



Novel monoethanolamine absorption using ionic liquids as phase splitter for CO₂ capture in biogas upgrading: High CH₄ purity and low energy consumption

Fanzhi Meng, Tongyao Ju, Siyu Han, Li Lin, Jinglin Li, Kailun Chen, Jianguo Jiang ^{*}

School of Environment, Tsinghua University, Beijing 100084, China



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ABSTRACT

Ionic liquid, as a green absorber, could be effectively combined with amine solution to obtain a mixed system that effectively improved the upgrading effect and reduced regeneration energy consumption in the biogas upgrading process. In this work, an aqueous biphase solvent consisting of 30 wt% monoethanolamine (MEA) and 40 wt% 1-butyl-3-methylimidazolium tetrafluoroborate (BF) was prepared, which had advantages such as excellent biogas upgrading effect, high CO₂ recycling loading and low regeneration energy consumption. The effect law of ionic liquid addition to amine solution on biogas upgrading and mass transfer characteristics was comprehensively evaluated through the analysis and prediction of physical parameters, and the excellent biogas upgrading characteristics of the mixed system and the favorable effect of ionic liquid on mass transfer were verified. The solvent effect of the ionic liquid could appropriately lower the energy barrier for the reaction to produce carbamate and improve the CO₂ capture effect. The higher polarity of the ionic liquid solvent also provided the driving force for the phase separation and accelerated the phase separation process. The distribution pattern of CO₂ loading with time and space was comprehensively studied by using amplified phase separator, covering the whole process variation of phase separation. The important role of intermolecular forces in the phase separation process was discussed, and the important reasons for the occurrence of phase separation in phase separators were explained.

1. Introduction

The rapid depletion of fossil energy sources has caused tremendous pressure on energy utilization and environment, so it was urgent to increase the development and utilization of renewable energy sources [1–3]. Biogas, as a green, safe and efficient renewable energy source, has attracted a lot of attention worldwide because of its high calorific value (15–30 MJ/Nm³) [4,5], which could be used to fuel engines in the transportation industry and thus solve energy problems. Although biogas contains a large amount of methane (CH₄, 45–70%), the impurity component carbon dioxide (CO₂, 30–55%) still severely reduces its calorific value [6,7]. Therefore, CO₂ capture of biogas by biogas upgrading technology was necessary.

As a relatively mature CO₂ capture technology, amine scrubbing technology had the advantages of fast absorption rate, large absorption capacity and regeneration, and was suitable for industrial large-scale biogas upgrading and CO₂ capture [8,9]. However, its regeneration

energy consumption was generally high, which greatly limited its commercial use [10,11]. Currently the most widely used was the 30 wt% monoethanolamine (MEA) aqueous solution, and new absorbents often used the 30 wt% MEA aqueous solution as a reference for industrial use [12–14]. Studies had shown that the latent and sensible heat of gasification of water during regeneration could be reduced by replacing all water with non-aqueous solvents, so a large number of amines scrubbing technologies based on non-aqueous solvents have emerged [15,16]. However, this technology still had many drawbacks, such as higher cost, environmental risks, difficulty in regeneration after oxidative degradation, and still required high sensible heat of regeneration, which made it rarely used for biogas upgrading and CO₂ capture in practical engineering [17,18]. The biogas upgrading process was also optimized by means of solid amines, Li et al. [19] and Qu et al. [20] impregnated Polyethylenimine (PEI) on nano-Al₂O₃ support and calcium silicate hydrate support with large pores, respectively, to enhance the CO₂ adsorption capacity and cycling stability of amine-based functional

* Corresponding author.

E-mail address: jianguoj@tsinghua.edu.cn (J. Jiang).

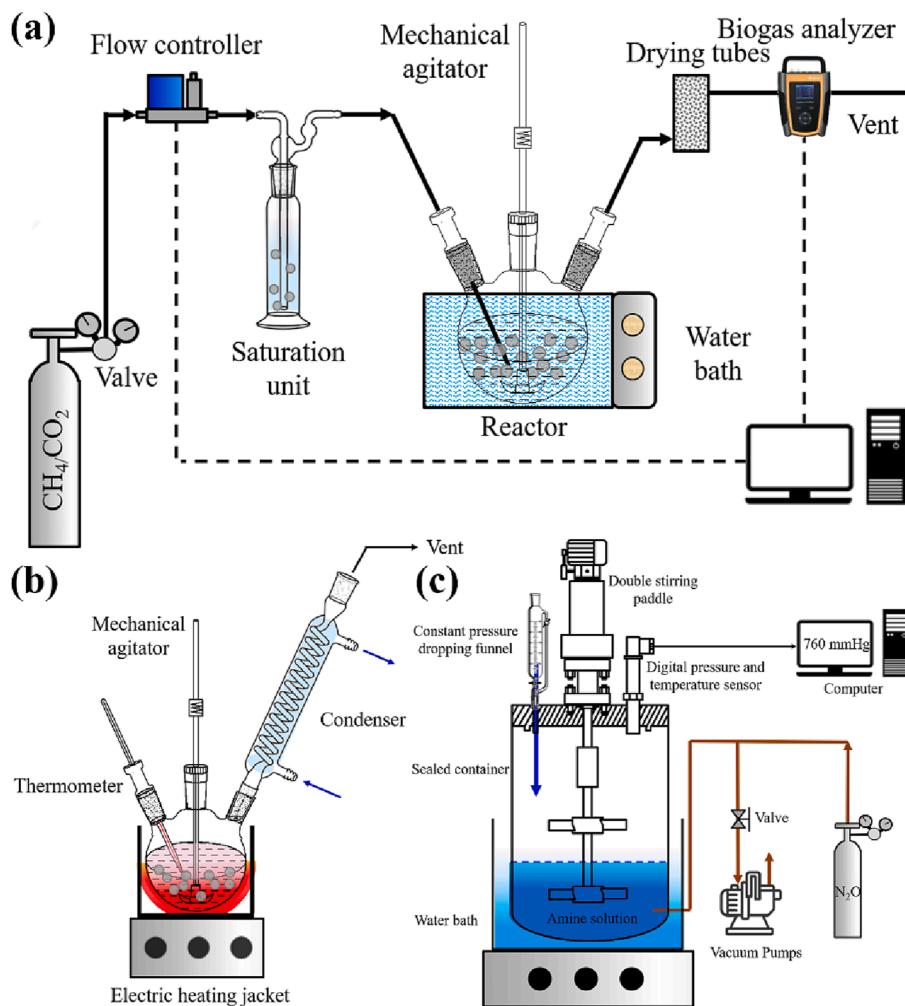


Fig. 1. Experimental device for biogas upgrading. (a) Absorption unit; (b) Desorption unit; (c) Gas-liquid parameter measuring unit.

adsorbents, but the solid amines scale application was still slightly less than that of liquid amines. Among them, ionic liquids (ILs) were gradually attracting attention as a new solvent with wide liquid temperature range, low vapor pressure, high thermal stability, easily regenerated and able to capture CO_2 [21,22]. But the large viscosity of ionic liquids seriously affected the mass transfer in the reaction process and brings inconvenience to the actual industrial use [23]. However, it had been shown that the addition of small amounts of water to ionic liquids could greatly improve the phenomenon of high viscosity, which made ionic liquids have great prospects for application in CO_2 capture [24].

In addition, phase splitting agents were also a major research direction for low energy consumption CO_2 capture recently [25,26], the rich amine solution after biogas upgrading could be divided into two phases (rich liquid phase and lean liquid phase) under the action of phase change absorber, the reaction product of CO_2 and amine carried a small amount of water enriched in the rich liquid phase [27,28], the rich liquid phase entered the desorption tower for regeneration and then mixed directly with the lean liquid phase into the absorption tower for biogas upgrading again [29], which could greatly reduce the energy consumption of desorption [30–32]. However, there were few studies on using ionic liquids as phase splitting agents.

Although the amine-ionic liquid–water three-phase mixed system could combine the advantages of both the amine absorber and the ionic liquid and could solve each other's problems in the application process [33,34], if the phase separation could be achieved by regulating the addition of ionic liquids, it could significantly reduce the direct energy loss caused by the heating of water and ionic liquids and improve the

overall thermal stability of absorbers while ensuring high CO_2 absorption rate and high CO_2 absorption [35]. This made the three-phase mixture of amine-ionic liquid–water solution had good potential for research [36,37]. Studies had shown that imidazolium-based ionic liquids were simpler to synthesize and had better water solubility, which facilitated the reaction process [38,39]. Among the common anions, the fluoride anion was more soluble in CO_2 , and the water solubility of both $[\text{BF}_6]^-$ and $[\text{NTf}_2]^-$ were poor except for $[\text{BF}_4]^-$ [40]. Therefore, 1-butyl-3-methylimidazolium tetrafluoroborate was often used in CO_2 capture processes as well, as a green absorber recognized for its better thermal stability. In addition, the insolubility of carbamate in ionic liquids allowed the possibility of phase separation after a certain level of CO_2 loading, which was crucial for the reduction of energy consumption in the subsequent reaction. Miao et al. [41] found that 1-butyl-3-methylimidazolium tetrafluoroborate (BF) could achieve the reduction reaction of CO_2 at room temperature thus increasing the net consumption of CO_2 . Taib et al. [42] found that the addition of 1-butyl-3-methylimidazolium tetrafluoroborate to MEA and accompanied by increasing reaction pressure facilitated the CO_2 capture process. Yoon et al. [43] prepared membrane materials using 1-butyl-3-methylimidazolium tetrafluoroborate that significantly improved CO_2 permeability and selectivity. Although a few studies on CO_2 capture by ionic liquids coupled with amine solutions has been carried out, none of them were concerned with the field of biogas upgrading and possible phase separation phenomena. Therefore, there were fewer studies of amine-ionic liquid–water three-phase mixed systems for biogas upgrading, and there was a lack of both gas–liquid equilibrium data and analysis of this system and

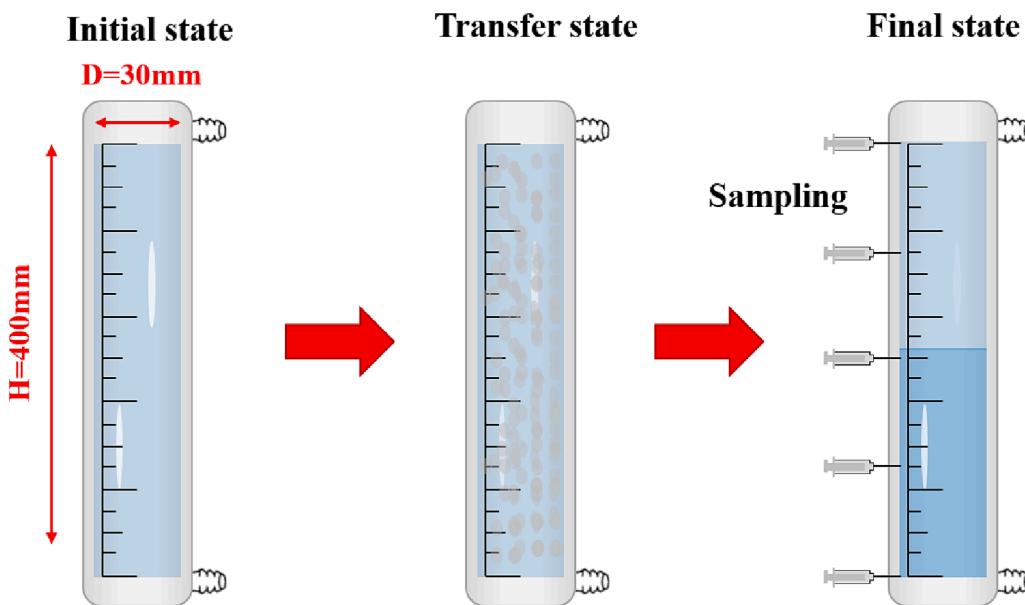


Fig. 2. Large scale phase separator for studying phase separation characteristics of biphasic solvents.

liquid–liquid partitioning phenomenon, and most importantly there was a lack of studies on ionic liquids in the field of phase separation, thus it was of good research value [44–46].

In this work, an aqueous biphasic solvent consisting of monoethanolamine and 1-butyl-3-methylimidazolium tetrafluoroborate was prepared for the CO₂ capture for biomethane preparation with low energy consumption. Based on the experimental study of various biogas upgrading characteristics and the calculation and prediction of physical parameters, the basic physical parameters of the mixed system, the biogas upgrading effect and phase separation characteristics were comprehensively studied, and the influence of ionic liquids on the mass transfer process was discussed. The reaction products and processes were investigated in detail in combination with ¹³C nuclear magnetic resonance (NMR) and Gaussian-based quantum chemical calculations. The CO₂ loading in the phase separation process at different time and space was discussed using an independently built amplified phase separator to further understand the phase separation kinetics of the mixed system.

2. Experimental and methodology

2.1. Materials

Monoethanolamine (MEA, purity ≥ 99%) and 1-butyl-3-methylimidazolium tetrafluoroborate (BF, purity ≥ 98%) obtained from Meryer were used to prepare aqueous biphasic solvents for CO₂ capture in the biogas upgrading process. The most commonly used aqueous 30 wt% MEA solution in industry was used as a measure, as reported in the study [17,47]. Simulated biogas was prepared with 65% purity CH₄ and 35% purity CO₂. The mixture of CO₂ and N₂ was prepared in a specific ratio.

2.2. Performance measurements of biphasic solvents

The optimal BF addition was determined by measuring the phase separation characteristics such as phase separation volume, separation rate, CO₂ enrichment efficiency and basic physical parameters such as density, viscosity, Henry coefficient, CO₂ diffusion rate and biogas upgrading performance such as methane purity, effective upgrading time and regeneration rate under different BF additions of MEA-BF aqueous biphasic solvent. The reaction process was based on a bubbling reaction unit, a regeneration unit and a Chittick titration unit

as shown in Fig.S1 and Fig. 1, where the viscosity was measured by a digital viscometer. The desorption heat of the biphasic solvent was calculated by the previously reported Gibbs Helmholtz equation, as detailed in the Supporting information. ¹³C NMR spectroscopy was used to quantify the reaction products and enrichment range of biphasic agents in the biogas upgrading process.

2.3. Amplified application of phase separator

The study of the amplification application of biphasic solvents was a key means to measure its usefulness. The amplified phase separator designed and fabricated independently in this paper was shown in Fig. S2 and Fig. 2, and the device was used to further research the phase separation characteristics after biogas upgrading. The selected optimal biphasic solvents were placed in a phase separator equipped with a thermostatic sandwich and maintained at 303.15 K under different CO₂ loadings, where the diameter and effective height of the phase separator were 30 mm and 400 mm, respectively. The CO₂ loading was measured and recorded every 15 mins from five equally spaced sampling ports (1 ml for each sampling port) located on the side of the device. The CO₂ loading of the biphasic solvent was plotted against time and space to analyze the phase separation characteristics.

2.4. Mechanistic analysis

Gaussian 09 was used to perform the quantum chemistry calculations, where density functional theory (DFT) was used to optimize the model of the reaction process of amine and CO₂ in mixed solvents, obtaining the full process reaction products and intermolecular interaction relationships, and analyzing the causes of phase separation generation. The solvation free energy of amines in solvents was achieved based on the universal solvation model (SMD). The visualization model was built with a combination of Multiwfn and VMD.

3. Results and discussion

3.1. Biogas upgrading characteristics and basic parameters of MEA-BF solvent

The results of biogas upgrading and regeneration for mixed amine systems with different BF additions were shown in Fig. 3(a) and Fig. 3(b)

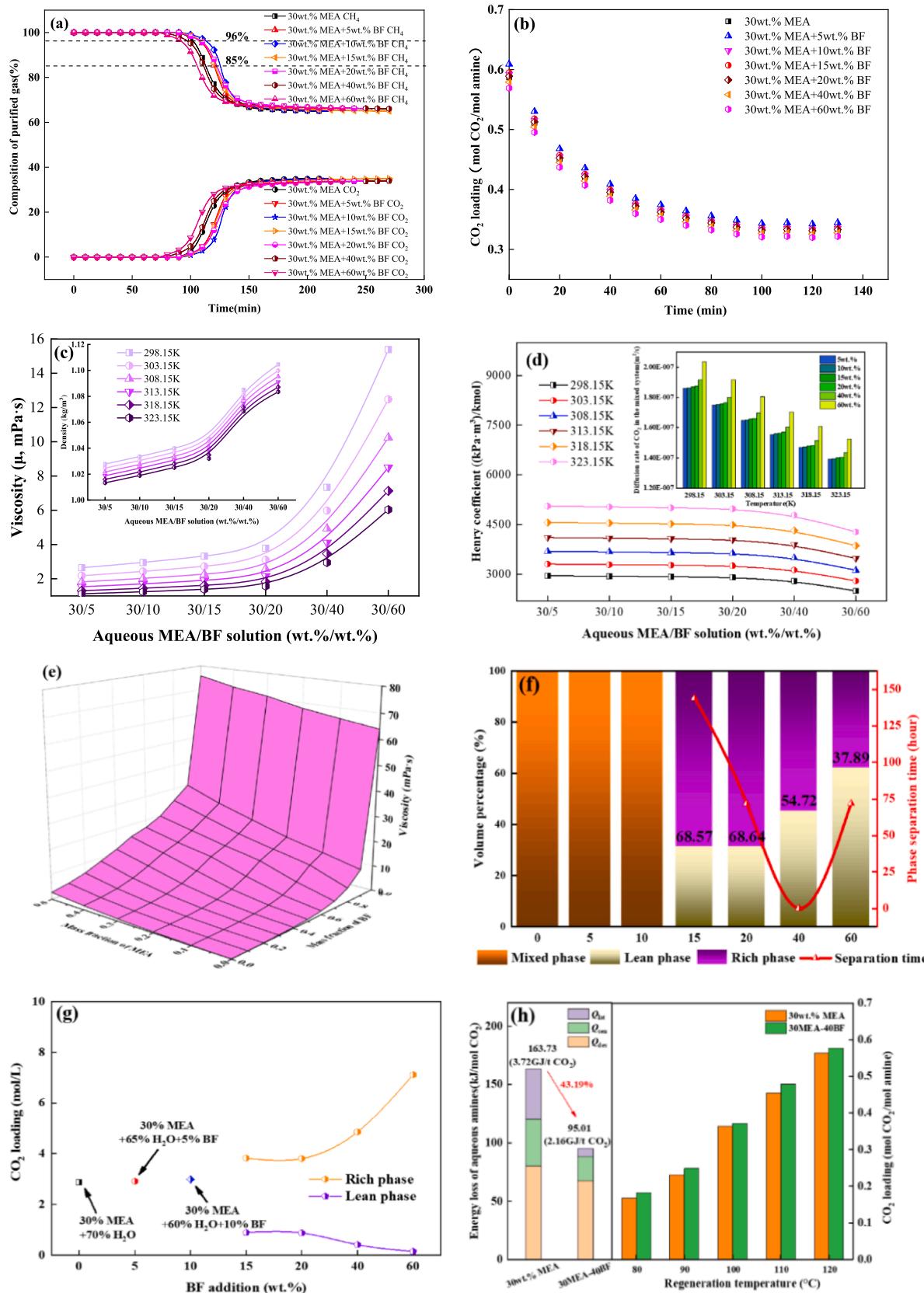


Fig. 3. Biogas upgrading effect and physical properties parameters of biphasic solvent. (a) Biogas upgrading process; (b) Solvent regeneration process; (c) Variation of density and viscosity with addition and temperature; (d) Variation of Henry coefficient and CO_2 diffusion rate with addition and temperature; (e) Effect of the content of each component of the mixed system on viscosity; (f) Variation pattern of phase separation time and volume; (g) Trend of CO_2 loading in the phase separation process; (h) Regeneration energy consumption and cycle CO_2 loading of 30MEA-40BF.

respectively, from which it could be seen that the BF additions had little effect on the methane purity of the upgraded biogas, all of which could reach 100%. This result could meet the requirements for biogas into grid and vehicle applications in China ($\geq 96\%$) and some EU countries ($\geq 85\%$), respectively. This was mainly because the CO₂ absorption kinetics decreased as the CO₂ loading increased during the biogas upgrading process, and the CO₂ could not be completely trapped, so the methane purity showed a decreasing trend and the CO₂ content gradually increased. Measured by the time to reach the required methane purity of the upgraded gas, there was a slight upward trend of biogas upgrading effect with increasing BF mass fraction, which was mainly due to the low effect of viscosity when the ionic liquid addition did not exceed 20 wt% and the improved absorption kinetics of mixed amines due to the physical absorption properties of BF on CO₂, which was consistent with the results in Fig. 3(c). The trends of the regeneration curves were generally consistent, but there was a slight difference between the initial and ending CO₂ loadings, which could be analyzed in conjunction with the data in Table S1, where the regeneration rate fluctuated between 56.46% and 56.64%. Combined with the CO₂ solubility data of mixed amine in Table S1, when the addition amount of BF reached 40 wt%, the viscosity of mixed amine increased slightly, but the solubility of CO₂ increased, so the biogas upgrading effect was basically the same as that of 30 wt% MEA solution. However, when the addition amount of BF reached 60 wt%, the viscosity increased sharply despite the obvious increase of CO₂ solubility, so the biogas upgrading effect showed a decreasing trend.

The biogas upgrading effect, CO₂ loading and regeneration rate of the mixed system were detailed in Table S1, and it could be clearly found that the regeneration rates of the samples were basically consistent, all around 56.5%. In this paper, the duration for which the methane purity of the upgraded biogas could reach 96% and 85%, respectively, was used as an index to measure the effectiveness of biogas upgrading of the samples, expressed as T_{96%} and T_{85%}, respectively. When T_{96%} was used as a measure, with the gradual increase of BF addition, the mixed amine had a better biogas upgrading effect than that of 30 wt% MEA solution (102.4 mins) at BF addition up to 40 wt%. When T_{85%} was used as a measure, the mixed amine also had better biogas upgrading than that of 30 wt% MEA solution (112.3 mins) when the BF addition did not exceed 40 wt%.

The physical parameters of aqueous MEA, BF and MEA/BF mixtures with different mass fractions at different absorption temperatures were investigated, and the data were shown in the Fig. S3 and Tables S1–S4 of the Supporting information. From the data in the Fig. S3, it could be found that the density and viscosity of the aqueous MEA, BF and MEA/BF mixtures showed an increasing trend with the increase of mass concentration at constant temperature. The density showed a linear trend with the increase of mass concentration, while the viscosity growth rate increased significantly with the increase of mass concentration. The viscosities of pure BF at 303.15 K, 313.15 K and 323.15 K were measured to be 65.21 mPa·s, 42.69 mPa·s and 29.88 mPa·s, respectively. Combining the results in Fig. S3(e), it was readily apparent that the viscosity decreased significantly when the ionic liquid BF was mixed with H₂O, which was the same as our expected application effect. It was worth noting that in the MEA-BF-H₂O system as shown in Fig. 3(c), the increase in viscosity was almost negligible until the mass concentration of BF increased to 20 wt%, and even remained at a lower level compared to pure BF until the mass concentration of BF reached 40 wt%, which was a very good conclusion for the MEA-BF-H₂O system. The density and viscosity also showed a decreasing trend with increasing temperature.

The results of Henry coefficient and CO₂ diffusion rate were shown in Fig. 3(d), and the calculation procedure was shown in the Supporting information. Combined with the physical solubility of CO₂ in amine solution in Fig. S3, it was easy to see that under the condition of the reaction temperature determination, the increase of the mass fraction of MEA had less effect on the Henry coefficient, while with the increasing

mass fraction of BF the Henry coefficient showed a decreasing trend, which was mainly because the larger particle volume of the liquid tended to have a higher solubility. And with the increasing reaction temperature, the Henry's constant showed an increasing trend. Since Henry coefficient plays an important role in gas–liquid phase mass transfer, especially a smaller Henry coefficient was more favorable for the reaction, so with the increasing mass fraction of ionic liquid BF, it was more favorable for the whole MEA-BF-H₂O system for CO₂ reaction mass transfer performance in the biogas upgrading process. From the Fig. 3(d), it could be found that the diffusion rate of CO₂ in the mixed system started to show an increasing trend when the BF was added at 40 wt% and 60 wt%. This further indicated that the addition of BF at 40 wt% had a good CO₂ capture effect.

In addition, in order to better establish the laws of variation of mass concentration, temperature on density, viscosity and Henry coefficient, the experimental results were fitted with semi-empirical equations, and the fitting results were shown in Table S6, and the detailed process was described in the Supporting information. The viscosity of the solution of MEA-BF-H₂O system plotted with the mass fractions of MEA and BF by combining the experimental data and the results of the fitted equations was shown in Fig. 3(e). It could be more intuitively found that the viscosity of the solution could be kept at a very low level when the mass fraction of MEA was 30 wt% and the mass fraction of BF was less than 50 wt%, which would be beneficial to the biogas upgrading process of this system. In addition, this further indicated that the viscosity in the amine-ionic liquid system would not increase sharply due to the addition of ionic liquid, which was of great significance for practical engineering applications.

Finally, in order to comprehensively analyze the physical parameters of the MEA-BF-H₂O system, all the relevant data of the mixed system were listed in Table S7. There was no difficulty to observe that when the mass fraction of BF was added below 20 wt%, the density and viscosity of the mixed system were lower but the Henry coefficient was larger, when it was greater than 60 wt%, the Henry coefficient of the mixed system was lower but the density and viscosity were larger, and when it was around 40 wt% could be simultaneously with the advantages of low density, low viscosity and low Henry coefficient.

It was worth noting that some of the MEA/BF aqueous solutions showed liquid–liquid stratification after biogas upgrading, in which no stratification occurred when BF was added at 5 wt% and 10 wt%, while stratification occurred when the addition amount was 15 wt% and 20 wt% and the stratification time was as long as 144 h and 72 h, respectively, which had a long stratification time. However, when the addition amount was 40 wt%, it only took 5 mins to achieve stratification, the result of stratification was shown in the Fig. 3(f) and Fig. S6, which had a good stratification effect. Finally, when the addition amount was 60 wt%, the stratification time grew again to about 72 h with a long stratification time. On the one hand, this indicated that with the increasing mass fraction of BF, the mixed system was more prone to stratification, and on the other hand, it showed that the rate of phase separation was faster only when the mass concentrations of MEA and BF in the system were close to each other. In addition, the separated solution could all return to the unseparated state after regeneration, but the sample with BF addition of 60 wt% remained in the separated state even after full desorption, which was because the CO₂ loading of the solution after desorption was still under the condition that made it result in the separated phase, which was consistent with the previous results, so this kind of mixed amine was not suitable to be used as a separator. Combined with the results in Fig. 3(g), it was not difficult to find that the volume of the rich phase after the aqueous 30MEA-40BF biphasic solvent splitting accounted for about 50% of the total volume, and almost all of the CO₂ was enriched in the rich phase, which was very beneficial to the regeneration and circulation process of the biphasic solvent. The energy consumption results of the optimal mixed amine (30MEA-40BF) with a BF addition of 40 wt% were obtained by the thermodynamic calculation method in the Supporting information, as shown in Fig. 3(h).

Table 1Energy consumption of different amines in the CO₂ capture process.

Absorption solution	Temperature change	Energy consumption	References
30MEA-40BF	363 K	2.16 GJ/tCO ₂	This work
TETA-DEEA	363 K	2.98 GJ/tCO ₂	[15]
TETA-DMCA	363 K	2.80 GJ/tCO ₂	[48]
TETA-DEEA	363 K	2.70 GJ/tCO ₂	[49]
TETA-DEAPD	363 K	2.72 GJ/tCO ₂	[48]
DEEA-MAPA	393 K	3.21 GJ/tCO ₂	[39]
AMP-HMDEA	/	3.43 GJ/tCO ₂	[39]
MEA-PZ	393 K	3.61 GJ/tCO ₂	[50]

The regeneration energy consumption of 30MEA-40BF was 43.19% lower than that of 30 wt% MEA, which greatly reduced the regeneration energy consumption, while the cyclic CO₂ loading of 30MEA-40BF increased with the increase of regeneration temperature. The energy consumption of some amine absorbers for carbon capture was summarized in Table 1, among which 30MEA-40BF had a low energy consumption and some value.

3.2. Reaction mechanism and intermolecular interactions of MEA-BF solvent

To further analyze the solutions after phase separation, ¹³C NMR analysis was performed on all samples used for biogas upgrading, and the results were shown in Fig. 4. Fig. 4(a) showed the ¹³C NMR spectra of

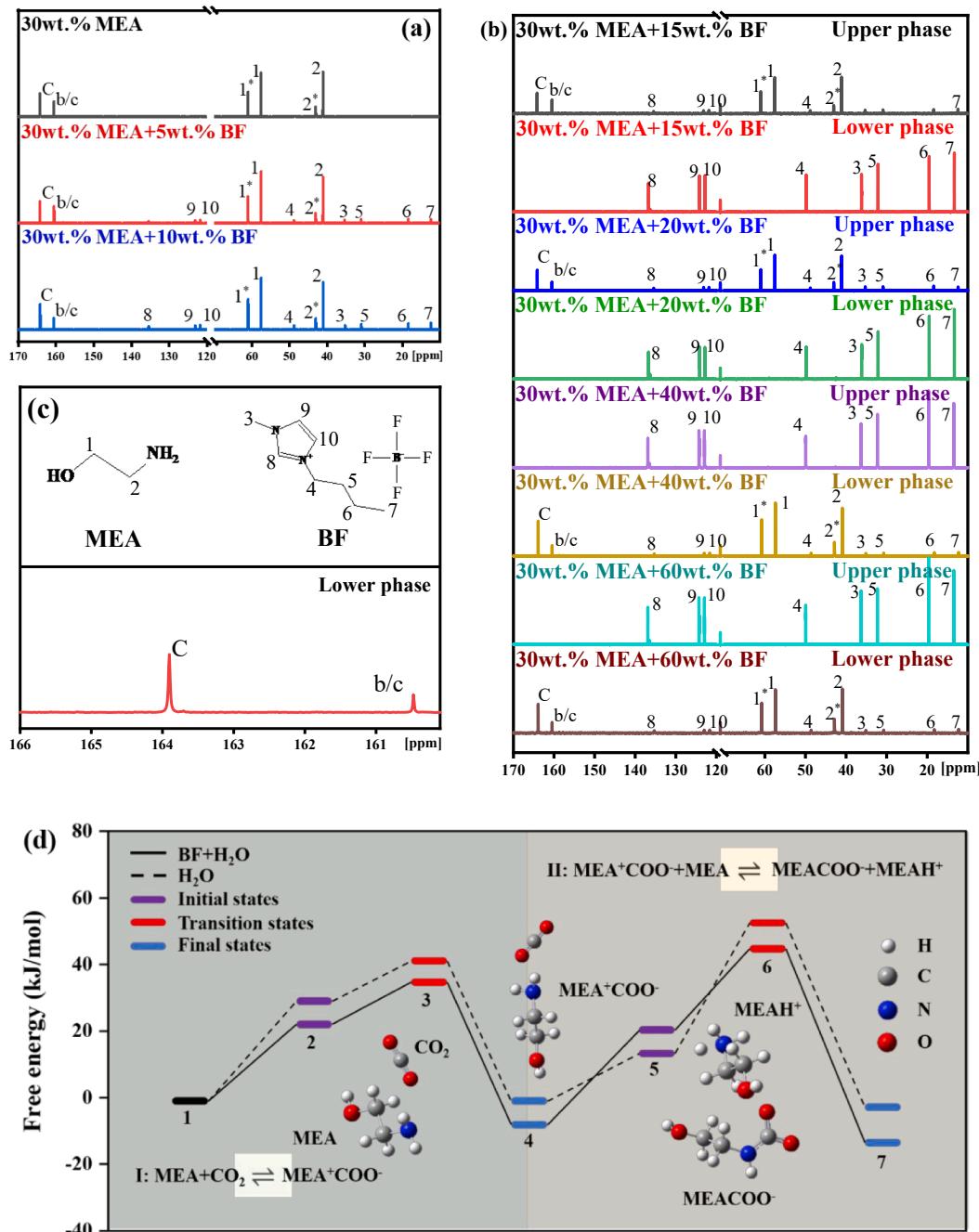


Fig. 4. Analysis of the reaction process of biphasic agents. (a) ¹³C NMR of the solvent without phase separation; (b) ¹³C NMR of the solvent with phase separation; (c) Molecular structure diagram and carbamate (C) and carbonate/bicarbonate (b/c) diagrams; (d) Free energy change diagram of the reaction pathway.

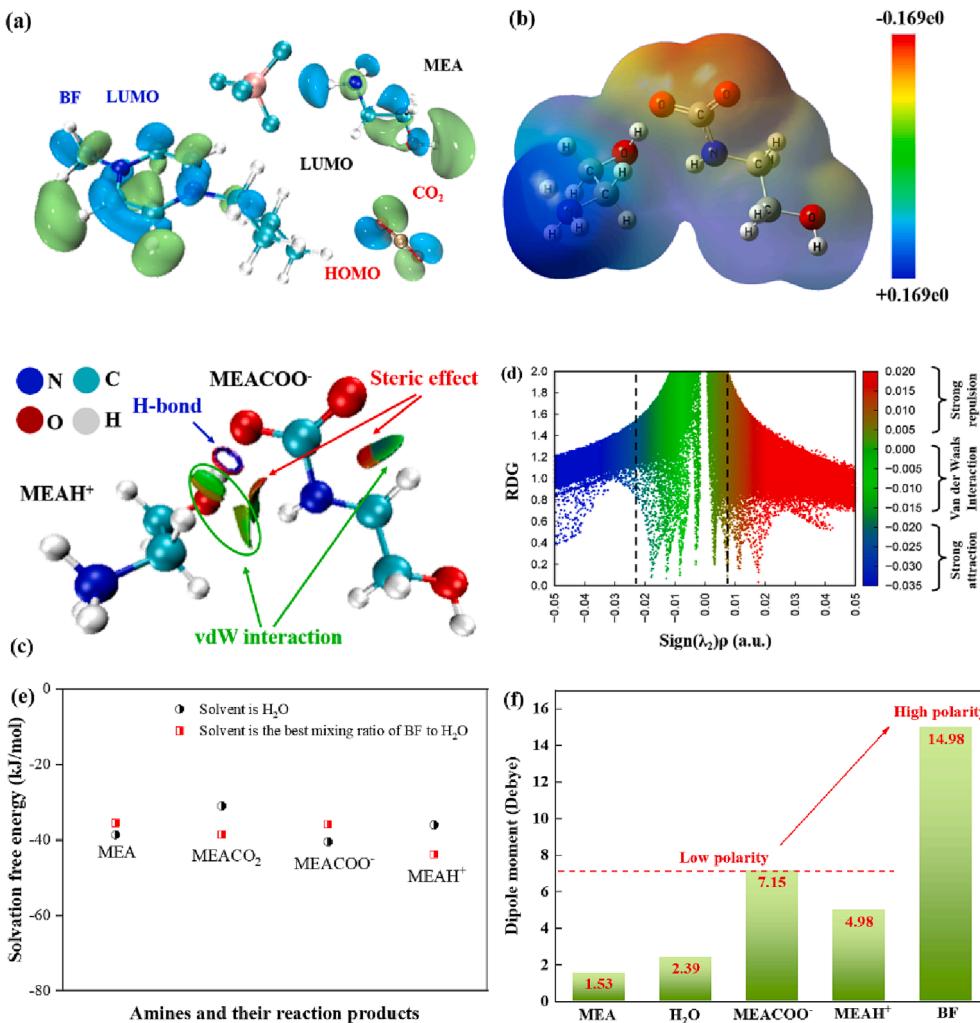


Fig. 5. Intermolecular interactions of biphasic agents. (a) Molecular orbital diagrams; (b) Electrostatic potential of reaction products; (c) Three-dimensional visualization of intermolecular forces of reaction products; (d) Reduced density gradient of reaction products; (e) Free energy of solvation of different substances; (f) Dipole moments of different species.

the amine solution without the phase separation phenomenon, and the chemical shifts of carbon in the MEA and BF structures were clearly observed and did not change significantly as the BF mass fraction was increased to 10 wt%. In addition, CO₂ was mainly present as carbamate and carbonate/bicarbonate after absorption, and Fig. 4(b) showed the ¹³C NMR spectra of each of the upper and lower layers of the mixed amine after phase separation, and a clear difference could be observed. The ¹³C NMR spectra in this paper were all plotted using a 1:1 ratio of internal standards, the interrelationships between peak heights were in general agreement with the integration results calculated by Delta 6.0 and could be used to roughly determine the interrelationships of substance contents. It could be clearly seen that MEA, protonated amines, carbamates and carbonate/bicarbonate were mainly concentrated in one phase, while BF was separately concentrated in the other, so the former and the latter were defined as rich and lean phases, respectively, for differentiation. When the addition amount of BF was 15 wt% and 20 wt%, the upper and lower layers were dominated by rich and lean phases, respectively, and when the addition amount of BF was 40 wt% and 60 wt%, the upper and lower layers were dominated by lean and rich phases, respectively. This was mainly due to the fact that as the CO₂ absorption increased, the density of the rich phase containing the carbamate increased, causing the relative density of the two phases to change and leading to a flip in the position of the two phases. When the concentration of ionic liquid was low, the proportion of amine and water

in the solution was larger, and the density of carbamate after saturation with CO₂ reaction was still low, so it was in the upper phase. As the concentration of ionic liquid increases, the carbamate combines with the remaining aqueous amine solution and the density increased thus the two phases reversed. Therefore, in practical engineering, it just needed to determine the concentration ratio of the solution for solving such problems. It was worth noting that since the ionic liquid was all enriched in the lean phase, it would directly enter the absorption tower for recycling and there was no regeneration loss. In addition, even into the regeneration tower there was no loss problem, on the one hand, the ionic liquid was physically absorbed without chemical reactions, on the other hand, the ionic liquid had a very low saturation vapor pressure, there was no volatility problem.

Due to the solvent effect, the quantum chemical calculation function of Gaussian 09 software was used to investigate the absorption mechanism of the biphasic agent, mainly including the reaction routes and energy consumption. The reaction process of MEA and CO₂ was relatively simple, and it was not difficult to find through Fig. 4(d) that the ionic liquid BF was not directly involved in both reactions, but its presence could effectively reduce the energy barrier of the reaction and accelerate the absorption as a result of the solvent effect of BF, which was consistent with the results in Fig. 3(a). In addition, the presence of solvent effects may weaken the effect of H-bonding on the electron density around the N atom of MEA, making it appear slightly elevated in

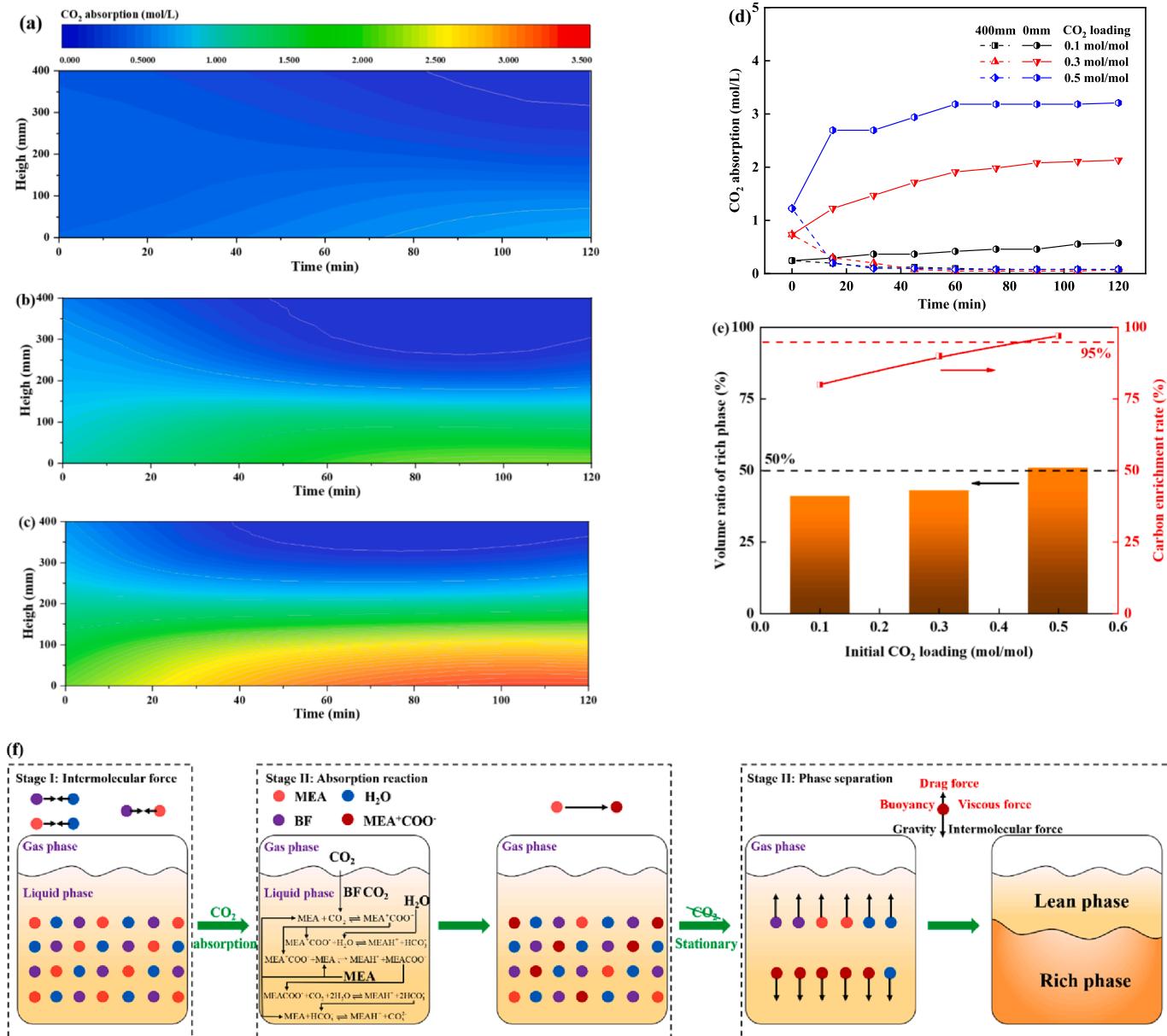


Fig. 6. Phase separation kinetics of 30MEA-40BF. (a) Space-time variation diagram of 30MEA-40BF biphasic agent at CO₂ loading of 0.1 mol CO₂/mol amine; (b) Space-time variation diagram of 30MEA-40BF biphasic agent at CO₂ loading of 0.3 mol CO₂/mol amine; (c) Space-time variation diagram of 30MEA-40BF biphasic agent at CO₂ loading of 0.5 mol CO₂/mol amine; (d) CO₂ in migration trend during phase separation with time; (e) Carbon enrichment rate and splitting volume of 30MEA-40BF; (f) Phase separation kinetic mechanism diagram.

basicity or nucleophilicity, which was beneficial for the reaction II to produce carbamates and protonated amines.

In order to further investigate the intermolecular interactions during the reaction, the molecular structure was visualized in three dimensions based on Gaussian quantum calculations in combination with Multiwfn and VMD. Combining the molecular orbital diagram in Fig. 5(a) and the calculation of the respective orbital energy levels showed that the HOMO orbital of CO₂ (the highest energy level of electron occupied orbital) provided electrons during the reaction, while the LUMO orbital of MEA (the lowest energy level of electron unoccupied orbital) served as the electron acceptor due to its lowest energy difference with the HOMO of CO₂. This was also confirmed by the Electrostatic Potential (ESP) results of the reaction products in Fig. 5(b), in which the N-bonds linked to the CO₂ and the surrounding region showed a more pronounced electronegativity, while the N-bonds linked to the H-bonds and the surrounding region showed a more pronounced electronegativity.

The intermolecular interactions were further explored in conjunction with the non-covalent interactions (NCI) in Fig. 5(c), where the equivalence surfaces of the protonated amine and carbamate ion pairs indicated the dominance of van der Waals forces, and the rest also included some repulsion forces due to the steric effect and attraction forces due to hydrogen bonding. The ion pair reduced density gradient (RDG) in Fig. 5(d) further indicated that the ion pair had a strong van der Waals effect within a certain range of $\text{sign}(\lambda_2)\rho$, and the electronegativity difference between the protonated amine and the carbamate also led to the formation of a strong hydrogen bond. The solubilization free energy of different components in Fig. 5(e) also revealed that the solubility of carbamate in mixed solvents was not as well as in water, and combined with the stronger interaction between carbamate and protonated amine it could be judged that the reaction products had a tendency to dissolve in water. In addition, the dipole moments of the substances in Fig. 5(f) also showed that the dipole moments of MEA, H₂O, MEACOO⁻ and

MEA + were close to each other and were lower than 7.15D, indicating the weak polarity. The dipole moment of the ionic liquid BF reached 14.98D, indicating the high polarity. Combined with the similar compatibility theory it could be judged that the reaction products would preferentially dissolve in water and separate out the BF, as reported by the results of ^{13}C NMR in Fig. 4(b). The amount of reaction products produced would also determine whether the positions of the lean and rich phases were flipped through the form of the rich phase density.

3.3. Dynamics analysis of phase separation for MEA-BF solvent

In order to simulate the phase separation process more intuitively in practice, the kinetic characteristics of phase separation of biphasic agents at 303.15 K with different CO_2 loadings (0.1, 0.3 and 0.5 mol $\text{CO}_2/\text{mol amine}$) were investigated with the scaled-up phase separator shown in Fig. S2. The CO_2 loadings of the biphasic agent in the phase separator at different times and spaces were plotted as Fig. 6(a)–(c). Where the color changed with the amount of CO_2 absorption and the equivalents between the different colors indicated the rate of CO_2 absorption change. From the figure, it was easy to find that the CO_2 loading in the biphasic agent showed different contour patterns with the change of height, and the contours gradually stabilized with time. And with the increasing initial CO_2 loading, the stabilization time was greatly reduced and the volume of the rich phase was maintained at about 50%, as shown in Fig. 6(c) and Fig. 6(e). From the results in Fig. 6(e), it could also be obtained that the carbon enrichment rate of the biphasic agent with CO_2 loading of 0.5 mol $\text{CO}_2/\text{mol amine}$ could reach more than 95%, which greatly improved the phase separation efficiency. The results in Fig. 6(d) also indicated that the phase separation rate was very weak when the CO_2 loading was low, and a CO_2 loading of 0.5 mol $\text{CO}_2/\text{mol amine}$ required less than 15 mins to achieve a very good separation. And with the increase of CO_2 absorption, the rate of phase separation would rapidly increase and the time required would rapidly decrease, and when the absorption increased to 0.58 mol $\text{CO}_2/\text{mol amine}$ at saturation, the phase separation time would not exceed 10 mins, which was consistent with the previous results.

In addition, it was found that the formation of phase separation was not instantaneous, but formed by the transfer and gradual fusion of many bubble-like clusters, and the rate of transfer tended to decrease with time, with the transfer of the phase separation interface also becoming more and more obvious. It was inferred from the experimental results that the components of the solution were temporarily in a more stable state at the beginning of the reaction, as shown in the first stage of Fig. 6(f). As the reaction proceeds the carbamate was formed, which had a strong affinity for water and was almost insoluble in ionic liquids (shown in Fig. 5(e) and Fig. 5(f)), causing a significant destabilization of the intermolecular interaction relationship in the system, as shown in the second stage in Fig. 6(f). The formation of initial agglomerates was caused by the incompatibility of substances with different polarities driven by intermolecular forces. The aqueous solution containing carbamate gradually moved downward, while the ionic liquid carried part of the water upward and thus the phase separation occurred. In the separation process, the rich phase was mainly affected by gravity and intermolecular forces, while the lean phase was mainly affected by drag force and buoyancy force, and the influence of viscous force was weak, as shown in the third stage of Fig. 6(f). This also indicated that as soon as the amount of carbamate produced by the reaction of MEA with CO_2 reached a certain amount, meaning that the CO_2 loading was increasing, the intermolecular forces between the reaction products and BF would increase and thus lead to the occurrence of phase separation.

4. Conclusions

The results showed that the MEA-BF-H₂O system could simultaneously have the advantages of low viscosity, low density, low Henry coefficient and high CO_2 diffusion rate when the ionic liquid BF was

added at 40 wt%, and the CO_2 saturation absorption, regeneration rate and outlet methane purity could reach 0.581 mol $\text{CO}_2/\text{mol amine}$, 56.46% and 100%, respectively, with very excellent biogas upgrading effect. In addition, the mixed system at this addition amount was able to achieve rapid phase separation of the rich amine in approximately 5 mins, where the results combined with amplified phase separator and ^{13}C NMR revealed that the separation rate of the recyclable ionic liquid, carbon enrichment rate and rich phase volume could reach 100%, around 96% and around 50% respectively, and its total regeneration energy consumption was reduced by 43.19% compared to the aqueous 30 wt% MEA, providing excellent phase separation performance.

In conclusion, the MEA-BF-H₂O system could make up for the disadvantages of each while ensuring the advantages of amines and ionic liquids remaining unchanged, achieving rapid CO_2 capture, high purity preparation of biomethane, low energy regeneration and recycling of ionic liquid in biogas upgrading process, with very excellent performance in biogas upgrading.

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

All data are in the manuscript

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.142296>.

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