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Heat duty, heat of absorption, sensible heat and heat of vaporization of 2–Amino–2–Methyl–1–Propanol (AMP), Piperazine (PZ) and Monoethanolamine (MEA) tri–solvent blend for carbon dioxide (CO$_2$) capture

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HIGHLIGHTS

- Absorption heat was estimated using specific heat capacity and temperature.
- Sensible heat of AMP–PZ–MEA blends is significantly lower than that of MEA.
- Vaporization heat of the amine blends is lower than MEA.
- Heat duty of the AMP–PZ–MEA blends is substantially lower than that of MEA.
- A developed model accurately predicted AMP–PZ–MEA specific heat capacity.

GRAPHICAL ABSTRACT
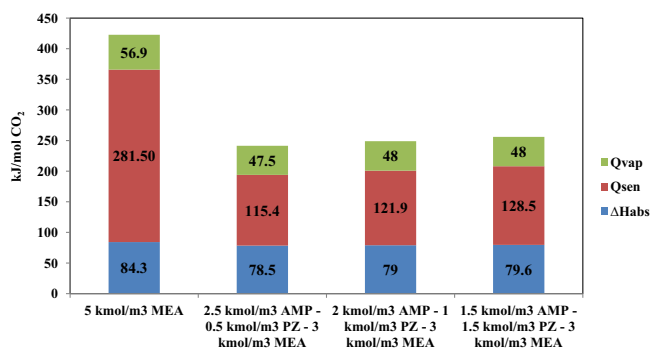
ABSTRACT

Chemical absorption using reactive amines for carbon dioxide (CO$_2$) capture is characterized by absorption heat, heat of desorption and heat duty for regeneration (Qreg, kJ/mol CO$_2$). This study experimentally investigated the heat duty of tri–solvent blends containing AMP–PZ–MEA and the individual contribution of desorption heat, sensible heat and heat of vaporization to heat duty. The experimental conditions for absorption were 15 v/v% CO$_2$ at 40 °C and atmospheric pressure while desorption was carried out 90 °C for loaded amine also at atmospheric pressure. The heat of desorption was experimentally determined using the specific heat capacity (kJ/kg °C) difference between the CO$_2$ free and CO$_2$ saturated amine solutions at the stated absorption conditions. Results showed that the heat duty of all the tri–solvent blends was significantly lower than that of the standard 5 kmol/m^3 MEA. Interestingly, the AMP–PZ–MEA tri–solvent blends exhibited only slightly lower heats of absorption when compared to MEA; however, they also showed significantly lower sensible heat and slightly lower heat of vaporization. Consequently, the tri–solvent blends exhibited significantly lower heat duties than the standard 5 kmol/m^3 MEA. In addition, a model analogous to a power law kinetic model was developed and used to predict the specific heat capacity of the AMP–PZ–MEA tri–solvent blends. The model accurately predicted the experimental results with an AAD of 0.59%. The overall results highlight the potential of using AMP–PZ–MEA blends for CO$_2$ capture.

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Nomenclature

ΔH_{des} heat of desorption, kJ/mol CO_2
Q_{sen} sensible heat, kJ/mol CO_2
Q_{vap} heat of vaporization, kJ/mol CO_2
Q_{reg} regeneration energy or heat duty, kJ/mol CO_2
Q heat flow, kJ
m mass, kg
C_p specific heat capacity, kJ/kg °C
C_{p0} product of specific heat capacity at standard condition and MEA molar concentration, kJ kmol/kg °C m^3
ΔT temperature difference, °C
C_{total} total concentration of species, mol/L
Cp_{molar} molar heat capacity, kJ/mole °C
C_{amine} amine concentration, kmol/m^3
αCO_{2_lean} CO_2 lean loading, mol CO_2/mol amine
αCO_{2_rich} CO_2 rich loading, mol CO_2/mol amine
P_{H2O} partial pressure of water, kPa
P_{CO2} partial pressure of CO_2, kPa
P_{sat} saturation pressure, kPa
x_{H2O_lean} water mole fraction in CO_2 lean amine

ΔH_{vap_H2O} latent heat of H_2O vaporization, kJ/mol
ΔH_{abs} heat of absorption, kJ/mol CO_2
ΔH_0 absorption heat at standard condition, kJ/mol CO_2
ΔT_{amine} temperature difference of an amine solution, °C
ΔT_{amine_i} temperature difference of an ith amine in a blended amine solution, °C
C_T total amine concentration, kmol/m^3
C_i concentration of ith amine in a blended amine solution, kmol/m^3
Ea   activation energy, kJ/mol
R   universal gas constant, 8.314×10^{-3} kJ/mol K

Greek letters
α thermal diffusivity, 1E8 m^2/s
λ thermal conductivity, mW/m K
ρ density, kg/m^3

1. Introduction

Absorption of carbon dioxide (CO_2) into reactive solvents such as amine solvents is the most mature and applied technology for CO_2 capture from natural gas processing, refinery gas, pre–combustion and post–combustion processes. Monoethanolamine (MEA), a primary amine, is regarded as the benchmark amine solvent for CO_2 capture. However, it is associated with high heat duty for regeneration (Q_{reg}, kJ/mol CO_2). According to previous studies, the heat duty of 5 kmol/m^3 MEA is in the range of 145.2–193.6 kJ/mol CO_2 (Knudsen et al., 2008; Ogawa et al., 2008; Kwak et al., 2012; Just, 2013; Dinca and Badea, 2013; Abu-Zahra et al., 2007; Alie et al., 2005; Pires et al., 2011; Singh et al., 2003). Other types of amine solvents like secondary and tertiary amines have shown to have lower heat duty compared to MEA as confirmed in an in–house experimental study. In addition, a primary sterically hindered amines like 2–amino–2–methyl–1–propanol (AMP) has attracted attention due to its lower heat duty compared to tertiary amine (methyldiethanolamine, MDEA). The low heat duty of AMP was also confirmed in an in–house experimental analysis.

Idem et al. (2006) as well as Aaron and Tsouris (2005) have stated that the regeneration energy could be as high as 70–80% of the entire operating cost of a CO_2 capture plant. This has led to increased research activities aimed at optimizing the formulation of amine blends that will offer a reduced energy of regeneration (Idem et al., 2006; Mangalapally and Hasse, 2011a, 2011b). The idea of blending amine solvents to reduce regeneration energy (heat duty) was first proposed by Chakravarty et al. (1985). Sakwattanapong et al. (2005) then reported lower regeneration energy of blended amine solvents when compared to single solvent MEA.

Regeneration energy is a combination of the heat of desorption (ΔH_{des}, kJ/mol CO_2), sensible heat (Q_{sen}, kJ/mol CO_2) and heat of vaporization (Q_{vap}, kJ/mol CO_2) as shown in Eq. (1).

$$Q_{reg} = \Delta H_{des} + Q_{sen} + Q_{vap} \tag{1}$$

Desorption heat is the amount of energy required to breakdown the species formed (carbamates, bicarbonates, carbonates) during amine–CO_2 reactions, and it greatly contributes to the energy required for regenerating the CO_2 loaded amine solution. It is generally assumed that the heat of desorption is of the same magnitude as the heat of absorption (Rayer and Henni, 2014; Oexmann and Kather, 2010; Quang et al., 2014). According to Abdulkadir and Abu-Zahra (2013), the heat of absorption obtained from calorimeter experiment is the combination of heats of dissolution and reaction of CO_2 and amine from zero loading to the final loading. In addition, the heat of absorption measured from calorimeter experiment has the ability to reflect heat effects due to both the physical solubility and chemical reaction between CO_2 and aqueous amine solution (El Hadri et al., 2017; Zhang and Chen, 2011; Kim and Svendsen, 2007; Kim et al., 2009). This is because CO_2 absorption in aqueous amine solution is a combination of physical dissolution and chemical reactions between CO_2 and the amine (Arcis et al., 2007; Xie et al., 2013; Huang et al., 2015).

Several authors (Kim et al., 2009, 2014; Chowdhury et al., 2011; Kim and Svendsen, 2007; Arcis et al., 2007; Coulier et al., 2016; Huang et al., 2015; McCann et al., 2008; El Hadri et al., 2017) have used different correlations and calorimetric experimental set–ups in determining the heat of absorption of amine solvents. Typically, the heat of absorption ranks in this order primary amine > secondary amine > tertiary amine for amines of similar structure and size.

Svensson et al. (2014) also stated that the integral heat of absorption is determined by dividing the total amount of heat released by the total amount of CO_2 absorbed up to the considered equilibrium point. On the other hand, the differential heat of absorption is determined by dividing the heat released by each addition of CO_2 by the amount of CO_2 absorbed with each addition (Svensson et al., 2014). The second heat that adds up to the heat duty (regeneration energy) is the sensible heat. This is the energy needed to increase the temperature of the CO_2 saturated amine solution (after absorption) to desorption (regeneration) temperature. Based on the correlations used by Conway et al. (2014) and Rochelle et al. (2002), for sensible heat to be reduced, the specific heat capacity (kJ/kg °C) and density (kg/m^3) of the CO_2 saturated amine solution should be small while the cyclic capacity (mol CO_2/L-amine soln.) should be high. Considering that high cyclic capacity leads to low sensible heat and low amine circulation rate (Singh, 2011; Aronu et al., 2011; Rochelle, 2009), therefore low sensible heat is proportional to low amine circulation rate. In addition, Maneeintr et al. (2009) stated that low amine circulation rate will lead to reduced absorber size. The last energy that makes up