CO₂ Absorption by Biphasic Solvents: Comparison with Lower Phase Alone

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Abstract — CO₂ Absorption by Biphasic Solvents: Comparison with Lower Phase Alone — The mixtures of 2 M 1,4-butanediamine (BDA) and 4 M 2-(diethylamino)-ethanol (DEEA) have been found to be promising biphasic solvents. This work identifies the composition of the lower phase using a DX-120 Ion Chromatograph (IC) and a Metrohm 809 Titrandp auto titrator. The cyclic capacitivities, cyclic loadings and reaction products of the biphasic solvent are compared with those of the aqueous solution with the same amine concentration as the lower phase of the biphasic solvent at the rich loading (2B4D) L using a fast screening facility and a JNM ECA-600 Nuclear Magnetic Resonance spectrometer (NMR). Their absorption rates at different loadings are also investigated using a Wetted Wall Column (WWC). The results show that the cyclic capacity and cyclic loading of (2B4D) L are almost the same as those of 2B4D. The absorption rate of (2B4D) L is higher than 2B4D at all the 3 tested loadings, except for the fresh solutions at CO₂ pressure lower than 10 kPa. NMR results show that the reaction products of (2B4D) L had more BDA bicarbamate, less BDA and less BDA carbamate than 2B4D. The CO₂ reaction products of (2B4D) L had twice as much carbonate/bicarbonate as with 2B4D and less BDA carbamate.
INTRODUCTION

Over the last decades, amine gas sweetening has become a proven technology for the CO₂ capture from natural gas. In recent years, amine based absorption has also been widely investigated for CO₂ capture in power plant, due to its high flexibility and easy retrofit for existing power plant (Rochelle, 2009). Development of solvents with high efficiency is regarded as one of the most crucial issues for CO₂ absorption. Many solvents, such as monoethanolamine (MEA), methyldiethanolamine (MDEA), diethanolamine (DEA) and piperazine (PZ), have been applied to capture CO₂ (Bishnoi and Rochelle, 2002; Derks and Dijkstra, 2005; Rinker et al., 2000; Rinker and Ashour, 2000). However, this absorption-desorption process always requires lots of energy and high operation costs during solvent regeneration. Therefore, to minimize the energy penalty is of great importance for this absorption-desorption system.

Recent years, some novel concepts, such as DMXTM (Raynal et al., 2011) and lipophilic amine solvents (Zhang X., 2007), have been proposed for the improvement of the energy performance. Zhang J. et al. (2011) did screening tests of dipropylamine (DPA), dimethylethylcyclohexylamine (DMCA) and other solvents. Tan (2010) studied the kinetics and thermodynamics of DPA and DMCA blend and found that the cyclic loading of this solvent can reach 0.7 mol CO₂/mol amine. The precipitation of the solvent at high loading, however, is still a challenge for this system. Raynal et al. (2011) explained the DMXTM process, which, according to their simulations, could remarkably reduce the reboiler heat duty to 2.3 GJ/t CO₂. Rojey et al. (2009) found that some solvents with special structures can separate into two liquid phases after absorption, but they did not give the particular structures. Hu (2009) pointed out that biphasic solvents should consist of several compounds, including at least one activator A and one solvent B, and that the mixture composition should be 20% A plus 80% B. However, Hu (2009) did not give the exact amines in the solvents. Bruder and Svendsen (2011) found that a blend of 5 M DEEA and 2 M MAPA separated into two phases after CO₂ absorption, with a cyclic loading higher than that of 5 M MEA. The lower phase, however, was found to be viscous, which affected the transition of the lower phase to the stripper.

Cyclic capacity ΔR, expressed as either \( C_{\text{amine}} \) or \( R_{\text{abs}} - R_{\text{des}} \), is an important characteristic of the solvent, where \( C_{\text{amine}} \) is the amine concentration, \( R_{\text{abs}} \) and \( R_{\text{des}} \) are the CO₂ concentrations in terms of moles per kilogram after absorption and desorption; \( z_{\text{rich}} \) and \( z_{\text{lean}} \) are rich and lean loading of the solvent, the difference of which is shown as cyclic loading, \( \Delta z \). Cyclic efficiency, \( \theta \), is the result of \( \Delta z \) divided by \( z_{\text{rich}} \). A promising solvent should have relatively higher cyclic capacity, cyclic loading and cyclic efficiency (Aronu et al., 2011).

About 30 solvents with various compositions, including solutions with Low Critical Solution Temperature (LCST) and other potential biphasic solvents, were screened in our previous research (Xu et al., 2012a,b, 2013a,b,c). Some of these biphasic solvents, such as 5 M TEA and 2 M BDA blended with 4 M DEEA, have been proven to have higher cyclic capacities, cyclic loadings or absorption rates than traditional 5 M MEA. Moreover, the aqueous solution of 2 M BDA mixed with 4 M DEEA (simplified as 2B4D hereafter) was found to have the best performance among the selected solvents, with 46% higher cyclic loading, 48% higher cyclic capacity and 11% higher cyclic efficiency than 5 M MEA, which will reduce the sensible heat requirement during regeneration (Svendsen et al., 2011).

It was found that the solution of 2B4D became two phases after CO₂ absorption using the fast screening facility on the absorption mode, with 97.4% of CO₂ existing in the lower phase and a total loading of 0.505 mol CO₂/mol amine. The weight percentages of the upper and lower phases after absorption on the absorption mode were 21.79% and 78.21%, respectively. The screening facility will be described in the experimental section. The amine and CO₂ distributions in the two phases were analyzed by IC in the previous studies. It was confirmed that the biphasic solvent separation is due to the fast reaction rate of BDA with CO₂ and the limited solubility of DEEA in the reaction products of BDA with CO₂. The reaction products of BDA in the two phases were then analyzed. The products was mainly BDA carbamate in the upper phase, while in the lower phase, at a total loading of 0.446 mol/mol amine, the mole fractions of BDA, BDA carbamate and BDA bicarbamate were 16.8%, 55.8% and 27.4% respectively (Xu et al., 2013c). Since most of the CO₂ absorbed existed in the lower phase after absorption, comparison of the alone lower phase and biphasic solvent is necessary to decide which one will be more efficient.

This paper will identify the composition of 2B4D lower phase after absorption. Then, the absorption and desorption properties of the alone lower phase of 2B4D (simplified as (2B4D)\text{l} hereafter), which has the same amine concentration as the 2B4D lower phase at rich loading, will be measured and compared with 2B4D. The absorption rates of 2B4D and (2B4D)\text{l} at different loadings will be compared with WWC. The reaction products of (2B4D)\text{l} with CO₂ during absorption will also be measured by NMR and compared with those of 2B4D.
1 EXPERIMENTAL

The chemicals used in this work, BDA (≥98 wt%), DEEA (≥99 wt%), dioxane (≥99.9 wt%) and D$_2$O (≥99.96 wt%) NaOH (≥96 wt%) from Aladdin Reagent Company, and CO$_2$ (≥99.9% pure), SO$_2$ (1.51% vol%, N$_2$ balanced) and N$_2$ (≥99.99% pure) from Beijing Huayuan Gas Company were used without further purification. Distilled deionized water was used for preparing the solutions. The amine concentrations were determined by titration against 0.2 N H$_2$SO$_4$ using a Metrohm 809 Titrando auto titrator.

The BDA and DEEA structures are shown Figure 1.

The absorption and desorption capacities, and the rich and lean loadings were measured using a fast screening facility, and the loadings were confirmed by the titration method. The absorption experiments were conducted at 40°C with the desorption at 90°C at atmospheric pressure. On “absorption mode”, CO$_2$ and N$_2$, controlled by mass flow controller, were used to simulate the flue gas with 12% of CO$_2$ in terms of volume. The total gas flow rate was 463 mL/min. The simulated flue gas went through the gas mixture first to mix intensively, and then to the reactor, which was made of glass and had a volume of about 150 mL. After reaction with solvent, the gas went to condenser, which was circulated by 3°C water. The condensed water went back to the reactor to avoid water losses, and then the acid washing, in case that amine vapor mixed with simulated gas and resulted in measurement error in IR CO$_2$ analyzer. After being dried by anhydrous calcium chloride, CO$_2$ concentration of the gas was measured by the IR CO$_2$ analyzer. Equilibrium was assumed to be reached when the outlet CO$_2$ concentration reached 12%. On “desorption mode”, N$_2$ was used to sweep the desorbed CO$_2$ to take turns in going through condenser, acid washing, drier and analyzer with a flow rate of 874 mL/min. Lean loading of solution was assumed to be reached when the outlet CO$_2$ concentration was less than 0.1%. This assumption has been verified in our previous work (Xu et al., 2012a). The volume of the fresh solution added in the reactor was 100 mL. The other details of the facility were described by Xu et al. (2012a).

A wetted wall column was used to investigate the absorption rate of the amine solution with a contact area of about 41.45 cm$^2$. The gas-liquid contactor was constructed from a stainless steel tube, measuring 11.0 cm in height and 1.2 cm in diameter. The gas-liquid contact region was enclosed by a 31.0 cm thick-walled glass tube, separated from a water bath. More details about the original WWC system can be found in our previous research (Liu et al., 2009, 2011, 2012). The experimental system used in this work shown in Figure 2 has two modifications from the original system. A saturator with the same temperature and pressure as the reactor was added before the gas entered the reactor. The gas side mass transfer coefficient was calibrated using SO$_2$ absorption into NaOH solution, to replace the previous one which was determined with CO$_2$ absorption into MEA solution.

For the analysis method, A Dionex DX-120 system with an IonPac Column CG17/CS17 was used to measure the individual amine concentrations in the two liquid phases. The CO$_2$ loading was determined by titration using the barium carbonate precipitation method (Hilliard, 2008). A JNM ECA-600 NMR from JEOL Company was used to analyze the reaction products in the solution in terms of $^{13}$C. As the natural abundance of $^{13}$C is 1.11%, the ordinary CO$_2$ was added into the solution for further analysis. CO$_2$ was added by bubbling the gas into the solution. The total loading was determined from the weight change of the solution after bubbling with CO$_2$, and the individual loadings of the upper and lower phases were titrated. Then, about 1 mL solution was added to a WG-5000-7-50 sample tube from Wilmad Company. Dioxane was used as an internal standard and a small amount of D$_2$O was added to the sample tube to get a signal lock. The magnetic field strength of the NMR was 14.096 T, with a $^{13}$C resonance frequency of 150.91 MHz. The quantitative $^{13}$C lasted 15 hours for each sample with a relaxation time of 20 seconds.

2 THEORY

2.1 Chemical Reactions

The chemical reactions of CO$_2$ with the amines in the solution can be addressed as follows:

Dissociation of carbon dioxide:

$$\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \quad (1)$$

Dissociation of bicarbonate ion:

$$\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad (2)$$

\[ 
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 \\
& \quad \text{H}_2\text{C} \quad \text{N} \quad \text{CH}_3 \\
\text{BDA} & \quad \text{DEEA}
\end{align*}
\]

Figure 1

BDA and DEEA structures.
Dissociation of protonated amine:

\[
\text{DEEAH}^+ + \text{H}_2\text{O} \rightarrow \text{DEEA} + \text{H}_3\text{O}^+ \tag{3}
\]

\[
\text{BDAH}^+ + \text{H}_2\text{O} \rightarrow \text{BDA} + \text{H}_3\text{O}^+ \tag{4}
\]

Dissociation of deprotonated BDA:

\[
\text{BDAH}_2^{2+} + \text{H}_2\text{O} \rightarrow \text{BDAH}^+ + \text{H}_3\text{O}^+ \tag{5}
\]

Formation of carbamate of BDA:

\[
\text{BDA} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{BDACOO}^- + \text{H}_3\text{O}^+ \tag{6}
\]

Formation of bicarbamate of BDA:

\[
\text{BDACOO}^- + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{BDA(COO)}_2^{2-} + \text{H}_3\text{O}^+ \tag{7}
\]

Dissociation of protonated carbamate:

\[
\text{BDAHCOO} + \text{H}_2\text{O} \rightarrow \text{BDACOO}^- + \text{H}_3\text{O}^+ \tag{8}
\]

2.2 Absorption Rate Calculation of WWC

Based on the two film model, the mass flux with chemical absorption can be described as follows, where the total resistance to mass transfer is divided as the sum of the resistance from gas side and liquid side, as Equation (9) shows:

\[
\frac{1}{k_g} + \frac{1}{k_G} = \frac{1}{K_G} \tag{9}
\]

The overall gas transfer coefficient, \(K_G\), can be calculated from the \(\text{Flux}, P_{\text{CO}_2,b}\), and \(P_{\text{CO}_2,\text{out}}\). \(K_G\) is fixed for a given temperature and amine concentration and can be calculated by the \(\text{Flux-CO}_2\) partial pressure curve:

\[
K_G = \frac{\text{Flux}}{P_{\text{CO}_2,b} - P_{\text{CO}_2}} \tag{10}
\]

where \(P_{\text{CO}_2,b}\) is the operational partial pressure of CO\(_2\) in the wetted wall column, which is the log mean average, as Equation (11) shows:

\[
\text{Figure 2}
\]

The experiment scheme of wetted wall column.
\[ P_{CO_2,b} = \frac{P_{CO_2,in} - P_{CO_2, out}}{\ln(P_{CO_2,in}/P_{CO_2, out})} \]  

The CO\(_2\) pressure in the gas-liquid contact face, \( P_{CO_2,i} \), can be calculated by Equation (12):

\[ k_g = \frac{\text{Flux}}{P_{CO_2,b} - P_{CO_2,i}} \]  

The gas side mass transfer coefficient \( k_g \) can be given by Equation (13):

\[ Sh = \alpha(Re \times Sc \times \frac{d_h}{h})^\beta \]  

where \( Sh = \frac{RTk_gd_h}{D_{CO_2}} \), \( Re = \frac{\rho g V_g d_h}{\mu_g} \), \( Sc = \frac{\nu}{D} \), \( d_h \) is the hydraulic diameter of the annulus and \( h \) is the length of the column. As Pacheco (1998) stated, the parameters \( \alpha \) and \( \beta \) are fitted based on the experimental data of SO\(_2\) absorption into 0.1 M NaOH solution. The fitted results will be presented in Section 3.3.

### 3 RESULTS AND DISCUSSION

#### 3.1 (2B4D)\(_L\) Identification and the Lean Loading Calculation

The amine and CO\(_2\) concentrations in the two phases were measured by IC and auto-titrator after the CO\(_2\) absorption by 2B4D reaching equilibrium using the fast screening facility on absorption mode. The measurement error has been evaluated in previous work and the results proven to be reliable (Xu et al., 2013c). At the rich loading, the BDA, DEEA and CO\(_2\) concentrations in the lower phase were 2.23, 2.40 and 3.29 mol/kg solution, which can be converted to the amine concentration of (2B4D)\(_L\) by subtracting the weight of CO\(_2\) in the solution. The actual BDA and DEEA concentrations in fresh (2B4D)\(_L\) solution were 2.61 and 2.81 mol/kg.

The absorption rates of 2B4D and (2B4D)\(_L\) at lean loadings were measured to compare their performance comprehensively. Thus, the lean loadings of 2B4D and (2B4D)\(_L\) were identified here. The 2B4D lean solution was got using the fast screening facility on desorption mode and the CO\(_2\) loading of the lean solution was titrated. The rich and lean solutions of (2B4D)\(_L\) were got using the fast screening facility on absorption and desorption mode, respectively. Then the CO\(_2\) loadings of (2B4D)\(_L\) rich and lean solution were titrated using the titrator. The CO\(_2\) and amine concentrations in 2B4D lean solution were the mixture of upper phase and the lean solution of lower phase, the same as would occur in actual application.

Table 1 presents the BDA, DEEA and CO\(_2\) concentrations in 2B4D upper and lower phases at lean and rich CO\(_2\) loadings, as well as those of (2B4D)\(_L\) solutions at lean and rich CO\(_2\) loadings. The amine and CO\(_2\) concentrations are between the concentrations for the upper phase solution and the lean solution of lower phase. Table 1 reveals that the (2B4D)\(_L\) lean solution has higher BDA concentration, lower DEEA concentration, slightly higher CO\(_2\) concentration and higher CO\(_2\) loading than 2B4D lean solution.

#### 3.2 Comparisons of the Cyclic Capacity and Cyclic Loading

Our previous works have confirmed the reliability of the screening and titration results (Xu et al., 2012a, 2013c).

| Solvent | BDA (mol/kg) | DEEA (mol/kg) | CO\(_2\) (mol/kg) | CO\(_2\) loading (mol/mol amine) |
|---------|--------------|---------------|------------------|-------------------------------|
| 2B4D    |              |               |                  |                               |
| Upper phase | 0.115   | 7.265         | 0.315            | 0.043                         |
| Lower phase rich | 2.233 | 2.400         | 3.291            | 0.710                         |
| Lower phase lean | 2.477 | 2.663         | 1.050            | 0.204                         |
| 2B4D lean | 2.200       | 3.906         | 0.943            | 0.154                         |
| (2B4D)\(_L\) |            |               |                  |                               |
| Fresh | 2.607        | 2.806         | /                | /                             |
| Rich  | 2.268        | 2.441         | 3.398            | 0.722                         |
| Lean  | 2.490        | 2.679         | 1.076            | 0.208                         |
Figure 3 shows the cyclic loadings and cyclic capacities of the 2B4D lower phase and \((2B4D)_L\), indicating that the cyclic capacity and cyclic loading of 2B4D and \((2B4D)_L\) are very similar. Therefore, \((2B4D)_L\) differs little from the lower phase of 2B4D in terms of the cyclic capacity and cyclic loading.

### 3.3 Comparison of Absorption Rate

The influence of the saturator added to the WWC system was investigated by titrating DEEA concentration against 0.2 N H\(_2\)SO\(_4\) using a Metrohm 809 Titrando auto titrator before and after the WWC tests of aqueous DEEA solution. The results listed in Table 2 confirm that the addition of the saturator effectively balanced the water in the system.

The parameters \(x\) and \(\beta\) in Equation (13) were determined with SO\(_2\) absorption into 0.1 M NaOH solution to determine the gas side mass transfer coefficient \(k_g\). The results are listed in Table 3 with a correlation in Figure 4.

Therefore, the correlated equation for the gas side mass transfer coefficient is Equation (14):

\[
Sh = 6.7097(Re \times Sc \times d_h/h)^{0.5036}
\]  

\(Sh\) = 3.3 Comparison of Absorption Rate

The CO\(_2\) absorption rates for 2B4D and \((2B4D)_L\) were measured with WWC system at 298.15, 313.15

### TABLE 2

| Sample       | Sample amount (g) | \(H_2SO_4\) (mL) | DEEA concentration (mol.kg\(^{-1}\)) |
|--------------|-------------------|-----------------|-----------------------------------|
| Before WWC   | 0.8880            | 17.8741         | 4.0538                            |
| After WWC    | 0.8531            | 17.1017         | 4.0374                            |

### TABLE 3

| Total flow rate (L/min) | \(P\) (MPa) | \(k_g \times 10^{10}\) (mol/Pa-cm\(^2\)/s) | \(Re \times Sc \times d_h/h\) | \(Sh\) |
|-------------------------|------------|------------------------------------------|-----------------------------|-------|
| 5.84                    | 0.13       | 8.38                                     | 43.39                       | 44.70 |
| 6.11                    | 0.15       | 7.47                                     | 45.38                       | 45.14 |
| 8.13                    | 0.17       | 7.89                                     | 60.35                       | 54.16 |
| 8.26                    | 0.14       | 9.07                                     | 61.35                       | 52.16 |
| 3.56                    | 0.16       | 5.10                                     | 26.43                       | 32.74 |
| 3.69                    | 0.16       | 5.56                                     | 27.42                       | 36.36 |
| 3.96                    | 0.17       | 5.52                                     | 29.42                       | 38.15 |
| 9.88                    | 0.17       | 8.67                                     | 73.32                       | 59.19 |
| 1.54                    | 0.17       | 3.39                                     | 11.46                       | 23.17 |
and 333.15 K with the CO$_2$ pressure of 3-25 kPa at loadings of 0 (fresh solution), half lean loading and lean loading, as presented in Tables 4 and 5.

The Flux of 2B4D and (2B4D)$_L$ at 0 loading, half lean loading and lean loading are compared in Figures 5 to 7. Figure 5 shows that the fresh 2B4D solution reacted faster than (2B4D)$_L$ with $P_{CO_2}$ lower than 8 kPa, while the absorption rate of the fresh (2B4D)$_L$ solution was higher than that of fresh 2B4D solution with $P_{CO_2}$ higher than 10 kPa. Figure 6 reveals that at half lean loading, the absorption rate of (2B4D)$_L$ was higher than that of 2B4D for $P_{CO_2}$ between 5 and 25 kPa. Figure 7 shows that at the lean loading, (2B4D)$_L$ reacted faster than 2B4D. For example, the mass flux of (2B4D)$_L$ at lean loading and 313.15 K was 37% higher than that of 2B4D. Comparing the 3 figures, at 313 K and $P_{CO_2} = 15$ kPa, the mass flux of fresh (2B4D)$_L$ solution was twice more than that at lean loading and the mass flux of fresh 2B4D was 2.2 times more than that at lean loading.

### 3.4 Comparison of the Reaction Products

As for the reaction products, our previous research has identified the carbon numbers, as shown in Table 6 (Xu et al., 2013c). The peaks positions of the fresh 2B4D solution NMR spectrum agreed well with those in the literature (Balaban et al., 1985; Parker et al., 2011). Comparison of the NMR data and the titration results showed that the NMR error was less than 8%. (Xu et al., 2013c)
TABLE 4
Kinetic parameters of CO₂ absorption into 2B4D solutions at 298.15, 313.15 and 333.15 K

| Solvent               | T (K) | Flux $\times 10^3$ (mol/m²/s) | $P_{CO_2}$ (kPa) | $k_g \times 10^6$ (mol/Pa/m²/s) | $P_{CO_2,i}$ (kPa) |
|-----------------------|-------|-------------------------------|-----------------|-------------------------------|-----------------|
| 2B4D fresh            | 298.15| 17.41                         | 5.80            | 8.55                          | 3.76            |
|                       |       | 23.24                         | 12.67           | 8.42                          | 9.91            |
|                       |       | 26.51                         | 20.02           | 8.41                          | 16.87           |
|                       |       | 34.06                         | 26.98           | 8.39                          | 22.92           |
|                       | 313.15| 18.96                         | 5.85            | 8.30                          | 3.56            |
|                       |       | 29.46                         | 12.93           | 8.27                          | 9.37            |
|                       |       | 37.07                         | 19.46           | 8.25                          | 14.97           |
|                       |       | 44.71                         | 26.25           | 8.23                          | 20.83           |
|                       | 333.15| 20.41                         | 5.68            | 8.17                          | 3.19            |
|                       |       | 35.39                         | 12.54           | 8.13                          | 8.19            |
|                       |       | 46.32                         | 19.07           | 8.05                          | 13.32           |
|                       |       | 59.59                         | 25.23           | 8.08                          | 17.85           |
| 2B4D half lean loading| 298.15| 12.68                         | 5.90            | 8.50                          | 4.41            |
|                       |       | 17.53                         | 13.65           | 8.43                          | 11.57           |
|                       |       | 20.52                         | 20.58           | 8.36                          | 18.13           |
|                       |       | 25.71                         | 27.43           | 8.35                          | 24.35           |
|                       | 313.15| 14.15                         | 6.06            | 8.31                          | 4.35            |
|                       |       | 19.89                         | 13.65           | 8.29                          | 11.26           |
|                       |       | 25.86                         | 20.26           | 8.22                          | 17.11           |
|                       |       | 33.74                         | 26.99           | 8.21                          | 22.88           |
|                       | 333.15| 15.80                         | 5.92            | 8.24                          | 4.00            |
|                       |       | 25.55                         | 13.20           | 8.10                          | 10.05           |
|                       |       | 33.01                         | 19.99           | 8.09                          | 15.90           |
|                       |       | 40.34                         | 26.49           | 8.07                          | 21.49           |
| 2B4D lean loading     | 298.15| 6.71                          | 6.57            | 8.46                          | 5.78            |
|                       |       | 11.11                         | 14.02           | 8.50                          | 12.71           |
|                       |       | 13.67                         | 20.93           | 8.50                          | 19.32           |
|                       |       | 15.12                         | 27.92           | 8.44                          | 26.12           |
|                       | 313.15| 10.00                         | 6.44            | 8.37                          | 5.25            |
|                       |       | 14.39                         | 13.77           | 8.36                          | 12.05           |
|                       |       | 19.24                         | 20.87           | 8.30                          | 18.55           |
|                       |       | 24.59                         | 27.74           | 8.28                          | 24.77           |
|                       | 333.15| 13.90                         | 6.20            | 8.19                          | 4.50            |
|                       |       | 21.36                         | 13.85           | 8.11                          | 11.22           |
|                       |       | 27.40                         | 20.15           | 8.21                          | 16.81           |
|                       |       | 35.21                         | 27.61           | 8.03                          | 23.23           |
| Solvent                  | $T$ (K) | $Flux \times 10^3$ (mol/m$^2$/s) | $P_{CO_2,b}$ (kPa) | $k_g \times 10^6$ (mol/(Pa$m^2$/s)) | $P_{CO_2,i}$ (kPa) |
|-------------------------|---------|----------------------------------|--------------------|--------------------------------------|---------------------|
| (2B4D)$_L$ fresh        | 298.15  | 9.55                             | 6.26               | 8.57                                 | 5.14                |
|                         |         | 23.65                            | 12.92              | 8.59                                 | 10.16               |
|                         |         | 34.75                            | 18.73              | 8.62                                 | 14.70               |
|                         |         | 47.85                            | 24.34              | 8.65                                 | 18.81               |
|                         | 313.15  | 13.33                            | 5.85               | 8.42                                 | 4.27                |
|                         |         | 29.51                            | 12.64              | 8.33                                 | 9.10                |
|                         |         | 41.44                            | 18.82              | 8.24                                 | 13.79               |
|                         |         | 57.43                            | 25.19              | 8.20                                 | 18.19               |
|                         | 333.15  | 18.30                            | 5.74               | 8.12                                 | 3.49                |
|                         |         | 35.16                            | 12.46              | 8.08                                 | 8.11                |
|                         |         | 49.63                            | 18.30              | 8.10                                 | 12.17               |
|                         |         | 63.44                            | 24.93              | 8.07                                 | 17.07               |
| (2B4D)$_L$ half lean loading | 298.15  | 11.68                            | 6.26               | 8.39                                 | 4.87                |
|                         |         | 17.63                            | 13.60              | 8.32                                 | 11.48               |
|                         |         | 23.40                            | 20.36              | 8.36                                 | 17.56               |
|                         |         | 31.14                            | 27.33              | 8.34                                 | 23.60               |
|                         | 313.15  | 13.88                            | 6.05               | 8.25                                 | 4.36                |
|                         |         | 25.17                            | 13.36              | 8.17                                 | 10.28               |
|                         |         | 33.56                            | 20.02              | 8.21                                 | 15.93               |
|                         |         | 41.47                            | 26.55              | 8.19                                 | 21.48               |
|                         | 333.15  | 16.36                            | 5.87               | 8.24                                 | 3.88                |
|                         |         | 31.10                            | 12.71              | 8.09                                 | 8.86                |
|                         |         | 42.45                            | 19.27              | 8.06                                 | 14.00               |
|                         |         | 54.68                            | 26.13              | 7.98                                 | 19.28               |
| (2B4D)$_L$ lean loading | 298.15  | 8.13                             | 6.53               | 8.45                                 | 5.56                |
|                         |         | 14.26                            | 14.19              | 8.44                                 | 12.50               |
|                         |         | 17.95                            | 20.47              | 8.43                                 | 18.34               |
|                         |         | 22.84                            | 27.61              | 8.42                                 | 24.90               |
|                         | 313.15  | 10.00                            | 6.56               | 8.32                                 | 5.36                |
|                         |         | 18.45                            | 13.95              | 8.30                                 | 11.73               |
|                         |         | 25.90                            | 20.36              | 8.28                                 | 17.23               |
|                         |         | 34.79                            | 27.11              | 8.26                                 | 22.90               |
|                         | 333.15  | 13.16                            | 6.34               | 8.13                                 | 4.72                |
|                         |         | 23.89                            | 13.60              | 8.00                                 | 10.62               |
|                         |         | 34.59                            | 20.05              | 8.03                                 | 15.74               |
|                         |         | 48.34                            | 26.24              | 8.05                                 | 20.24               |
TABLE 6
Identification of carbon atoms in NMR spectrum (Xu et al., 2013c)

| Component          | Structure and identification |
|--------------------|-------------------------------|
| DEEA/DEEAH⁺       | ![Structure](image1)          |
| BDA/BDAH⁺/BDAH₂²⁺  | ![Structure](image2)          |
| BDACOO⁻/HBDACOO   | ![Structure](image3)          |
| BDA(COO⁻)₂        | ![Structure](image4)          |
| CO₃²⁻/HCO₃⁻        | ![Structure](image5)          |

Figure 8
NMR spectrum of (2B4D)₄ at the loading of 0.361 mol/mol amine. a) Up field part spectrum; b) low field part spectrum.
In this work, the quantitative NMR spectrum of (2B4D)$_L$ at five various loadings were acquired. The loadings of all solutions were controlled by the amount of CO$_2$ bubbled into the solution and verified by titration against 0.2 N H$_2$SO$_4$. The five loadings were 0.113, 0.219, 0.361, 0.532 and the rich loading 0.735 mol CO$_2$/mol amine.

The NMR results of the solution with the 0.361 mol/mol loading are shown in Figure 8 as an example. Referring to the NMR spectrum for fresh 2B4D solution (Xu et al., 2013c), the BDA and DEEA positions can be easily recognized and the positions of D1, D2, D3, D4, B1 and B2 can be identified in the figure. B3, B4, B5 and B6 represent BDA carbamate, the peak areas of which must be equal and close to those of B1 and B2, so they can also be identified in the spectrum. Then, the remaining peaks are B8 and B9 in Figure 8a. The peaks in Figure 8b are B7, B10 and 11. As previous researchers have pointed out, due to the fast proton exchange with water, it is not possible to distinguish signals of amine from protonated amine, or carbonate from bicarbonate. Thus, the position of these peaks in the spectra are the average of the chemical shift of amine and proton amine, or carbonate and bicarbonate (Jakobsen et al., 2005, 2008; Hartono et al., 2007). Thus in the following tables and figure legends of all species represent species and their protonated forms. For example, BDA represents the sum of BDA, BDAH$^+$ and BDAH$_2$CO$_3$.$^2^+$. The NMR results in this paper are compared with the titration results to verify its accuracy, as shown in Table 7. The CO$_2$ concentration measured by the NMR result is the sum of BDA carbamate, bicarbamate and carbonate/bicarbonate. The difference between the NMR and titration results indicates the accuracy of NMR results of this work.

The concentrations of the various (2B4D)$_L$ species at different loadings are shown in Figure 9. It is obvious that BDA concentration decreased from 1.859 mol/kg solution at the loading of 0.113 mol/mol to 0.206 mol/kg at the rich loading of 0.735 mol/mol. The BDA carbamate concentration first increased and then decreased slightly after the loading of 0.532 mol/mol, possibly due to the formation of bicarbamate. BDA bicarbamate kept increasing with increased loading. BDA bicarbamate concentration was higher than the BDA concentration at high loadings. The carbonate/bicarbonate concentration increased sharply after the loading of 0.532 mol/mol as a result of DEEA reaction with CO$_2$.

Figure 10 presents the species mole fraction variations of BDA with the increased loading. Since the total BDA concentration did not vary much during the absorption, the tendency of mole fractions is similar to the variations in Figure 9. Figure 10 also demonstrates that at higher loadings, the mole fraction of BDA bicarbamate was relatively high. At rich loading, the mole fractions of BDA, BDACOO$^-$ and BDA(COO)$_2$$^{2-}$ were 10.62%, 51.23% and 38.15%, respectively.
Figure 11 illustrates the distribution of CO$_2$ in terms of BDACOO$^-$, BDA(COO)$_2$$^-$ and CO$_3^{2-}$/HCO$_3^-$.
The current NMR spectrum, unfortunately, had no peaks around 125 ppm, which would indicate free CO$_2$. As the results of Jokobsen et al. (2005) and Suda et al. (1996) proved that the free CO$_2$ was less than 5% of its total amount in the solution, the free CO$_2$ in the solution was neglected in this work. Given that BDA bicarbonate has two carbon atoms, its mole fraction in the figure is twice as its actual fraction. Figure 11 shows that at the beginning, the CO$_2$ formed BDA carbamate, while the BDA carbamate fraction decreased and bicarbonate increased with increasing CO$_2$ loading. At the rich loading, CO$_2$ in the solution was distributed as 33.64% carbamate, 50.10% bicarbonate and 16.26% carbonate/bicarbonate.

Figure 11 also compares the CO$_2$ distribution between 2B4D lower phase and (2B4D)$_L$ at different loadings. The CO$_2$ distribution in 2B4D lower phase can be referred to Xu et al. (2013c). It shows that in (2B4D)$_L$ solution, the mole fraction of CO$_2$ existed in terms of carbamate was more than that in 2B4D lower phase, while the mole fractions of CO$_2$ in terms of bicarbonate and carbonate/bicarbonate were slightly higher than those in 2B4D lower phase.

The reaction products and the BDA and CO$_2$ distributions in 2B4D and (2B4D)$_L$ at the rich loading are compared in Figure 12. Figure 12a shows that the (2B4D)$_L$...
reaction products had more BDA bicarbamate than the 2B4D products, with less BDA and less BDA carbamate. Figure 12b demonstrates that the CO2 reaction products of (2B4D)l had twice as much carbonate/bicarbonate as 2B4D and less BDA carbamate. The reason for more BDA bicarbamate of (2B4D)l is that the BDA concentration in (2B4D)l was almost constant during absorption, while the equivalent BDA concentration (including BDA carbamate and bicarbamate) in the 2B4D lower phase kept decreasing while approaching the rich loading. The BDA concentration of 2B4D lower phase at different loadings can be referred to Xu et al. (2013c).

CONCLUSIONS

The present study identifies the (2B4D)l composition with 2.607 mol/kg BDA and 2.806 mol/kg DEEA. The cyclic capacity and cyclic loading of (2B4D)l are almost the same as those of 2B4D. For reaction conditions of 298.15, 313.15 and 333.15 K and CO2 pressure of 3-25 kPa, the absorption rates of fresh (2B4D)l solution, (2B4D)l solutions at half lean loading and lean loading are higher than those of fresh 2B4D solution, and 2B4D solutions at half lean loading and lean loading, respectively, except for the fresh solutions at CO2 pressure lower than 10 kPa.

NMR measurements of the reaction products of (2B4D)l show that in (2B4D)l solution, the BDA bicarbamate concentration increases with increasing CO2 loading, while the BDA carbamate concentration decreases a little at loadings greater than 0.532 mol/mol. The reaction products of (2B4D)l have more BDA bicarbamate, less BDA and less BDA carbamate than 2B4D. The CO2 reaction products of (2B4D)l have twice as much carbonate/bicarbonate as with 2B4D and less BDA carbamate. Further study on the performance of (2B4D)l is necessary.

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