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Energy Procedia 37 (2013) 869 – 876

Energy

Procedia

GHGT-11

# $^{13}\text{C}$ -NMR Spectroscopic Study on Chemical Species in Piperazine–Amine– $\text{CO}_2$ – $\text{H}_2\text{O}$ System before and after Heating

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## Abstract

Chemical reactions associated with the absorption of  $\text{CO}_2$  into aqueous solutions of blends of piperazine (PZ) with *N*-methyldiethanolamine (MDEA), etc. were studied by  $^{13}\text{C}$ -NMR spectroscopy. The coexistence of PZ and MDEA enhanced the initial apparent rate of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  formation. This result can be explained by considering that PZ monocarbamate rapidly formed works as an organocatalyst in the formation reaction of  $\text{HCO}_3^-$ . Concentration changes of chemical species in  $\text{CO}_2$ -absorbed aqueous amine solutions upon heating (80 °C, 30 min) were studied by  $^{13}\text{C}$ -NMR spectroscopy. Carbon dioxide regeneration originates mainly from  $\text{HCO}_3^-/\text{CO}_3^{2-}$ , and not from carbamate and carbonate.

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**Keywords:**  $^{13}\text{C}$ -NMR; amine; piperazine; carbamate; carbon dioxide.

## 1. Introduction

Aqueous solutions of alkanolamines are widely used as absorbers for removing  $\text{CO}_2$  from flue gas of fossil-fueled power plants [1]. An aqueous solution of an alkanolamine absorbs  $\text{CO}_2$  chemically at room temperature and releases  $\text{CO}_2$  at high temperature. Primary amines such as 2-aminoethanol (MEA), 2-amino-2-methyl-1-propanol (AMP), etc., secondary amines such as 2-(isopropylamino)ethanol (IPAE), etc. and tertiary amines such as *N*-methyldiethanolamine (MDEA), 1-dimethylamino-2-propanol

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(DMA2P), etc. were used as potential candidate absorbers. Their chemical structures are shown in Fig. 1. Since a single amine solution did not show high performance, a blend of two or three amines was used as an absorber. In particular, piperazine (PZ, see Fig. 1f) was used as a so-called "activator" together with an alkanolamine such as MDEA and IPAE. However, the role of PZ remains unclear from a standpoint of molecular chemistry.

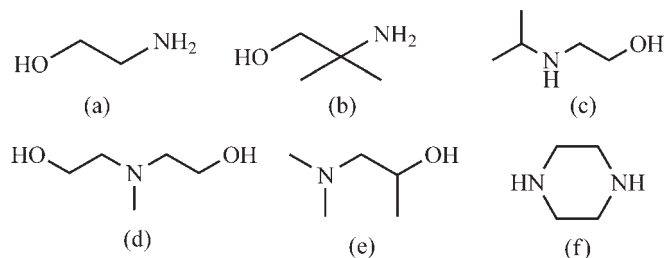


Fig. 1. Chemical structures of amines: (a) MEA; (b) AMP; (c) IPAE; (d) MDEA; (e) DMA2P; (f) PZ.

It has been demonstrated [2–10] that <sup>13</sup>C-NMR spectroscopy is a powerful tool for qualitative and quantitative studies of chemical species formed in aqueous solutions containing amines and CO<sub>2</sub>. It was elucidated that amines react with CO<sub>2</sub>, forming ionic species such as bicarbonate ion (HCO<sub>3</sub><sup>-</sup>), carbonate ion (CO<sub>3</sub><sup>2-</sup>), protonated amines, amine carbamates, and amine carbonates, etc. It is believed that a carbamate molecule is formed through the deprotonation of the zwitterion of amine and CO<sub>2</sub> in the presence of a proton acceptor such as an amine or a water molecule. In the aqueous solutions, CO<sub>2</sub> reacts with alkanolamines either directly or via the acid-base buffer mechanism to form HCO<sub>3</sub><sup>-</sup>. Recently, a density functional theory study [11] suggests that amine, CO<sub>2</sub>, and H<sub>2</sub>O molecules react directly to form HCO<sub>3</sub><sup>-</sup>. The reaction mechanism has not been fully clarified yet.

In this paper we focus on quantitative <sup>13</sup>C-NMR studies on concentration changes of chemical species in an aqueous solution of a blend of PZ with an amine (MDEA, DMA2P, or IPAE) in the course of CO<sub>2</sub> absorptions and on those upon heating as a simple model of CO<sub>2</sub> regeneration.

## 2. Experimental

### 2.1. Sample preparation

Samples of MEA (Tokyo Chemical Industry), AMP (Acros Organics), IPAE (Tokyo Chemical Industry), MDEA (Tokyo Chemical Industry), DMA2P (Tokyo Chemical Industry), and PZ (Acros Organics) were used without further purification. In the experiments of CO<sub>2</sub> absorption kinetics, CO<sub>2</sub> gas was bubbled through an aqueous solution of an amine or a blend at a rate of 150 mL/min. The concentration of PZ was 5 or 10 wt%, and that of an amine was 20 or 30 wt%. In the absorption-regeneration experiments, CO<sub>2</sub> gas was bubbled through an aqueous solution of an amine or a blend at a rate of 50 mL/min at 50 °C for 60 min; the solution was heated at 80 °C for 30 min as the CO<sub>2</sub> regeneration process. The concentrations of MEA, AMP, and MDEA were 20 wt%, and that of PZ was 10 wt%. A blend of 10 wt% PZ and 20 wt% amine (MDEA, DMA2P or IPAE) was used.

### 2.2. <sup>13</sup>C-NMR measurements

The <sup>13</sup>C-NMR spectra of a D<sub>2</sub>O solution containing an amine or a blend were measured at room temperature on a JEOL JNM-500ECX 500 MHz NMR spectrometer by using the inverse gated proton

decoupling method. Because of a long spin-lattice relaxation time, the holding time between scans was set to be 1 min. 128 scans were accumulated for each spectrum. As the standard of chemical shifts, 3-trimethylsilyl-1-propanesulfonic acid- $d_6$  sodium salt was added into the sample solution.

### 3. Results and discussion

#### 3.1. $CO_2$ -absorption kinetics

The  $^{13}C$ -NMR spectrum of an aqueous solution of a blend of PZ (10 wt%) and MDEA (20 wt%) and that after 50-min bubbling of the  $CO_2$  gas are shown in Figs. 2a and 2b, respectively. The observed bands have been assigned on the basis of the data in the literature [3, 8]. The assignments of the bands are listed in Table 1. The number of each carbon atom is shown in the chemical structures below. It should be noted that it is not possible to distinguish the signals originating from MDEA and protonated MDEA, because of the fast exchange of a proton between them. Thus a single band is assigned to both the species MDEA/MDEAH $^+$ . The chemical shift of this band shifts with increasing  $CO_2$ -bubbling time because the contents of these species are changed. Similar assignments have been made to another species and its protonated species such as  $HCO_3^-$  and  $CO_3^{2-}$ .

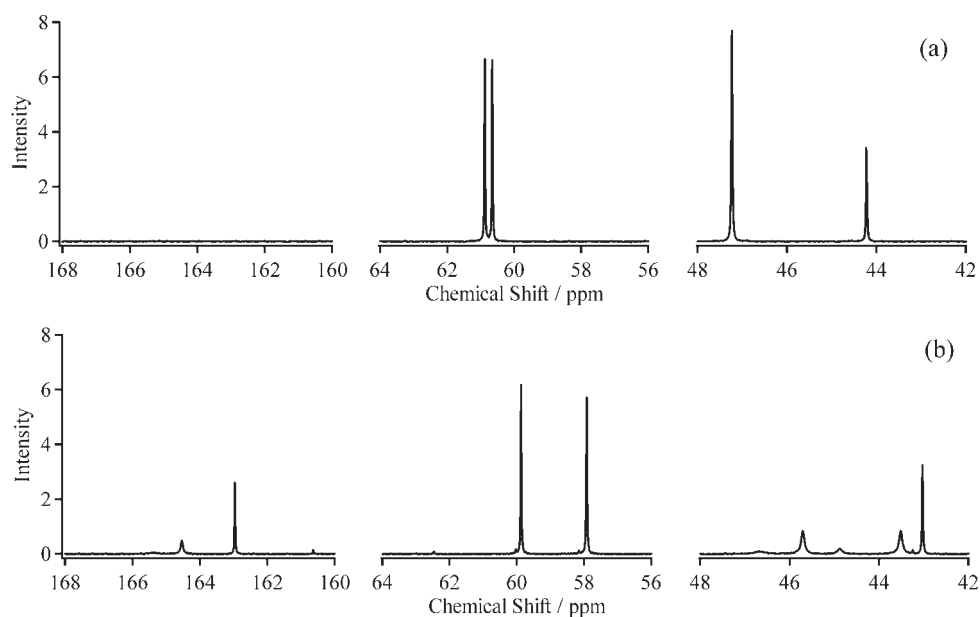


Fig. 2.  $^{13}C$ -NMR spectra of (a) an aqueous solution of a blend of PZ (10 wt%) and MDEA (20 wt%) and (b) after 50-min  $CO_2$  bubbling.

The following species were observed: (i) MDEA and its protonated species; (ii) MDEA carbonate and its protonated species; (iii) PZ and its protonated species; (iv) PZ monocarbamate and its protonated species; (v) PZ biscarbamate; (vi)  $HCO_3^-$  and  $CO_3^{2-}$ . This result is consistent with the previous report [8].

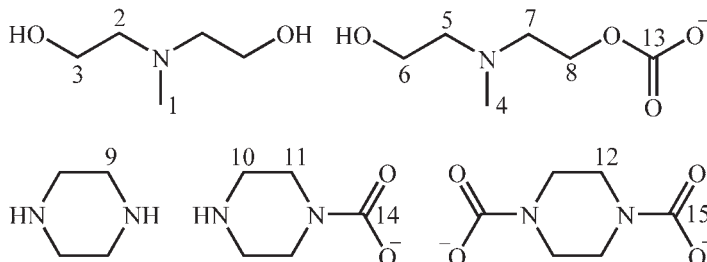
The intensity of a band attributed to each species was converted to the concentration of the species. The concentration of each species is plotted as a function of  $CO_2$ -bubbling time for an aqueous solution of

MDEA (20 wt%), PZ (10 wt%), PZ (10 wt%)–MDEA (20 wt%) blend, and PZ (10 wt%)–MDEA (30 wt%) blend in Figs. 3a-3d, respectively.

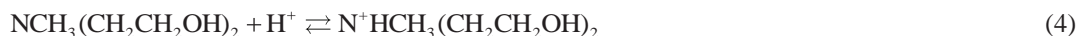
Table 1. Assignments of observed bands in PZ–MDEA–CO<sub>2</sub>–H<sub>2</sub>O system.

chemical shift / ppm	Species	Numbering <sup>a)</sup>
44.2–43.0	MDEA and its protonated species	1
43.4–43.2	MDEA carbonate and its protonated species	4
44.2–43.5	PZ monocarbamate and its protonated species	11
47.2–44.9	PZ and its protonated species	9
45.9–45.7	PZ monocarbamate and its protonated species	10
46.7	PZ biscarbamate	12
60.9–57.9	MDEA and its protonated species	3
58.6–58.1	MDEA carbonate and its protonated species	6
60.7–59.9	MDEA and its protonated species	2
60.1–60.0	MDEA carbonate and its protonated species	5
63.0–62.5	MDEA carbonate and its protonated species	8
161.1–160.6	MDEA carbonate and its protonated species	13
163.9–163.0	HCO <sub>3</sub> <sup>-</sup> and CO <sub>3</sub> <sup>2-</sup>	—
164.6–164.5	PZ monocarbamate and its protonated species	14
165.4	PZ biscarbamate	15

<sup>a)</sup> The numbering of carbon atoms is shown in the chemical structures below.



In the MDEA–CO<sub>2</sub>–H<sub>2</sub>O system (Fig. 3a), the concentration of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> increases with increasing time. The initial apparent rate of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> formation from 0 to 10 min was 0.049 mol/L·min. Probably, this rate depends on the rate of CO<sub>2</sub> absorption into the solution. The concentration of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> becomes equilibrium at 50 min. The formation of a small amount of carbonate indicates that carbonate does not play an important role in the CO<sub>2</sub> absorption-regeneration process. In the acid-base buffer mechanism, equilibrium reactions can be written as follows:



In the termolecular mechanism [11], the following reaction will proceed.

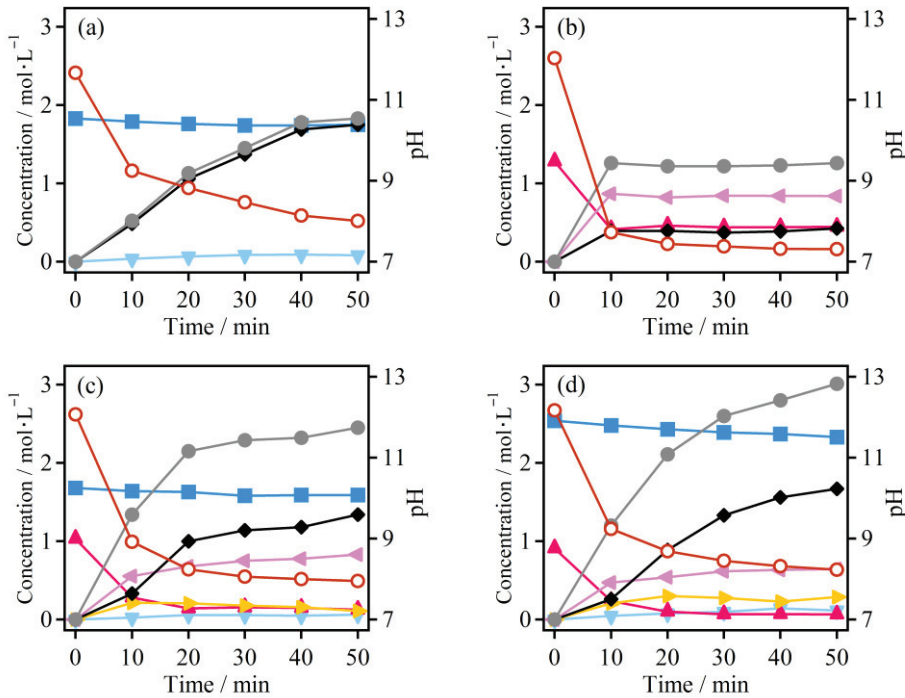
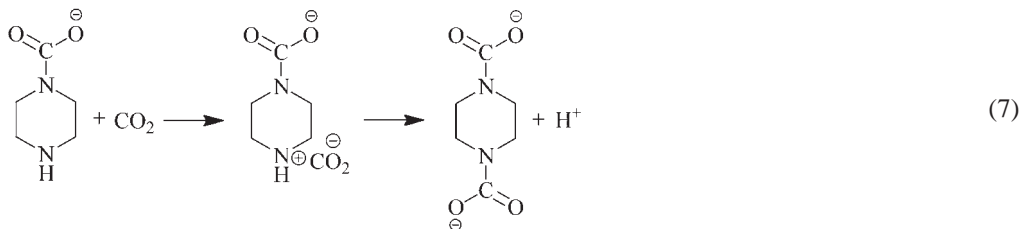
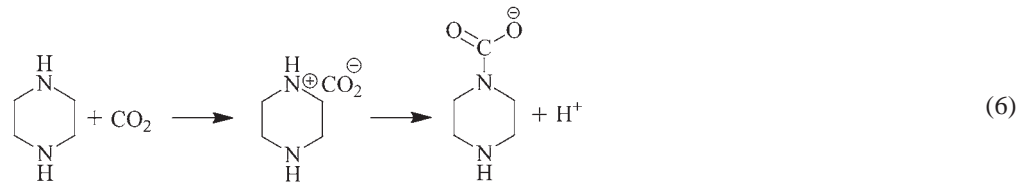


Fig. 3. Concentrations (mol/L) of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  (◆), MDEA (■), carbonate (▼), PZ (▲), PZ monocarbamate (◀), PZ bis-carbamate (▶), total  $\text{CO}_2$  equivalent content (●), and pH (○) in aqueous solutions of (a) MDEA (20 wt%), (b) PZ (10 wt%), (c) PZ (10 wt%)-MDEA (20 wt%), and (d) PZ (10 wt%)-MDEA (30 wt%) as a function of  $\text{CO}_2$ -bubbling time.

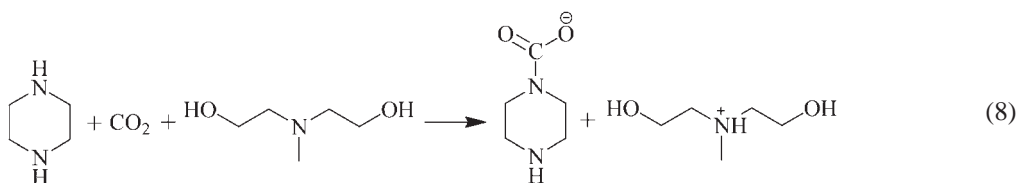
In the PZ- $\text{H}_2\text{O}$ - $\text{CO}_2$  system (Fig. 3b), the concentrations of monocarbamate and  $\text{HCO}_3^-/\text{CO}_3^{2-}$  increase. The concentration of monocarbamate is higher than that of  $\text{HCO}_3^-/\text{CO}_3^{2-}$ . It is believed that a carbamate molecule is formed from the zwitterion of PZ and  $\text{CO}_2$ . Thus, the following reactions are proposed:



The initial apparent rate of PZ monocarbamate formation from 0 to 10 min was 0.087 mol/L·min. The initial rate of the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  formation from 0 to 10 min was 0.040 mol/L·min.

In the PZ (10 wt%)-MDEA (20 wt%)- $\text{CO}_2$ - $\text{H}_2\text{O}$  system (Fig. 3c), the initial rate of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  formation from 0 to 10 min was 0.033 mol/L·min; this is smaller than that (0.049 mol/L·min) in MDEA (20 wt%)- $\text{CO}_2$ - $\text{H}_2\text{O}$  system. This decrease is due to the rapid formation of PZ monocarbamate. In this system, the rate of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  formation from 10 to 20 min was 0.066 mol/L·min, whereas in the MDEA (20 wt%)- $\text{CO}_2$ - $\text{H}_2\text{O}$  system the corresponding rate was 0.058 mol/L·min. This result indicates that the coexistence of PZ and MDEA enhances the rate. Similar rate enhancements were also observed for PZ (10 wt%)-MDEA (30 wt%)- $\text{CO}_2$ - $\text{H}_2\text{O}$ , PZ (5 wt%)-MDEA (20 wt%)- $\text{CO}_2$ - $\text{H}_2\text{O}$ , and PZ (10 wt%)-DMA2P (20 wt%)- $\text{CO}_2$ - $\text{H}_2\text{O}$  systems. This enhancement of the apparent rate was observed for tertiary amines MDEA and DMA2P. Since the rate of  $\text{CO}_2$  absorption is low for tertiary amines, this rate enhancement with PZ carbamate can be observed.

In order to explain this rate enhancement, we consider a novel mechanism of  $\text{HCO}_3^-$  formation-decomposition reactions as follows. The formation reaction of PZ monocarbamate can be expressed as follows:



A proton generated from the reaction of PZ and  $\text{CO}_2$  is accepted by an MDEA molecule. In addition, we assume the decomposition reaction of PZ monocarbamate as follows:



The combination of Eqs (8) and (9) leads to Eq (5). In Eq (5) PZ monocarbamate does not appear. Thus, the PZ monocarbamate molecule helps the formation of  $\text{HCO}_3^-$  like an organocatalyst. Since similar reactions associated with PZ biscarbamate are possible, the PZ biscarbamate molecule also may help the formation of  $\text{HCO}_3^-$  as an organocatalyst.

### 3.2. $\text{CO}_2$ regeneration upon heating

Molar concentrations of the chemical species in amine- $\text{CO}_2$ - $\text{H}_2\text{O}$  system before and after heat-treatment for MEA, AMP, MDEA, and PZ are shown in Fig. 4. In an MEA aqueous solution bubbled with  $\text{CO}_2$ , the concentrations of carbamate and  $\text{HCO}_3^-/\text{CO}_3^{2-}$  were 1.34 and 0.79 mol/L, respectively. After heat-treatment, the concentration of carbamate increased to 1.55 mol/L. This suggests that carbamate is not decomposed to  $\text{CO}_2$  and MEA upon heating. The concentration of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  species decreased to 0.37 mol/L; 0.42 mol/L of  $\text{CO}_2$  was regenerated from the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  species. In an AMP aqueous solution bubbled with  $\text{CO}_2$ , the concentrations of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  and carbonate were 2.26 and 0.05 mol/L, respectively. After heat-treatment, the concentrations of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  and carbonate

decreased to 1.84 and 0.04 mol/L, respectively. In an MDEA aqueous solution bubbled with CO<sub>2</sub>, the concentration of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> was 1.32 mol/L; upon heating, the concentration decreased to 0.76 mol/L. The 0.56 mol/L of CO<sub>2</sub> was regenerated from the HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> species. In an aqueous solution of PZ bubbled with CO<sub>2</sub>, there exist HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> (0.31 mol/L), PZ monocarbamate (0.75 mol/L), and PZ biscarbamate (0.03 mol/L). The concentrations of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, monocarbamate, and biscarbamate were changed to 0.24, 0.63, and 0.10 mol/L, respectively. This result indicates that mono- and bis-carbamates are not decomposed to PZ and CO<sub>2</sub>.

Carbon dioxide is mainly saved in an aqueous amine solution as the chemical species of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, monocarbamate, and biscarbamate. Carbonate may be ignored because the concentration of carbonate is low. The observed data suggests that upon heating, the regeneration of CO<sub>2</sub> mainly originates from the HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> species. This is probably attributed to the temperature dependence of chemical equilibrium in reactions (1)–(4).

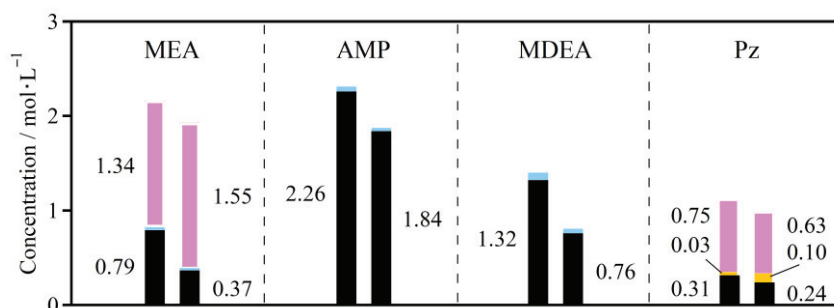


Fig. 4. Concentrations of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> (black), monocarbamate (pink), biscarbamate (yellow), and carbonate (blue). Bars in the left- and right-hand sides for each amine are before and after heat-treatment, respectively.

The concentrations of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, PZ monocarbamate, PZ biscarbamate, and amine carbamate in the aqueous solution of a PZ blend with an amine such as MDEA, DMA2P, or IPAE before and after heat-treatment are listed in Table 2.

Table 2. Concentrations (mol/L) of HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>, PZ monocarbamate, PZ biscarbamate, and amine carbamate before and after heating.

species	heating	equivalent CO <sub>2</sub> change	MDEA	PZ	PZ–MDEA	PZ–DMA2P	PZ–IPAE
HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	before		1.32	0.31	1.00	1.42	1.25
	after		0.76	0.24	0.40	0.64	0.78
		$\Delta_1$	-0.56	-0.07	-0.60	-0.78	-0.47
PZ monocarbamate	before		—	0.75	0.74	0.68	0.67
	after		—	0.63	0.59	0.55	0.50
		$\Delta_2$	—	-0.12	-0.15	-0.13	-0.17
PZ biscarbamate	before		—	0.03	0.18	0.27	0.29
	after		—	0.10	0.22	0.40	0.44
		$\Delta_3$	—	0.07	0.04	0.13	0.15
		$\Delta_2 + 2\Delta_3$	—	0.02	-0.07	0.13	0.13
carbamate	before		—	—	—	—	0.0
	after		—	—	—	—	0.0
		$\Delta_4$	—	—	—	—	0.0
		$\Delta = \Delta_1 + \Delta_2 + 2\Delta_3 + \Delta_4$	-0.56	-0.05	-0.67	-0.65	-0.34

Table 2 shows the concentration changes upon heating in HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> ( $\Delta_1$ ), PZ monocarbamate ( $\Delta_2$ ), PZ biscarbamate ( $\Delta_3$ ), amine carbamate ( $\Delta_4$ ) and total equivalent CO<sub>2</sub> content ( $\Delta = \Delta_1 + \Delta_2 + 2\Delta_3 + \Delta_4$ ). In

this equation  $\Delta_3$  is times by 2, because a biscarbamate molecule is made from two  $\text{CO}_2$  molecules. In all the solutions,  $\Delta_1$  decreases upon heating, indicating that  $\text{HCO}_3^-/\text{CO}_3^{2-}$  species contribute to  $\text{CO}_2$  regeneration. On the other hand, the sum of the equivalent  $\text{CO}_2$  contents in PZ monocarbamate and biscarbamate  $\Delta_2 + 2\Delta_3$  increases for PZ–DMA2P and PZ–IPAE and decreases for PZ–MDEA. The total equivalent  $\text{CO}_2$  change  $\Delta = \Delta_1 + \Delta_2 + 2\Delta_3 + \Delta_4$  is large for PZ–MDEA and PZ–DMA2P. The observed data suggests that the regeneration of  $\text{CO}_2$  upon heating mainly originates from the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  species. Carbamate has a negative effect in  $\text{CO}_2$  regeneration upon heating.

#### 4. Conclusions

We have studied the concentration changes of chemical species in an aqueous solution of a blend of PZ and an amine such as MDEA, DMA2P, or IPAE as a function of  $\text{CO}_2$ -bubbling time by  $^{13}\text{C}$ -NMR spectroscopy. At the beginning of the reaction, PZ carbamate was formed. The coexistence of PZ and MDEA or DMA2P enhanced the initial rate of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  formation. This result probably indicates that PZ monocarbamate rapidly formed works as an organocatalyst in the formation reaction of  $\text{HCO}_3^-$ . We have studied the concentrations of chemical species in  $\text{CO}_2$ -absorbed aqueous amine (MEA, AMP, MDEA, PZ, PZ–MDEA, PZ–DMA2P, and PZ–IPAE) solutions upon heating (80 °C, 30 min) by  $^{13}\text{C}$ -NMR spectroscopy. The results indicate that  $\text{CO}_2$  regeneration originates from the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  species, and not from mono- and bis-carbamates and carbonate.  $^{13}\text{C}$ -NMR spectroscopy is a powerful tool for qualitative and quantitative analyses of chemical species in amine absorbers of  $\text{CO}_2$ .

#### Acknowledgements

The authors are grateful to Professors H. Nakai and N. Kanomata, and Dr. H. Yamamoto of Waseda University for valuable discussion and suggestions.

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