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Aqueous piperazine/N-(2-aminoethyl) piperazine for CO_2 capture

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Abstract

A novel blend of piperazine (PZ) with N-(2-aminoethyl) piperazine (AEP) has been proposed as a superior solvent for CO_2 capture from coal-fired flue gas. Blending PZ with AEP can remediate the precipitation issue of concentrated PZ while maintaining its high CO_2 absorption rate, and high resistance to degradation. Although PZ/AEP has a lower CO_2 capacity than concentrated piperazine, its higher heat of absorption may offset the negative effect on energy consumption. PZ/AEP also shows a milder nitrosamine issue than concentrated piperazine. A novel method for synthesizing AEP using PZ and monoethanolamine (MEA) was also developed to lower the solvent cost in industry application.

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Keywords: Solvent blend; Piperazine; Aminoethylpiperazine; CO_2 capture; Degradation; Nitrosamine

1. Introduction

Amine scrubbing has shown the most promise for effective capture of CO_2 from coal-fired flue gas [1]. Aqueous monoethanolamine (MEA) with a concentration between 15–30 % has been previously used in similar applications such as CO_2 removal from natural gas and hydrogen, and is currently considered the state-of-the-art technology for CO_2 absorption/stripping because of its effectiveness for CO_2 capture and

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low cost of production. However, the low resistance to degradation, and low CO_2 capacity and CO_2 absorption rates of MEA lead to high capital and energy cost when MEA is used for CO_2 capture from coal-fired flue gas.

Concentrated piperazine (PZ) has been proposed as a possible alternative to 30 wt % MEA for CO_2 capture from coal-fired flue gas [2]. PZ has about twice the CO_2 absorption rate and CO_2 capacity, and greater resistance to oxidative and thermal degradation than 30 wt % MEA, which can lower the heat duty for the stripper in amine scrubbing systems by approximately 5–10% [3].

In spite of desirable characteristics, the application of concentrated PZ in industry may be limited by solid precipitation at both lean and rich CO_2 loading [3]. At room temperature (22 ˚C), 8 m PZ requires a loading of 0.25 mol CO_2/mol alkalinity to stay in solution and also forms solids at high CO_2 loading.

Blending solvents already in use is one approach to combine desirable characteristics. A novel PZ-based blend, piperazine/N-(2-aminoethyl) piperazine (PZ/AEP), was investigated in this study to remediate the precipitation of concentrated PZ without sacrificing its CO_2 capacity and absorption rate, resistance to degradation, and other desirable characteristics.

2. Materials and Methods

2.1. Solution preparation

Aqueous PZ/AEP was prepared by melting anhydrous PZ (99%, Alfa Aesar, Ward Hill, MA) in water and AEP (99%, Alfa Aesar, Ward Hill, MA) mixture, and gravimetrically sparging CO_2 (99.5%, Matheson Tri Gas, Basking Ridge, NJ) to achieve the desired CO_2 concentration. The concentration of CO_2 was determined by total inorganic carbon (TIC) analysis, described by Hilliard [4].

2.2. Solvent solubility

The solid solubility of PZ/AEP with a total N concentration of 16 m was measured in a water bath over a range of PZ/AEP molar ratio (5/2, 4/2.67, 3/3.33), CO_2 loading (from 0 to 0.4 mol CO_2/mol alkalinity), and temperature (from 0 to 50 °C). The solid solubility measurements were based on visual observations and the method was described in detail by Freeman [5]. Solutions with desired properties were heated up to 50 °C in a water bath to melt precipitates in solution with lean CO_2 loading. While cooling slowly, the temperature at which the solution first began to crystallize or precipitate was regarded as the crystallizing transition temperature. Finally, the solution was heated again to carefully observe the temperature when the crystals fully melt and this was noted as the melting transition temperature. The difference between crystallizing and melting transition temperature, which is also called hysteresis, was minimized to 1 °C or less for most of the measured points by giving enough equilibrium time and repeating the melting-crystallizing process at transition temperatures.

2.3. Viscosity measurements

Viscosity of 5 m PZ/2 m AEP was measured using a Physica MCR 300 cone and plate rheometer (Anton Paar GmbH, Graz, Austria). The method was also described by Freeman [5]. The average value and standard deviation calculated from 10 individual measurements for each sample was reported.

2.4. Thermal degradation

Thermal degradation was measured in ½-inch OD 316 stainless steel thermal cylinders. Cylinders were filled with 7 mL of amine solution with around 3 mL of headspace, sealed with two Swagelok® end caps, and placed in forced convection ovens maintained at the target temperature. Individual cylinders were removed from the ovens at each sampling point and then analyzed for degradation products, degradation rate, and CO_2 loading, using a Dionex ICS-2500 cation ion chromatograph, a Dionex ICS-3000 modular Dual Reagent-Free anion ion chromatograph (Dionex Corporation) and an infrared CO_2 analyzer (Horiba Instruments Inc., Spring, TX). The details of the experimental apparatus, procedure, and analytical methods are described by Freeman [5, 6].

2.5. Oxidation

Oxidative degradation experiments for 8 m PZ and 2 m AEP spiked with 0.05 mM Cr^{3+}, 01 mM Ni^{2+}, 0.4 mM Fe^{2+} and 0.1 mM Mn^{2+} were conducted in a low gas flow agitated reactor with 100 mL/min of a saturated 98%/2% O_2/CO_2 gas mixture fed into the reactor headspace. The duration of the experiment is 2 weeks and 3 ml samples were taken every two to three days and water was added periodically to maintain the water balance of the reactor contents. The liquid samples were analyzed for PZ, AEP, and degradation products using ion chromatography. The details of the experimental apparatus, procedure, and analytical methods are described by Sexton [7].

2.6. Nitrosamine formation and decomposition

Nitrosamine formation and decomposition experiments were conducted in ⅜-inch Swagelok thermal cylinders using a similar method to thermal degradation experiments. 5 m PZ/2 m AEP or 2 m AEP solutions with 0.3 mol CO_2/mol alkalinity were prepared and spiked gravimetrically with 40 mmol/kg of sodium nitrite ($NaNO_2$) immediately before being placed into convection ovens at 100 °C and 150 °C. The details of the experimental apparatus, procedure, and analytical methods are described by Fine [8].

2.7. CO_2 absorption rate and solubility

CO_2 absorption rate and equilibrium partial pressure in 5 m PZ/2 m AEP were measured from 20 to 100 °C using a wetted wall column (WWC), which countercurrently contacted an aqueous 5 m PZ/2 m AEP solution with a saturated N_2/CO_2 stream on the surface of a stainless steel rod with a known surface area to simulate the situation of CO_2 absorption in a absorber. The detailed description of wetted wall column measurement has been given by Li [9].

2.8. High temperature vapor-liquid equilibrium

The total pressure of 5 m PZ/2 m AEP loaded with CO_2 was measured from 100 to160 °C using a sealed autoclave (SA). The partial pressure of CO_2 was calculated by subtracting the partial pressure of N_2 and water from the measured total pressure. The pressure of water was assumed to follow Raoult's

Law and the pressure of amine was neglected. The experimental method and calculation of CO_2 partial pressure are described in detail by Xu [10].

2.9. Synthesis of N-(2-aminoethyl) piperazine

The synthesis of N-(2-aminoethyl) piperazine from PZ and MEA in the presence of CO_2 was conducted using a method similar to that of thermal degradation experiments. 7 m PZ/2 m MEA with 0.3 mol CO_2/mol alkalinity was placed in ½-inch OD 316 stainless steel thermal cylinders , which were then sealed and placed in a convection oven held at 150 °C. Cylinders were removed periodically and samples were analyzed using ion chromatography.

3. Results and Discussion

3.1. Solid solubility of PZ/AEP

The melting transition temperature of PZ/AEP with variable amine concentration ratio (5/2, 4/2.67, 3/3.33) over a range of CO_2 loading from 0 to 0.4 mol/mol alkalinity is shown in Fig. 1. The transition temperature for non-blended 8 m PZ from Freeman [3] is also shown in Fig. 1 for comparison. As the proportion of PZ in the blend decreases, the transition temperature decreases. For 5 m PZ/2 m AEP, a CO_2 loading of approximately 0.20 mol/mol alkalinity is required to maintain a liquid solution without precipitation at room temperature (22 °C), which is lower than 0.25 mol/mol alkalinity required for 8 m PZ. Unlike 8 m PZ, which also precipitates when CO_2 loading reaches 0.44 mol CO_2/mol alkalinity [3], no precipitate was observed for the three blends at rich CO_2 loading (until CO_2 reached its solubility limit under atmospheric pressure, which is about 0.4 mol CO_2/mol alkalinity in the three blends). Therefore, this blend has a lower solvent solubility limit at lean loading, and is free from precipitation at rich loading under atmospheric pressure.

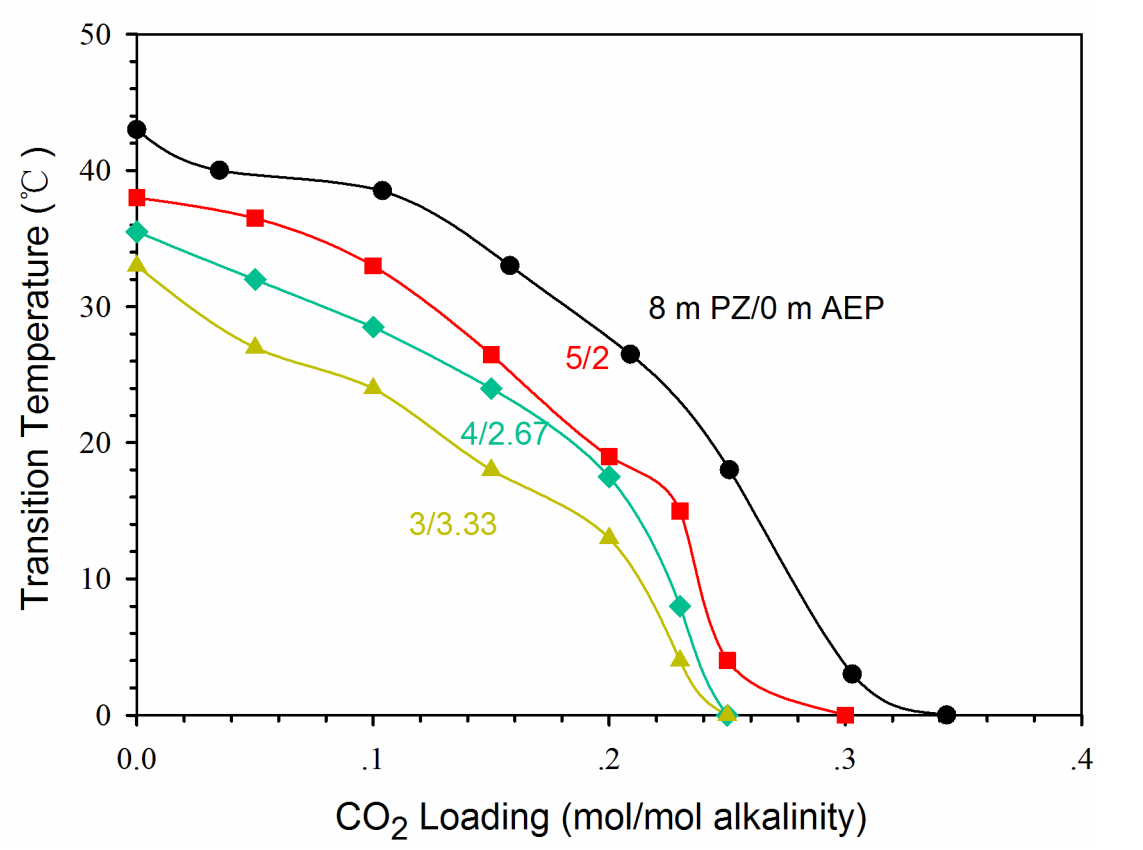

Fig. 1: Liquid-Solid transition temperature for PZ/AEP with different amine ratios, ●: 8 m PZ/0 m AEP [3]; ■: 5 m PZ/2 m AEP; ♦: 4 m PZ/2.67 m AEP; ▲: 3 m PZ/3.33 m AEP.

3.2. Viscosity

Viscosity of 5 m PZ/2 m AEP with 0.2 and 0.3 mol CO_2/mol alkalinity was measured at 20 °C, 40 °C, and 60 °C (Table 1). The results suggests that the viscosity of this blend is comparable to that of non-blended 8 m PZ [3] (i.e., 11.96 cP for 5 PZ/2 AEP compared to 9.99 cP for 8 m PZ at 0.30 mol CO_2/mol alkalinity and 40 °C). The data also demonstrate the expected trend that viscosity increases with increasing CO_2 concentration and decreasing temperature.

Table 1. Viscosity of 5 m PZ/2 m AEP from 20 to 60 °C.

CO_2 Loading	Viscosity (cP)		
(mol/mol alkalinity)	20 °C	40 °C	60 °C
0.20	21.92 ± 0.068	9.843 ± 0.082	5.88 ± 0.162
0.30	24.75 ± 0.090	11.96 ± 0.108	7.78 ± 0.720

3.3. Thermal Degradation

The thermal degradation of 5 m PZ/2 m AEP was measured for 20 weeks with 0.3 mol CO_2/mol alkalinity at 150 °C and 175 °C. After the 20-week experiment, the loss of PZ and AEP at 150 ˚C was approximately 10% and 30%, respectively, while at 175 ˚C the amines were almost entirely degraded (Figs. 2 and 3). From these results it can be concluded that 5 m PZ/2 m AEP is thermally stable up to 150 ˚C but not 175 °C.

The thermal degradation of 5 m PZ/2 m AEP is compared to that of 5.33 m non-blended AEP and 8 m PZ [11] (Figs. 2 and 3), and their apparent first order rate constants (k_1) for thermal degradation is given in Table 2, along with the data for 7 m MEA. The PZ in this blend degrades at the same rate as in 8 m PZ at both temperatures (Fig. 2). However, the AEP in the blend degraded much more slowly than in 5.33 m AEP with 0.3 mol CO_2/mol alkalinity (Fig. 3). This could have two explanations: 1) compared to 2 m AEP, due to the competition of PZ for H^+, this blend produced less protonated AEP, which is likely to be the initiating species required for the initial reactions of thermal degradation [6, 11, 12]; 2) as PZ is one of the major products for AEP thermal degradation, its presence may inhibit the degradation of AEP [13]. The overall amine degradation rate of this blend is on the same scale as that of 8 m PZ, while much smaller than that of 5.33 m AEP and 7 m MEA.

Table 2. Apparent first order rate constant (k_1) for thermal degradation of PZ/AEP and other related solvents.

Amine	Components	Loading mol/mol alkalinity	$k_1 \times 10^{-9}$ (s^{-1}) 150 °C	175 °C
PZ	5 m PZ/2 m AEP	0.3	10.2	162
AEP	5 m PZ/2 m AEP	0.3	27.9	388
PZ/AEP	5 m PZ/2 m AEP	0.3	15.2	201
[11]PZ	8 m PZ	0.3	6.1	140
AEP	5.33 m AEP	0.3	365	2022
[13]MEA	7 m MEA	0.4	807	N/A

N/A: not available

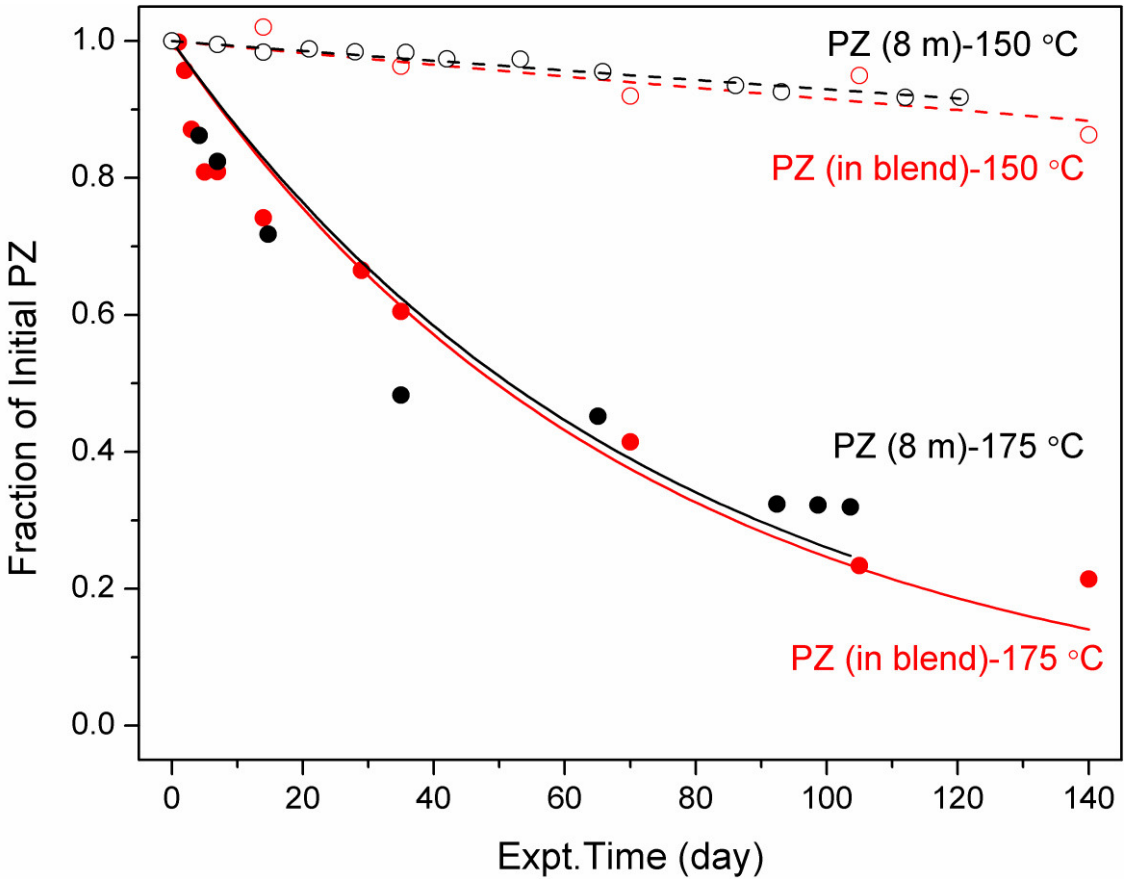

Fig. 2. Comparison of PZ loss in 5 m PZ/2 m AEP and 8 m pure PZ [11] in thermal degradation at 0.3 mol CO_2/mol alkalinity.

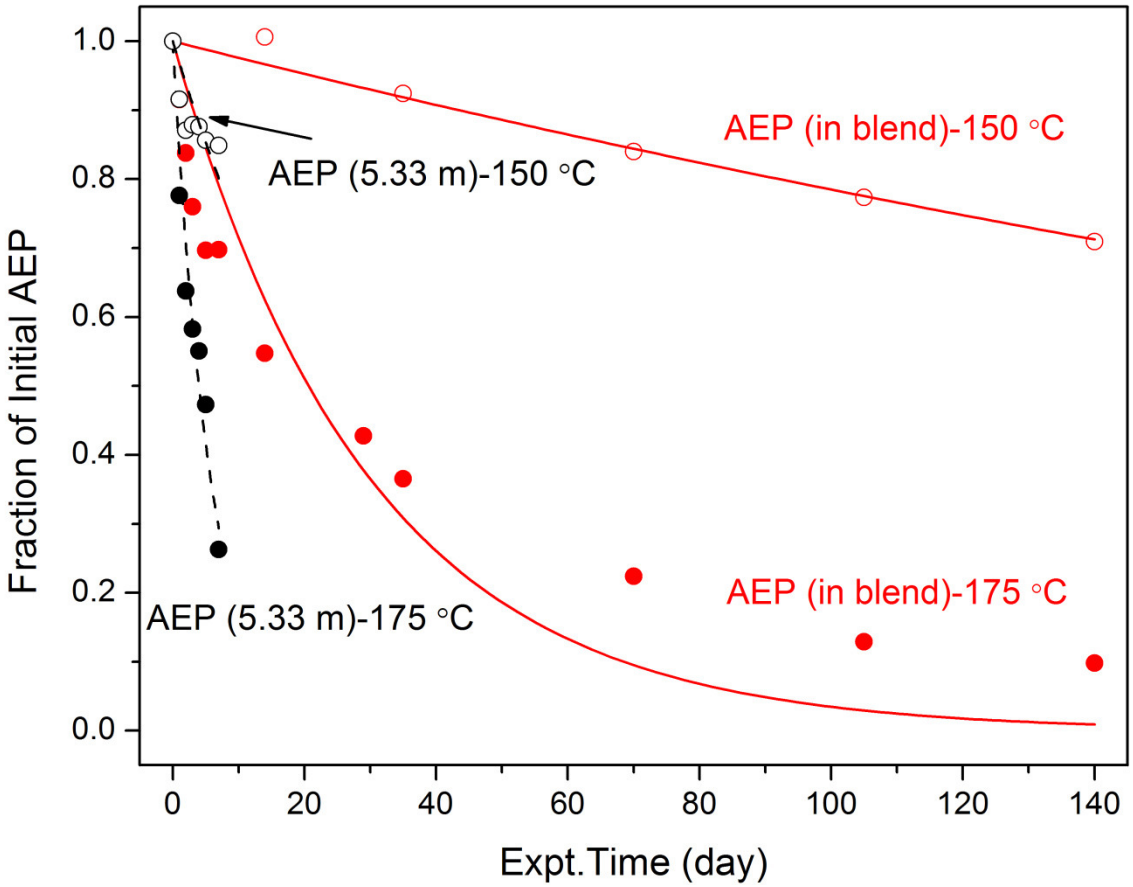

Fig. 3. Comparison of AEP loss in 5 m PZ/2 m AEP and 5.33 m pure AEP in thermal degradation at 0.3 mol CO_2/mol alkalinity.

The effect of CO_2 on the degradation of PZ and AEP in 5 m PZ/2 m AEP at 175 °C is given in Fig. 4. The increase of CO_2 accelerated the degradation of both PZ and AEP in this blend. This can be ascribed to the increased protonated PZ/AEP species present in solution, which are likely to be the initiating species required for the initial reactions of thermal degradation [6, 11, 12].

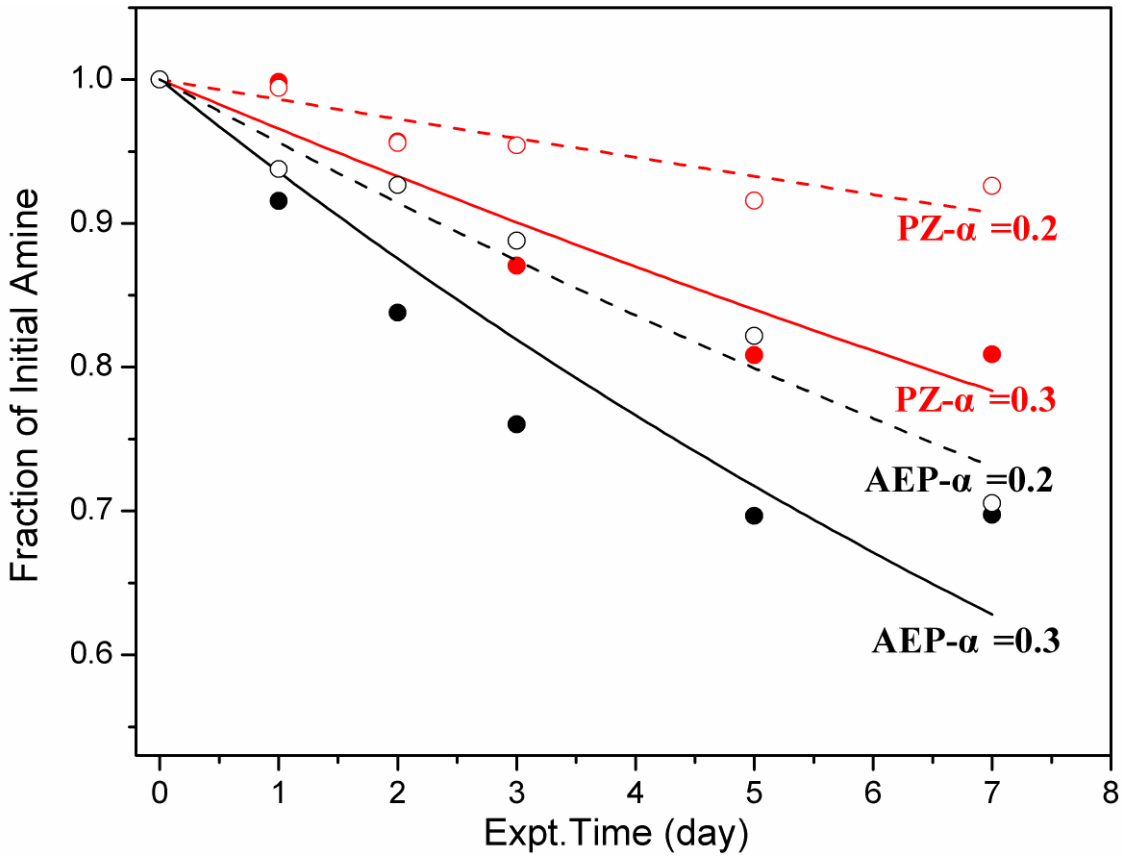

Fig. 4. Effect of CO_2 on the degradation of PZ and AEP in 5 m PZ/2 m AEP at 175 °C (Dashed line: 0.2 mol CO_2/mol alkalinity; solid line: 0.3 mol CO_2/mol alkalinity).

The thermal degradation products of 5 m PZ/2 m AEP at 175 °C are shown in Fig. 5. It can be seen that NH_4^+ and total formate, the sum of formate and N-Formyl PZ, were the two major products for the thermal degradation, while 1,1'-(1,2-ethanediyl)bis-PZ (PEP), 1-Ethyl PZ, Triethylenediamine (TEDA), total 1-[2-[(2-aminoethyl)amino]ethyl] PZ (AEAEPZ), the sum of AEAEPZ and AEAEPZ Urea, and N,N"-di(2-aminoethyl) piperazine (DAEP) were the minor ones. As the retention time of TEDA is too close to that of 1-Ethyl PZ on cation ion chromatography, we quantified them as a combination. All the products showed a fast phase in the first 1–3 weeks, followed by a slow rate or steady-state concentration at longer time.

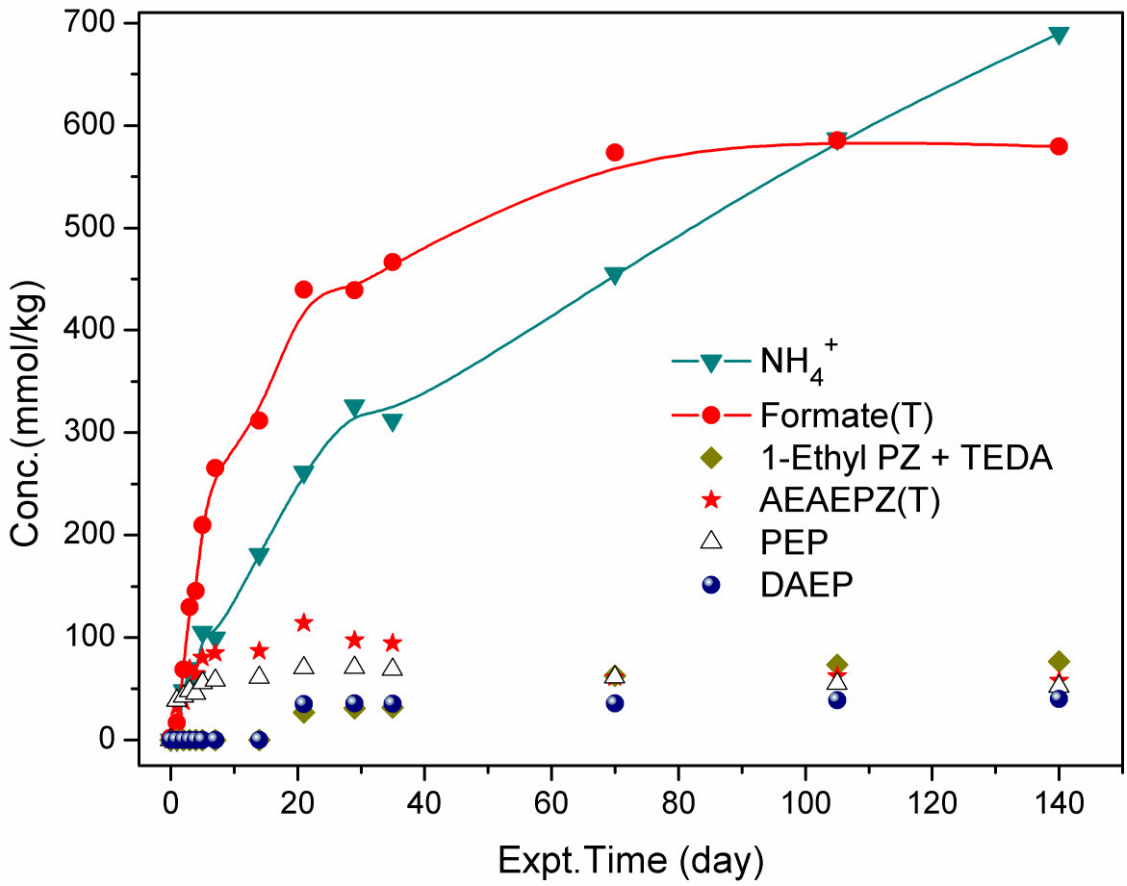

Fig. 5. Degradation products from thermal degradation of 5 m PZ/2 m AEP with 0.3 mol CO_2/mol alkalinity at 175 °C.

PZ, AEP, and CO_2 loss are compared to the production of NH_4^+ and total formate during thermal degradation of 5 m PZ/2 m AEP with 0.3 mol CO_2/mol alkalinity at 175 °C (Fig. 6). The rate of PZ/AEP decrease is much larger than the rate of NH_4^+ increase in the first week, indicating some degradation pathways that do not produce NH_4^+ may also occur in the first week. This non-NH_4^+ production pathway could be the reaction between two PZ molecules to produce AEAEPZ and AEAEPZ urea [6].

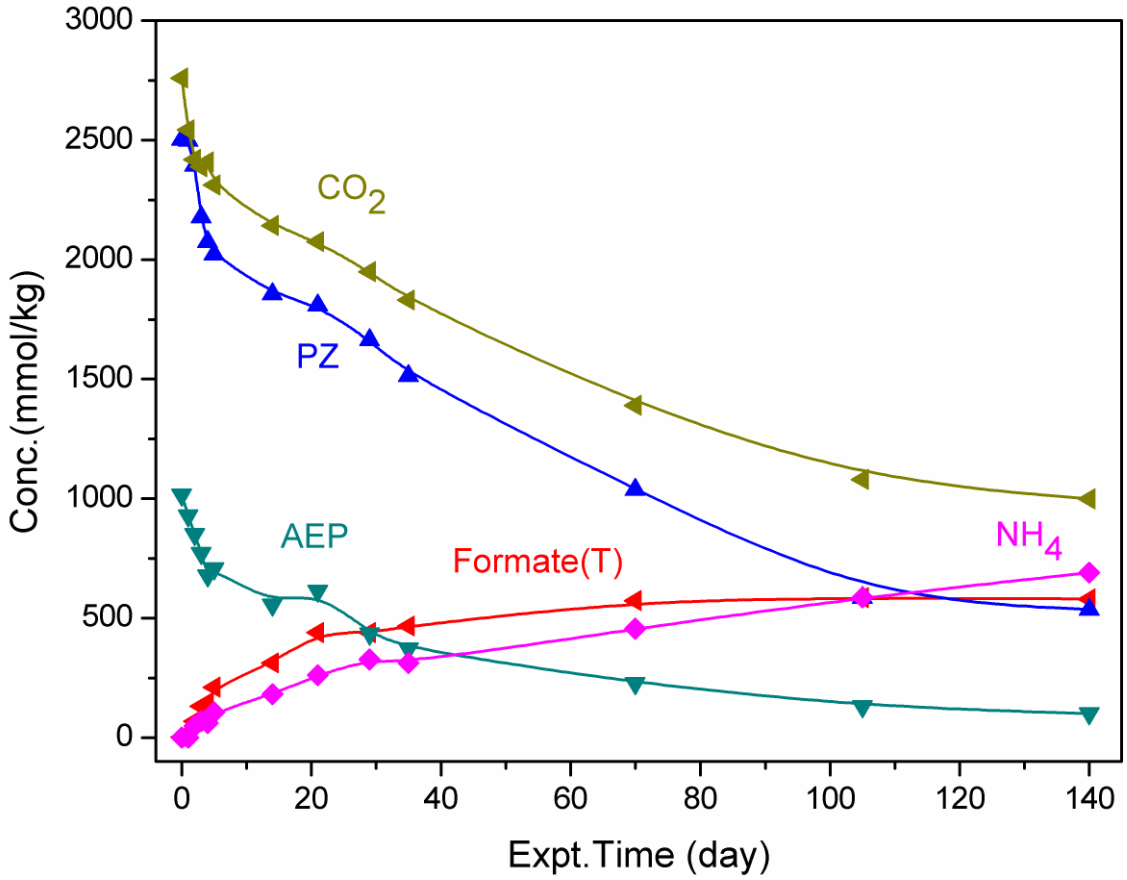

Fig. 6. PZ, AEP, and CO_2 loss and generation of major degradation products for 5 m PZ/2 m AEP with 0.3 mol CO_2/mol alkalinity at 175 °C.

3.4. Oxidative degradation

Sexton [7] and Freeman [5] have shown that PZ oxidizes significantly slower than MEA under similar conditions, and that the generation rate of total formate (formate and formyl amides) can represent the oxidation rate of PZ under different conditions in low gas flow experiments. In this work, oxidation of 8 m PZ, 2 m AEP and 5 m PZ/2 m AEP at 70 °C in the presence of 0.1 mM Mn^{2+} and with the typical SSM mixture (0.4 mM Fe^{2+}, 0.05 mM Cr^{3+} and 0.1 mM Ni^{2+}), was investigated. The generation of total formate is shown in Fig. 7, compared to that in 8 m PZ [5] and 7 m MEA in the absence of Mn^{2+} under similar conditions. It can be seen from Fig. 7 that Mn^{2+} did not have a significant catalytic effect on the oxidation of PZ. In terms of the production of total formate, the oxidation of 2 m AEP and 5 m PZ/2 m AEP was comparable to that of 8 m PZ, but significantly slower than that of 7 m MEA.

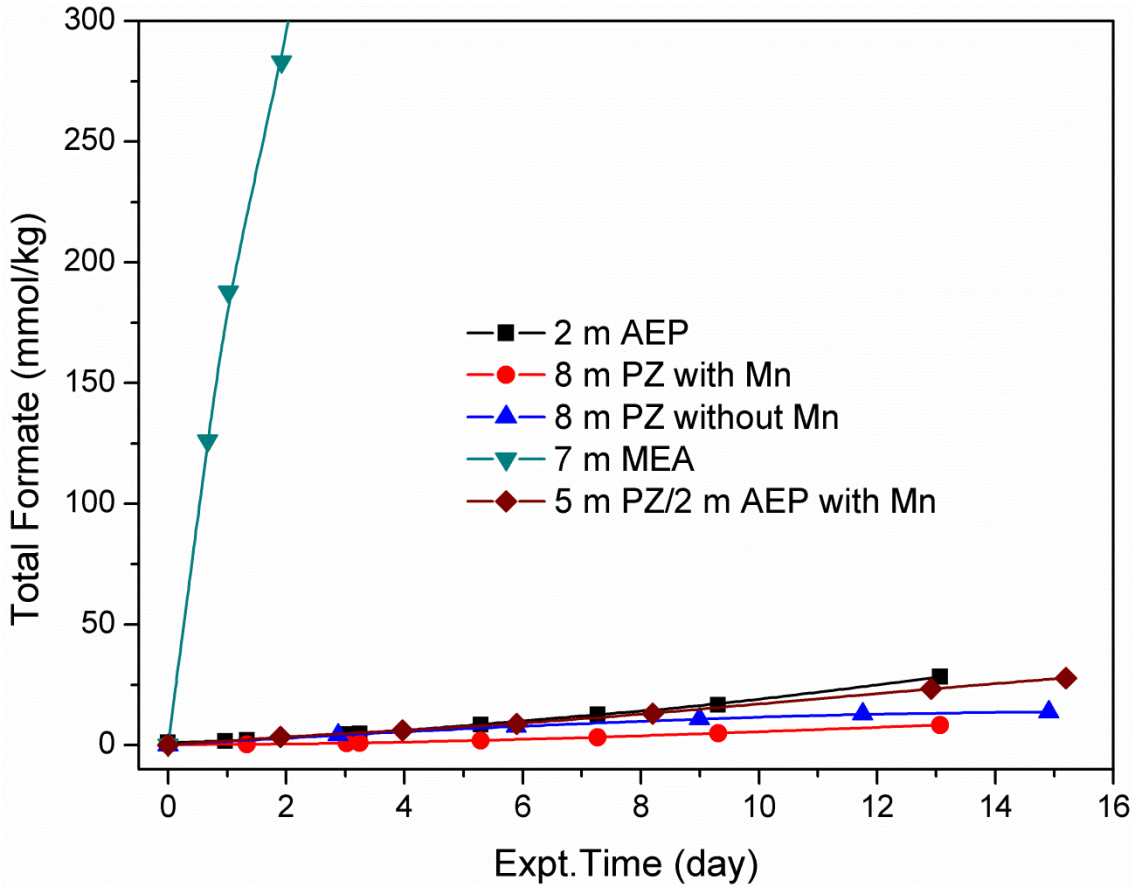

Fig. 7. Comparison of total formate production in 8 m PZ with Mn^{2+}, 8 m PZ without Mn^{2+} [5], 2 m AEP and 7 m MEA at 70 °C.

3.5. Nitrosamines

Nitrosamines, which are likely to be carcinogenic and can be formed through nitrosation of secondary amines [8], may be important when using amines containing secondary amine nitrogens in CO_2 capture. The formation of nitrosamines in 5 m PZ/2 m AEP was compared to that in 8 m PZ and 2 m AEP at 0.3 mol CO_2/mol alkalinity and 100 °C (Fig. 8). As can be seen from Fig. 8, the formation rate of total nitrosamine (mono-nitroso-PZ (MNPZ) and mono-nitroso-AEP (MNAEP)) in 5 m PZ/2 m AEP is similar to the formation rate of MNPZ in 8 m PZ [8]. However, the formation of MNAEP in this blend is slower than that in 2 m AEP. This can be ascribed to the competition between PZ and AEP for CO_2 in blend. Compared to 2 m AEP, this blend produced less AEP carbamate species, which are likely to be the initiating species required for the initial reactions of nitrosation and first order to the formation rate of MNAEP [8].

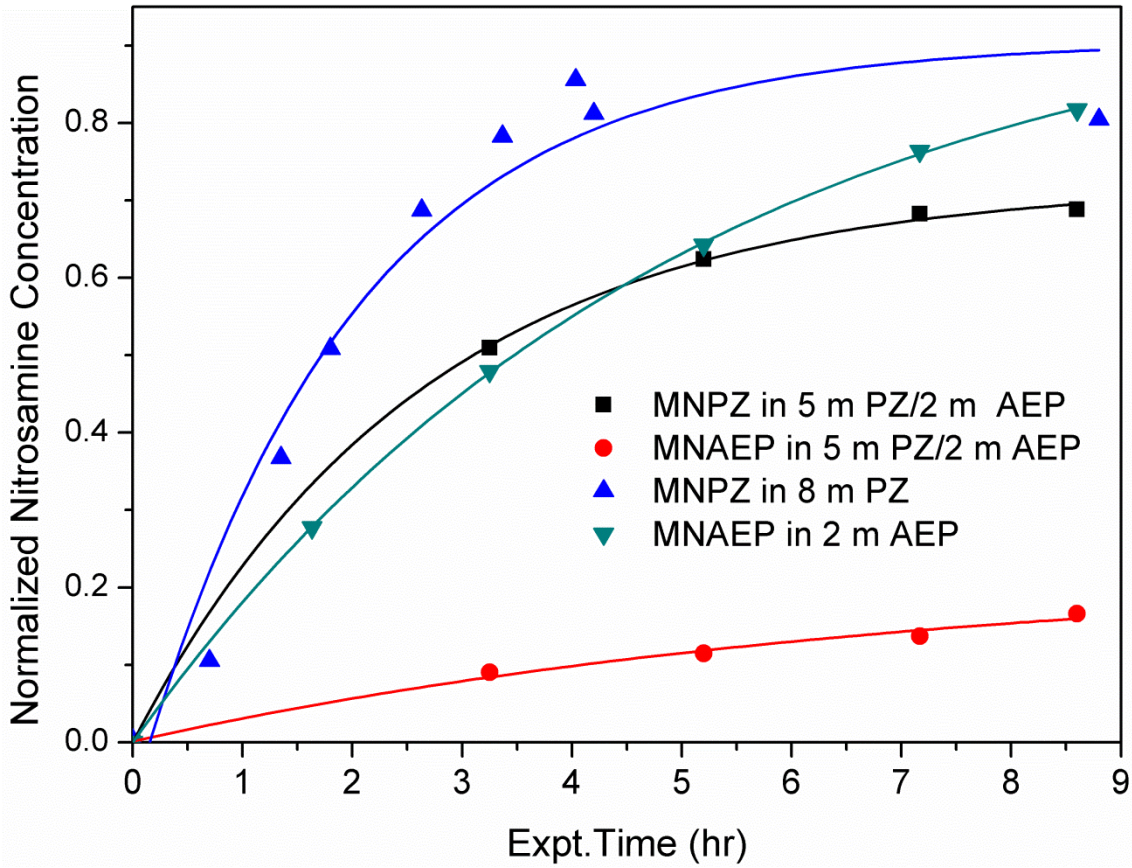

Fig. 8. Nitrosamines formation in 5 m PZ/2 m AEP at 100 °C, compared to that in 8 m PZ [8] and 2 m AEP.

The decomposition of nitrosamines in 5 m PZ/2 m AEP was investigated at 0.3 mol CO_2/mol alkalinity and 150 °C, compared to that in 8 m PZ and 2 m AEP under similar conditions (Fig. 9). As can be seen from Fig. 9, the decomposition of MNPZ and MNAEP in 5 m PZ/2 m AEP is on the same scale as that of that of MNPZ in 8 m PZ. However, the decomposition of MNAEP in 5 m PZ/2 m AEP is much faster than that of MNAEP in 2 m AEP. This may be ascribed to the high amine concentration in this blend compared to 2 m AEP, though the mechanism for thermal decomposition of nitrosamine is still unclear at this moment. Together with the formation results, these results indicate that PZ/AEP may have a similar nitrosamine issue to individual PZ.

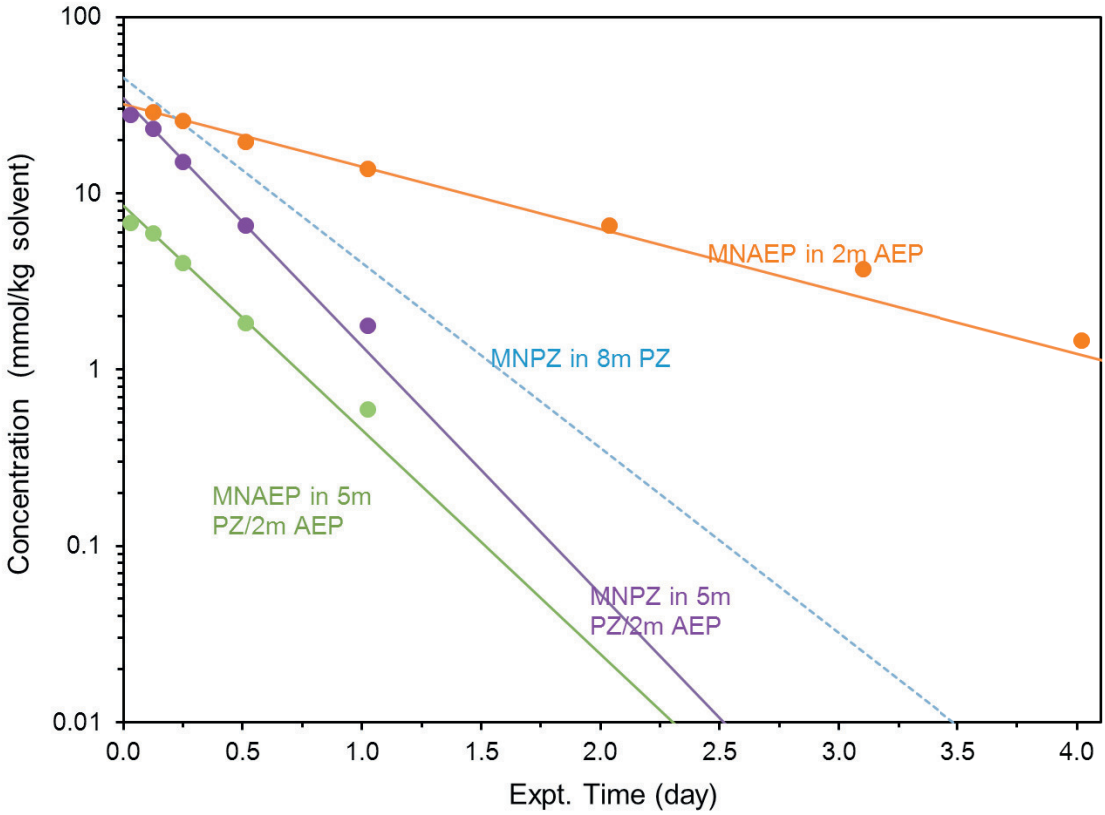

Fig. 9. Nitrosamine decomposition in 5 m PZ/2 m AEP at 150 °C, compared to that in 8 m PZ [8] and 2 m AEP.

3.6. CO_2 solubility

The CO_2 solubility in loaded 5 m PZ/2 m AEP was measured from 40 to 160 °C (Fig. 10). CO_2 equilibrium partial pressure, P_{CO2} (Pa), was regressed using the following empirical model Eq. 1 as a function of temperature, T (K), and CO_2 loading, α (mol CO_2/mol alkalinity), in the liquid phase.

$$\ln P_{CO2} = 39.83 - 11105 * \frac{1}{T} - 15.47 * a + 22167 * \frac{a^2}{T} \quad (1)$$

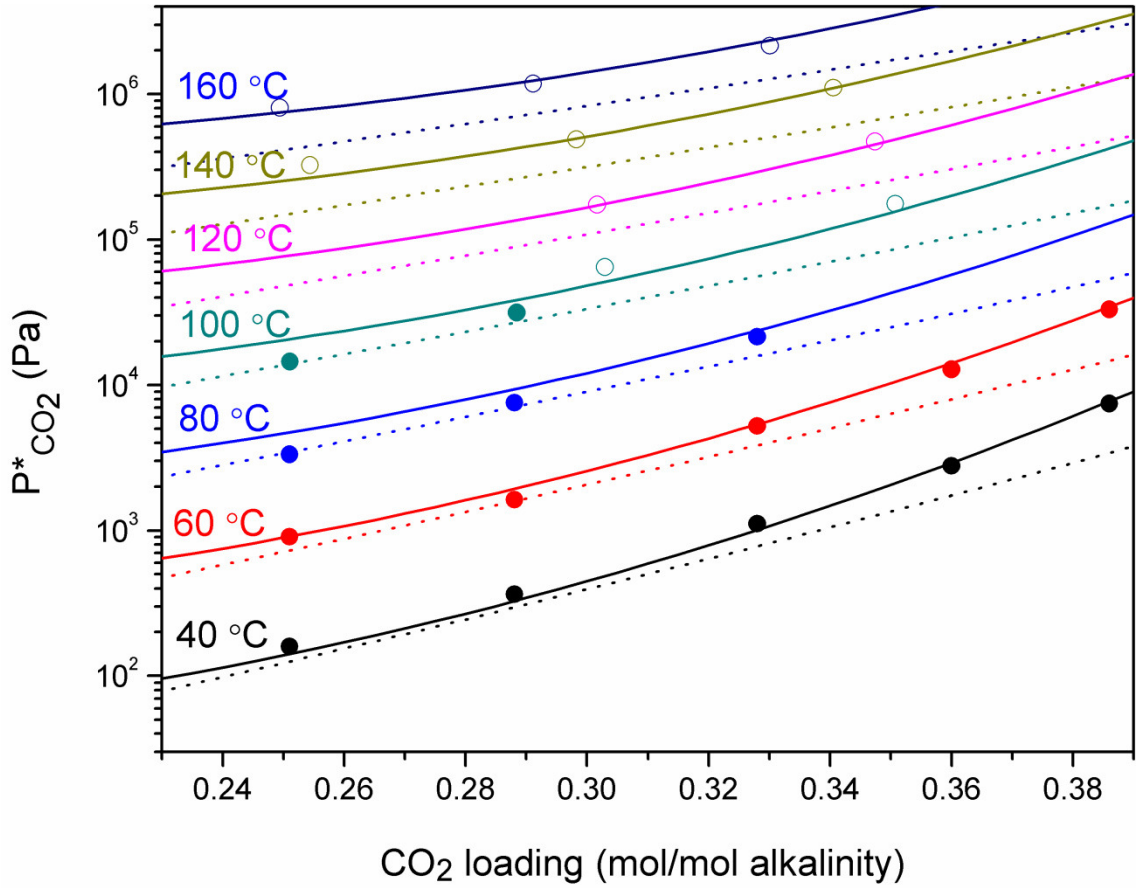

Fig. 10. CO_2 solubility for 5 m PZ/2 m AEP (Solid lines: 5 m PZ/2 m AEP equation model; Solid circles: measured data for 5 m PZ/2 m AEP using WWC; Open circles: measured data for 5 m PZ/2 m AEP using SA; Dashed lines: 8 m PZ equation model from Xu [10].

The CO_2 partial pressure of 8 m PZ is also given in Fig. 10 for comparison [10]. From Fig. 10 we can see that CO_2 partial pressure of 5 m PZ/2 m AEP is consistently higher than that of 8 m PZ from 40 to 160 °C, indicating a lower CO_2 solubility in this blend. Based on the difference in the equilibrium CO_2 partial pressure from 5 to 0.5 kPa at 40 °C, the working capacity of 5 m PZ/2 m AEP (0.67 mole per kg amines + water) is lower than that of 8 m PZ [9] (0.79 mole per kg amines + water), but still much higher than that of 7 m MEA (0.47 mole per kg amines + water) [14].

3.7. Absorption rate

CO_2 absorption rate into 5 m PZ/2 m AEP were studied in a wetted wall column from 20 to 100 °C with loading from 0.25 to 0.39 mol CO_2/mol alkalinity. The liquid-film mass coefficients (k_g') of CO_2 absorption into 5 m PZ/2 m AEP are shown in Fig. 11. To compare kg' in 5 m PZ/2 m AEP to that in 8 m PZ on the same basis, the rate data are plotted against partial pressure of CO_2 instead of CO_2 loading. T compare kg' at variable temperature, the rate data of 5 m PZ/2 m AEP at 20 to 100 °C are plotted as a function of the equilibrium partial pressure of CO_2 at 40 °C. Compared to 8 m PZ, at 40 °C the blend has

similar rate. Similar to other amines studied in CO_2 capture [14], temperature has a negative effect on CO_2 absorption rate into 5 m PZ/2 m AEP, especially at rich CO_2 loading.

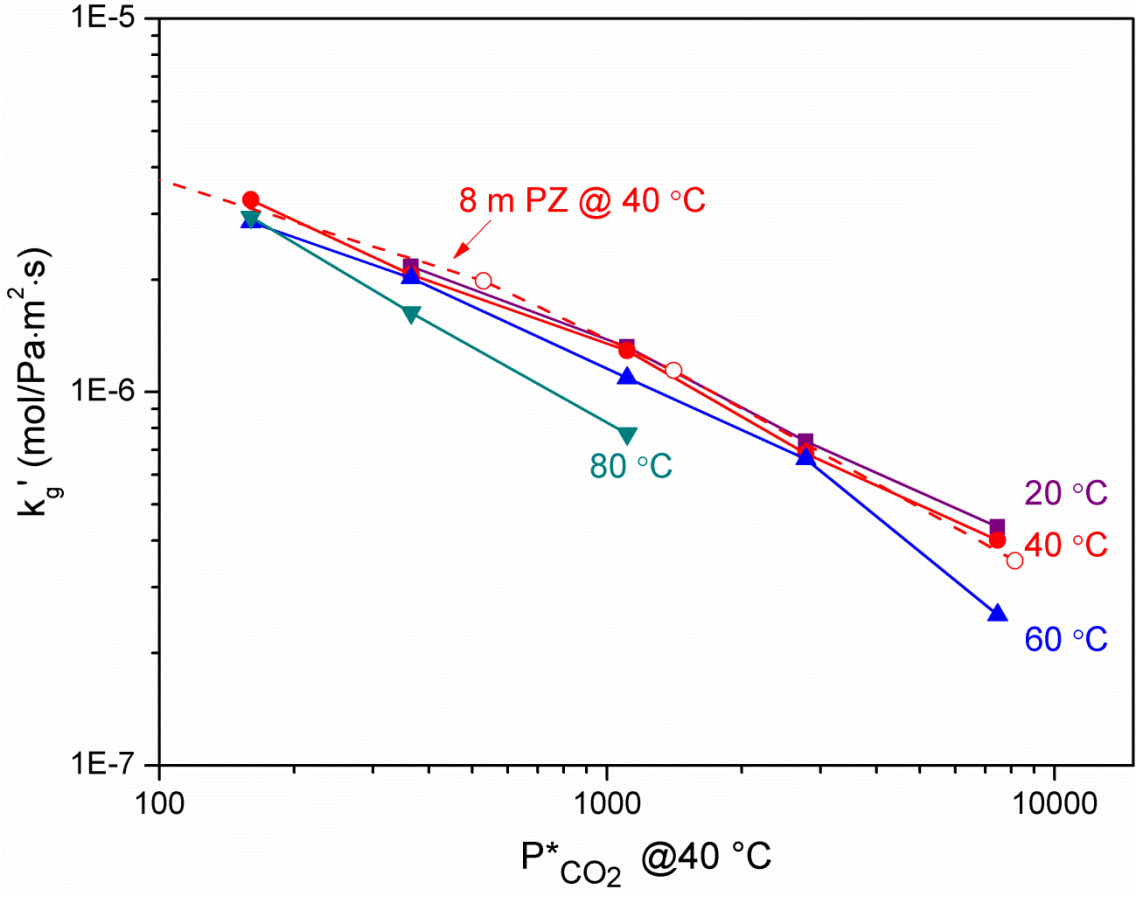

Fig. 11. Mass transfer coefficients (kg') in 5 m PZ/2 m AEP (solid lines) from 20 to 80 °C, compared to that in 8 m PZ (dashed line) at 40 °C.

3.8. Synthesis of N-(2-aminoethyl) piperazine

Since AEP is the dominant thermal degradation product in 7 m MEA/2 m PZ [13], the synthesis of AEP was studied at 150 °C with an initial loading of 0.3 mol CO_2/mol alkalinity with two blends: 7 m PZ/2 m MEA and 6 m PZ/4 m MEA. A combined AEP/DAEP yield of 68% was obtained with 89% of the total alkalinity present as PZ, AEP, or DAEP over 840 hours in 7 m PZ/2 m MEA. A combined AEP/DAEP yield of 52% was obtained with 77% of the total alkalinity present as PZ, AEP, or DAEP in 6 m PZ/4 m MEA. Ureas appear to be the greatest contributor to alkalinity loss. These results show that PZ/AEP can be achieved by starting with PZ/MEA, leading to cost reduction in obtaining the solvent.

4. Conclusions

The blend 5 m PZ/2 m AEP has a larger solid solubility window than 8 m PZ. In 5 m PZ/2 m AEP, a CO_2 loading of 0.20 mol/mol alkalinity is required to avoid precipitation at 22 °C, which is lower than

0.25 mol/mol alkalinity required for 8 m PZ. No precipitate was observed in PZ/AEP at rich CO_2 loading. The viscosity of 5 m PZ/2 m AEP is comparable to 8 m PZ.

5 m PZ/2 m AEP is thermally stable up to 150 °C but not 175 °C. Thermal degradation of this blend is comparable to 8 m PZ, but significantly slower than 7 m MEA. In terms of the production of total formate, the oxidation of 5 m PZ/2 m AEP is comparable to that of 8 m PZ, but significantly slower than that of 7 m MEA, and Mn^{2+} does not have a significant catalytic effect on the oxidation of PZ.

The working capacity of 5 m PZ/2 m AEP (0.67 mole per kg amines + water) is lower than that of 8 m PZ (0.79 mole per kg amines + water), but still much higher than that of 7 m MEA (0.47 mole per kg amines + water). Kinetics measurements have shown that compared to 8 m PZ, at 40 °C 5 m PZ/2 m AEP has similar CO_2 absorption rates.

The formation and decomposition of nitrosamine in PZ/AEP is similar to that in PZ.

PZ/AEP can be synthesized in situ by thermal degradation of PZ/MEA.

Compared to 8 m PZ, the greater solvent solubility and comparable CO_2 absorption and degradation rates, indicate that 5 m PZ/2 m AEP is a superior solvent for CO_2 capture by absorption/stripping.

Acknowledgements

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