# CHAPTER 1

# INTRODUCTION

## 1.1. Generalities

The issue of global warming which is associated with the increase of carbon dioxide gas emissions to the environment has received a great interest all over the world. With more stringent air pollution control regulations, removing carbon dioxide from process gas streams becomes an urgent necessity in many industries. Carbon dioxide has to be removed from its many sources not only because it can cause corrosion to process equipment but it also has a commercial value. In natural gas it will degrade the heating value whereas in manufacturing of ammonia it will poison the catalyst.

Aqueous alkanolamine technology has been found to be effective in removing acidic gases such as $CO_2$ from process gas streams. This technology is widely used in the ammonia production, coal gasification and petroleum refineries. This process is based on absorption with simultaneous chemical reactions in the liquid phase. The reactions involved in this process depend mainly on the type of alkanolamine used. When reacted with primary or secondary amines, $CO_2$ forms stable carbamates which are responsible for limiting the maximum stoichiometric carbon dioxide loading to 0.5 mol of $CO_2$ /mol of amine. However, at high $CO_2$ partial pressure loading higher than 0.5 can be obtained due to the hydrolysis of carbamate ions which generates free amines. These free amines can further react with additional

$CO_2$. The carbamate formation is also believed to be responsible for the high $CO_2$ absorption rates in aqueous solutions of primary and secondary amines. On the other hand, tertiary amines do not form carbamates and consequently are characterized by high $CO_2$ loading capacity approaching 1.0 mol of $CO_2$/mol of amine but slow reaction rate. The solvent circulation rate in the amine sweetening plant contributes about 50 to 70% of the initial investment and another 10 to 20 % from the regeneration energy requirement. In the operating cost, 70% of the cost comes from the regenerating process excluding the labor cost (Astarita et al., 1983)]. This cost analysis indicates that the choice of alkanolamine solvent has a great impact on the overall cost of the gas-sweetening unit. One way to optimize the operation of amine units efficiently, is to change the type of amine used.

Conventional alkanolamine technology uses single amines such as MEA, DEA and MDEA. With the recent developments in this technology, more attractive solvents are becoming available in the market. Sartori and Savage identified the advantage of using aqueous sterically hindered amines such as AMP to absorb $CO_2$. Chakravaty et al.(1986) proposed the use of blended amines consisting of a mixture of tertiary and primary or secondary amines in order to gain the characteristics of each solution. Another important development is the use of activated amine solutions which consist of a conventional amine doped with small amounts of an accelerator (activator) that enhances the overall $CO_2$ absorption rate. An example of such activator which has been the focus of many investigators is piperazine (PZ). Activated MDEA technology which uses piperazine as the activator has been used successfully for $CO_2$

removal in ammonia plants and this process is well known as a low energy consumption process (Appl et al., US Pat. No. 4,336,233).

In order to design high efficiency absorption facilities, accurate data on vapor liquid equilibrium, physical properties, kinetics, transport and thermodynamic properties of the systems are required. Physical properties such as density are required for engineering design. In addition, there is an interest to use the volumetric data to study the effect of pressure on thermodynamic properties and to understand the molecular interactions in mixtures (Maham et al., 1994). Regardless, whether it is pure or mixture, in phase equilibria, most thermodynamic properties of interest can be calculated from thermal and volumetric measurements for any substance (Prausnitz et. al, 1999).

Knowledge on the equilibrium solubility of the $CO_2$ aqueous alkanolamine solutions is essential to determine the amount of feed solution to be circulated to treat a given feed gas and to calculate the maximum amount of $CO_2$ gas present in the regenerated amine. Furthermore, the development and validation of any mathematical model require reliable data on the equilibrium solubility of carbon dioxide in the alkanolamine solvents.

## 1.2. Aim and Scope of Work

The great importance of the volumetric properties of alkanolamine-$H_2O$ systems and their carbon dioxide equilibrium loading is reflected in the tremendous number of publications devoted to these two areas.

A comprehensive set of data on density and volumetric properties of aqueous solutions containing conventional alkanolamines and their blends is available in the open literature. However, the density of PZ+ $H_2O$ and PZ + DEA + $H_2O$ systems has not been published. Thus, it is the interest of this work to measure the density of these systems. Redlich-Kister equation of excess molar volumes is used to correlate the density data and generalized sets of interaction parameters are generated from this work.

Only a few studies on solubility of $CO_2$ in aqueous activated amine solutions have been published in the literature. Xu et al. (1998) and Liu et al. (1999) studied on the $CO_2$ solubility in activated MDEA in which piperazine was used as the activator. They found that piperazine is beneficial to the ultimate $CO_2$ loading. Recently, Dang and Rochelle (2003) studied the absorption rate and solubility of $CO_2$ in aqueous activated MEA solution using wetted wall column. They reported that piperazine decrease the equilibrium pressure and enhance the reaction rate of the system.

Despite the importance of piperazine as activator, there is a lack of experimental data on $CO_2$ solubility in aqueous solution of pure PZ. Recently, Kamps et al. (2003) presented data and a model describing the phase equilibrium for the absorption of

$CO_2$ into aqueous piperazine and PZ + MDEA + $H_2O$ systems. Their experimental solubility data were collected at high $CO_2$ partial pressures (> 70 kPa) and relatively high PZ concentrations (>2.0 M). Therefore, one of the aims of this work is to present additional data on $CO_2$ solubility in aqueous PZ at low $CO_2$ partial pressures (0.1-100 kPa) and at total piperazine concentration ranging from 0.1-1.0 M which corresponds to the typical concentration range of PZ in activated solvents.

In addition this work presents the first data on $CO_2$ solubility in activated DEA solutions. All solubility data are correlated according to Kent and Eisenberg model and a simple speciation model for the $CO_2$-PZ-$H_2O$ system is also presented.

Therefore, the objectives of this work are:

1) To measure the density of aqueous solutions of piperazine, DEA and activated DEA.
2) To develop a generalized set of parameters for density calculation of aqueous piperazine and activated DEA solutions.
3) To provide reliable VLE data on the absorption of $CO_2$ into aqueous solutions of piperazine and activated DEA.
4) To compare the experimental results obtained with the predictions from the mathematical model using the Kent and Eisenberg approach.

## 1.3. Structure of the thesis

This thesis consists of six main chapters including this chapter.

***Chapter 2: Literature Review***

This chapter presents a review on historical and theoretical background of amine gas treating systems. The development on density correlation based on Redlich Kister equation and reaction mechanisms in the amine system studied are also presented in this chapter. Previous works done on density of aqueous alkanolamine and $CO_2$ solubility into aqueous alkanolamine system by many investigators were reviewed. This include various methods used to measured the $CO_2$ solubility in the aqueous alkanolamine system.

***Chapter 3: Experimental methods and techniques***

It provides the information on the experimental section. It covers the material used, solution preparation and procedures for measuring the density and $CO_2$ solubility in the amine system studied.

***Chapter 4: Results and discussions***

This chapter consists of two parts: in the first part a detailed analysis of the density data is reported. The density analyses include excess molar volume values, comparison of the density behavior between the amine systems studied, and determination of generalized set of interaction parameters for density calculations. The second part deals with the $CO_2$ solubility study, this section discusses on the effect of piperazine concentration, $CO_2$ partial pressure and temperature on $CO_2$ solubility. The $CO_2$ absorption performance in the amine systems studied is compared to other amine systems which are available in the open literature.

***Chapter 5: Solubility and speciation modeling.***

This chapter deals with the modeling of the $CO_2$-PZ-$H_2O$ system using the Kent and Eisenberg approach. Based on several assumptions, speciation profiles for this system are also developed. This model is also extended to the PZ-DEA-$H_2O$ system.

Finally, chapter 6 presents the conclusions drawn from this study and a series of recommendations for future work.