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Absorption heat, solubility, absorption and desorption rates, cyclic capacity, heat duty, and absorption kinetic modeling of AMP–DETA blend for post–combustion CO_2 capture

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ABSTRACT

This study investigated the absorption heat, equilibrium CO_2 solubility, absorption and desorption rates, cyclic capacities, heat duty, and absorption kinetic modeling of amine blends containing AMP and DETA. The AMP and DETA concentrations were varied (1–2.5 kmol/m^3 and 0.5–2 kmol/m^3, respectively) while the total amine concentration was constant at 3 kmol/m^3. The absorption experiment was conducted at 15 %v/v CO_2 and 313 K while the desorption temperature was at 363 K. Experimental results revealed that the absorption rates, cyclic capacities and desorption rates of some AMP–DETA blends were higher than those of 5 kmol/m^3 MEA. The absorption heat of the blends is comparable to that of MEA while the heat duty of some AMP–DETA blends are much lower than that of 5 kmol/m^3 MEA. The optimal amine blend was confirmed to be 2 kmol/m^3 AMP – 1 kmol/m^3 DETA. A model similar to the power law kinetic model showed that CO_2 composition in the feed gas affected the initial absorption rates as compared to AMP/DETA molar concentration ratio. The model predicted the initial absorption rate with a %AAD of 0.52%. These results provide good prospects for AMP–DETA blends towards CO_2 capture.

1. Introduction

Carbon dioxide (CO_2) capture using a post–combustion capture process has continued to gain considerable attention due to the need to reduce carbon emissions from the generated flue gas. The most reliable and economical technology for CO_2 capture is by absorption using amine–based solvents [29]. Another merit of amine–based solvent technology is the ability to handle large volumes of flue gas and remove up to 90% of the CO_2 in the flue gas [23,2,24]. Amine–based solvents are classified as primary (monoethanolamine, MEA, secondary (diethanolamine, DEA and tertiary amines (methyldiethanolamine, MDEA. Other special types of amines known as sterically hindered amines (2–amino–2–methyl–1–propanol, AMP and polyamines (piperazine, PZ; diethylenetriamine, DETA have also attracted interest due to their high CO_2 absorption capacity, high mass transfer, and/or very fast kinetics and low heat duty [4,10,26,20,22].

The benchmark amine solvent is the primary amine MEA due to the high mass transfer, low cost and fast kinetics during amine–CO_2 reaction [16,3]. However, high energy is required to regenerate the MEA solvent which can be as high as 70–80% of plant operating cost [1,14]. This major drawback has led to the application of blended amine solvent which was first proposed by Chakravarty et al. [6]. Blending amine solvents will utilize the potentials of individual solvents in the blend while reducing their individual problems. Several bi–solvent blends of amine solvents have been studied and reported results include increased CO_2 loading, high cyclic capacity, lower regeneration energy heat duty or desorption energy) and increased absorption rate [25,14,5,27,17]. In recent studies [20,22,18,33], tri–solvent blends and quad–solvent blends (AMP–PZ–DETA–MEA) of amine solvents has shown to outperform single solvent MEA in terms of CO_2 loading, regeneration energy, CO_2 absorption rates and desorption rates.

The objective of this study is to experimentally investigate the equilibrium CO_2 loading, initial absorption and desorption rates, cyclic capacity, absorption heat and heat duty of an amine bi–solvent blend containing AMP and DETA. AMP was chosen because of its high absorption capacity and desorption rate while DETA two primary amino groups and one secondary amino group) was chosen due to its high absorption capacity and absorption rate [10,11,26,20,22]. Amine blends involving DETA has also been previously reported to have enhanced initial absorption rates [20,22,19,21]. The concentration of AMP and DETA were varied 1–2.5 kmol/m^3 and 0.5–2 kmol/m^3, respectively while the total amine concentration was kept at 3 kmol/m^3.

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A model analogous to the kinetic power law model was used to analyze the contribution of AMP/DETA molar ratio, CO_2 mole fraction in the feed gas and absorption temperature towards the initial absorption rate of the blend.

2. Experimental

2.1. Chemicals and equipment

DETA (99%) was obtained from Sigma–Aldrich, St. Louis, MO, USA. AMP (99%) was bought from ACROS ORGANICS, New Jersey, USA, while MEA was acquired from Merck KGaA, Darmstadt, Germany. Hydrochloric acid (HCl, 37%) was supplied by RCI Labscan Limited, Thailand. Methyl orange (0.10%) indicator and 1 kmol/m^3 HCl was used to analyze the amine concentration as well as their CO_2 loadings. Eqs. (1) and 2) were used to determine the molar concentration of the aqueous amine solution [20,22]. Praxair Inc., Bangkok, Thailand supplied all the nitrogen (N_2, 99.99%) and CO_2 (99.99%) cylinders used for this study. The materials for the experimental study were all used without any additional purification.

$$C_{amine} = \sum_i \left(\frac{V_{HCl,endpoint} \times C_{HCl}}{C_N \times V_s} \times C_i \right) \quad (1)$$

$$C_N = \sum_i (n_{N,i} \times C_i) \quad (2)$$

where; $V_{HCl\_endpoint}$ is the HCl volume at endpoint (mL), C_{HCl} is the HCl concentration (kmol/m^3), V_s is the volume of amine sample used for titration (mL), C_i is the desired concentration of each amine solvent in the aqueous amine solution (kmol/m^3), C_N is the total concentration of amino groups in the aqueous amine solution (kmol/m^3) while n_{N_i} is the number of amino groups present in each amine solvent in the blended amine solution.

2.2. CO_2 absorption experimental procedure

Fig. 1 displays the experimental set–up used for the CO_2 absorption process which is similar to those detailed by Tontiwachwuthikul et al. [31]. The absorption reactor and humidifier (saturator) are both placed inside the temperature controlled water bath (Memmert, GmbH + Co. KG Schwabach FRG, Germany, with a precision of 273.1 K). All condensable species were recovered by the aid of a circulating bath (Peter Huber Kältemaschinenbau GmbH, Germany, model CC–K6 with temperature range between 248 K and 473 K and temperature stability of ± 273.02 K) which supplied the condenser cooling water. The flow rates of the gas N_2 (0–350 mL/min) and CO_2 (0–350 mL/min) were controlled by mass flow controllers (Electronic AALBORG GFC-17, with range of 0–500 mL/min and ± 1.5% accuracy) to maintain the desired CO_2 composition (%) in the mixed gas. In a mixed gas (CO_2 + N_2) the total gas flow rate is 350 mL/min and when pure CO_2 was used for initial absorption rates, the flow rate of CO_2 was set at 350 mL/min. A portable infrared (IR) CO_2 analyzer (Quantek Instruments, Inc., Grafton, MA, USA, model 906 ranging from 0.0% to 100% CO_2 with 0.1% accuracy) was used to determine the actual CO_2 composition in the mixed gas. The desired amine concentration was prepared gravimetrically using a mass balance (Sartorius AG Gottingen Germany, model TE214S, with accuracy of ± 0.1 mg).

During each experimental run the desired volume of amine solution (70 mL) and deionized water (20 mL) are loaded into the absorption reactor and saturator respectively. Prior to the start of each experiment, the absorption reactor and saturator are placed inside the water to attain the desired thermal equilibrium (313 K). This is then followed by passing the mixed dry gas (15 %v/v CO_2 and 85 %v/v N_2) through the saturator (wet mixed gas) and to the absorption reactor. A condenser is located downstream of the absorption reactor top exit to recover all condensable components (H_2O and amine). This will also help maintain the amine concentration throughout the duration of the experiment. Acidification technique was used to determine the amine concentration and CO_2 loadings [13]. All absorption experiments took between 2 and 3 h to reach equilibrium. Equilibrium was reached when two consecutive CO_2 loadings showed a difference of ± 2%. Absorption capacity of all amine solutions were reported in this work as the product of equilibrium CO_2 loading by amine molar concentration. At time intervals (10 min) CO_2 loadings (αCO_2, mol CO_2/mol amine) are taken until equilibrium is reached. The absorption capacity is plotted against time in a graph and initial absorption rates (I_{abs_rate}, mol CO_2/min) are determined as the slope of the linear portion of the graph. The accuracy of the results was ascertained by conducting the experiments three times and the difference in CO_2 loadings were ± 0.02 mol CO_2/mol amine.

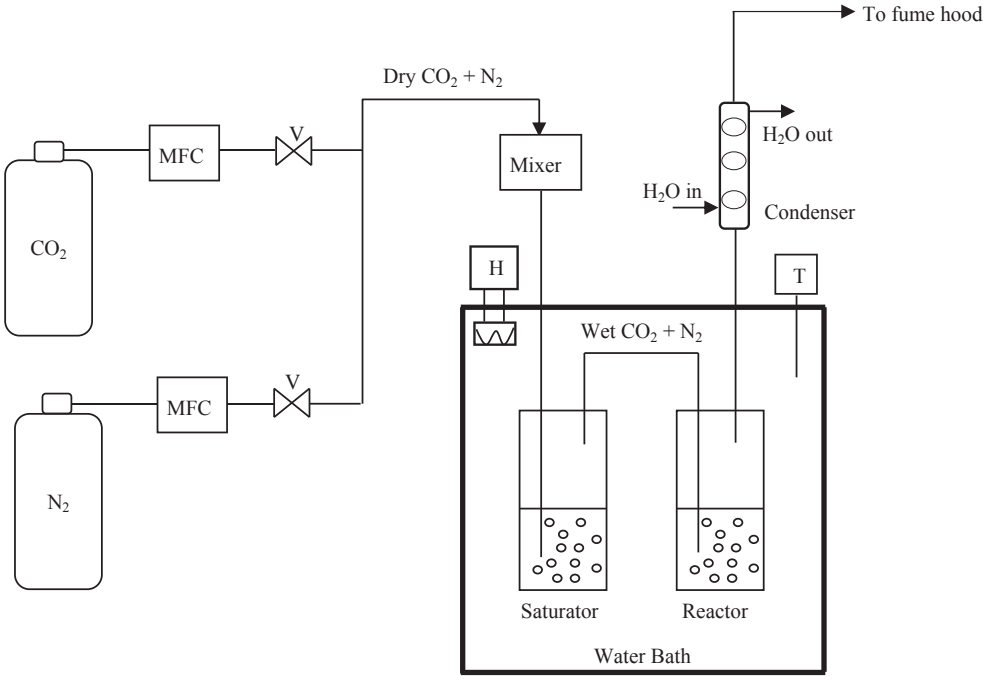

Fig. 1. Experimental set–up for CO_2 absorption.