# CHAPTER I

# INTRODUCTION

Carbon dioxide ($CO_2$) is part of the greenhouse gases (GHGs) which continue to cause damaging effect to the global environment. $CO_2$ is produced from fossil fuels during post combustion, pre-combustion, oxyfuel, and industrial processes. $CO_2$ is not the most severe GHG, but it's the highest emitted which makes it the most unavoidable anthropogenic GHG (Kangwanwatana *et al.*, 2013). Capture of $CO_2$ through absorption is known as one of the most reliable and economical processes (Singh *et al.*, 2009). More so, with the advent of $CO_2$ enhanced oil recovery (EOR), several research studies are underway to develop oil reserves more economically (Nonthanasin *et al.*, 2013).

Most commonly used solvents are the conventional amines covering primary alkanolamines; monoethanolamine (MEA) and diglycolamine (DGA), secondary alkanolamines; diethanolamine (DEA) and diisopropanolamine (DIPA) and tertiary alkanolamines; methyldiethanolamine (MDEA) and triethanolamine (TEA). Other amines classified as a sterically hindered amine like 2-amino-2-methyl-1-propanol (AMP) and cyclic diamine, piperazine (PZ) are also available commercially.

In recent times, amine solvents have been promoted for $CO_2$ capture to utilize the merit of high reaction rate of $CO_2$ with the promoting agent(s), which can be blended with the merits of the high loading capacity of tertiary amines or hindered amines and the relatively low cost of regeneration of the promoting solvent (Balsora, and Mondal, 2011). The highly reactive cyclic diamine PZ and the reactive MEA have both been used as potential promoters (activators), and research on this combination is available in literature and commercial application (Yang *et al.*, 2010; Bruder *et al.*, 2011; Samanta and Bandyopadhyay, 2009; Austgen *et al.*, 1991; Mandal *et al.*, 2001; Dash and Bandyopadhyay, 2013; Bishnoi, 2000)

The success recorded by blending two solvents to enhance $CO_2$ capture, is gradually leading to ternary and quartenary amine blends (Haghtalab *et al.*, 2014; Esmaeili and Roozbehani, 2014). This research work is then focused on the equilibrium solubility of $CO_2$ in the novel ternary blend of AMP based solvent promoted with PZ – MEA blends. This was experimentally studied and investigated considering the absorption temperature range 25 – 60 °C, $CO_2$ partial pressure range 2 – 100 kPa. At 40 °C and 93.93 kPa $CO_2$ partial pressure, the concentrations of PZ and MEA promoters were varied between 0.5 M – 1 M and 2 – 4 M, respectively, while the AMP concentration was kept constantly at 2 M. This high concentration of the AMP-PZ-MEA ternary blend was chosen for experimental investigation because it leads to an increase in the absorption working capacity (aWC). Several researchers (Freeman *et al.*, 2010b; Bruder and Svendsen, 2012; Aboudheira *et al.*, 2003; Dugas and Rochelle, 2009; Yang *et al.*, 2010) have successfully studied $CO_2$ solubility in high concentrations of MEA, PZ, and blends of MEA-PZ and AMP-PZ which showed higher absorption working than their respective low concentrated solutions. The various concentrations of the ternary blend indicated higher equilibrium $CO_2$ loading (6.9 – 19 %) and absorption working capacity (aWC) between 13.8 – 48.3 % compared to the standard 5 M MEA. The very high concentrations (6 – 7 M) of the AMP – PZ – MEA ternary blend also showed high absorption working capacity (5.4 – 16.2 %) than the optimal AMP – PZ binary blend (3 M AMP – 1.5 M PZ). Higher absorption working capacity will most often translate to lower amine circulation rate in the $CO_2$ capture plant, which will reduce the energy of regeneration. The absorption working capacity is usually seen as more relevant parameter compared to the $CO_2$ loading. It represents the amount of $CO_2$ the amine solution can carry in the absorption section, which leads to more capture of $CO_2$ and hence reduced amine circulation rate. This reduced circulation rate is mostly beneficial in the regeneration section. Absorption working capacity can be calculated by multiplying the equilibrium $CO_2$ loading of the amine solution ($\alpha CO_2$) by its molar concentration (Equation 1.1).

$$\text{aWC} = \alpha CO_2 \left(\frac{mol\ CO_2}{mol\ amine}\right) \times Amine\ Conc\ \left(\frac{mol\ amine}{L\ of\ solution}\right) \quad 1.1$$

The influence of MEA and PZ concentrations, $H_2O$/PZ molar ratio, and possibility of precipitation were also studied, and the solvent combination of 2 M AMP – 0.5 M PZ – 3 M MEA was finally selected for further equilibrium $CO_2$ loading analysis considering its high $H_2O$/PZ molar ratio (very minimal possibility of forming solid precipitates). The results were reported as a function of $CO_2$ partial pressures at the investigated temperatures. In addition, the energy penalty during regeneration was predicted using a validated ProMax® 3.2 $CO_2$ capture plant simulation. The simulation results showed 10 – 24.7 % energy reductions compared to 5 M MEA and 5 – 15 % reductions compared to 3 M AMP – 1.5 M PZ.