Chapter One

INTRODUCTION
Nowadays, the global warming issue caused by emission of greenhouse gases (GHGs) has become a matter of great concern. The Inter-governmental Panel on Climate Change (IPCC) has reported that anthropogenic activities result in the production of GHGs such as carbon dioxide (CO₂), methane (CH₄), chlorofluorocarbons (CFCs) and nitrous oxide (N₂O), which significantly contribute to global warming (Choi et al., 2007). Of these gases, CO₂ has the greatest impact on global warming (see Fig. 1.1), causing approximately 55% of the observed global warming (Houghton et al., 1990). CO₂ plays an important role in the ecological system, since photosynthesis and food production depends on it as a carbon source. The concentration of CO₂ in earth's atmosphere has reached approximately 391 ppm (parts per million) by volume as of 2011 and rose by 2.0 ppm/yr during 2000-2009 (Kargari and Ravanchi, 2012). This current concentration is substantially higher than the 280 ppm concentration present in pre-industrial times, with the increase largely attributed to rapid industrialization and fast deforestation. Since CO₂ emission normally increases with increasing energy consumption, intensive efforts should be made towards energy conservation and promotion of energy efficiency. By the year 2030, energy demand is projected to increase tremendously, thereby increasing CO₂ emissions to about 90% higher than 1990 levels (Li et al., 2007). According to the United Nations Framework Convention on Climate Change (UNFCCC) in Kyoto, 1997, a commitment to reduce CO₂ emissions by 6% below the 1990s level was made by several countries (Choi et al., 2007).

CO₂ is a major component of natural gas and various industrial gases such as those in fossil-fuel-fired power plants, various chemical process industries, petrochemical refineries and steel & cement production units being the prime sources of CO₂ emissions. Due to the increasingly stringent environmental regulations, along with exploitation of poorer quality crudes and natural gas, CO₂ removal and its subsequent recovery from gas streams has gained considerable industrial importance. On account of the discharge standards for CO₂, flue gases from thermal power stations need to be treated. Similarly, it is necessary to remove CO₂ from the refinery off-gas to meet the desired specifications. CO₂ acts as a detrimental contaminant which poisons the catalyst in the ammonia manufacturing process by formation of excess methane (Astarita et al., 1983). Being acidic in nature, CO₂ also causes corrosion of pipes and process equipments. CO₂ must be removed from natural gas,
before it is directed to transmission lines, as it reduces the heating value of the gas. In an analogous way, coke oven gas must be freed from CO₂ before it can be used as a fuel. CO₂ thus recovered can be suitably used for the manufacture of methanol, carboxylic acids of phenols, dimethyl carbonate and dry ice (Vaidya and Kenig, 2009).

Based on the requirements, there are several technologies being used for CO₂ capture, such as absorption, adsorption, cryogenic methods, membrane separation and biological fixation (Rao and Rubin, 2002). Absorption represents the most important physico-chemical operation to remove CO₂ from gaseous streams. Absorption can be realized by using either physical solvents or chemical solvents or a mixture of both. Physical solvents such as water, methanol (Rectisol process), dimethyl ethers of polyethylene glycol (Selexol process), N-methyl-2-pyrrolidone (Lurgi’s Purisol process) and propylene carbonate (Fluor solvent process) have been used for CO₂ capture. Reactive absorption involves chemical solvents such as potassium carbonate (Benfield process) or alkanolamines (Girbotol process). Sulfinol process licensed by Shell Oil Company in the U.S. and by Shell International Petroleum Maatschappij (SIPM) in the Netherlands employs a mixture of physical and chemical solvents (Kohl and Nielsen, 1997). The Sulfinol solvent comprises sulfolane, an alkanolamine (usually diisopropanolamine or N-methyl diethanolamine) and water. A typical process flow diagram of a CO₂ absorption unit is given in Fig. 1.2 (Ahmadi et al., 2008). The unit consists of (i) an absorption section where CO₂ is removed from a gas stream by a liquid solvent and (ii) a regeneration section where the absorption capability of the used solvent is restored. In the absorption section, the gas stream containing CO₂ is passed upward through the absorption column, counter-current to the liquid solvent entering the column at the top. In this stage, CO₂ is transferred from the gas stream to the liquid solvent. This provides a treated gas, with low CO₂ content, passing out of the column top and a rich solvent, with high CO₂ content, leaving the column at the bottom. The rich solvent is then heated in a rich-lean heat exchanger, and enters the regeneration column at a point near the top of the column. In the regeneration section, the rich solvent is heated in a hot steam reboiler, located at the bottom of the regeneration column, which strips out the CO₂. Thus, the absorbed CO₂ is recovered at the top of the column. Finally, the lean solvent, with low CO₂ content, from the regeneration column is pumped through the rich-lean heat exchanger and a cooler, prior to re-introduction to the absorption column. The absorption column
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operates at low temperatures (40-60°C) and high pressures, while the regeneration column operates at high temperatures (100-120°C) and low pressures (1.5-2 atm) (Wang et al., 2011).

Reactive absorption using alkanolamines is by far the most widely used technique. The hydroxyl group in alkanolamines serves to reduce the vapour pressure and increase the water solubility, while the amino group provides the necessary alkalinity in water solution for the absorption of acid gases (Kohl and Nielsen, 1997). The reversible nature of the reaction between CO₂ and alkanolamines is exploited for the closed loop absorption-desorption system. Based on the number of hydrogen atoms attached to the nitrogen of the amino group, alkanolamines are classified as primary, secondary and tertiary. The most important characteristic of an amine is its reactivity. In case of alkanolamines, reactivity towards CO₂ decreases in the order primary > secondary > tertiary. All amines are relatively weak bases and CO₂ is a weak acid. Therefore, the salts that are formed, easily dissociate to their original compounds in the regeneration process, by the application of thermal energy to break the acid-base bonds. Primary and secondary alkanolamines react rapidly with CO₂ to from carbamates. However, the heat of absorption associated with carbamate formation is high, thereby resulting in high solvent regeneration costs (Vaidya and Kenig, 2007a). Furthermore, the CO₂ loading capacity of these alkanolamines is low (0.5 mol CO₂/mol amine). Tertiary alkanolamines do not possess a hydrogen atom attached to the nitrogen atom, as in the case of primary and secondary alkanolamines. Thus, the carbamation reaction cannot take place, resulting in a low reactivity with CO₂. Instead, tertiary amines facilitate the CO₂ hydrolysis reaction forming bicarbonates. The reaction heat released in bicarbonate formation is lower than that of carbamate formation, thus reducing solvent regeneration costs. Moreover, tertiary amines have a high CO₂ loading capacity (1 mol CO₂/mol amine). The high reaction rates of primary or secondary amines can be combined with high equilibrium capacity and easier regeneration of tertiary amines by using amine blends. This results in great savings in energy requirements that currently account for as much as 70% of the total operating cost (Chakravarty et al., 1985). Thus, aqueous blends of primary or secondary amines with tertiary amines can be very attractive for bulk CO₂ removal. However, despite the technical feasibility, the economic penalty poses a huge barrier to the implementation of this technology at large scale. Solvent optimization and
advanced process integration are two efficient ways to reduce the cost (Rochelle, 2009).

Monoethanolamine (MEA) as a primary amine, diethanolamine (DEA) as a secondary amine and N-methyl diethanolamine (MDEA) as a tertiary amine are the most popular absorbents (Li et al., 2007). However, high energy requirement resulting in high solvent regeneration cost, low CO₂ loading capacity, reduced scrubbing efficiency on account of amine decomposition and degradation, and corrosion in the equipment and piping are some of the major drawbacks that limit the usage of these amines (Olah et al., 2011). MEA has a high vapour pressure, and hence, it is not suitable for low pressure operations due to possible evaporation losses (Kohl and Nielsen, 1997). The discovery of novel, alternative amine-based solvents, which are attractive for CO₂ capture, constitutes an important challenge. N,N-diethyl monoethanolamine (DEMEA) represents a candidate amine having good potential for the bulk removal of CO₂ from gaseous streams (Vaidya and Kenig, 2008). It comprises two ethyl groups replacing the hydrogen atoms of the amino group in MEA. Diethylamine (produced from ethanol) and ethylene oxide (obtained from the oxidation of ethylene, which in turn can be prepared by dehydration of ethanol) react to form DEMEA. Ethanol, which is the major raw material for the manufacture of this amine, can be prepared from agricultural products and/or residues. Thus, DEMEA represents an especially promising absorbent, as it can be prepared from renewable resources. Being a tertiary amine, it’s reactivity with CO₂ is low. The absorption rates of CO₂ in aqueous DEMEA solutions can be enhanced by addition of small amounts of primary or secondary amines known as ‘absorption activators’ or ‘promoters’. In this study, the kinetics of CO₂ absorption in activated DEMEA solutions was investigated. Also, the equilibrium solubility of CO₂ in DEMEA and activated DEMEA solutions was determined. N-ethyl monoethanolamine (EMEA), a secondary alkanolamine which can be prepared from renewable resources, also represents a promising absorbent for CO₂ capture. Moreover, it is co-produced with DEMEA. In this study, the reaction mechanism and kinetics of CO₂ absorption in aqueous EMEA solutions was explored, too.

Knowledge of the absorption rates is essential for design of the absorption column and prediction of its performance. The rate of absorption depends on volumetric mass transfer co-efficient (hydrodynamic parameter) and solubility of solute gas in the absorbent (thermodynamic parameter). It is also decided by the
enhancement factor, which in turn depends on the kinetic parameters. If the kinetic rate constants and solubility of CO₂ in the absorbent are higher, the desired specifications with respect to CO₂ can be achieved in a lesser volume of the contactor. The lesser volume is reflected in a shorter column as the diameter of the column is decided by hydrodynamic consideration, namely, flooding in a counter-currently operated column and flow regime in a co-currently operated column. For the absorption of CO₂ in alkanolamines, a totally co-currently operated column is not used due to the finite reversible nature of the reaction (Vaidya and Mahajani, 2005).

Hydrogen sulfide (H₂S) is present along with CO₂ in a variety of gas streams. Selective removal of H₂S from CO₂ containing gases lowers the capital and operating costs of the treating process substantially (Blauwhoff et al., 1984). Increasing the selectivity reduces the solvent circulation rate and therefore the steam consumption in the regenerators and, moreover, reduces the dimensions of the sulphur recovery and tail-gas units. As the reaction between H₂S and aqueous alkanolamines involves only a proton transfer, this reversible reaction can be considered to be infinitely fast (Danckwerts and Sharma, 1966) and hence the absorption rate is entirely mass transfer controlled under practical conditions. The CO₂ reaction with alkanolamines, however, proceeds at a finite rate. Thus, from a purely kinetic point of view, the selectivity for H₂S depends solely on the CO₂ reaction rate.

CO₂ absorption occurs in response to a partial pressure driving force from gas to liquid. The net driving force for absorption is the difference between the CO₂ partial pressure in the bulk gas phase and the equilibrium CO₂ partial pressure. Knowledge of the equilibrium partial pressure of CO₂ over the amine solution is essential, particularly for the design of the top portion of the absorber. The CO₂-slip in the top portion of the absorber depends upon the equilibrium partial pressure of CO₂ over the amine solution and has a bearing effect on the overall costing of the gas processing unit. Commonly, the dependence of equilibrium partial pressure of CO₂ on the loading capacity of the absorbent is determined. Due to reversibility of the CO₂ reaction with alkanolamines, there is always a finite concentration of CO₂ in the regenerated solution. This results in equilibrium partial pressure of CO₂, also known as back pressure. It can be determined as the ratio of the concentration of CO₂ in the bulk liquid to its physical solubility. The loading solubility can be represented as molar solubility, i.e. moles of CO₂ absorbed per mole of amine.
Thus, in this chapter, a brief introduction to CO$_2$ sequestration has been given. Chapter 2 reviews the literature on reactive absorption of CO$_2$ in amines. Individual amines as well as amine mixtures have been surveyed. Also, previous studies on equilibrium solubility of CO$_2$ in aqueous amine solutions and amine blends have been reported. The reaction mechanisms and mass transfer characteristics are discussed in Chapter 3. The experimental setup and procedure, used in this work, are described in detail in Chapter 4. The study of acceleration of the CO$_2$ reaction with DEMEA in aqueous solutions by the primary amines (MEA and diglycolamine, DGA) and the secondary amines (DEA and EMEA) is discussed in Chapter 5. In the sixth chapter, the work on efficacy of three diamines, i.e. piperazine (PZ), N-(2-aminoethyl)ethanolamine (AEEA) and 1,6-hexamethyl diamine (HMDA) as promoters in aqueous DEMEA solutions is explored. Also, kinetic data of the CO$_2$ reaction with DEMEA-HMDA blend is presented. In Chapter 7, the outcome of CO$_2$ absorption into aqueous blends of chemical (DEMEA+PZ) and physical (Sulfolane) solvents is discussed. Chapter 8 constitutes the equilibrium solubility data of CO$_2$ in DEMEA and (DEMEA+PZ) blend for low CO$_2$ partial pressures. Based on these measurements, the dependence of the CO$_2$ partial pressure on the loading is determined using simple mathematical correlations. A comparative study of effectiveness of three secondary amines, i.e. EMEA, DEA and diisopropanolamine (DIPA) for CO$_2$ capture, and kinetics of the reaction between CO$_2$ and EMEA is presented in Chapter 9. Some exploratory work on amine degradation is reported in Chapter 10. The eleventh chapter constitutes summary and conclusions. The scope for future work is discussed in Chapter 12.
**Figure 1.1:** Relative contributions of GHGs (Houghton et al., 1990)
Figure 1.2: Schematic diagram of absorber-regenerator arrangement (Ahmadi et al., 2008)