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Carbon dioxide capture and regeneration with amine/alcohol/water blends

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ABSTRACT

Non-aqueous low boiling chemicals have been considered as potential solvents for amines in post-combustion carbon dioxide capture by chemical absorption. In this study, a set of simplified experiments was devised to evaluate the overall capture and regeneration performances of five absorbents, including a 7 m monoethanolamine solution, a piperazine/diethylenetriamine/water solution, a piperazine/diethylenetriamine/diethylene glycol/water blend, a piperazine/diethylenetriamine/methanol/water blend, and a piperazine/diethylenetriamine/methanol solution. Among the five absorbents, the blend that used methanol and water as the solvent achieved a high absorption efficiency, a high desorption efficiency, and a low regeneration energy penalty. In addition, this blend did not suffer the problems of piperazine crystal formation in absorbents at low temperatures or precipitation in carbon dioxide rich solutions. The results showed that low boiling solvents could be used to reduce the regeneration energy penalty, and that efficient regeneration at a low temperature was possible. Analysis indicated that the critical factor for evaluating regeneration energy penalty was the specific solvent loss, which was defined as the amount of accompanying solvent loss per unit of carbon dioxide removed during regeneration.

1. Introduction

The increasing carbon dioxide (CO_2) concentration in the atmosphere caused by anthropogenic CO_2 emissions from burning fossil fuels contributes greatly to global warming (IPCC, 2005; Smith, 1993). Post-combustion CO_2 capture using amine-based absorbents in an absorption/stripping system has been considered as one of the most promising technologies to effectively capture CO_2 from many power plants and industrial applications (Rochelle, 2009). In this technology, a highly active absorbent is required to efficiently capture CO_2 from flue gases containing a low CO_2 concentration (<15 vol% CO_2), and the absorbent is mostly requested to have low energy penalty. The system of CO_2 capture using 7 m monoethanolamine (MEA) solutions is commercialized and is regarded as a standard to evaluate the overall CO_2 capture performances of various absorbents due to its high absorption rate. However, this MEA system suffers two major disadvantages, including low saturated loading (~0.5 mol CO_2/mol amine), which restricts its absorption efficiency, and a high regeneration energy penalty (typically 2.8–3.5 GJ/ton CO_2) (Figueroa et al., 2008; Olajire, 2010; Pires et al., 2011).

Amine blends have drawn growing interest in the area of improving absorption efficiency, due to the advantages brought by the integration of various absorbents. Monoethanolamine/piperazine (MEA/PZ), monoethanolamine/diethylenetriamine (MEA/DETA), and PZ/DETA blends have been found to improve either the average absorption rate or saturated CO_2 loading (Chang et al., 2013; Zhu et al., 2012). Absorption performance can be further enhanced by increasing mass transfer rate in an advanced reactor. In the investigation of CO_2 capture with amine-based absorbents in a rotating packed bed (RPB), PZ/DETA blends have been found to show higher absorption efficiency than MEA/PZ blends (Cheng et al., 2013; Cheng and Tan, 2011; Yu et al., 2012). Nevertheless, a challenge for PZ-contained absorbents is poor PZ solubility in water at a low temperature (the saturated PZ concentration of aqueous solution is ~3.6 m at 30 °C), and this PZ solubility problem may limit the use of absorbents containing high PZ concentrations (Freeman et al., 2010).

Abbreviations: $BaCl_2$, barium chloride; $BaCO_3$, barium carbonate; CO_2, carbon dioxide; DEG, diethylene glycol; DETA, diethylenetriamine; HCl, hydrochloric acid; H_2O, water; MEA, monoethanolamine; MeOH, methanol; N_2, nitrogen; NaOH, sodium hydroxide; PZ, piperazine; RPB, rotating packed bed.

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Nomenclature

C_P	heat capacity, J/kg·K
ΔH_j^{vap}	molar enthalpy of vaporization of solvent component *j*, kJ/mol
ΔH_{abs}	heat of absorption, kJ/mol CO_2
Δm_{CO_2}	mass of the CO_2 removed, g
$m_{solution}$	mass of the solution, g
Δn_j	amount of solvent loss, mol
Δn_{CO_2}	amount of CO_2 removed, mol
$P_{CO_2}^{sat}$	equilibrium partial pressure of CO_2, kPa
q_{desorp}	heat of absorption, GJ/ton CO_2
q_r	regeneration energy penalty, GJ/ton CO_2
$q_{sensible}$	sensible heat, GJ/ton CO_2
$q_{solvent}$	latent heat of vaporization, GJ/ton CO_2
R	gas constant, kJ/K mol
t	time, s
T	temperature, K
T_{bj}	normal boiling point of solvent *j*, K
T_{cj}	critical temperature of solvent *j*, K
T_R	regeneration temperature, °C
ΔT	temperature difference, K

Greek letters

α or $\alpha(t)$	CO_2 loading, mol CO_2/mol amine
α^*	saturated loading, mol CO_2/mol amine
$\Delta\alpha$	cyclic loading, mol CO_2/mol amine
τ	characteristic time of the first-order system, s

On the other hand, non-aqueous absorbents comprised of amidine/alcohol or guanidine/alcohol solutions have been found to reversibly react with CO_2 and are suggested to reduce regeneration energy penalties at low regeneration temperature due to their low heat capacity and low binding energy (Heldebrant et al., 2011, 2008, 2009; Jessop et al., 2005; Liu et al., 2006; Phan et al., 2008). Similarly, non-aqueous absorbents comprised of amine and alcohol are discovered to have low heat capacity, low heat of vaporization, low binding energy, and high cyclic loading, thus leading to a substantially reduced regeneration energy expenditure at low regeneration temperature (Barbarossa et al., 2013; Barzagli et al., 2013; Lail et al., 2012, 2011). Despite such remarkable regeneration performance, CO_2 capture with non-aqueous absorbents suffers several problems, such as an increase in viscosity, precipitation in CO_2-rich solutions, and liquid phase separation due to water accumulation.

Most of the previously proposed non-aqueous absorbents have higher boiling solvents than water. The underlying assumption is to reduce the amount of solvent loss during regeneration. However, high boiling solvents may lead to a higher regeneration temperature and higher latent heat of vaporization, thus the net amount of regeneration energy may not be actually reduced. Higher boiling solvents also tend to have higher viscosity, which leads to lower mass transfer efficiency during absorption. The main purpose of this study was to demonstrate that blended absorbents consisting of PZ, DETA, water and low boiling alcohols such as methanol (MeOH) may also be considered. Methanol has been used as a physical absorbent for CO_2 (Olajire, 2010), and it is a good solvent for PZ (Parker, 2003). The mixed solvent made of water and methanol would avoid the sharp viscosity increase of the absorbent after absorbing CO_2. Although methanol is more volatile than water, it has a lower molar enthalpy of vaporization and a lower boiling point. Thus, the regeneration energy penalty may be reduced without losing absorption performance. In the subsequent discussion, the absorption and desorption performance indices of a PZ/DETA blend in various solvents, such as water, methanol, mixtures of diethylene glycol (DEG) and water, and mixtures of methanol and water, were evaluated using two simple experiments. These performance indices were also benchmarked against a 7 m MEA solution.

Table 1
Summary of the constituents of the five absorbents used in this work.

No.	System	Solute concentration (m)			Solvent content (mol%)	
		PZ	DETA	MEA	Alcohol	H_2O
1	MEA	0	0	7	0	100
2	PZ/DETA/H_2O	4	4	0	0	100
3	PZ/DETA/DEG/H_2O	4	4	0	50	50
4	PZ/DETA/MeOH/H_2O	4	4	0	50	50
5	PZ/DETA/MeOH	4	4	0	100	0

2. Materials and methods

2.1. Absorbent preparation

Table 1 shows a summary of the constituents of five absorbents and their respective abbreviations studied in this work. Benchmarking 7 m aqueous MEA solutions were prepared by stirring the mixtures of MEA (99.0%, Tedia) and deionized water over 12 h. Meanwhile, all the PZ/DETA-based systems were prepared by heating the mixtures of PZ (99.0%, Fluka-Sigma–Aldrich), DETA (99.0%, Fluka-Sigma–Aldrich), and solvents (deionized water and/or alcohol (DEG, 99.0%, Acros Organics; methanol, 99.8%, Fluka-Sigma–Aldrich)) at 50 °C until PZ crystals completely melted into solutions. The amine concentration of prepared absorbents was analyzed by hydrochloric acid (HCl) titration method with an automatic potentiometric titrator (Metrohm, 702 SM Titrino), and the water content was analyzed by Karl Fischer titration using a Karl Fischer titrator (Metrohm, 701 KF Titrino). The uncertainty in the absorbent constituent was determined to be ±1%.

2.2. Absorption experiment

Fig. 1 shows the schematic view of the experimental apparatus for measurement of the absorption rate and the solubility of CO_2. First, the input gas with a flow rate of 13.33×10^{-6} m^3/s (800 ml/min), which was regulated by a gas flow controller, passed through a saturation flask containing deionized water. The water-saturated gas was then injected into a 250 μm^3-reactor in which it reacted with absorbents (0.12 kg) and formed a CO_2-absorbed solution. The unreacted gas was discharged from the gas vent of the reactor. To observe whether the reaction was finished, a branch of the discharged gas passing through a desiccator was sent into a CO_2 analyzer (Gas Data GFM130). When the CO_2 concentration of the discharged gas was within 99% of the CO_2 concentration of the inlet gas, the operation of a system would end.

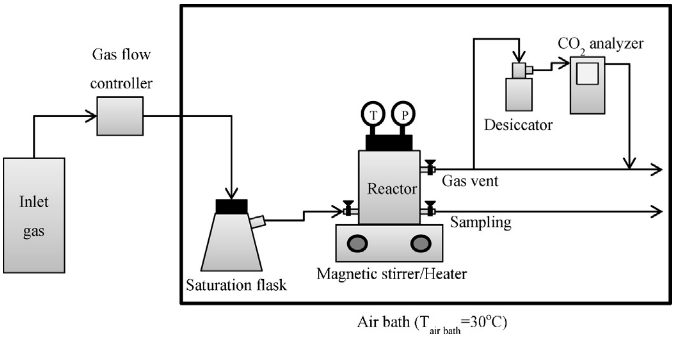

Fig. 1. Schematic diagram of the apparatus for the absorption experiment.