

Phase separation characteristics in biphasic solvents based on mutually miscible amines for energy efficient CO₂ capture

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Abstract—One of the challenges with regard to the aqueous amine-based CO₂ capture process is the considerable energy requirement for solvent regeneration. To overcome this challenge, a biphasic solvent was employed in this study. Here, the phase separation behavior of amine blends depending on the characteristic structures of the solvent component was investigated using a turbidity measurement apparatus. Amines were classified as (1) primary/secondary amines or tertiary/sterically hindered amines depending on the CO₂ reaction species, such as carbamate and bicarbonate (2) alkyl and alkanolamines, depending on the presence of a hydroxyl group, (3) chain and cyclic amines, and (4) mono- and polyamines depending on the molecular structure. Easy phase separation occurred in solvent blends containing polyamines such as DETA (diethylenetriamine), TETA (triethylenetetramine), and DEEA (2-(diethylamino) ethanol). The types with the greatest potential were the DETA/DEEA blended solvents. A phase separation could be determined based on the difference in the reaction rate with CO₂ and the low solubility between the carbamate species of DETA and DEEA.

Keywords: Biphasic Solvents, Solvent Screening, CO₂ Capture, Regeneration, DEEA, DETA

INTRODUCTION

Thus far, the absorption process, which uses an aqueous amine solvent, is the most mature technology for CO₂ capture from post-combustion flue gases. Although monoethanolamine (MEA)-based CO₂ capture is known to be effective, it requires a considerable amount of energy during the solvent regeneration step due to the large latent heat of water. It has been reported that nearly 30% of the energy of a power plant is diverted to the CO₂ capture process [1]. Some researchers have made efforts to improve the carbon capture capacity and to reduce the energy requirement for the regeneration of aqueous amine solvents. Among these efforts, phase-change absorbents (biphasic solvents) have received increasing amounts of attention.

The CO₂ capture process using a biphasic solvent features liquid-liquid phase separation of the solvent upon CO₂ absorption. Due to the difference in the density, the loaded CO₂ is enriched in the bottom phase and lean in the top phase. The CO₂-lean phase is recycled to the absorption column, and only the CO₂-rich phase is transferred to the stripping column for regeneration [2]. A schematic diagram of the CO₂ capture process with biphasic solvents is shown in Fig. 1. In this process, the CO₂ in flue gas is absorbed by a solvent. The CO₂-rich solvent from the absorption column is sent to

a decanter in which two aqueous phases are formed. The CO₂-rich top phase is preheated in a heat exchanger by the hot, regenerated solvent from the stripping column and then fed into the stripping column. The regenerated solvent from the stripper as well as the lean solution from the decanter are mixed and recycled to the absorber. This process reduces the amount of solvent required for CO₂ stripping, reducing the energy requirement for regeneration.

There have been several studies of the CO₂ capture process using biphasic solvents. The IFP (French Institute of Petroleum) Energies Nouvelles disclosed N,N-dimethylbenzylamine (DMBzA) and N,N,N',N'-tetramethyl-1,6-hexane-diamine (TMHDA) as DMXTM solvents that can form two liquid phases during CO₂ absorption [3,4]. However, these solvents have several disadvantages, such as a slow absorption rate. Bruder and Svendsen reported an aqueous biphasic solvent composed of 2-(diethylamino) ethanol (DEEA) and 3-(methylamino) propylamine (MAPA). This solvent can increase the cyclic capacity and improve the equilibrium curves [5]. A similar study of the CO₂ capture process was carried out by Xu et al. involving a blend of 1,4-butanediamine (BDA) and DEEA. They found that 2M BDA blended with 4M DEEA had higher cyclic capacity and loading than 5M MEA [6].

For the phase separation of absorbents, a thermal-induced miscibility gap upon modest heating was also used, known as the thermomorphic biphasic solvent (TBS) system. In TBS systems, aqueous partially miscible solvents, also referred to as lipophilic amines, exhibit deep regeneration at temperatures well below the solvent boiling point. Due to the limited aqueous solubility, a thermomorphic miscibility gap can be induced during regeneration [7].

Ye et al. screened approximately fifty aqueous amine-based sol-

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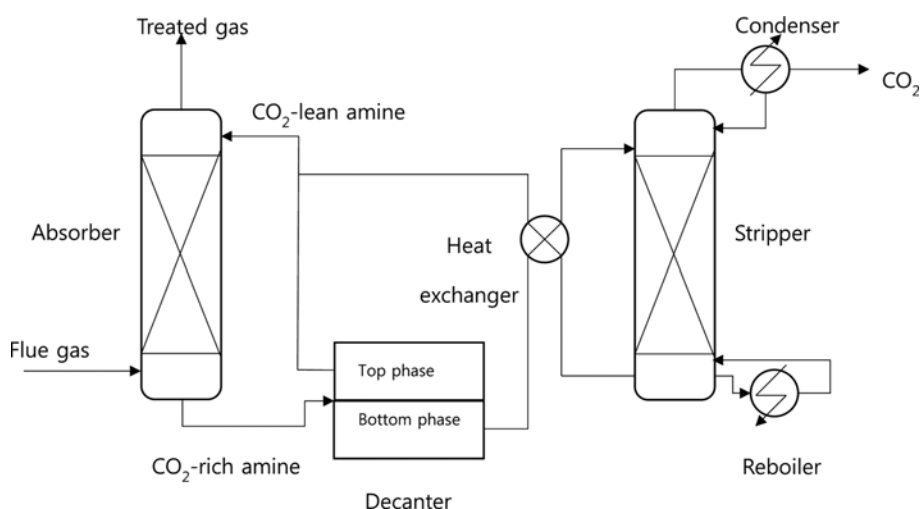


Fig. 1. Schematic diagram of CO₂ capture process by biphasic solvents.

vent blends of absorption accelerators A and regeneration promoter B, such as monoamine+DMCA, monoamine+DEEA, polyamine+DMCA, and polyamine+DEEA. They reported that a biphasic solvent blend with an accelerator A containing 3-4 N and 4-6 C atoms was favorable for obtaining both high absorption capacity and desorption pressure levels. They suggested a solvent blend composed of TETA and DEEA as the most desirable type [8].

While most of these studies concentrated on the absorption performance of biphasic solvents, few have focused on the characteristics of biphasic formation. In this study, a screening guide for the development of an aqueous amine-based biphasic solvent is suggested. Following this guide, several amine combinations were selected and their phase separation characteristics, in this case the phase separation time, phase volume ratio, and CO₂ concentration in each phase were investigated.

EXPERIMENTAL

1. Selection of Amine Components

There are three categories for biphasic amine solvents for CO₂

capture.

- (1) Aqueous amine+Aqueous amine (mixed aqueous amines)
- (2) Lipophilic amine+Aqueous amine (thermomorphic)
- (3) Alkanolamine+Ionic liquid

Considering the feasibility and cost of the CO₂ capture process, we selected mixed aqueous amines in this study. The biphasic solvents used in this study are represented as an A-B-H₂O system, in which each component is fully miscible. Component A possesses at least one primary or secondary amino group. It functions as an absorption accelerator due to its ability to form a carbamate with CO₂. Component B has a tertiary amino group. It has a high CO₂ loading capacity due to its ability to form bicarbonate with CO₂. Component B can function as a regeneration promoter.

Components A and B have the following criteria:

- (1) Moderate vapor pressure
- (2) At least one amine with a loading value for CO₂ of more than 0.5 (mol CO₂/mol amine)
- (3) Miscible with water in order to form a homogeneous solvent mixture under low loading
- (4) A high CO₂ distribution difference between the top and bot-

Table 1. Structure and properties of amines used in this study

			Compound	Molecular weight	Boiling point (°C)	Vapor pressure (mmHg)
Alkylamine	Monoamine	Secondary	DPA	101.19	110	20.1 (25 °C)
		Tertiary	TEA	101.19	88.6-89.8	51.7-63.8
	Polyamine	Primary	DETA	103.17	204.1	0.08
			TETA	146.24	266.6	<0.01
		Tertiary	TMPDA	130.23	NA	145-146
Alkanolamine	Monoamine	Primary	MEA	75.11	158.1	0.53
		Secondary	DEA	105.14	271	<0.01
		Tertiary	DEEA	117.19	161.1	0.75
	Steric hindered	Primary	AMP	89.14	165	<1 (25 °C)

DPA (dipropylamine), TEA (triethylamine), DETA (diethylenetriamine), TETA (triethylenetetraamine), TMPDA (N,N,N',N'-tetramethyl-1,3-propanediamine), MEA (monoethanolamine), DEA (diethanolamine), DEEA (2-(diethylamino)ethanol), AMP (2-amino-2-methyl-1-propanol)

tom phases

(5) A high phase volume ratio of the top to bottom phase. The volume of the bottom phase must be as low as possible.

The preliminary amine combinations for biphasic solvents are shown in Table 1. Considering the operating temperature in the absorber and the vapor pressure of the amine, we concluded that primary and secondary monoalkylamines except for dipropylamine (DPA) are not adequate for component A. Most tertiary monoalkylamines are not suitable for biphasic solvents due to their low water solubility and high vapor pressure.

The poly-alkylamines which contain a primary amino group are 1,4-diaminobutane (BDA), diethylenetriamine (DETA) and triethylenetetramine (TETA). Because a biphasic solvent using BDA has already been developed, this was excluded [6]. The poly-alkanolamines containing a tertiary amino group are 2-(diethylamino) ethanol (DEEA), N-methyl-diethanolamine (MDEA), and triethanolamine (TEA). For easy phase separation, DEEA was used as component B because it is less hydrophilic than the others. The final combinations for the biphasic solvents are shown in Table 2.

The amines used in this study were MEA (>99 wt%), TEA (>99 wt%), DEEA (99.5 wt%), DETA (>99.0 wt%), AMP (>95 wt%), TMPDA (>99 wt%) and DPA (>99 wt%). All were from Sigma-Aldrich and prepared with deionized water without further purification.

All the solvents tested in this study were composed of two amines (amine A and amine B) and water. Biphasic solvents were prepared by mixing amine A and amine B with deionized water. Amines A and B function as a rate accelerator and a CO₂ absorption capacity enhancer, respectively. The total amine concentration was kept at 5.5 mol/L, which is similar to that of conventional MEA (5 mol/L

MEA). The water content in the biphasic solvents was very important for easy phase separation; therefore, the water content was below 45 wt% for all the solvents. The molar ratio of A to B was kept at 2.5 : 3.0 for all solvents.

2. Experimental Procedure

The screening experiments of the absorption by biphasic solvents were carried out in 250 mL glass bubble columns with 100 mL of the prepared solvents at 50 °C. Pure CO₂ gas at a flow rate of 100 mL/min controlled with a mass flow controller was bubbled through the column at atmospheric pressure. Such a low gas flow rate into the bubble column is required for accurate observations of the interface between the top and bottom phases, as the interface can be broken by gas bubbling. The bubble column was maintained at a constant operating temperature by a water-conducting jacket. To avoid water and amine loss, the condenser was cooled by 4 °C. After the phase separation step began, the samples in both phases were collected at 1, 2, 3, and 4 hr.

The CO₂ loadings (g CO₂/L solvent or mol CO₂/L solvent) in each phase were determined by titration with a hydrochloric acid (HCl) solution and the blended amine compositions were determined by GC (Agilent Technologies 7890).

RESULTS AND DISCUSSION

As shown in Table 3, we observed three different types of phase separation behavior in this study. Type I blended amines maintained a single phase during CO₂ absorption. Type II blended amines underwent a transition from an initially single phase to two immiscible phases after a critical CO₂ concentration was reached. In type III, a solid phase was formed after CO₂ absorption. Representative

Table 2. Solvent combination for biphasic absorbents: (a) Carbamate forming amine+bicarbonate forming amine, (b) Bicarbonate forming amine+bicarbonate forming amine

(a)				
		Primary alkanolamine	Primary polyamine	
Secondary and tertiary alkylamine		MEA/TEA	DETA/TEA, DET/DPA	
Tertiary alkanolamine		MEA/DEEA	DETA/DEEA	
Steric hindered alkanolamine		MEA/AMP	DETA/AMP	
Secondary polyamine		MEA/TMPDA	DETA/TMPDA	
(b)				
	Tertiary alkylamine	Tertiary alkanolamine	Steric hindered alkanolamine	Tertiary polyamine
Tertiary alkylamine	-	DEEA/TEA	AMP/TEA	TMPDA/TEA
Tertiary alkanolamine	-	-	AMP/DEEA	TMPDA/DEEA
Steric hindered alkanolamine	-	-	-	TMPDA/AMP
Tertiary polyamine	-	-	-	-

Table 3. Type of phase transition behavior in several blended amines

Type	Description	Blended amines
I	Single phase→single phase	MEA/TEA, MEA/DEEA, MEA/AMP, DETA/TEA, DETA/AMP, DEEA/TEA, AMP/TEA, AMP/DEEA, TMPDA/TEA
II	Single phase→2 phases (aqueous biphasic)	DETA/DEEA, TMPDA/DEEA, MEA/TMPDA
III	Single phase or 2 phases→2 phases (liquid-solid phase)	DETA/DPA, TMPDA/AMP

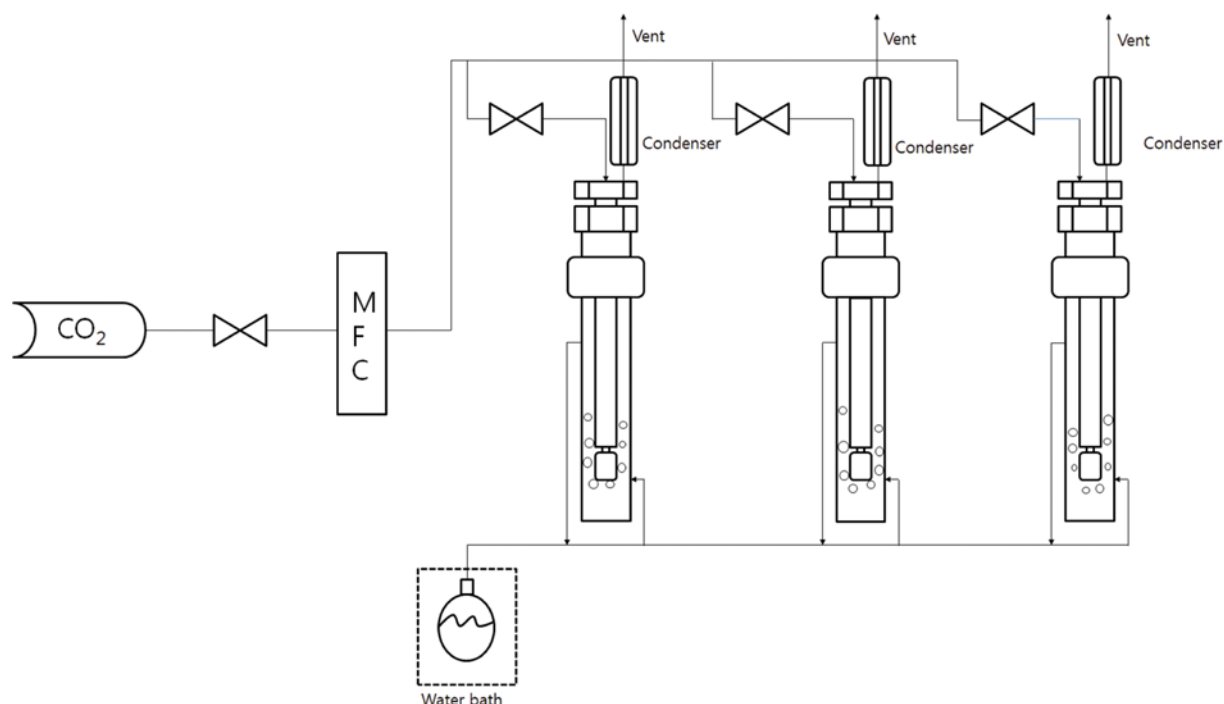


Fig. 2. Solvent screening apparatus.

	20 min	90min	120min	remark
Type II (DETA/DEEA)				Total amine concentration=5.5mol/L Mol of DETA:mol of DEEA=2.5:3.0
Type III (TMPDA/AMP)				Total amine concentration=5.5mol/L Mol of TMPDA:mol of AMP=2.5:3.0

Fig. 3. Phase separation behavior in each type solvents after CO₂ absorption.

photographs of the type II and III before and after CO₂ absorption are shown in Fig. 3.

Type I solvents are not suitable as biphasic solvents because the flow rate of the solvent required for CO₂ stripping cannot be reduced. During the progress of solvent screening, TEA was considered as component B because it is less hydrophilic. However, TEA was not effective for phase separation due to its high vapor pressure.

In Type III solvents, carbamate was found in a crystalline form after bubbling CO₂ through a glass column. Reports of precipitation by AMP carbamate are available in the literature [9,10]. The formation of solid precipitates in the absorber can plug the packing in the absorption and can cause fouling in heat exchangers [8]. The solid precipitate was also observed in the DETA and DPA blended solvent during CO₂ absorption.

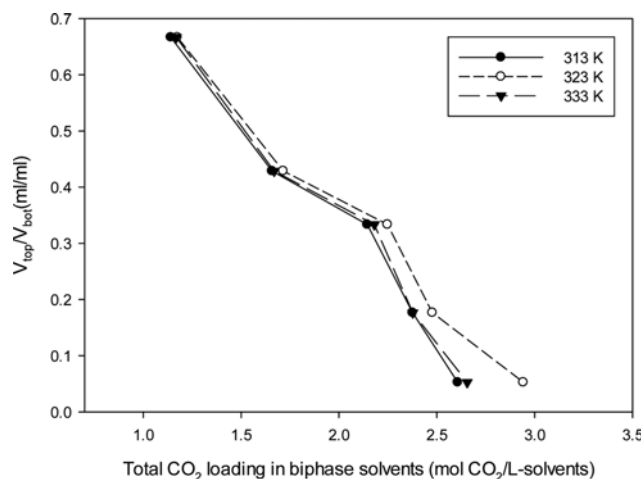


Fig. 4. Phase volume ratio of top to bottom phase with total CO_2 loading and operating temperature. (DEEA : DETA=2.5 mol : 3.0 mol).

In the type II solvents, the DEEA/DEEA blended amine showed the clearest biphasic formation during CO_2 absorption. Fig. 4 shows the phase volume ratio of top to bottom with the total CO_2 loading and the operating temperature. The volumetric portions of the bottom phase increased during CO_2 absorption but did not depend on the operating temperature. The change in the volumetric portions over the total CO_2 loading can be explained by the difference in their reaction rates and the limited solubility of DEEA in the DETA carbamate. Because DETA contains a primary amine group and DEEA contains a tertiary amine group, the reaction rate of DETA with CO_2 is faster than that of DEEA. At the initial time of absorption, DETA carbamates are formed. Due to the limited solubility of DEEA in the reaction products of DETA carbamate and its comparatively low density, phase separation occurred and the DEEA was transferred into the upper phase. At lower loadings, the DETA concentration increased in the lower phase and decreased in the upper phase, while the DEEA concentration increased in the upper phase and decreased in the lower phase. When DETA is sat-

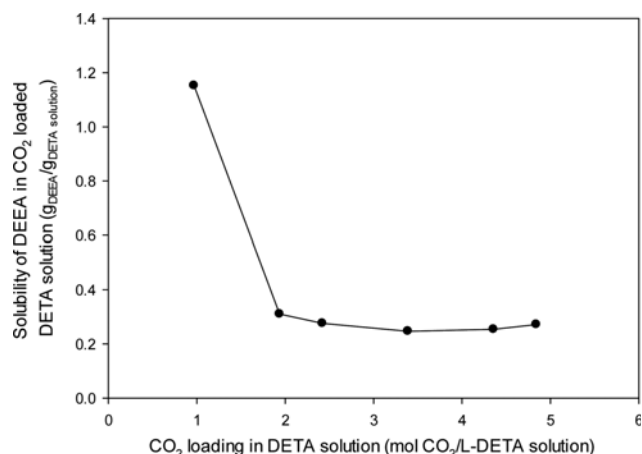


Fig. 5. Solubility of DEEA in CO_2 loaded 3.0 mol/L DETA aqueous solution at 313 K.

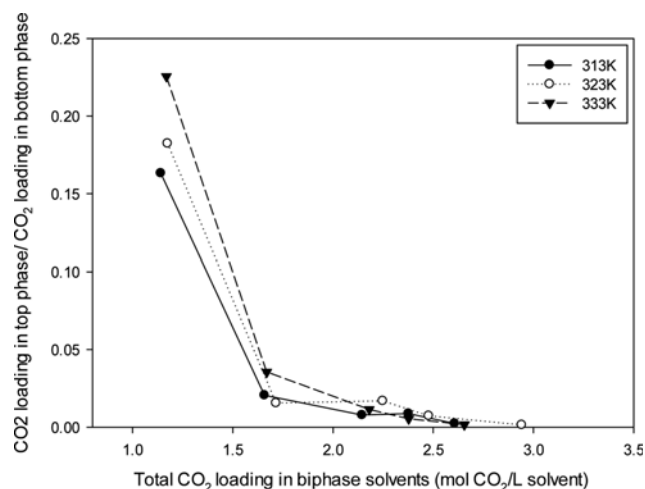


Fig. 6. CO_2 distribution in each phase after CO_2 absorption (Total amine concentration=5.5 mol/L, mol of DEEA : mol of DETA=2.5 : 3.0).

urated with CO_2 , the DEEA in the top phase begins to move into the bottom phase. The DEEA concentration decreases in the upper phase, while its concentration increases in the bottom phase. Therefore, the amount of amine in the bottom phase gradually increases with the loading value.

The phase separation mechanism described above can be verified by measuring the DEEA solubility in a CO_2 -loaded DETA solution, as shown in Fig. 5. In the DEEA solubility experiments, 3.0 mol/L DETA solutions were prepared with various CO_2 loadings by feeding CO_2 into the solutions. DEEA was then added to those solutions at 313 K. The measurement results of the solubility show that DEEA was fully miscible with the DETA solution at CO_2 loadings lower than 1 mol CO_2 /LDETA solution, while two phases formed at loadings greater than 1 mol CO_2 /LDETA solution.

As shown in Fig. 6, the amount of CO_2 distributed into the top phase was decreased through absorption. This result can be also explained by the previous mechanism.

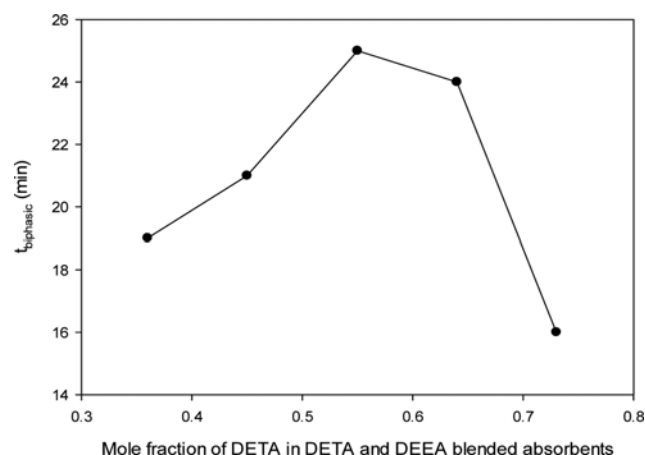


Fig. 7. Effect of amine blending ratio on the beginning time of phase separation (Total amine concentration=5.5 mol/L, Operating temperature=50 °C).

The effect of the amine blending ratio on the start time of phase separation is presented in Fig. 7. The total mole number of amines was maintained constant during the change in the mole fraction of DETA. The start time of phase separation remained proportional to the DETA composition in blended amine solvents up to 0.5 mole fraction of DETA in total amine, whereas the start time of phase separation decreased with the DETA composition in the range exceeding 0.5 mole fraction of DETA. At low CO₂ loading, DETA preferentially reacts with CO₂ and DETA carbamates move into the bottom phase until the full loading value is reached. Accordingly, the start time of phase separation is proportional to the composition of DETA. However, in the range exceeding more than 0.5 mole fraction of DETA, the start time of phase separation was decreased due to the solubility limitation of DEEA for DETA carbamate. The solubility limitation of DEEA in the reaction products of amine and CO₂ has already reported by Xu et al. In CO₂ absorption by a blend of BDA and DEEA, they reported that the solubility of DEEA in the reaction products of BDA and CO₂ is limited and DEEA is a reactant at high loadings [6].

TMPDA/DEEA blended solvents also showed biphasic formation during CO₂ absorption. DETA is a polyamine with two primary amine groups and one secondary amine group, while TMPDA has the tertiary amine groups only. Because the reaction rates of TMPDA and DEEA with CO₂ are slow, their blended solvent took a considerable amount of time to form a biphasic compared to DETA and DEEA. At a ratio of 2:2.5 (mol:mol) TMPDA+DEEA, it took 6.5 hours to transit one phase into two phases. For a fast reaction with CO₂, a small amount of piperazine was added to the TMPDA+DEEA blended solvents. Due to the enhancement of the reaction rate, phase separation was immediate during CO₂ absorption. It is presumed that most reaction products of piperazine and CO₂ and DEEAH⁺ are in the bottom phase and that TMPDA is in the top phase. According to results from the CO₂ absorption experiments in this study, DETA+DEEA, TMPDA+DEEA and MEA+TMPDA showed a transition from a single phase to two phases. Among these, DETA+DEEA exhibited excellent phase separation behavior and a high CO₂ loading capacity.

CONCLUSION

We investigated the phase separation characteristics of several

biphasic solvents. Although DETA/DEEA, TMPDA/DEEA and MEA/TMPDA showed a transition from a single phase to two phases, the biphasic solvent composed of DETA and DEEA was the most promising blend in this screening study. After absorption, most of the CO₂ was concentrated in the bottom phase. Biphasic formation with CO₂ loading can be explained by the different reaction rates of DETA and DEEA with CO₂ and the solubility limit of the DEEA with regard to DETA carbamate. This explanation can be verified by measuring the DEEA solubility in a CO₂-loaded DETA solution.

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REFERENCES

1. S. Seo, L. D. Simoni, M. Ma, M. A. Desilva, Y. Huang, M. A. Stadtherr and J. F. Brennecke, *Energy Fuels*, **28**, 5968 (2014).
2. S. Zheng, M. Tao, Q. Liu, L. Ning, Y. He and Y. Shi, *Environ. Sci. Technol.*, **48**, 8905 (2014).
3. M. Aleixo, M. Prigent, A. Gilbert, F. Porcheron, I. Mokbel, J. Jose and M. Jacquin, *Energy Procedia*, **4**, 148 (2011).
4. L. Raynal, P. Alix, P.-A. Bouillon, A. Gomez, M. le F. de Nailly, M. Jacquin, J. Kittel, A. di Lella, P. Mougin and J. Trapy, *Energy Procedia*, **4**, 779 (2011).
5. P. Bruder and H. F. Svendsen, *Energy Procedia*, **23**, 45 (2012).
6. Z. Xu, S. Wang and C. Chen, *Int. J. Greenh. Gas Control*, **16**, 107 (2013).
7. J. Zhang, Y. Qiao and D. W. Agar, *Chem. Eng. Res. Des.*, **90**, 743 (2012).
8. Q. Ye, X. Wang and Y. Lu, *Int. J. Greenh. Gas Control*, **39**, 205 (2015).
9. M. Hasib-ur-Rahman, M. Siaz and F. Larachi, *Int. J. Greenh. Gas Control*, **6**, 246 (2012).
10. M. Hasib-ur-Rahman and F. Larachi, *Environ. Sci. Technol.*, **46**, 11443 (2012).