayun Company, China, accuracy 1%). The temperature of water bath was maintained at 313.15 K (accuracy  $\pm$  0.5 K), and equilibrium was assumed when the outlet CO<sub>2</sub> concentration reached 12 vol%. A separating funnel was used to separate the upper and lower phases, and the properties of both phases, including CO<sub>2</sub> loading, mass percentage, and viscosity, were analyzed. The viscosities of the absorbents at different CO<sub>2</sub> loadings and temperatures were measured using a digital rotational viscometer (Brookfield Viscometer, DV-II + Pro, accuracy 1%).

In the desorption mode, 45 g of the CO<sub>2</sub>-rich phase solutions were added to a 100 mL three-necked flask, which was warmed using an oil bath (Fig. S1). The temperature of the oil was 120 °C (accuracy  $\pm$  1 °C). A magnetic rotor was placed at the center of flask. An electronic soapfilm flowmeter (BL-1000, range 1–1000 mL/min, accuracy 1%) was used to record the amount of CO<sub>2</sub> released in process. The water vapor was condensed using ice water and collected.

## 2.3. NMR analysis

The species distribution in the loaded biphasic solvent was analyzed via  $^{13}$ C NMR (Agilent DD2-600 MHz). 1,4-Diaxone was used as the internal reference standard and deuterated water was added to the sample to obtain a signal lock. The parameters used for quantitative  $^{13}$ C NMR were delay time, D1 = 60 s and number of scans, NS = 300.

## 2.4. Regeneration energy

Regeneration energy (*Qreg*) consists of three parts: reaction heat (*Qreac*), sensible heat (*Qsens*) and latent heat (*Qlatent*), which can be calculated as follows [14]:

$$Qreg = Qreac + Qsens + Qlatent$$
(1)

$$Qreg = \frac{-\text{Habs}}{MrCO2} + \frac{Cp \cdot msol \cdot \Delta T}{mCO2} + \frac{nw}{MrCO2 \cdot nCO2} \Delta H_w^{vap}$$
(2)

where Habs is the reaction heat of CO<sub>2</sub> absorption in kJ/mol, tested using a calorimeter (C80, Setaram), *MrCO2* is the CO<sub>2</sub> molecular weight, 44 g/mol, *Cp* is the heat capacity in kJ/(kg·K), measured using the Aspen plus software, *msol* is the mass of the CO<sub>2</sub>-rich phase solution in kg,  $\Delta T$  is the difference between the CO<sub>2</sub>-rich and CO<sub>2</sub>-lean solution temperatures, assumed to be 10 K, *mCO2* and *nCO2* are the mass and the amount of desorbed CO<sub>2</sub>, in kg and mol, respectively, calculated using a soap film flowmeter, *nw* is the moles of water evaporated in mol, condensed using ice-water, and  $\Delta H_w^{vcp}$  is the heat of water evaporation in kJ/mol.

#### 2.5. Molecular dynamics simulations

Molecular dynamics simulations were carried out using a Gromacs 2018.8 [38], and the following simulation steps were performed on each solution: An initial equilibrium was attained to minimize the system energy. Then a 1 ns equilibrium simulation was performed under an NVT ensemble to heat the system to the desired temperature. The NPT ensemble simulations, consisting of a 1 ns equilibrium simulation and a

Table 1Simulation results of MEA aqueous solutions.

T/K	c (MEA) (mol/ L)	ho (kg/m <sup>3</sup> ), sim	ρ (kg/ m <sup>3</sup> ), exp [40]	D(MEA) $\cdot 10^{-9}$ , $(m^2/s)$ , sim	D(MEA) $\cdot 10^{-9}$ , $(m^2/s)$ , exp [40]	$D(H_2O)$ $\cdot 10^{-9}$ , $(m^2/s)$ , sim
298.15	1	981.9	999.1	1.07	1.00	4.06
	2	985.4	1001.6	0.98	0.91	3.06
	5	1007.8	1010.0	0.75	0.69	1.64
313.15	1	976.7	993.6	1.58	1.42	4.82
	2	981.3	996.1	1.27	1.30	4.02
	5	1002	1003.5	0.95	1.04	2.66



Fig. 1. The mass ratios of the upper and lower phases at different mass ratios of  $DGM/H_2O$  (with 5M MAE).

2 ns isothermal-isobaric simulation, ensured the appropriate density and pressure of the solvents. Lastly, a 2 ns NVT simulation was performed and the simulation trajectories were noted every 1 ps. The temperature (298.15 K) and pressure (1.01 kPa) were maintained using the Nose-Hoover and Berendsen and Parrinello-Rahman thermostats, respectively. An OPLS-AA force field was chosen, and water was used as the

Table 2
The chemical shifts of the carbons in the loaded 2M1.5D system.

Signal number	Chemical shift (ppm)	Assignment
1	34.97-35.10	3 Н
2	52.32-52.45	$\sim$ $^{N}$
3	60.59-60.72	HO
4	29.51-29.64	5
5	44.34-44.47	
6	55.76-55.90	4
7	60.59-60.72	N _ OH
8	58.54-58.71	$\sim \sim \sim$
9	69.93-70.09	5 6 7
10	71.51-71.68	
11	164.98-165.11	
$HCO_{3}^{-}/CO_{3}^{2-}$	163.41-163.62	8 9 9 8
		11
		coo
		Ń N
		HO' V V

SPC model for a good consistency of the experimental results [39]. MEA, MAE, DGM, MAECOO<sup>-</sup>, MAEH<sup>+</sup>, and CO<sub>2</sub> molecular structures were obtained by a Gaussian software and optimized at the B3LYP-6-311 level.

An aqueous MEA solution was chosen to verify the consistency between the simulation and experimental results. The density and the component diffusion coefficients were calculated for three concentrations of the MEA solutions (Table 1). The relative deviations in the density and the diffusion coefficients were 1.1% and 7.6%, respectively.

#### 3. Results and discussion

#### 3.1. Phase-separation behavior

## 3.1.1. Influence of the mass ratio of $DGM/H_2O$ on phase change

As shown in Fig. 1, the phase ratio (mass ratio of the CO<sub>2</sub>-rich phases) is related to the mass ratio of DGM/H<sub>2</sub>O. In this study, the lower phase was the CO<sub>2</sub>-rich phase. With an increase in the amount of water, the phase ratio decreased, and phase separation phenomenon was not observed for water concentrations higher than 75%. For biphasic solvents, only the rich phase is sent to the stripper tower; therefore, a decreasing phase ratio can cut down the sensible heat. However, a very low phase ratio may increase the viscosity of the rich phase. Therefore, the mass ratio of DGM/H<sub>2</sub>O was maintained at approximately 7:3.



Fig. 2.  $^{13}$ C NMR spectra of the upper and lower phases of the loaded 2M1.5D solvent (with 1,4-dioxane at  $\delta = 67.15$  ppm as the reference).

## Table 3

Species distribution in the upper and lower phases obtained by NMR spectroscopy and ion chromatography.

Total loading (mol/kg)	Phase	NMR (mol/kg)				ion chromatography (mol/kg)			
		MAE <sup>a</sup>	3DMA1P <sup>b</sup>	DGM	$HCO_3^-$	$CO_3^{2-}$	MAE <sup>a</sup>	3DMA1P <sup>b</sup>	
1.32	Upper Lower	0.33 3.36	1.08 1.83	6.25 1.28	- 1.53	_ 0.70	0.29 3.17	1.06 1.68	
									•

The average absolute relative deviation (AARD) is 8.08%. AARD =  $\frac{1}{n} \sum_{i=1}^{n} \left( \frac{NMR - chromatography}{chromatography} \right)$ 

a MAE species, including molecular, protonated, and carbonated MAE

b 3DMA1P species, including molecular and protonated 3DMA1P



Fig. 3. Amine concentration in the 2M1.5D solvent at different CO<sub>2</sub> loadings.

# 3.1.2. NMR analysis

The  $^{13}$ C NMR spectra of the loaded 2 M1.5D (2 M MAE/1.5 M 3DMA1P/3.5 M DGM) solvents are shown in Fig. 2. The corresponding molecular structures with carbon assignments and chemical-shift ranges are shown in Table 2. The species distribution in the upper and lower phases (Table 3) was obtained via NMR and ion chromatography. According to the zwitterion and base-catalyzed hydration mechanisms [41,42], the products of the reaction between MAE and CO<sub>2</sub> were carbamates, while those of the reaction between 3DMA1P and CO2 were carbonates and bicarbonates. According to the NMR results, the upper phase was the organic phase, dominated by DGM, and the lower phase was the aqueous phase. The absorption products, such as the protonated MAE, carbonated MAE and  $HCO_3^-/CO_3^{2-}$ , were concentrated in this phase. 3DMA1P existed in both the phases and had a higher concentration in the lower phase. Fig. 3 shows the migration of the amine species at different CO<sub>2</sub> loadings. The biphasic solvent 2M1.5D started showing phase separation at a CO<sub>2</sub> loading of 0.28 mol/mol. With increasing CO<sub>2</sub> loading, MAE and its derivatives accumulated in the lower phase. The 3DMA1P also moved to the lower phase, but at a lower rate.

#### 3.1.3. Phase-separation mechanism

The phase separation could be explained by the salting-out mechanism [43] by analyzing the species migration. MAE was miscible with DGM; however, after absorbing  $CO_2$ , it formed a carbamate whose solubility in DGM is much lower than MAE. During absorption, the amount of carbamate increased up to a certain  $CO_2$  loading, beyond which it separated out to form a new phase. The hydrophobicity and polarity of the amine are crucial parameters for the phase-change behavior [44].

Preliminary experiments (Supplementary Material) were conducted



Fig. 4. Phase-change behavior and ionic logP values of various amine/DGM/  $\rm H_2O$  solutions.

to screen the novel biphasic solvents. The phase-changing results were used to explain the phase-separation mechanism as shown in Fig. 4 (red and blue represent phase separation and homogeneity, respectively). The logP values, which were obtained using ChemDraw software, indicated the degree of hydrophobicity. Lower logP values indicated better water solubility. DGM is lipophilic organic solvent whose logP = -0.22; therefore, lipophilic substances dissolve more readily in it than hydrophilic substances. However, upon reaction with CO<sub>2</sub>, MAE is ionized, and its hydrophilicity decreases, resulting in a lower solubility in DGM. The MAE ions were then transferred to the aqueous phase, resulting in phase separation. There has been some research on the relation between logP and phase separation. Zhao et al. [45]studied amine-organic solvent-water systems and proposed that the solubility of the CO2-absorption product in organic solvents would decrease with logP. Shen et al. [46] studied primary/secondary amine-tertiary amine-water systems and found the a large difference between the logP values of the primary and tertiary amines benefited phase separation. In the preliminary experiment, the AMP/DGM/H<sub>2</sub>O solution undergoes precipitation, because the solubility of the carbamate of AMP is low both in water and DGM.

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

# 3.2.1. MAE/DGM/water solvent

To understand the influence of DGM on the absorption performance, absorption rate, and absorption loading of 5M MAE/DGM/water solution were investigated. The absorption loading and rate results are shown in Fig. 5. The solutions with DGM/water mass ratios in the range of 4:6–10:0 separated into two phases, with more than 98% of the absorbed  $CO_2$  concentrated in the lower phase. It can be seen from



Fig. 5. (a)  $CO_2$  absorption loading and (b) absorption rate in MAE/DGM/H<sub>2</sub>O solutions with different mass ratios of DGM to water (with 5M MAE).

Table 4  $CO_2$  loadings of phase separation point in MAE/DGM/H<sub>2</sub>O solutions (with 5 M MAE).

DGM: water	10:0	3:1	7:3	6:4	5:5	4:6
Phase separation loading(mol/ mol)	0.25	0.16	0.22	0.25	0.32	0.39

Fig. 5a that a higher initial mass ratio of DGM results in a lower absorption loading.  $CO_2$  loading of the MAE/DGM solution was 20% lower than that of the MAE/H<sub>2</sub>O solution.

Fig. 5 b shows that all the absorption rates in MAE/DGM/H<sub>2</sub>O solution decreases sharply at different  $CO_2$  loadings, and these loadings were exactly same as the  $CO_2$  loadings of the phase separation point as shown in Table 4. Consequently, by defining the loading of phase separation point as the boundary, the absorption progress can be divided into two stages. In the first stage, amine–DGM solution has a higher  $CO_2$  absorption rate than the amine–water solution, and the absorption rate increases with the DGM concentration. This could be because DGM facilitates absorption [23] and a solution with a higher DGM concentration has stronger mass transfer ability with  $CO_2$ , thus increasing the absorption rate. In the second stage, the effect is reversed, and the solution with a lower DGM concentration has faster absorption rate. This



Fig. 6. (a)  $CO_2$  absorption loading, cyclic capacity, and regeneration efficiency at various molar ratios of MAE/3DMA1P (b)  $CO_2$  regeneration performance.

could be because the solution begins to separate into two phases, the carbamates are concentrated in the lower (CO<sub>2</sub>-rich) phase, and the viscosity increases rapidly over a short period. Therefore, the diffusion of  $CO_2$  is hindered, which slows the absorption.

#### 3.2.2. MAE/3DMA1P/DGM/water solvent

The absorbed CO<sub>2</sub>, in the form of the carbamate, bicarbonate, and carbonate, was concentrated in lower phase of the biphasic solvents, leading to a rapid increase in their viscosity, thereby hindering CO<sub>2</sub> diffusion and absorption and increasing the load on the heat exchanger. As the reaction mechanism for primary/second amines is different than that for the tertiary amine, the CO<sub>2</sub> absorbed by the tertiary amine would generate  $CO_3^{2-}/HCO_3^{-}$  ions instead of carbamate, which could have decreased the viscosity [5], so the tertiary amine (3DMA1P) was selected to replace a portion of the secondary amine. As shown in Fig. 6 a, through the screening experiment, six types of solvents were subjected to phase separation. Since the viscosity of the CO2-rich phase of 5 M MAE/DGM/H<sub>2</sub>O was still high (32.12 mPa·s) at 313.15 K, the molar ratio of MAE/DGM was changed to 4:0 from 5:0 to reduce its viscosity. CO<sub>2</sub> absorption loading, cyclic capacity, and regeneration efficiency of different molar ratios of MAE/3DMA1P solutions were investigated. The absorption loading and cyclic capacity of 30 wt% MEA were 2.55 mol/ kg and 0.91 mol/kg, respectively: lower than the literature-reported values [14] for poor desorption condition. When the molar ratio of MAE/3DMA1P was 2:1.5, the cyclic capacity was approximately 1.59 mol/kg (0.45 mol/mol), which was 74.2% higher than that of 30 wt% MEA and 52.7% higher than that of the MAE/DGM/H<sub>2</sub>O solvent.

#### Table 5

CO<sub>2</sub> loading distribution and viscosity at 313.15 K.

MAE/ 3DMA1P/ DGM	Upper phase (mol/kg)	Lower phase (mol/kg)	Mass ratio	Viscosity of the lower phase (mPa·s)
4M/0/3.5M	0.02	3.07	58.3%	17.00
3M/1 M/3.5M	0.07	3.11	56.3%	17.20
2M/2 M/3.5M	0.06	2.44	55.9%	16.42
2M/1.5M/ 3.5M	0.08	2.53	59.4%	13.12
2M/1 M/3.5M	0.05	2.03	66.6%	8.23
1.5M/1.5M/ 3.5M	0.06	1.99	55.3%	9.40



Fig. 7. Viscosity of 2M1.5D at different CO<sub>2</sub> loadings and temperatures.

Replacing a portion of the MAE with 3DMA1P increased the cyclic capacity and increasing the 3DMA1P concentration resulted in a higher regeneration efficiency. When the amine molar ratio was 1.5:1.5, the regeneration efficiency was 75%, which was 2.1 times that of 30 wt% MEA. The desorption performance is shown in Fig. 6b. The desorption rates of the biphasic solvent are approximately twice that of 30 wt% MEA. This could be attributed to the conversion of the CO<sub>2</sub> absorbed by 3DMA1P to bicarbonate, which is unstable and can be more readily decomposed than carbamate. However, there was a decrease in absorption loading due to a lower absorption rate for 3DMA1P than MAE. Table 5 shows the CO<sub>2</sub> loading of the upper and lower phases and the mass ratio of lower phase. Considering the higher absorption loading and cyclic capacity, the molar ratios of 4:0, 3:1, 2:1.5, 2:2, 2:1 (henceforth referred to as 4MOD, 3M1D, 2 M1.5D, 2M2D, 2M1D) were chosen to analyze heat regeneration.

## 3.3. Viscosity

The viscosity of 2 M1.5D is shown in Fig. 7. The viscosity of the lower phase increased with the CO<sub>2</sub> loading due to the self-concentrating effect of the MAE carbamate products [46,47]. In contrast, an increase in the temperature of solution decreased the lower-phase viscosity. The viscosity of the lower phase was maximum (13.12 mPa·s) at a CO<sub>2</sub> loading of 0.68 mol/mol and a temperature of 313 K.

## 3.4. Regeneration energy

The regeneration heats of different biphasic solutions are shown in Fig. 8 a. The desorption time was maintained at 30 min to decrease the



Fig. 8. (a) Regeneration heat of MAE/DGM/H<sub>2</sub>O and 30 wt% MEA solutions (b) regeneration heat of 2M2D for 5 cycle experiments.

influence of the evaporation of water. The biphasic solutions exhibit a lower regeneration heat (22.1-38.7%) than 30 wt% MEA, especially in terms of the latent and sensible heats. The latent heat is closely related to the water content in the solution, comparing 2M1D, 2M1.5D and 2M2D, with decreasing water content, the latent heat decreased from 0.94, 0.75 to 0.42 GJ/ton CO2. Notably, comparing 3M1D and 2M2D, the regeneration heat decreased from 2.53 to 2.33 GJ/ton CO2, which showed that with the increase of the molar ratio of 3DMA1P, the regeneration heat could be lower. The lowest regeneration heat was 2.33 GJ/ton CO2 for 2M2D, which could be advantageous for energy conservation. In order to evaluate the changes of regeneration heat after circulation, and a circulation experiment with five cycles was performed, as shown in Fig. 8 b. It can be seen that there was no significant change in the regeneration heat, and the deviations were all lower than 3% compared to the first cycle, which indicated that 2M2D was stable and suitable for reuse.

#### 3.5. Molecular dynamics simulations

The liquid structure was investigated to understand the interactions between various species, for which the radial distribution functions (RDFs) and coordination numbers were calculated (using Eqns. 5 and 6



**Fig. 9.** Calculated  $g_{N-Hw}(r)$  and  $g_{N-Ow}(r)$  of the (a) unloaded 5M MAE and (b) unloaded 5M MAE/3.5M DGM aqueous solutions; calculated (c)  $g_{N-C}(r)$  and (d)  $g_{N-N}(r)$  of the unloaded/loaded 5M MAE/3.5M DGM aqueous solution; (e) calculated  $g_{002-C}(r)$ ,  $g_{009-C}(r)$ , and  $g_{00G-C}(r)$  of the unloaded 5M MAE/3.5M DGM aqueous solution; (f) calculated  $g_{N1-O09}(r)$  of the unloaded/loaded 5M MAE/3.5M DGM aqueous solution.

provided in the Supplementary Material). The calculated RDFs of select atom pairs are shown in Fig. 9. Three types of solutions were studied: 5 mol/kg MAE aqueous solution and unloaded and loaded MAE/DGM aqueous solutions (molar ratio 5:3.5). Fig. 9a and 9b show the pair interactions between the nitrogen atoms of MAE and the hydrogen and oxygen atoms of water. Fig. 9a shows a small peak at 0.30 nm and a larger peak at 0.48 nm corresponding to the N-O<sub>w</sub> pair; the former formed due to hydrogen bonding between the amine and the hydroxyl group of water, and the latter due to intermolecular forces. The N-H<sub>w</sub> pair showed a similar pattern, with a peak at 0.18 nm in the 0.4–0.53 nm region. The order of peaks indicates that the water molecules were arranged in the H<sub>w</sub>-O<sub>w</sub>-H<sub>w</sub> order away from the nitrogen atom. After the addition of DGM to the system, the amplitude of peaks corresponding to the N-H<sub>w</sub> and N-O<sub>w</sub> pairs increased and the coordination number of  $g_{N-Hw}(r)$  increased from 0.42 to 0.58 (Fig. 9b–9e), indicating an increase in the number of water molecules surrounding the MAE molecules and enhancing the solvent effect of the MAE molecules. The N-C interaction showed a slight decrease, but the N-N interaction was enhanced with an increase in the coordination number  $g_{N-N}(r)$  from 0.31 to 0.48, indicating clustering of the MAE molecules. This could be attributed to the hydrophilicity of MAE, which tends to cluster with water and itself with an increasing DGM concentration. As more water molecules surrounded the MAE molecules, the viscosity of the solvent layer increased, hindering CO<sub>2</sub> absorption.



Fig. 10. The coordination number  $g_{Nl-O09}(r)$  at different mass ratios of DGM/  $H_2O$  (with 5M MAE).

Fig. 9e shows the interaction between DGM and  $CO_2$  molecules; the coordination numbers of which were 0.58, 0.49, and 0.48 for the  $g_{O02-C}(r)$ ,  $g_{O09-C}(r)$ , and  $g_{O0G-C}(r)$  pairs, respectively. Notably, the coordination number of  $g_{OW-C}(r)$  was only 0.21, indicating a superior  $CO_2$ -absorption ability of DGM than water. Therefore, at the initial absorption stage, the solution with a higher DGM concentration exhibited a faster absorption rate.

Fig. 9f indicates a drastic decrease in the MAE–DGM interaction after the conversion of MAE to its carbamate. Fig. 10 shows the coordination number  $g_{\rm NI-O09}(r)$  at various DGM/H<sub>2</sub>O mass ratios. The number of DGM molecules surrounding the MAE molecules increased with the water content in both the unloaded and loaded solutions, indicating that water promotes the miscibility of MAE and DGM. The coordination number  $g_{\rm NI-O09}(r)$  dropped sharply (to the range of 0.23–0.28) after CO<sub>2</sub> absorption, and phase separation occurred below 0.24.

## 4. Conclusion

Herein, we propose the novel biphasic solvent, MAE/3DMA1P/ DGM/H<sub>2</sub>O, for CO<sub>2</sub> capture with a low regeneration energy. The cyclic loading was 74.2% higher than that of 30 wt% MEA; the desorption rate and regeneration efficiency were both approximately twice that of 30 wt % MEA. Further, with the addition of the tertiary amine 3DMA1P, the regeneration heat decreased to 2.33 GJ/ton CO<sub>2</sub>, the viscosity of the CO<sub>2</sub>-rich phase decreased to 8–17 mPa·s, and the phase ratio was 55–60%. The species distribution in the upper and lower phases was obtained by NMR and ion chromatography analysis and the phasechange mechanism was explained by the salting-out theory. Finally, MD simulations were used to investigate the liquid structure and dynamic properties of MAE/DGM/H<sub>2</sub>O solutions, confirming an increase in the CO<sub>2</sub> absorption rate with DGM concentration. The interaction between the atoms was also elucidated.

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#### CRediT authorship contribution statement

Hangtian Hu: Conceptualization, Software, Formal analysis, Investigation, Writing – original draft. Mengxiang Fang: Resources, Supervision, Writing – review & editing. Fei Liu: Methodology, Writing – review & editing. Tao Wang: Resources, Supervision, Writing – review & editing. Zhixiang Xia: Resources. Wei Zhang: Funding acquisition. Chunliang Ge: Funding acquisition. Jingjuan Yuan: Funding acquisition.

# **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.

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apenergy.2022.119570.

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#### H. Hu et al.

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