



Capacity and absorption rate of tertiary and hindered amines blended with piperazine for CO₂ capture



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HIGHLIGHTS

- 21 tertiary and hindered amines blended with PZ have been studied for CO₂ capture.
- The optimum pK_a of a tertiary amine blended with PZ is around 9.1.
- A generic Aspen Plus[®] model for PZ/tertiary amine has been developed.
- Hindered amines show similar CO₂ VLE to tertiary amines in PZ blends.
- PZ/2E-4 M-IMI and PZ/HMPD are promising solvents for CO₂ capture from flue gas.

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ABSTRACT

Aqueous piperazine (PZ) blended with a tertiary or hindered amine combines the high CO₂ capacity of the tertiary or hindered amine with the fast rate of PZ. For flue gas CO₂ capture, the optimum pK_a (that which offers the highest CO₂ cyclic capacity) of a mono-tertiary amine blended with PZ is 9.1. A generic Aspen Plus[®] model for PZ/tertiary amine was developed to predict the CO₂ vapor-liquid-equilibrium (VLE) from the pK_a of the tertiary amine. The polarity of the tertiary amine also affects the CO₂ solubility of the PZ/tertiary amine. Hindered amines that form little carbamate show similar CO₂ VLE to tertiary amines with the same pK_a, when blended with PZ. The CO₂ absorption rate of most 2.5 m PZ/2.5 m tertiary amines was slightly slower than 2.5 m PZ, probably due to the higher viscosity of the blends.

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1. Introduction

Chemical absorption using aqueous amine is the most applicable technology for flue gas CO₂ capture from fossil fuel combustion. Its maturity has been proved in other industrial gas treating processes (Astarita et al., 1983), and its high energy efficiency compared to other alternative technologies, such as oxy-combustion, physical adsorption, and membrane separation (Rochelle, 2009) makes it an excellent choice. Its commercial application may be impeded by the high capital and energy costs that result from the low CO₂ partial pressure and high flow rate of flue gas (Catalanotti et al., 2014; Clark and Herzog, 2014; Finkenrath, 2012).

CO₂ cyclic capacity and CO₂ absorption rate are the two most important parameters that determine the capital cost and energy cost of an amine solvent for CO₂ capture. With higher CO₂ cyclic capacity, less solvent is required to remove the same amount of

CO₂, reducing the sensible heat requirement for solvent regeneration and the size of the cross heat exchanger. A faster absorption rate reduces the amount of packing required for the same CO₂ removal, which leads to a lower absorber cost.

Concentrated piperazine (PZ) has been proposed as a new baseline for amine scrubbing (Rochelle et al., 2011). 8 molal (m) PZ (40 wt% PZ) has double the CO₂ absorption rate and capacity, and much better thermal stability than the benchmark solvent, 30 wt% monoethanolamine (MEA) (Rochelle et al., 2011). However, PZ and its zwitterionic carbamate have limited water solubility so solid precipitation may occur (Freeman et al., 2010; Ma et al., 2012), which may limit its application. Blending other useful amines with less concentrated PZ (2–3 mPZ) is a way to address the solid precipitation of PZ, while maintaining the good performance of concentrated PZ. PZ blended with a tertiary or hindered amine, such as PZ/*n*-methyl-diethanolamine (MDEA) and PZ/2-amino-2-methyl-1-propanol (AMP), usually combines the high CO₂ capacity of the tertiary and hindered amine with the fast rate of PZ (Adeosun et al., 2013; Bishnoi and Rochelle, 2002; Chen and Rochelle, 2011;

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Kumar and Kundu, 2012; H. Li et al., 2013; Seo and Hong, 2000).

In this work, 21 novel tertiary and hindered amines (Table 1) blended with PZ have been studied for their CO₂ capacity and absorption rate, and compared to PZ/MDEA and PZ/AMP. The effect of the structural features of tertiary and hindered amines on the CO₂ capacity and absorption rate of the blends has also been investigated. More details of this work are reported in Du (2016).

2. Experiment methods

2.1. Solution preparation

All amines studied in this work were reagent grade chemicals from commercial sources. Aqueous PZ/tertiary amines and PZ/hindered amines were prepared by melting anhydrous PZ in mixtures of distilled de-ionized water and tertiary amines or hindered amines, and gravimetrically sparging CO₂ (99.5%, Matheson Tri Gas, Basking Ridge, NJ) to achieve the desired CO₂ concentration. The CO₂ was determined by total inorganic carbon (TIC) analysis, described in detail previously (Freeman et al., 2010).

2.2. Viscosity measurement

Viscosity of some of the PZ/tertiary amines with variable CO₂ loading was measured at 40 °C using a Physica MCR 300 cone-and-plate rheometer (Anton Paar GmbH, Graz, Austria). The method was described in detail previously (Freeman et al., 2010).

2.3. CO₂ solubility by FTIR

CO₂ solubility in PZ/tertiary amines and PZ/hindered amines were measured at 40 °C and normal CO₂ loading range in a stirred reactor coupled with a hot gas FTIR analyzer (Fourier Transform Infrared Spectroscopy, Temet Gasmet Dx-4000) as shown in Fig. 1. This was the same method and apparatus used by Nguyen (2013) to measure amine volatility. The 1 L glass reactor was filled with approximately 500 mL of target solution and agitated at 350 ± 5 rpm. Temperature of the solution was controlled by circulating heated dimethylsilicone oil in the outer jacket. The reactor is open to the atmosphere through the small gap between the agitator shaft and tube wall, in order to maintain a pressure close to 1 atm but negligible solvent evaporation loss. Vapor from the headspace of the reactor was circulated at a rate of ~5–10 L/min. by a heated sample pump to the FTIR through Teflon line. The line, the pump cell, and FTIR analyzer were all maintained at 180 °C to prevent the material in gas from condensation. After the gas passed through the FTIR, it was returned to the reactor through another heated line maintained at 95 °C to maintain water balance and heat balance in the reactor. The concentration of CO₂ in the gas were directly measured using the FTIR software (Calcmeter) with a measured calibration for CO₂. The details of the experimental apparatus, procedure, and calibration methods were described previously by Nguyen (2013).

2.4. CO₂ solubility and absorption rate by WWC

The CO₂ solubility and CO₂ absorption rate in some of the PZ/tertiary amines were measured at 40 °C and normal CO₂ loading range using a wetted wall column (WWC) (Fig. 2), which counter-currently contacted an aqueous amine solution with a saturated N₂/CO₂ stream on the surface of a stainless steel rod with a known surface area to simulate the situation of CO₂ absorption in an absorber.

The amine solution circulated through the WWC at (Q_{liquid}) approximately 4 mL/s. The total flow rate of the gas (Q_{gas}) was

5 standard liter (STL)/min. Variable CO₂ partial pressure in the gas mixture was achieved by mixing N₂ with pure CO₂ or diluted CO₂ in N₂ (~5000 ppm). The pressure in the chamber (P_{tot}) was controlled using a needle valve directly downstream of the WWC chamber. In this work, the WWC was operated with P_{tot} at 138 or 276 kPa (20 or 40 psig). The temperature of the amine solution coming out from the WWC chamber was controlled at 40 °C using oil baths. The temperature of the gas entering the WWC chamber was controlled at 40 °C using the heated saturator. The CO₂ in the gas ($P_{\text{CO}_2, \text{out}}$) exiting from top of the WWC chamber was measured continuously by an infrared CO₂ analyzer (Horiba VIA-510 analyzer). The inlet CO₂ ($P_{\text{CO}_2, \text{in}}$) was measured by bypassing the WWC chamber to the CO₂ analyzer.

The difference in gas phase CO₂ before and after the WWC chamber was used to calculate the CO₂ flux of absorption/desorption (N_{CO_2}), as described in Eq. (1).

$$N_{\text{CO}_2} = \frac{(P_{\text{CO}_2, \text{in}} - P_{\text{CO}_2, \text{out}})}{P_{\text{tot}}} \cdot Q_{\text{gas, sat}} \cdot \frac{1}{V_{\text{M}, \text{A}}} \quad (1)$$

In Eq. (1), $Q_{\text{gas, sat}}$ is the total flow rate of the saturated gas; V_{M} is the molar volume of an ideal gas; A is the total gas-liquid contact area.

Typically, four to six measurements with different $P_{\text{CO}_2, \text{in}}$ were made for each CO₂ loading with half for absorption and the other half for desorption. The calculated N_{CO_2} from Eq. (1) should form a straight line when plotted against the logarithmic mean of the driving force at the top and the bottom of the column (Fig. 3), as described by Eqs. (2) and (3).

$$N_{\text{CO}_2} = K_{\text{G}} (P_{\text{CO}_2} - P_{\text{CO}_2}^*)_{\text{LM}} \quad (2)$$

$$(P_{\text{CO}_2} - P_{\text{CO}_2}^*)_{\text{LM}} = \frac{(P_{\text{CO}_2, \text{out}} - P_{\text{CO}_2}^*) - (P_{\text{CO}_2, \text{in}} - P_{\text{CO}_2}^*)}{\ln \left(\frac{P_{\text{CO}_2, \text{out}} - P_{\text{CO}_2}^*}{P_{\text{CO}_2, \text{in}} - P_{\text{CO}_2}^*} \right)} \quad (3)$$

In Eq. (2), $P_{\text{CO}_2}^*$ is the equilibrium CO₂ partial pressure of the solution and K_{G} is the overall gas side mass transfer coefficient. $P_{\text{CO}_2}^*$ can be obtained by trial and error until the linear fit of these flux points passes through the origin, which means that N_{CO_2} is zero when the driving force is zero with the correct $P_{\text{CO}_2}^*$. The slope of the linear fit is the K_{G} . The liquid mass transfer coefficient (k_{g}') can be calculated by subtracting the gas film resistance ($1/k_{\text{g}}$) from the overall resistance ($1/K_{\text{G}}$) (Eq. (4)).

$$\frac{1}{k_{\text{g}}'} = \frac{1}{K_{\text{G}}} - \frac{1}{k_{\text{g}}} \quad (4)$$

The gas film mass transfer coefficient (k_{g}) was calculated using a pre-determined correlation for this wetted wall column (Bishnoi and Rochelle, 2000). The wetted wall column measurement was described in detail previously (Li, 2015; Du, 2016).

3. Results and discussion

3.1. CO₂ solubility of PZ/tertiary amines

3.1.1. Effect of pK_{a} of tertiary amines

Fig. 4 shows the CO₂ solubility in 2.5 m PZ/2.5 m tertiary amine with variable pK_{a} at 40 °C, compared to 2.5 m PZ. These tertiary amines have similar values of the Henry's law constant for the amine at 40 °C ($H_{\text{am}} = 20\text{--}100$ Pa) (Du, 2016), which minimizes the effect of solution polarity on CO₂ solubility. At extreme values of pK_{a} the tertiary amines do not buffer at the operating range of the solvent. At low pK_{a} (HEMOR at pK_{a} 7.01) the tertiary amine does

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