

CO₂ Capture from Flue gas using Amino acid salt solutions



Benedicte Mai Lerche

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By

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“As the true method of knowledge is experiment, the true faculty of knowing must be the faculty which experiences.

This faculty I treat of”.

–**William Blake**, *All Religions Are One*, “The Argument” (1788).

Summary

By implementing carbon dioxide (CO_2) capture, it is possible to clean the flue gas from coal-fired power plants, so that it is almost completely free of this greenhouse gas. The most advanced techniques towards practical application are based on chemical absorption, where CO_2 in the flue gas is chemically bonded by a solvent, usually an aqueous solution of amines, resulting in a cleaned gas being released to the atmosphere. Heating of the solution, desorbs the CO_2 and regenerates the solvent, which is then ready for a new round of absorption. The captured CO_2 can then be compressed and sent to storage.

Typical solvents for the process are based on aqueous solutions of alkanolamines, such as mono-ethanolamine (MEA), but their use implies economic disadvantages and environmental complications. Amino acid salt solutions have emerged as an alternative to the alkanolamines, partly because they are naturally occurring substances, and partly because they have desirable properties, such as lower vapor pressures and higher stability against oxidative degradation. One important feature of these new solvents is the formation of solids upon CO_2 absorption, which happens especially at higher CO_2 loadings and/or amino acid salt concentrations. The formation of solids poses challenges, but it also holds the promise for improving the efficiency of the capture process.

This project focuses on phase equilibrium experiments of five CO_2 + amino acid salt + H_2O systems, at conditions relevant for the CO_2 capture process. Also,

attention is given to the chemical compositions of the precipitations, which forms as a result of CO₂ absorption into the five amino acid salt solutions.

Phase equilibrium data are needed to develop safe and economically viable capture processes. Two different experimental apparatuses were used. One was developed specifically for this project and is based on an analytical semi-flow method. The other has recently been developed in another project, and is based on a synthetic method. The semi-flow method was used for measurements at 10 kPa CO₂ partial pressure, total pressure equal to the atmospheric pressure and temperatures of 298 K, 313 K and 323 K; these conditions cover the absorber part of the capture process. The apparatus based on the synthetic method was used to obtain data at different pressures and temperatures up to 353 K (80 °C), which is the maximum operation temperature of some of the components in the apparatus. Ideally, measurements in the full temperature range for desorption, which usually needs approximately 393 K (120 °C), would be desirable.

Using the two apparatuses, CO₂ solubility in aqueous solutions of MEA and the potassium salts of taurine, glycine, L-alanine, L-proline and L-lysine were examined. It was found that all of the tested amino acid salt solutions have the potential to replace MEA. Nevertheless, solutions of the potassium salt of L-lysine showed the best properties.

The chapters of this thesis are organized as follows:

Chapter 1 is a brief introduction to the central issues of this work, setting the subject of the project in perspective to the issues of global warming and CO₂ capture and storage (CCS).

Chapter 2 explains the principle behind the chemical absorption of CO₂ from flue gas, emphasizing on the issues involving the solvent.

Chapter 3 is dedicated to the concept of using amino acids salt solutions as solvents in CO₂ capture, it includes a description of general amino acids chemistry and an outline of the chemical reactions involved in CO₂ absorption into amino acids salt solutions.

Chapter 4 deals with building and validation of the new apparatus for measuring of CO₂ solubility based on the semi-flow method. A validation study of CO₂ solubility in aqueous solutions of MEA is presented.

Chapter 5 focuses on determination of the chemical compositions of the precipitations, which arise in the five amino acid salt solutions upon CO₂ absorption. The solutions were saturated with CO₂ at 298 K, using the apparatus based on the semi-flow method. The precipitates were isolated and analyzed with XRD.

Chapter 6 concerns a CO₂ solubility study using the apparatus based on the semi-flow method; CO₂ solubility were examined in aqueous solutions of MEA and the five amino acid salts, with concentrations between 2 and 8 molal and temperatures around 298 K, 333 K and 323 K.

Chapter 7 describes a CO₂ solubility study using the apparatus based on the synthetic method. CO₂ solubility in aqueous solutions of the potassium salts of L-lysine and L-proline, with concentrations of 3.5 molal and 7 molal respectively, were studied at CO₂ partial pressures up to about 760 kPa, and temperatures around 313 K, 333 K and 353 K. Similar data were obtained with solutions of 7 molal MEA, at the same temperatures and at CO₂ partial pressures up to around 2.3 MPa

Chapter 8, concludes on the accomplishments of the project, and finally addresses considerations concerning future work.

Resumé (Dansk)

Ved at implementere kuldioxid (CO_2) fangst eller såkaldt ” CO_2 capture” er det muligt at rense røggassen fra kulfyrede kraftværker, således at den næsten er helt fri for denne drivhusgas. De teknikker, som er længst udviklede frem mod praktisk anvendelse, bygger på kemisk absorption, hvor CO_2 i røggassen bindes kemisk af en opløsning kaldet et solvent, sædvanligvis en vandig opløsning af aminer, hvilket resulterer i, at en rensset gas frigives til atmosfæren. Opvarmning af opløsningen desorberer CO_2 gassen igen og regenerer solventet, som så er klar til en ny runde absorption. Den indfangede CO_2 kan derefter komprimeres og deponeres. Typiske solventer til denne proces er baseret på vandige opløsninger af alkanolaminer såsom mono-ethanolamin (MEA), men deres anvendelse indebærer økonomiske ulemper og miljømæssige komplikationer. Aminosyre salt opløsninger har vundet interesse, som alternativ til alkanolaminerne, dels fordi de er naturligt forekomne, og dels fordi de har ønskværdige egenskaber; såsom lavere damptryk og højre stabilitet over for oxidativ nedbrydning. Et vigtigt træk ved disse nye solventer er dannelsen af udfældninger, som følge af CO_2 absorptionen, hvilket sker især ved høj CO_2 optagelse og/eller høje aminosyre salt koncentrationer. Dannelsen af udfældning er en udfordring, men kan muligvis også forbedre effektiviteten af ” CO_2 capture” processen.

Arbejdet i dette projekt vedrører faselige vægts eksperimenter for fem CO_2 + aminosyre salt + H_2O systemer, ved forhold som er relevante for ” CO_2 capture”

processen. Desuden fokuseres der på den kemiske sammensætning af de udfældninger, der dannes ved CO₂ absorption i de fem aminosyre salt opløsninger.

Faselige vægts data er nødvendige, for at udvikle sikre og økonomisk rentable ”CO₂ capture” processer. To forskellige eksperimentelle apparaturer blev anvendt. Et blev bygget som del af dette projekt, og er baseret på en analytisk semi-flow metode, det andet er for nylig blevet konstrueret, som del af et andet projekt, og er baseret på en syntetisk metode. Apparaturet som bygger på semi-flow metoden blev anvendt til måling ved CO₂ partialtryk på omkring 10 kPa, total tryk omkring atmosfæriske tryk og temperaturer omkring 298 K, 313 K og 323 K; disse betingelser dækker absorber delen af ”capture” processen. Apparaturet baseret på den syntetiske metode blev anvendt til at opnå data ved andre tryk og temperaturer op til 353 K (80 °C), hvilket er den maksimale driftstemperatur for nogle af komponenterne i apparatet. Ideelt set ville målinger i hele temperaturområdet for desorption, som normalt kræver omkring 393 K (120 °C), være ønskværdig.

Ved anvendelse af de to beskrevne apparaturer, blev CO₂ opløseligheden i vandige opløsninger af MEA og kaliumsaltene af taurin, glycin, L-alanin, L-prolin og L-lysin undersøgt. Det blev konstateret, at alle de testede aminosyre salt opløsninger har potentiale til at erstatte MEA. Men opløsninger af kaliumsaltet af L-lysin udviste de bedste egenskaber.

Kapitlerne i denne afhandling er organiseret som følger:

Kapitel 1 er en kort introduktion til de centrale problemstillinger i dette arbejde, projektets emne sættes i perspektiv til spørgsmålet omkring global opvarmning og CO₂ fangst og lagring.

Kapitel 2 forklarer princippet i den kemiske absorption af CO₂ fra røggas, med specielt fokus på problemstillinger omkring solventet.

Kapitel 3 omhandler konceptet, CO₂ fangst fra røggas ved hjælp af aminosyre salt opløsninger. Kapitlet indeholder en beskrivelse af generel aminosyre kemi og en oversigt over de kemiske reaktioner, der er involveret i CO₂ absorption med aminosyre saltopløsninger.

Kapitel 4 vedrører konstruktion og validering af det nye apparatur til måling af CO₂ opløselighed baseret på semi-flow metoden. En valideringsundersøgelse med CO₂ opløselighed i vandige opløsninger af MEA præsenteres.

Kapitel 5 fokuserer på bestemmelse af den kemiske sammensætning af de udfældninger, som opstår ved CO₂ absorption i de fem aminosyre saltopløsninger. Opløsningerne blev mættet med CO₂ ved 298 K, ved anvendelse af apparaturet baseret på semi-flow metoden. Udfældningerne blev isoleret og analyseret med XRD.

Kapitel 6 vedrører et CO₂ opløseligheds studie udført med apparaturet baseret på semi-flow metoden; CO₂ opløselighed blev undersøgt i vandige opløsninger af MEA og de fem aminosyre salte ved koncentrationer mellem 2 molal og 8 molal og temperaturer omkring 298 K, 333 K og 323 K.

Kapitel 7 beskriver et CO₂ opløseligheds studie udført med apparaturet baseret på den syntetiske metode. CO₂ opløselighed i vandige opløsninger af kalium saltet af L-lysin og L-prolin, ved de respektive koncentrationer af 3,5 molal og 7 molal, blev undersøgt ved CO₂ partialtryk op til ca. 760 kPa, og temperaturer omkring 313 K, 333 K og 353 K. Lignende data blev opnået med opløsninger af 7 molal MEA ved samme temperaturer og CO₂ partialtryk op til ca. 2.3 MPa

Kapitel 8, konkluderer på de opnåede resultater, og til slut gives overvejelser omkring fremtidigt arbejde.

Preface

The present thesis is submitted for partial fulfillment of the requirements for the Ph.D. degree at the Technical University of Denmark (DTU). The work was carried out at the Center for Energy Resources Engineering (CERE) in the Department of Chemical and Biochemical Engineering at DTU, under the supervision of Associate Professor Kaj Thomsen and Professor Erling H. Stenby. The Ph.D. was financed by the companies DONG Energy and Vattenfall, and I express my gratitude for their economic support.

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Kongens Lyngby, August 2012

Benedicte Mai Lerche

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Chapter 1

Introduction

According to the United Nations (UN) climate panel, the temperature on earth will increase between 1.8 °C and 4°C until the year 2100 due to global carbon dioxide (CO₂) emissions. The main contributor to global CO₂ emissions is fossil fuel combustion, and a significant challenge is thus facing the energy industry in how to meet the growing energy demand while managing emissions of CO₂ [1].

To halt the change in the global climate, CO₂ emissions must be reduced by more than 80% by the middle of this century. At the same time most scenarios show that the supply of primary energy will continue to be dominated by fossil fuels for several decades, before we can truly base the world's energy supplies on renewable energy [1]. In this context, there is a growing recognition that it is important for the energy industry to develop and implement technologies for CO₂ capture [2,3].

CO₂ capture technologies comprise ways to separate CO₂ from flue gas, before the flue gas is released into the atmosphere. The objective is to obtain pure CO₂ streams that can be compressed and then transported to a storage location, where it can be stored away from the atmosphere; overall this is called CO₂ capture and storage (CCS) [4,5]. It is generally estimated that the capture part represents about

80% of the global cost of CCS, while the rest is distributed between transport and storage [6]. CO₂ capture is the focus of this project.

CO₂ capture has the potential for large reductions (approximately 80-90%) of CO₂ emissions from fossil fuel power plants, and its implementation would thus allow fossil fuels to be burned with low emissions of CO₂ [4]. There are a number of technologies available; those based on capturing CO₂ from flue gas, after a normal combustion process, are referred to as post-combustion capture [5]. The advantage of such techniques is that they do not interfere with the normal combustion process, and they can thus be retrofitted into existing power plants with relative ease. [4]

The leading technology for post-combustion CO₂ capture is chemical absorption, in which a chemical solvent reacts reversibly with the CO₂ in flue gas. During contact with the flue gas, the solvent chemically binds the CO₂, resulting in a cleaned gas being released to the atmosphere. Heating of the CO₂ rich solution releases the CO₂ from the solvent, which is hereby regenerated and ready for another round of absorption [7]. The CO₂ is compressed and subsequently transported for sequestration into the deep ocean, aquifers or depleted oil and gas wells. However, storing the CO₂ is an expensive option with no opportunity for profit to displace the cost of the capture process [8]. An alternative to storage is utilization of the gas. CO₂ can be injected into oil fields to increase the mobility of the oil, as well as reduce its viscosity and thereby enhance oil recovery (EOR) [6]. Various other industries also involve the applications of CO₂; such as supercritical

processes, food and beverage carbonation, dry ice and urea production and the soda ash industry [9]. Presently, processes where CO₂ is used as a raw-material in the production of polyurethanes are under development. Polyurethanes are polymers that have applicability in a large amount of different industrial products, thus having the potential for large consumptions of CO₂ [10]. Nevertheless, currently most industries consume very small quantities of CO₂ when compared to the overall emissions from power generation [8].

The chemical absorption process is at present the most mature and viable CO₂ capture technology. Available solvents are almost exclusively based on aqueous alkanolamine solutions [7,11]. Unfortunately, CO₂ capture using alkanolamine solutions entails economic drawbacks, as well as environmental complications, making the large scale implementation of the process difficult [7,11-14]. Because CO₂ capture is gaining importance, there is a need for the development of new solvents that have the ability to capture CO₂ in both a cost efficient and environmental safe manner.

Amino acid salt solutions have emerged as possible alternatives to the alkanolamine solutions [11]. In comparison with alkanolamines, amino acid salts have several desirable properties promising high performance in CO₂ capture from flue gas [11,15]. One important feature of these new solvents is the formation of solids upon CO₂ absorption, which happens especially at higher CO₂ loadings and/or amino acid salt concentrations. The formation of solids poses

challenges, but it also holds the promise for improving the efficiency of the capture process [16,17]. The concept of using amino acid salt solutions for CO₂ capture is new and information regarding the subject is lacking in the open literature. This thesis aims at furthering the understanding of the potential use of these new solvents in CO₂ capture.

The focus of this work is phase equilibrium behavior of CO₂ + amino acid salt + H₂O systems, at conditions relevant for CO₂ capture. The project concerns an experimental study of CO₂ solubility in aqueous solutions of the potassium salts of taurine, glycine, L-alanine, L-proline and L-lysine, as well as aqueous solutions of mono-ethanolamine (MEA) by different methods. For this, a new experimental set-up based on an analytical semi-flow method was designed and built. The semi flow method was used for measurements at 10 kPa partial pressure of CO₂, total pressure equal to the atmospheric pressure and temperatures of 298 K, 313 K and 323 K. Experiments at 313 K, 333 K and 353 K with CO₂ partial pressures up to around 760 kPa in the case of the amino acid salts and around 2.3 MPa in the case of MEA, were conducted in a recent developed apparatus [9], using a synthetic method. MEA is the alkanolamines most studied in regard to CO₂ capture, and represents a reference system, to which new solvents can be compared [6]. The obtained results, allow for the direct comparison of the performance of the tested amino acid salts to that of MEA. Also, attention is given to the chemical composition of the precipitations, which forms as a result of CO₂ absorption into the selected amino acid salt solutions.

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Chapter 2

CO₂ capture by chemical absorption

Flue gas from coal-fired power plants contains approximately 10 mol % CO₂, which can be captured by chemical absorption [1,2]. Even though chemical absorption is the most mature CO₂ capture technology, the process entails serious economic and environmental complications, which have to be addressed, before large scale implementation can become a reality [2]. Capturing CO₂ from the flue gas of power plants first gained attention, not because of global warming, but because of the need for CO₂ for application in EOR. As mentioned in the introduction (Chapter 1) the injection of CO₂ into an oil field can enhance the productivity of the reservoir. CO₂ capture plants for EOR purposes were constructed in USA in the late 1970s and the early 1980s, but when the oil price dropped in the middle of the 1980s, the captured CO₂ was too expensive, and the plants were closed [1].

CO₂ capture by chemical absorption makes use of the temperature dependent reversibility of the chemical reaction between CO₂ and a solvent [2]. Available solvents are almost exclusively based on aqueous solutions of alkanolamines, i.e., molecules that carry both hydroxyl (-OH) and amine (-NH₂, -NHR, and -NR₂) functional groups on an alkane backbone [3,4].

A typical CO₂ capture system using chemical absorption (with an alkanolamine based solvent) is presented in Figure 2.1.

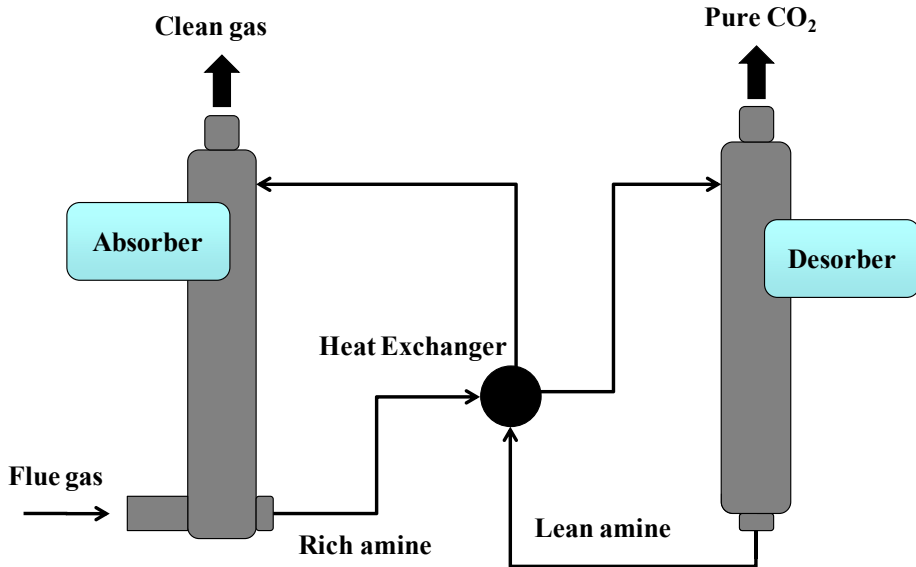


Figure 2.1: CO₂ capture from flue gas by chemical absorption. (The alkanolamine solution is abbreviated amine).

Before the flue gas is introduced in the capture system SO₂ and NO_x are removed in order to prevent formation of unwanted by-products, such as sulphates and nitrates [1]. The flue gas is then cooled and fed into the bottom of the absorber column, containing the solvent. The flue gas rises through the column, and at absorber temperature, typically around 313 K (40 °C), the alkanolamine solution chemically binds the CO₂ resulting in a clean gas being released to the atmosphere at the top of the column. It is possible to remove most of the CO₂ and recoveries are typical in the range of 80 to 95% [2]. When working with volatile solvents,

such as alkanolamines, a water wash section is needed, to remove solvent droplets or solvent vapor, before the cleaned gas is released into the atmosphere, this is important both economically and environmentally [1]. The solution containing the bound CO₂ (rich amine) is pumped to the top of the desorber column. Here the temperature is elevated to about 393 K (120 °C), reversing the chemical equilibrium, resulting in release of the CO₂ and regeneration of the solvent. A gas phase, consisting only of CO₂ and steam, is taken out at the top of the desorber. The water is removed by condensation, and the pure CO₂ gas is compressed [1,2]. The regenerated solvent (lean amine), is pumped back to the absorber column for another round of CO₂ absorption. This way the solvent is permanently recycled between the absorber and the desorber columns [1].

CO₂ capture in the described manner is energy demanding, and estimates are that almost 30 % of the energy produced by the power plant would have to be devoted to run the CO₂ capture process, possibly doubling the cost of the electricity produced [5]. The large energy penalty is mostly due to the large amount of heat needed to release the CO₂ from the alkanolamine solution in the desorber [1]. Also electric energy is required for blowing the flue gas through the absorber tower, solvent pumping and the subsequent compression of the pure CO₂ product [2,6]. In addition, the cost of the process stems from several operational problems, such as corrosion issues and solvent degradation and evaporation [1,7,8]. Flue gases from coal fired power plants contain around 4% oxygen, and oxidative degradation of alkanolamines in flue gas atmospheres are reported [7]. Thermal degradation and degradation by carbamate polymerization can also be a problem

[1,6]. The degradation is an economic burden as the solvent needs to be replaced at regular intervals [6]. In addition the degradation products may have unfavorable characteristics, such as being toxic and corrosive [6]. There is an increasing environmental concern regarding the use of alkanolamines, due to the formation of very toxic degradation products, which can be released with the cleaned gas [7,9]. Mastering the environmental impact of CO₂ capture is very important, as the reduction in CO₂ emissions should not come at the price of other environmental risks. One approach to make the process both more economical efficient as well as environmental safe is to find solvents with more favorable characteristics for CO₂ capture.

2.1. Solvents for CO₂ capture

When considering solvents for the chemical absorption process, CO₂ absorption rate, CO₂ solubility, heat of absorption, solvent volatility and stability as well as its environmental safety and price are the essential factors directly related to the cost-efficiency and environmental impact of the capture process [1,10].

- The absorption rate determines the height of the absorber tower; with a fast rate the tower height can be reduced, thereby lowering the capital investment cost [1].
- A high CO₂ solubility will limit the amount of solvent needed to capture a certain amount of CO₂, thus reducing the amount of used pump power, as well as decrease the heat requirements for regeneration [1,10].

- A low heat of CO_2 absorption is important for lowering the energy requirements in the desorber [1].
- The solvent should have low vapor pressure, as to avoid losses during the process. There can be solvent evaporation together with the cleaned gas, as the absorber is operated at atmospheric pressure. There can also be problems with evaporation of solvent in the desorber, where the pressure usually is only slightly above atmospheric pressure. However, sometimes the desorber is operated at higher pressures, preventing the loss of solvent during regeneration [1,10].
- Resistance to degradation is important in order not to lose solvent, but also to avoid the possible formation of toxic or corrosive degradation products [6].
- If a solvent is toxic or leads to toxic degradation products, this will prohibit its use [1].
- Finally, the price of the solvent is an important factor [1].

The chemistry of the absorption is in large controlled by the equilibrium constants of the reactions involved. High equilibrium constants will result in a high energy consumption upon solvent regeneration (high heat of absorption) while low equilibrium constants will result in CO_2 not being absorbed to any significant degree [5]. It is therefore not an issue of simply finding the solvent with strongest or weakest bonding to CO_2 , there is rather some intermediate values that will provide an optimum trade-off between uptake of CO_2 and energy consumption of

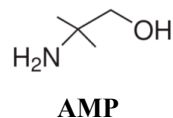
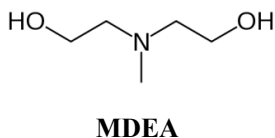
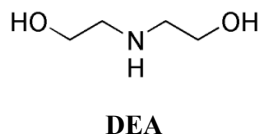
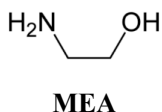
the process [6]. It shall be mentioned that if a solvent, has a high heat of absorption, but at the same time allows for regeneration at high pressure, the amount of energy used for evaporation of water in the desorption step will be reduced, and the energy requirement for the following compression of the CO₂ gas will be decreased [10].

2.1.1. Alkanolamines

CO₂ absorption into alkanolamine solutions occurs mainly as a result of the amine group of the alkanolamine molecule. It has been suggested that at very high pH, CO₂ can react with the hydroxyl groups of the molecule; however, this reaction is in general not expected to play a significant role in industrial CO₂ capture processes, as the pH of the systems are usually not high enough [6]. Different types of amines vary significantly in how they react with CO₂, in respect to both mechanism and kinetics. Tertiary amines (NR₃) differ from primary (RNH₂) and secondary amines (R₂NH), and sterically hindered amines differ from non-sterically hindered amines [6,11]. In addition the exact chemical structure of the specific amine is of importance [12].

Typical alkanolamine solvents include MEA, diethanolamine (DEA), N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP). Considering the mentioned alkanolamines they are classified as follows: MEA is a primary amine, DEA is a secondary amine, MDEA is a tertiary amine; whereas AMP is classified as a sterically hindered primary amine; sterically hindered

amines have substituent's attached to the α -carbon (the carbon next to the amine group) [9,11].



The alkanolamine most studied in regard to CO₂ capture is MEA; the advantage of MEA is its fast reaction with CO₂, which allows for limiting the height of the absorber tower. In addition, the price of the solvent is relatively low [1,10]. However for MEA as for many non-sterically hindered primary (or secondary amines) it has been observed that the high reaction rate comes at the expense of high heat of absorption [13]. This relation is thought to be caused by the fact that the reaction with CO₂ leads to formation of stable carbamates (RNHCOO⁻), which also have the disadvantage of creating a low CO₂ solubility [6,10,11]. A more detailed explanation of the circumstance for and the consequences of the formation of stable carbamates will be given in Chapter 3. In addition MEA is degraded in the oxygen rich atmosphere of flue gas and at elevated temperatures; the later prohibits the desorber being operated at elevated pressure. Generally, the

concentration of MEA in the solution is limited to 30 wt% due to problems with degradation products causing corrosion of the equipment [1,10].

Tertiary amines such as MDEA are also being considered. They do not form carbamate, but only absorb CO₂ by bicarbonate formation. They have lower heat of absorption and higher CO₂ solubility [6,10]. However, the rate of absorption is slow compared to primary and secondary amines [14].

In order to overcome the problematic trade-off between capture rate and energy consumption during regeneration, two different approaches are being explored. One is to use sterically hindered amines the other is to use blends of the different classes of amines [1].

Sterically hindered amines such as AMP have one or more substituent's attached to the α -carbon [11]. Molecular groups attached to the α -carbon, has been observed to make the formed carbamate less stable [6,11]. Generally, introduction of this type of steric hindrance to the amine group has been found to increase the CO₂ solubility and lower the heat of absorption [10,11]. The reactivity of the sterically hindered amines towards CO₂ is very similar to that of the tertiary amines, however it has been found that the rate of reaction of CO₂ with AMP is significantly higher than with MDEA [10], showing that sterically hindered amines could be a promising option for CO₂ capture [10].

In order to combine the advantages from different classes of amines, blends of amines are investigated. The idea is to combine a solvent presenting a low heat of absorption with a fast reacting solvent [10]. Most formulations of the blended amines are tertiary amine-based. MDEA is gaining recognition as the key component of the blended amines because of its low energy requirements for regeneration and high CO₂ solubility [9]. An addition of a relative small amount of a primary amine, such as MEA, or secondary amine, such as DEA, into the MDEA solution enhances the rate of capturing, while maintaining the advantages of MDEA [9]. The fast reacting amine in this process is often called a promoter [1].

Numerous alkanolamine based solvents are presently being studied and some also tested on a larger scale [10]. However, alkanolamines are inherently problematic, due to their volatility, oxygen degradability, and the formation of toxic degradation products [15]. Solvents with more favorable characteristics for CO₂ capture are thus being requested. Only if an energy efficient and environmental safe solvent can be found, the chemical absorption process for CO₂ capture will have the potential for large scale implementation.

2.1.2. New types of solvents

In the search for new solvents for the chemical absorption process, the majority of studies centers on ionic liquids, ammonia, and amino acid salt solutions.

Recently, a significant number of works were published on the use of ionic liquids as solvents in CO₂ capture [5,16-27]. Ionic liquids are salts consisting of anions and cations, but unlike common salts they are liquids even below 373 K (100 °C). Ionic liquids have the advantage of very low vapor pressures, together with high thermal and chemical stability. In addition, these liquids can be used without added water. With CO₂ absorption in common ionic liquids the CO₂ molecules are stored in the cavities between the ions. Adding functionalized groups, such as free amine groups to the ionic liquids, the CO₂ absorbing ability can be increased. These liquids are promising new solvents, but their design is difficult, and different research groups are currently working on synthesizing ionic liquids suitable for CO₂ capture [5].

Aqueous ammonia is another possibility for replacing the alkanolamines [10]. Unlike alkanolamines, ammonia is stable against degradation and does not cause corrosion problems. Another advantage is the potential low heat requirements; it has been observed that the heat of absorption in the case of ammonia is lower than with MEA. However, a challenge with ammonia is its high vapor pressure [10,28]. There are two variants of the process, depending on the temperature of absorption. In the chilled ammonia process, absorption takes place at low temperature 275-283 K (2-10 °C), having the advantage of limiting the ammonia

evaporation in the absorber, as well as decreasing the flue gas volume. This process allows precipitation of several ammonium carbonate compounds in the absorber. The other variant of the process absorbs CO₂ at ambient temperature 298-313 K (25-40 °C) and does not involve precipitation [10,28].

This thesis concentrates on using amino acid salt solution as solvents for CO₂ capture by chemical absorption. CO₂ absorption using amino acids is a biomimetic approach to CO₂ captures, due to its similarity to CO₂ binding by proteins such as for example hemoglobin [29]. As amino acid are either primary or secondary amines and often also sterically hindered, many of the same consideration as mentioned in this chapter for the alkanolamines also apply for the amino acids salt solutions. Although being more expensive than alkanolamines, a number of advantages make amino acid salt solutions attractive solvents. The next chapter is dedicated to the subject of amino acid salt as CO₂ capturing agents.

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Chapter 3

Amino acid salt solutions for CO₂ capture

Aqueous alkaline salts of amino acids, usually potassium salts but also lithium and sodium salts, are considered alternatives to the currently used alkanolamines [1-3]. Amino acids have the same amine functionality as alkanolamines, and alkaline amino acid salt solutions thus behave similar towards CO₂ in flue gas [4]. Compared to the solutions of alkanolamines, amino acid salt solutions are characterized by low vapor pressures and higher stability towards oxidative degradation [1]. In addition, they are expected to be environmentally friendly as amino acids are present in nature [5,6]. When absorbing CO₂ into amino acid salt solutions precipitation of the reaction products might occur [1,7]. The appearance of solids offers interesting advantages as well as drawbacks. The main negative aspects are the possible plugging and fouling of the gas-liquid contactors and heat-transfer surfaces [1]. Advantages are explained by the fact that precipitation of the reaction products, decreases their concentration in the liquid phase, which shifts the reactions towards the formation of more products, thereby increasing the CO₂ absorption by the solvent [3,8,9]. Depending on the chemical nature of the

precipitation, there are possibilities for the (temporary) storage of CO₂, and thereby new process opportunities [2]. In addition, the presence of the solid particles in the liquid phase will most likely influence the kinetics of the absorption [1]. Solid particles of the reaction products might enhance mass transfer at the gas-liquid interphase, due to favorable interactions between the small particles and the dissolved gas phase [1]. On the other hand their presence could increase the viscosity, and thereby lower the diffusivity of the gas in the liquid [1]. The occurrence of precipitation is challenging and adaption of equipment and process design is needed in order to handle the slurry and proper benefit from its formation [3,8]. Knowing the chemical composition of the precipitation is crucial, as different precipitates will lead to different absorption behavior and require different regeneration conditions [10].

3.1. Chemical nature of amino acids

To be able to discuss the possibilities of using amino acid salt solutions as solvents in CO₂ capture, knowledge of the chemical nature of amino acids is required. An overview of the chemistry of amino acids is thus presented in this section.

Chemically amino acids are molecules having both amine and carboxylic acid functional groups [11]. In biochemistry the term amino acid most often refers to α -amino acids, with the general structure shown in Figure 3.1 [12].

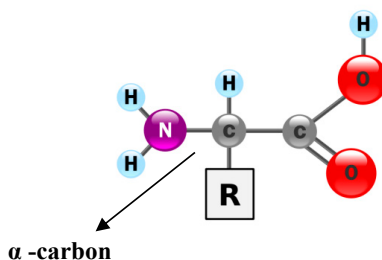
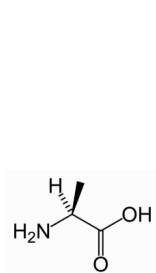


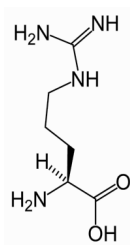
Figure 3.1: The general structure of an α -amino acid [13].

In α -amino acids the amine and the carboxylic acid groups are both attached to the α -carbon. The chemical variety of the α -amino acids comes from the difference in the side chain R, which is an organic substituent also attached to the α -carbon [14].

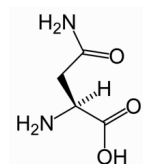
20 different amino acids are coded for in the genes of all organisms and incorporated into proteins. These amino acids are called standard or proteinogenic (meaning protein building) amino acids [12], and they are all α -amino acids. The complete structures of the standard amino acids are shown on page 24. The amino acids are drawn in a three-dimensional representation, illustrating the tetrahedral bonding about the α -carbon [12]. All the standard amino acid except glycine have an asymmetric α -carbon and can thus exist in two stereoisomer forms called L and D enantiomers, but only L enantiomers are found in proteins [12].



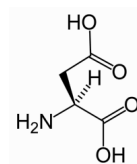
L-alanine



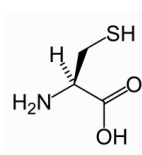
L-arginine



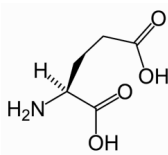
L-asparagine



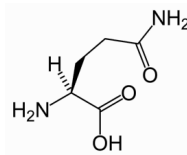
L-aspartic acid



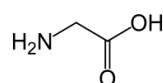
L-cysteine



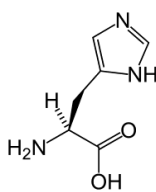
L-glutamic acid



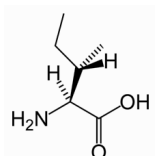
L-glutamine



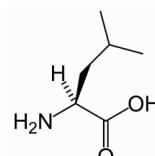
Glycine



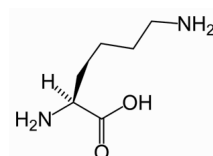
L-histidine



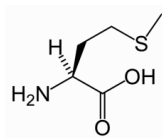
L-isoleucine



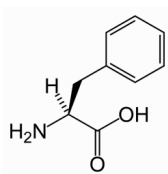
L-leucine



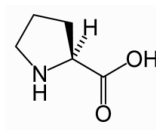
L-lysine



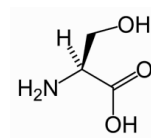
L-methionine



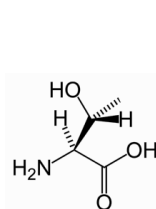
L-phenylalanine



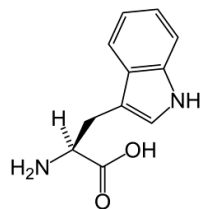
L-proline



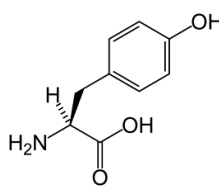
L-serine



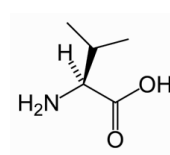
L-threonine



L-tryptophan



L-tyrosine



L-valine

As seen, 19 of standard amino acids are primary amines and differ only in the nature of their side chain. Proline, however, is a secondary amine whose nitrogen and α -carbon atom are part of a five-membered ring. It is important to note that all the standard amino acids except for glycine are sterically hindered amines [11].

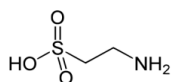
The standard amino acids contain a remarkable collection of chemical diversity. Many ways have been proposed to categorize the standard amino acids into groups based on the chemical feature of the side chains [12]. One way to group the standard amino acids is according to whether the side chain is basic, acidic, uncharged polar or non-polar, as given in Table 3.1 [15].

Table 3.1: Grouping of the 20 standard amino acids based on the chemical property of the side chain [15].

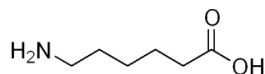
Chemical property of side chain				
	Basic	Acidic	Non polar	Uncharged polar
20 Standard Amino Acids	Lysine	Aspartic acid	Alanine	Asparagine
	Arginine	Glutamic acid	Valine	Glutamine
	Histidine	-	Leucine	Serine
	-	-	Isoleucine	Threonine
	-	-	Proline	Tyrosine
	-	-	Phenylalanine	-
	-	-	Methionine	-
	-	-	Tryptophan	-
	-	-	Glycine	-
	-	-	Cysteine	-

The standard amino acids are not the only amino acids to occur in nature. Others called non-standard amino acids appear in living organisms, some are found in proteins, others play important roles in the metabolism of the organism [12]. Not all of the non-standard amino acids are α -amino acids and not all of the non-standard amino acids, which are α -amino acids, are L-enantiomers [12].

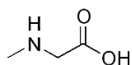
Standard as well as non-standard amino acids have been studied by different researchers in regard to CO₂ capture. The non-standard amino acids include taurine, 6-aminohexanoic acid, sarcosine, β -alanine, 2-methyl alanine and ornitine:



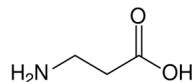
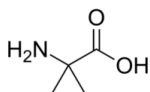
Taurine



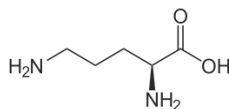
6-aminohexanoic acid



Sarcosine

 β -alanine

2-methyl alanine



Ornitine

Taurine is not strictly an amino acid, as it lacks the carboxylic acid group. It does contain a sulfonic acid group and may be called an amino sulfonic acid. But it is called an amino acid, even in scientific literature [16].

The representation of the amino acids given so far, although chemically correct, ignores an important fact. As amino acids have both the active groups of a carboxylic acid and an amine, they undergo an internal acid-base reaction [11]. The pKa of the carboxylic acid and the amine groups in amino acids are about 2 and 10 respectively. Therefore, an internal transfer of a proton from the carboxylic acid group to the amine group takes place, yielding the dipolar ion or the zwitterion form of the amino acid. Zwitter comes from the German word meaning "hybrid" [11,12].

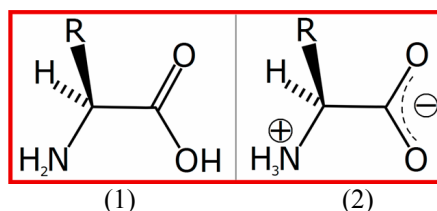


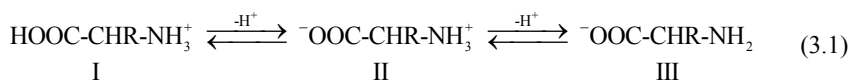
Figure 3.2: An amino acid, in its (1) unionized form and (2) zwitterionic form.

Amino acid zwitterions are a kind of internal salt, and have many of the physical properties associated with inorganic salts. Thus amino acids are crystalline, have high melting points, and are soluble in water but insoluble in hydrocarbons [11]. Amino acids zwitterions are amphoteric, meaning that they can react as acids or as bases depending on the circumstances. In aqueous acidic solution the carboxylate anion accepts a proton to yield the cation form of the amino acid; in aqueous basic

solution, the ammonium cation loses a proton to form the anion form of the amino acid [11]. As explained in the next section the amphoteric nature of amino acids is important when considering them as solvents for CO₂ capture.

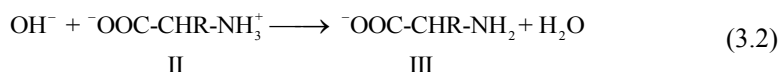
3.2. Chemistry of CO₂ absorption into amino acid salt solutions

Considering an amino acid with the generic formula HOOC-CHR-NH₂ dissolved in water, the following equilibriums are established, in which the amino acid takes its zwitterion form (II) [1].

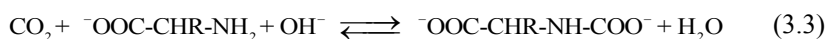


R stands for the side chain

The addition of an equimolar amount of strong base (such as potassium hydroxide) fully shift the equilibrium to the active form of the amino acid (III), having an amine group (-NH₂) similar to the active group in alkanolamines [1,8]:



The absorption of CO₂ by the amino acid salt follows the typical path of a primary or secondary amine, involving the formation of carbamate and bicarbonate, here the reactions are presented with an amino acid of primary amine functionality [1,4,8]:





The hydroxyl ions used in Reaction 3.3 and 3.4 are produced by the action of the amino acids as weak bases in an aqueous solution [4,17,18]:



Reaction 3.6 shall also be considered. This reaction, which is called base catalyzed bicarbonate formation is according to Donaldsen and Nguyen [18] distinct in mechanism from the action of the amine as a base producing hydroxyl ions (Reaction 3.5), which can then react with CO_2 (Reaction 3.4). Reaction 3.6 is mainly considered in the case of tertiary amines (which do not form carbamates), but the reaction may also play a role in the case of primary and secondary amines, especially if bicarbonate formation is abounded [17,19].



The kinetics of the CO_2 absorption is dominated by the carbamate formation (Reaction 3.3), which happens instantaneously [7,20,21]. In contrast base catalyzed bicarbonate formation (Reaction 3.6) is significantly slower [21]. As CO_2 is an acidic gas, the pH will decrease with the CO_2 absorption. The contribution from Reaction 3.4 to the kinetics of the absorption process can be important at very low CO_2 loadings, where the pH of the solution is high [4,20,21]. However, at increasing CO_2 absorption this reaction becomes slow compared to the reactions involving the amines [21].

Once formed, the carbamate can undergo hydrolysis/breakdown to produce bicarbonate and free amine (Reaction 3.7), the liberated amine can then react with another molecule of CO₂; thus hydrolysis of the carbamate leads to increased CO₂ absorption [7]. The degree of hydrolysis is determined by parameters such as, concentration of the amine, solution pH, and the chemical stability of the carbamate [7,22,23].



As described in Chapter 2, substituents at the α -carbon create instability in the formed carbamate molecule; this instability can lead to carbamate hydrolysis [7]. The steric hindrance would be expected to slow the rate of the initial reaction with CO₂ to some extent, but as 1 mol of amine is released upon hydrolysis of 1 mol of carbamate, there is more amine available for reaction with CO₂, and a counteracting increase in rate is possible [7,24].

It can be realized, that the CO₂ absorption is increased when the absorbed CO₂ is present as bicarbonate; this is because there exists a 1:1 ratio for CO₂ and amine in the case of bicarbonate formation, whereas this ratio is 1:2 for carbamate [7]. Bicarbonate formation takes place by Reaction 3.6 and through the overall Reactions 3.4+ 3.5, and 3.3+ 3.5+ 3.7, whereas carbamate is formed by the overall Reaction 3.3+ 3.5. In addition it is expected that solutions containing a higher proportion of bicarbonate to carbamate will undergo desorption at a greater rate and produce a “leaner” desorbed solution [7].

For a certain CO₂ amino acid salt system, the position of the individual equilibria and the speciation of the system will change throughout the absorption process [20], and under conditions with high amino acid salt concentration and/or high CO₂ loading, precipitation of the reaction products may occur, due to the formation of complexes and the salting-out effect [1,2].

The way a specific amino acid salt reacts with CO₂ will depend on many factors including the structure of the amino acid, meaning is it a primary or secondary amine, is it sterically hindered amine, and are there more than one amine group in the molecule, also each amino acid has its own unique structure that will affect the way it reacts with CO₂. The pK_a value of the amine group will play a role; as well will the solubility of the molecule at absorber conditions. Equally important for use in CO₂ capture, is the stability against degradation at the conditions of the process.

There are a number of different amino acids with different properties, which could in principle be used to capture CO₂ from flue gas, but so far only few amino acids have been tested. As mentioned in Chapter 1, this project concerned the study of five amino acids (taurine, glycine, L-alanine, L-proline and L-lysine). Other amino acids are mentioned in the following chapters in connection with presenting and discussion of literature data. This chapter includes the structures of all the amino acids (standard as well as non-standard), which are mentioned throughout the thesis.

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Chapter 4

A new flow apparatus for measuring CO₂ solubility

4.1. Abstract

As mentioned, coal-fired power plants exhaust flue gas contains approximately 10 mol % CO₂, which can be captured by chemical absorption in an appropriate solvent. This chapter describes a new experimental set-up designed to perform such studies. The apparatus applies a semi-flow method as one of the phases is flowing (gas phase), while the other is stationary (solution). In order to validate the experimental set-up, studies of the solubility of CO₂ in aqueous solutions of MEA with molal (m) concentrations between 0.52 m and 7 m, were performed at temperatures ranging from 298 K to 323 K. The results were compared to experimental data from literature, and to values calculated with the Extended UNIQUAC model.

4.2. Introduction

The principle of the constructed apparatus is versatile, in that it can be used to study the solubility of any gas in a solvent. However, the focus of this work is CO₂ solubility at conditions resembling the chemical absorption process connected to a coal fired power plant [1,2]. The set-up was therefore operated at a CO₂ partial pressure of 10 kPa, total pressure equal to the atmospheric pressure and temperatures between 298 K and 323 K. As MEA is the most commonly studied solvent regarding CO₂ absorption from gaseous streams, there are available literature data on the CO₂ + MEA + H₂O system [3-9], and thermodynamic models for the system exist [10]. The setup was used to study CO₂ solubility in aqueous solutions of MEA; in addition to validations of the apparatus, the obtained results add to the available phase equilibrium data on this ternary system.

4.3. Experimental methods to study gas solubility

The availability of reliable phase equilibrium data of a CO₂ + solvent mixture is essential to the optimization of a capture process involving that specific solvent. Quality phase equilibrium measurements allow the development of high accuracy models for the process and thus the design of a more efficient, safe, and economical feasible capture plant [11]. Different experimental techniques can be used to obtain phase equilibrium data of CO₂ amine systems. The equipments are designed to measure pTx data of the phases at the thermodynamic equilibrium, with T and p being the same in the coexisting phases [12]. The variable commonly

fixed is temperature, whose constancy is provided by contact with a heat reservoir, often a water bath or a temperature chamber [13]. The absorption takes place in a cell often made of stainless steel, although it can also be made of other materials including glass. A stainless steel cell is appropriate for higher pressures, whereas a glass cell is conveniently used for low pressure measurements [12,13]. In contrast to a stainless steel cell, a glass cell allows a visual inspection of the absorption process, enabling the observation of phenomena such as foaming or precipitation. In order to have a high mass-transfer rate of the gas into the liquid, a good mixing of the phases is necessary. The most common and most simple way of mixing the phases, is by magnetic stirring of the liquid phase [13].

Categorization of a method depends on how the composition of the phases at equilibrium is determined. The classification used here is in agreement with Fonseca et al. [14]. According to the authors there are two fundamental different classes of phase equilibrium techniques, analytical and synthetic depending on whether the composition of the phases at equilibrium are determined analytically or indirectly by measuring, phase volumes and densities and subsequently using these properties in calculations involving material balances [14].

Both analytical and synthetic methods have been used in the study of CO₂ solubility [9,12,15-21]. An analytical method with monitoring of the CO₂ content in the gas phase was the approach taken in this work. Our apparatus applies a semi-flow method, which has already been applied to the study of CO₂ solubility [12,16,17]. Semi-flow techniques for CO₂ solubility studies are characterized by

the flowing of the gas phase, while the liquid phase remains stationary in the equilibrium cell. A flow regulator provides a stable flow of gas, of known composition, to a thermostated cell containing the solution [12,14]. The CO₂ content of the effluent stream is continuously monitored using an analytical sensor, most commonly based on infrared spectroscopy. The equality of the CO₂ concentration in the inlet stream and outlet stream means that equilibrium has been reached [12,13]. Sometimes, only the composition of the effluent gas stream is analyzed, and used to calculate the composition of the liquid phase at equilibrium [14]. Another possibility is to analyze the liquid phase directly for example by a titration method [16,17].

4.4. Materials and methods

4.4.1. A new apparatus to measure gas solubility

Figure 4.1 shows a schematic representation of the developed experimental set-up. The equilibrium cell is a 250 cm³ cylindrical glass container placed in a thermostatic water bath, with an operating temperature range from 243 K to 423 K, stabilizing the temperature of the cell. The solvent is kept in a double wall glass column, with water from the thermostatic bath circulating in its outer layer, thermostating the solvent before its transfer to the cell. The gas mixture containing the CO₂ is brought into the system from a high-pressure vessel. The mixture first goes through a flow controller, passing then through a glass spiral in the water bath, which acts as heat exchanger, before entering the cell. A magnetic stirrer is used to promote the agitation of the liquid phase, thereby increasing the mass

transfer rate between the two phases. The flow controller, FC (Bronkhorst High-Tech B.V., Netherlands) controls the flow rate of the gas. A 3-wire platinum resistance thermometer (Pt 100) is placed in contact with the solution, through a port in the cell, measuring the temperature with a precision of ± 0.1 K. A pH probe can be placed in an additional port in the cell. Throughout the experiment, a non-dispersive infrared (NDIR) CO₂ sensor (GMTP221 acquired from and calibrated by Vaisala, Finland) measures the concentration of CO₂ in the effluent gas with a precession equal to or better than 3.5% of the reading. The water-saturated effluent gas leaving the cell passes through a condenser with a temperature around 273 K, condensing the water back into the solution; another thermostatic bath (not represented in Figure 4.1) provides the chilled liquid for the condenser. After the condenser, the dry effluent gas passes through a heat exchanger, which heats it back to ambient temperature, before reaching the CO₂ sensor. All the connections of the system are air-tight, with the gas only having the possibility to exit through the vent, thereby passing the CO₂ sensor. The CO₂ sensor, the platinum resistance thermometer and the optional pH meter are connected to an A/D converter, which is connected to a computer that records the data every fifth second.

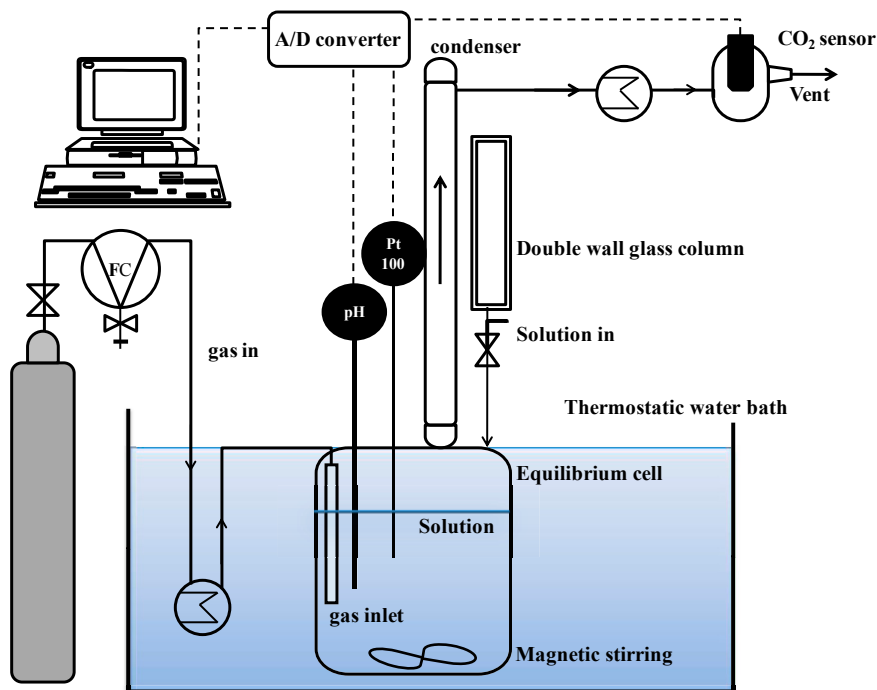


Figure 4.1: Schematic representation of the developed apparatus for the measurement of CO₂ solubility by means of a semi-flow method.

In order to use the recorded CO₂ readings to calculate the solubility of CO₂, specific considerations regarding the gas flow and analysis are needed. In a preliminary study it was concluded that a gas flow rate of approximately $1 \text{ dm}^3 \cdot (\text{min})^{-1}$ combines a complete absorption of CO₂ with an acceptable time frame for the experiments. The flow controller was calibrated with a CO₂/N₂ gas mixture at ambient temperature and pressure, using a bubble flow meter (Gilian Gilibrator 2, Calibration system from Sensidyne, USA). The flow of gas was determined to be $1.088 \text{ dm}^3 \cdot (\text{min})^{-1}$ at 101.147 kPa and 295 K. This value corresponds to a total molar flow of $7,48 \cdot 10^{-4} \text{ mol} \cdot (\text{sec})^{-1}$. As the pressure and temperature of the

laboratory does not change significantly, the variations of the mole flow are considered to be negligible, this value of total molar flow being valid for all experiments.

The output signal of the CO₂ sensor is proportional to the molecular density, and is influenced by variations in pressure, temperature and water vapor. Assuming an ideal gas, the CO₂ readings were corrected for differences between the sensor's calibration pressure (101.3 kPa), and the atmospheric pressure in the laboratory, measured by a manometer (quartz mano 2100 from Crouzet, France) at the start of each experiment. The temperature in the laboratory was assumed to be equal to the sensor's calibration temperature (298 K), the accuracy of this assumption has been evaluated, and found to be negligible (below 1 %) in the calculations of the final CO₂ solubility. Almost all water is removed from the effluent gas by the condenser, and the gas reaching the CO₂ sensor is thus assumed to be dry. The validity of this assumption has been confirmed by the agreements of the readings of the sensor on the dry gas (before the solvent is added to the cell) to the readings of the sensor after equilibrium of the system has been reached.

4.4.2. Chemicals and experimental procedures

Aqueous solutions of MEA were prepared using deionized water. MEA was acquired from Sigma-Aldrich, with a mass fraction superior to 0.99. The solutions were prepared gravimetrically, in an analytical balance Mettler-Toledo PR1203, with a precision of 0.001 g. Solutions were prepared in the concentration unit

molality (m), $\text{mol amine} \cdot (\text{kg H}_2\text{O})^{-1}$, instead of the more common unit molarity (M), $\text{mol amine} \cdot \text{dm}^{-3}$. Since molality is not volume based, it is temperature independent. The gas mixture with 10.0 ± 0.2 mol % CO_2 in nitrogen was acquired from Linde/AGA.

The experimental procedure starts by adding the solvent solution to the double walled column, which is then weighed, using the analytical balance. The gas flow is turned on, and the experimental set-up is filled with the CO_2 containing gas mixture. After about 15 min, the data collection program is started and a baseline is recorded, corresponding to the initial CO_2 concentration. With the gas flowing continuously, the solvent is added to the equilibrium cell, by opening a valve connecting the double wall column to the cell. The valve is closed, leaving some solution in the column, as not to add air to the system. The concentration of CO_2 in the effluent gas decreases because of absorption in the solution, increasing subsequently to its initial value, as the solution becomes saturated with the CO_2 . Figure 4.2 shows the CO_2 concentration in the outlet gas as a function of time for a typical experiment. Data collection from the CO_2 sensor, platinum resistance thermometer and optional pH meter are continued until equilibrium is reached. After the experiment, the double wall column containing the remaining unloaded solvent is weighed, using the same analytical balance, in order to determine the amount of solution used in the experiment.

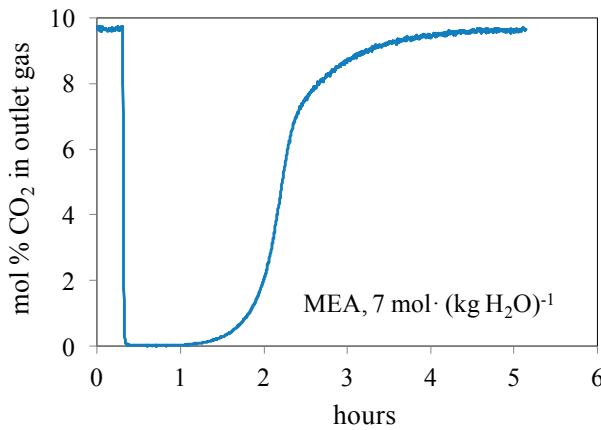


Figure 4.2: Typical curve for the CO₂ signal (concentration of CO₂ in the outlet gas as function of time). The curve is from an experiment with 7 m MEA at 298 K.

4.4.3. Calculating CO₂ solubility

The total amount of CO₂ absorbed by the solvent is found by integrating the differences between the molar flows of CO₂, in and out of the system over time:

$$n_{\text{CO}_2(\text{absorbed})} = \int \left(n_{\text{CO}_2(\text{In})} - n_{\text{CO}_2(\text{Out})} \right) dt \quad (4.1)$$

Where $n_{\text{CO}_2(\text{In})}$ is equal to the total mol flow of the inlet gas $n_{\text{Total}(\text{In})}$ multiplied the mol fraction of CO₂ in the inlet gas, $x_{\text{CO}_2(\text{In})}$, and $n_{\text{CO}_2(\text{Out})}$ is equal to the total mol flow of the outlet gas $n_{\text{Total}(\text{Out})}$ multiplied the mol fraction of CO₂ in the outlet gas, $x_{\text{CO}_2(\text{Out})}$. The $n_{\text{Total}(\text{In})}$ has a constant value given by the flow controller. However, $n_{\text{Total}(\text{Out})}$ varies throughout the experiment, due to variations in the CO₂ absorption.

$n_{\text{Total (Out)}}$ can be expressed in terms of the mol flow of nitrogen, $n_{\text{(nitrogen)}}$:

$$n_{\text{(nitrogen)}} = (1 - x_{\text{CO}_2(\text{In})}) \cdot n_{\text{Total (In)}} \quad (4.2)$$

The total mol flow of the outlet gas:

$$n_{\text{Total (Out)}} = \frac{n_{\text{(nitrogen)}}}{(1 - x_{\text{CO}_2(\text{Out})})} \quad (4.3)$$

$n_{\text{CO}_2(\text{Out})}$ can thus be calculated, followed by the calculation of $n_{\text{CO}_2(\text{absorbed})}$ by Equation 4.1. CO_2 solubility is usually expressed as loading (α), $\text{mol CO}_2 \cdot (\text{mol amine})^{-1}$ [22]. The loading is readily obtained, by dividing the total amount of mol CO_2 absorbed by the number of moles of amine examined. The latter is derived from the relation between the mass of solution used in the absorption experiment and the mass of solution prepared. The method provides the determination of the CO_2 loading of a solvent with a precision of 2.4 %.

4.5. Results and discussions

In order to validate the apparatus, solubility of CO_2 in solutions of MEA with concentrations between 0.52 m and 7 m was studied at 298 K, 313 K and 323 K. The phase equilibrium results of the validation study are listed in Table 4.1. The table presents the conditions of each experiment, together with the obtained CO_2 loading values. Listed are also the loading values calculated using the Extended UNIQUAC model [10], as well as the deviation (Dev.) between the model and this work.

Table 4.1: Results obtained for the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ around 298 K, 313 K and 323 K, with MEA concentration between 0.52 m and 7 m, 10 kPa partial pressure of CO_2 and total pressure equal to the atmospheric pressure, compared to calculations of the Extended UNIQUAC model [10].

m	p_{Total}	p_{CO_2}	T	α This work	α Model	Dev.
mol MEA · (kg H_2O) ⁻¹	kPa	kPa	K	mol CO_2 · (mol amine) ⁻¹	mol CO_2 · (mol amine) ⁻¹	%
0.52	101.13	9.8	297.5	0.75	0.71	6.1
0.52	100.18	9.7	297.4	0.76	0.71	6.4
2.00	100.47	9.7	297.7	0.63	0.61	4.0
2.00	100.46	9.6	297.7	0.61	0.61	0.7
7.02	101.41	9.8	297.7	0.55	0.54	2.1
7.00	101.12	9.8	297.6	0.54	0.54	0.1
7.00	100.98	9.7	297.5	0.54	0.54	0.3
2.00	100.09	9.4	312.9	0.55	0.56	-1.7
2.00	100.37	9.5	313.0	0.56	0.56	-0.1
7.00	102.44	9.8	311.7	0.52	0.51	1.0
7.00	99.48	9.3	313.0	0.50	0.51	-0.5
0.52	101.31	9.7	321.7	0.61	0.62	-0.7
0.52	99.40	9.5	321.7	0.64	0.62	3.0
2.00	99.55	9.3	322.2	0.54	0.53	1.3
2.00	100.90	9.7	321.5	0.55	0.53	2.5
2.00	100.99	9.7	321.4	0.53	0.53	-1.0
7.00	100.87	9.7	321.7	0.50	0.49	2.0
7.00	101.82	9.8	321.4	0.50	0.49	1.6

Figure 4.3 depict the results obtained in this work (Table 4.1) together with data obtained by Lee et al. [6] and values calculated using the Extended UNIQUAC model [10]. Each of the loading values of this work is represented as the mean value from at least two experiments, repeated at the same conditions of temperature and MEA concentration. The error bars show the standard deviation, where they are absent, the deviation was below or equal to $0.001 \text{ mol CO}_2 \cdot (\text{mol amine})^{-1}$.

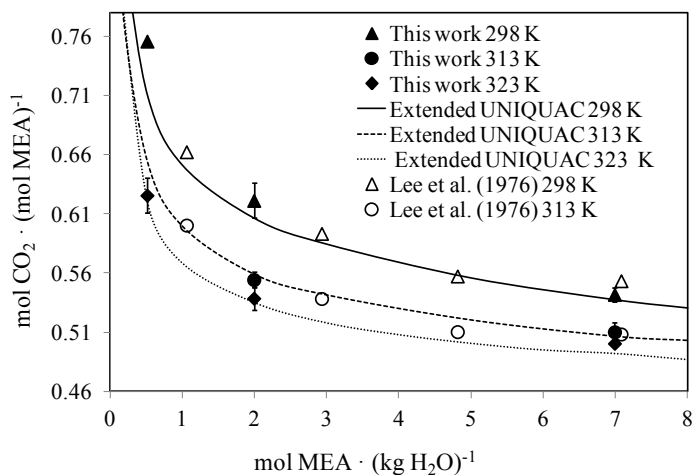


Figure 4.3: Results, showing the CO₂ loading as a function of the MEA concentration, for the system CO₂ + MEA + H₂O obtained in this work at 298 K, 313 K and 323 K, with MEA concentrations between 0.52 m and 7 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure. The data of this work are compared with calculations of the Extended UNIQUAC model [10], and with data from literature [6].

Figure 4.3 shows that there is good agreement between data obtained in this study and data from literature [6], despite some deviation from the Extended UNIQUAC model [10].

Figures 4.4, 4.5 and 4.6 show further comparisons of this work with literature. Tendency lines of the literature data are displayed. In the case of more than one literature source, the line was obtained from all the sources.

Figure 4.4, presents the results obtained in this work with 0.52 m MEA, at 298 K and 323 K compared to data of Mason and Dodge [4].

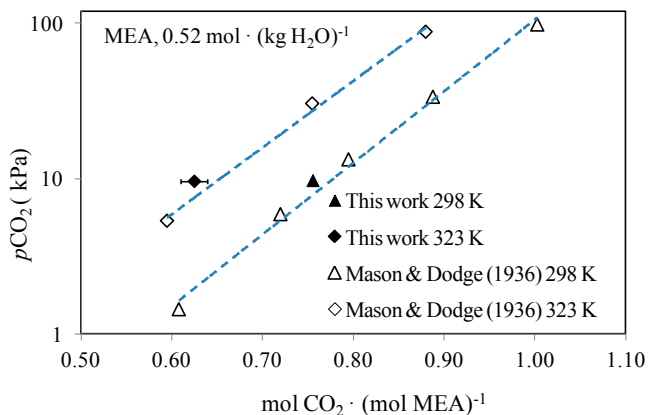


Figure 4.4: Results for the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work at 298 K and 323 K, with a MEA concentration of 0.52 m, CO_2 partial pressure of 10 kPa, and total pressure equal to the atmospheric pressure. The results are compared to literature [4]. The lines in the plot are given for eye guidance.

In Figure 4.5 the results obtained in this work with 7 m MEA at 298 K and 323 K are compared to data from Mason and Dodge [4] and Lee et al. [6].

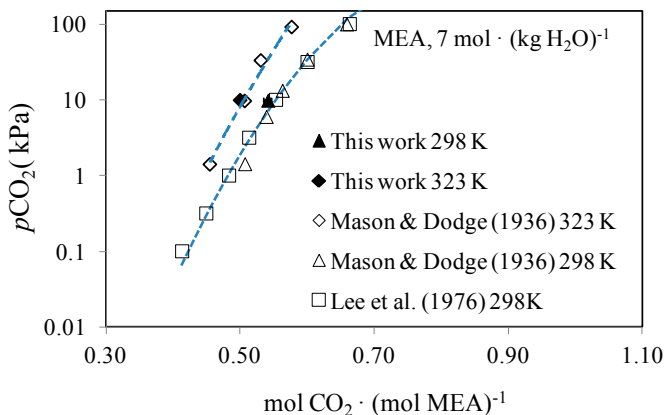


Figure 4.5: Phase equilibrium data of the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work at 298 K and 323 K, with a MEA concentration of 7 m, CO_2 partial pressure of 10 kPa and a total pressure equal to the atmospheric pressure. The results are compared to data from literature [4,6]. The lines in the plot are given for eye guidance.

Figure 4.6 presents the data obtained in this work at 7 m and 313 K compared to data from Lee et al [5,6] and Shen and Li [3].

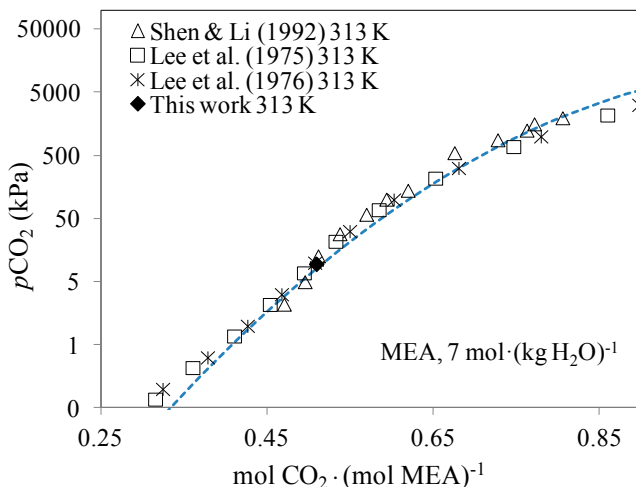


Figure 4.6: Results of the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work at 313 K, with a MEA concentration of 7 m, CO_2 partial pressure of 10 kPa, and a total pressure equal to the atmospheric pressure. The results are compared to data from literature [3,5,6]. The line in the plot is given for eye guidance.

It was found that the loading values obtained in this work deviate from the tendency lines of the literature data by less than 3%, which shows that there is very good agreement between this work and the given literature sources.

The presented apparatus was built with the purpose of studying CO_2 solubility in amino acid salt solutions. One of the important issues with amino acid salt solutions is their ability to form precipitation when absorbing CO_2 . The fact that the presented set-up utilizes an equilibrium cell made of glass allows for a visual inspection of the precipitation process. During the work with developing the new apparatus two different glass equilibrium cells were constructed. Figure 4.7 is an

image of the cell pictured in Figure 4.1. This cell has a vertical glass tube as the gas inlet, which is suitable for experiments where precipitation occurs, as it limits the tendency for plugging of the equipment.



Photo: Christian Ove Carlsson

Figure 4.7: Image of the cell shown in Figure 4.1. The gas inlet is a vertical glass tube.

Figure 4.8 shows an image of another cell which was fabricated during this work; here the gas inlet is a glass sieve. The sieve has the function of gas distributor and thus the advantage of enhancing the gas liquid mass transfer. But, in case of precipitation, the disadvantage is, that the sieve is prone to clogging. In both of the cells, the tube from the gas vessel is connecting to a glass spiral, fastened on the outer side of the cell. As mentioned this glass spiral functions as a heat exchanger,

heating the gas (to the temperature of the water bath) before the gas enters the cell, getting in contact with the solution. There is direct contact from the glass spiral to the gas inlet (glass tube or sieve).



Photo: Christian Ove Carlsson

Figure 4.8: Image of a second equilibrium cell fabricated during this work. The gas inlet is a glass sieve.

The ports of the cells are for connections to the condenser, thermometer, and double walled column (containing the solvent solution), as well as to the optional pH probe. The pH probe allows for the measurement of pH during the absorption, giving information about the activity of H_3O^+ (and OH^-) in the liquid phase, which is a vital input for understanding the speciation and in turn the reaction mechanism

of a system under study [23]. The cells have more ports than applied in the presented work, these apertures can be used for different purposes, including sampling of the liquid phase; and if not used, they are closed off, during the experiment. Both types of cells can be used as the equilibrium cell in the presented apparatus, but in the case of precipitation the cell depicts in Figure 4.7 is the most suitable.

4.6. Conclusions

A new apparatus for measuring CO₂ solubility by means of a semi-flow method was built. The apparatus was validated by studying CO₂ solubility in aqueous solutions of MEA. Besides validating the apparatus, the obtained results add to the available phase equilibrium data on the system CO₂ + MEA + H₂O. The obtained results were compared to experimental data from literature [3-6] and to calculations of the Extended UNIQUAC model [10]. The results obtained in this work are in very good agreement with literature data. A good agreement between the results and the Extended UNIQUAC model can also be observed. This confirms the quality of the new apparatus, and its ability to obtain high quality data.

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Chapter 5

Precipitation in CO₂ amino acid salt systems

5.1. Abstract

An important feature of amino acid salt solutions is the formation of solids upon the reaction with CO₂, which happens especially at high CO₂ loading and/or high amino acid salt concentration. As a consequence of the novelty of these systems, much is still unclear regarding the precipitation, including its chemical nature. In this work aqueous solutions of the potassium salt of glycine, taurine, L-alanine and L-proline at 7 m and L-lysine at 4.5 m were saturated with CO₂ at 298 K, using the semi-flow method presented in Chapter 4, operating at a 10 kPa partial pressure of CO₂ and a total pressure equal to the atmospheric pressure. The resulting precipitates were isolated, and their chemical compositions were determined by X-ray diffraction (XRD).

5.2. Observations from literature

One of the first observations of the solid formation was made by Hook [1] during his study of absorption of pure CO₂ from a 100 kPa gas reservoir into 2.5 M aqueous solution of the potassium salts of different amino acids, including glycine, alanine and 2-methyl alanine, at 295 K. Hook [1] used ¹³C nuclear magnetic resonance spectroscopy (NMR) to analyse the precipitate. The analysis indicated that there were 2 mol of amino acid per mole of CO₂, and it was concluded that the precipitates were carbonate salts of the amino acid zwitterion $[(\text{KO}_2\text{CR}^-\text{NH}_2\text{R}^+)_2\text{CO}_3^{2-}]$ [1].

Kumar et al. [2] argued that, as the crystallization in Hooks [1] experiments was observed at very high CO₂ loadings > 0.9 for some amino acids (for example alanine), the dissolved CO₂ should be present predominantly as bicarbonate species rather than carbonate, since at high CO₂ loadings the pH of the solution is low [2]. With the study performed by Hook [1] as basis, Kumar et al. [2] performed an investigation on the crystallization phenomena occurring during the absorption of CO₂ into aqueous solutions of the potassium salts of taurine at 298 K. Using ¹³C NMR to analyse the crystallized solid the authors concluded, that the precipitated material was the protonated amino acid, i.e., the zwitterionic form of taurine.

Majchrowicz et al. [3] examined the tendency of aqueous solutions of the alkaline salts of taurine, β -alanine, sarcosine and L-proline to form solids at 293 K and 313K and CO₂ partial pressures relevant for CO₂ capture. According to Majchrowicz et al. [3] lithium based solutions precipitate more easily than sodium

based, which in turn precipitate more easily than the potassium based solutions. The authors report the identity of the formed solids to be the zwitterion of the amino acid in the case of taurine, whereas more complex species containing CO₂ were found for β -alanine, sarcosine and L-proline [3]. In a recent paper, Majchrowicz and Brilman [4] report precipitation of potassium bicarbonate, when absorbing CO₂ in a 3 M solution of the potassium salt of L-proline at 285K and CO₂ partial pressures above 6 kPa. In another work, Majchrowicz et al. [5] examined the solids precipitating upon the absorption of CO₂ into aqueous solutions of the potassium, sodium and lithium salts of different amino acids. The solutions were flushed with CO₂ to obtain the precipitate. Elemental analysis (CHN), atomic absorption spectroscopy (AAS), XRD, ¹³C and ¹H NMR were used to identify the chemical composition of the solid products formed. In the case of taurine, the precipitation was found to be the zwitterionic form of the amino acid for all three alkali salt systems. In the case of the potassium salt of L-alanine and 2-methyl alanine the precipitates were also identified as the zwitterionic form of the amino acid, whereas the potassium salt of 6-aminohexanoic acid precipitated mainly as potassium bicarbonate. For the sodium salts of L-alanine, 2-methyl alanine and 6-aminohexanoic acid the precipitates consisted of a mixture of compounds containing both sodium bicarbonate and the amino acid, with the amino acid being present either as the bicarbonate salt, the zwitterion or the amino acid salt [5]. Notably, in the case of precipitation of the latter, the CO₂ loading of the solution would decrease. In this case the precipitation is a disadvantage, as the reactant is lost.

This outline of data from literature underlines the individuality and complexity of the different CO₂ amino acid salt systems, and the need for investigation of the chemical composition of the solid formation for a specific system of interest.

5.3. Materials and methods

5.3.1. Chemicals and preparation of solutions

All chemicals were acquired from Sigma Aldrich, having a mass fraction superior to 0.99 in the case of taurine, glycine, L-alanine and L-proline; superior to 0.98 in the case of L-lysine and superior to 0.85 in the case of potassium hydroxide. The gas mixture with 10.0 ± 0.2 mol % CO₂ in nitrogen was acquired from Linde/AGA.

All solutions were prepared gravimetrically in an analytical balance (Mettler-Toledo PR1203) with a resolution of 0.001 g, using deionised water. The precise purity of the potassium hydroxide was determined by titration with 0.1 M aqueous solution of HCl. The amino acid salt solutions were prepared by neutralizing the amino acid with an equimolar amount of base, according to Reaction 3.2. The amount of water formed, together with the water content of the potassium hydroxide were taken into account in the calculation of the final concentration of the amino acid salt solutions. As the reaction is exothermic, the mixing of the chemicals was performed with cooling, in order not to lose water from the solution. In the case of the solutions of L-lysine and L-alanine, an ultrasonic bath was needed in order to dissolve the mixture.

5.3.2. CO₂ saturation of the solutions

The aqueous solutions of the potassium salt of glycine, taurine, L-alanine and L-prolin at 7 m and L-lysine at 4.5 m were loaded with CO₂ until equilibrium at 298 K, using the equipment presented in Chapter 4. As mentioned this experimental set-up, is based on a semi-flow method [6,7] with analysis of the effluent gas. A gaseous mixture containing 10 mol % CO₂ in nitrogen is bubbled through the solvent, at a total pressure close to atmospheric pressure. The concentration of CO₂ in the effluent stream is continuously analyzed, using a non-dispersive infrared sensor (NDIR). The experiments are characterized by an initial decrease in the amount of CO₂ in the effluent stream, followed by an increase back to its initial value, as the solution becomes saturated with the CO₂. All experiments were performed twice, with the pH of the solution being measured continuously in one of the experiments.

5.3.3. XRD study of the precipitates

Precipitation occurred as a result of the CO₂ absorption in case of all five amino acid salt solutions. From experiments without pH measurement, the solid was isolated by vacuum filtration and dried in a silica desiccator, before being subjected to the XRD study. Only solids from experiments without pH measurement were examined; in order to avoid any interference from the electrolyte solution (KCl) of the pH probe on the chemical composition.

X-ray diffraction patterns were collected on a Huber G670 Imaging strip Guinier camera equipped with a focusing quartz monochromator using Cu $K\alpha_1$ radiation. The data were collected in the range 3° to 100° in steps of 0.005° in 2θ and accumulated for 10 min per pattern. The different phases were identified via a Search/Match procedure. The crystal structures of the identified phases were retrieved from the inorganic crystal structure database (ICSD) [8], and from the Cambridge crystal structure database (CCDS) [9], and subsequently fitted to the observed powder patterns using the Rietveld method [10]. In the Rietveld method the least square method is used to refine the theoretical powder pattern of an identified phase until it matches the measured profile. If there are several phases in the sample, these can be optimized simultaneously and the percentage composition of the sample can be calculated.

5.4. Results and discussions

The identified and fitted phases obtained in this study are presented in Table 5.1. The table also presents the experimental conditions of pressure, temperature and pH at equilibrium, together with the initial amino acid salt concentrations. The initial amino acid salt concentrations were chosen considering that an aqueous solution of 30 wt% MEA, corresponding to 7 m, represents a reference to which new solvents can be compared [11]. As the amino acids taurine, glycine, L-alanine and L-proline all contain one amine group (as MEA), 7 m solutions of the potassium salt of these amino acids were studied. L-lysine contains two active amine groups, which both participate in the reaction with CO_2 , thus the

corresponding concentration for L-lysine would be 3.5 m. But, when it was found, that precipitation did not occur with this solution under the given experimental conditions, the concentration was increased to 4.5 m, which then led to precipitation in the experiments.

Table 5.1: XRD results showing the chemical composition of the solids isolated from five CO₂ saturation experiments. The table presents, pressure, temperature and pH at equilibrium as well as initial amino acid salt concentration for each experiment.

Amino acid salt mol · (kg H ₂ O) ⁻¹		p_{Total} kPa	$p\text{CO}_2$ kPa	T K	pH	Chemical composition of precipitation
Taurine	7.00	100.57	9.6	297.5	8.6	100 % Taurine zwitterion
Glycine	7.00	100.74	9.6	297.5	8.8	73 % Glycine zwitterion, 27 % KHCO₃
L-alanine	7.00	100.96	9.5	298.1	9.0	67 % L-alanine zwitterion, 33 % KHCO₃
L-lysine	4.50	100.63	9.5	297.7	9.1	100 % KHCO₃
L-proline	7.05	100.28	9.5	297.6	9.4	100 % KHCO₃

An example of a Rietveld XRD fit is shown in Figure 5.1. None of the diffraction patterns showed signs of other phases, or significant amorphous contributions. The rest of the Rietveld fits are presented in the Appendix of this thesis.

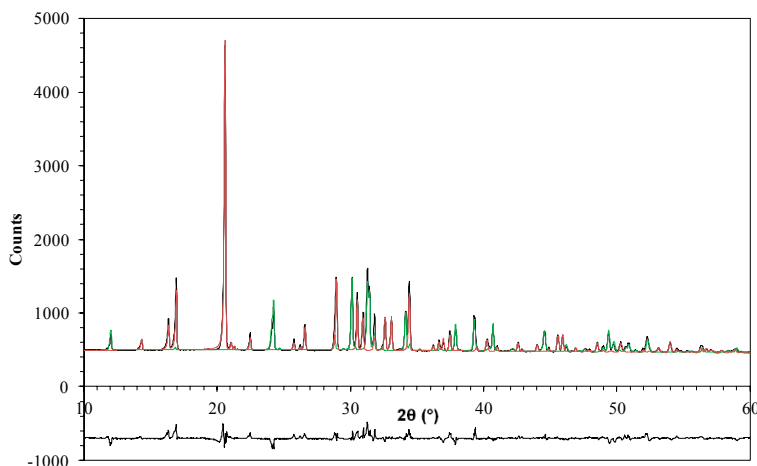


Figure 5.1: Rietveld XRD fit of L-alanine and potassium bicarbonate to the powder pattern of the precipitation, occurring with the absorption of CO_2 into a 7 m solution of the potassium salt of L-alanine. Powder patterns; Black (top): Observed pattern; Black (bottom): Difference between observed and fitted pattern; Green: Potassium bicarbonate; Red: L-alanine.

Table 5.1 shows that the chemical compositions of the solids obtained in this study consist in either the zwitterion form of the amino acid, potassium bicarbonate, or a mixture of the two. These findings are in good agreement with findings by other authors as will be outlined below. Carbamate was not detected, and to our knowledge it has never been reported as part of the crystallized material in previous studies.

For potassium taurate the precipitation was determined to be the pure zwitterion of the amino acid (Table 5.1), which was also found in experiments performed by Kumar et al. [2] and Majchrowicz et al. [5], see Section 5.2.

In the case of potassium glycinate the precipitation consisted in a mixture of potassium bicarbonate and the zwitterion form of glycine (Table 5.1). Although

works on the absorption of CO₂ into salt solutions of glycine are available in literature [12-16], there has been no report of solid formation for these systems by other authors. To our assessment, either the initial amino acid salt concentration or the degree of CO₂ loading in their experiments has been too low for any precipitation to occur.

For CO₂ absorption into the potassium salt of L-alanine, Hook [1] reports a solid consisting of 2 mol of amino acid per mole of CO₂ (see Section 5.2), which is very close to the result obtained in this work (Table 5.1), when taking into consideration that the carbonate found by Hook [1] is likely to be bicarbonate, as explained by Kumar [2]. Majchrowicz et al. [5] found the precipitation in the case of the potassium salt of L-alanine to consist in the pure zwitterion of L-alanine. This discrepancy between results can be explained by the different experimental procedures; Majchrowicz et al. [5] formed their solid by flushing the amino acid salt solution with pure CO₂, whereas both ours and Hook's [1] experiment involved long equilibration times. Clearly, the kinetics can be an important factor when comparing different experiments.

In the case of CO₂ absorption into solutions of the potassium salts of L-proline, Majchrowicz and Brilman [4] report precipitation consisting of potassium bicarbonate, which is in concordance with our findings (Table 5.1).

L-lysine is not among the amino acids studied in regard to CO₂ capture, and there is no literature regarding the precipitation occurring with this amino acid.

5.4.1. Chemical considerations

As described in Chapter 3, a set of equilibrium reactions are part of the absorption process, with the position of the individual equilibria varying depending on the specific system, i.e., the specific amino acid salt solution, the partial pressure of CO₂ and the temperature.

For a given system the pH at equilibrium is dictated by the base strength of the amino acid. For the studied amino acids, the base strength is as follows taurine < glycine < L-alanine < L-lysine < L-proline [17], which corresponds with the alkalinity trend of the equilibrium pH, as seen in Table 5.1. Here, the base strength of L-lysine is considered to be an average of its two amine groups. The results presented in Table 5.1 imply a relation between the bicarbonate contents of the formed solids and increased alkalinity of the system. Even though, there is no direct connection between the quantity of a formed species and the chemical nature of the precipitation, it can be considered that a high base strength of the amino acids favors the production of hydroxyl ions (Reaction 3.5) which then combine with CO₂ forming bicarbonate (Reaction 3.4). Also favored by a high base strength of the amino acid is base catalyzed bicarbonate formation (Reaction 3.6). As explained in Chapter 3, this reaction is less important than the carbamate formation. However, according to da Silva [11], this reaction can be important especially if bicarbonate formation is dominant. In addition, carbamate hydrolysis (Reaction 3.7) also produces bicarbonate. As explained in Chapter 3 Section 3.2, it has been demonstrated that one of the reasons to render the carbamate instable

is substitution at the α -carbon [1]. Thus L-alanine and L-lysine are presumed to involve greater carbamate hydrolysis, than glycine and taurine. In the case of L-proline, which has a cyclical amine functionality, the carbamate is likely to be more stable [4,18], and in this case the high base strength of L-proline is possibly accounting for the bicarbonate formation.

Another issue is the solubility of the amino acid zwitterion [2,19]. As shown in Table 5.1, the experiments with taurine, glycine and L-alanine resulted in the precipitation of the zwitterion form of the amino acid, which means that for these 3 amino acids the concentration of the zwitterion exceeded its solubility limit at the conditions of equilibrium. In their study of CO₂ absorption into solutions of potassium taurate Kumar et al. [2] found, that the concentration of the zwitterion of taurine at the point of crystallization did not differ significantly from the solubility of taurine in water. The absence of zwitterion precipitation in the case of L-proline can possibly be explained by the fact that L-proline has very high water solubility compared to other amino acids [17]. In the case of L-lysine the equilibrium pH of 9.1 means that the isoelectric point of the amino acids has been passed during the absorption [17], and the pH is presumably low enough to render the zwitterion concentration of L-lysine under its precipitation limit.

5.5. Conclusions

Five amino acid (potassium) salt solutions were saturated with CO₂ at 298 K, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure. The chemical compositions of the precipitations, which occurred as a result of the absorption, were determined by XRD. The solids consisted of either the pure zwitterion form of the amino acid, pure potassium bicarbonate or a mixture of the two. These findings are in agreement with the results published by other authors for similar systems. In the case of solids containing bicarbonate, there is the opportunity to temporarily store the CO₂, opening new possibilities for the capture process. Especially interesting in this regard are the solutions of L-proline and L-lysine, showing the highest base strengths, and forming precipitates consisting of pure potassium bicarbonate.

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Chapter 6

CO₂ solubility in five amino acid salt solutions

6.1. Abstract

This chapter addresses the solubility of CO₂ in aqueous solutions of the potassium salts of taurine, glycine, L-alanine, L-proline and L-lysine, at concentrations between 2 m and 8 m. The experiments were carried out at a CO₂ partial pressure around 10 kPa, total pressure equal to the atmospheric pressure and temperatures of 298 K, 313 K and 323 K. The experimental setup was presented in Chapter 4, and is based on a semi-flow method. The obtained results with the amino acid salt solutions are compared to similar data obtained with aqueous solutions of MEA.

6.2. Introduction

Designing of a CO₂ capture process using an aqueous amino acid salt solution requires phase equilibrium data on the system at CO₂ partial pressures of interest to the process. In addition, it is important to have knowledge of the conditions for which a given system changes from a non-precipitating to a precipitating system. This chapter addresses these issues for solutions of the potassium salts of taurine, glycine, L-alanine, L-proline and L-lysine. CO₂ solubility in solutions of alkaline salts of taurine, glycine, L-alanine and L-proline, have been included in studies by other authors, but to our knowledge, there are no reports on studies involving solutions of L-lysine. Furthermore, the data obtained in this work include a wide concentration range, not previously presented by other authors for any CO₂ + amino acid salt + water system.

Experiments with the amino acid salt solutions are compared with the corresponding experiments with MEA performed in this work using the semi-flow method. Some of the data with MEA were produced as part of the validation of the apparatus and are given in Table 4.1; presenting tabulated data of MEA in this chapter, it will be indicated when the data are reproduced from Chapter 4.

Influences of amino acid salt concentration and temperature on the CO₂ solubility and precipitation occurrence were investigated. The influence of increasing the concentration of MEA and the amino acid salt solutions between 2 m and 8 m was studied at 313 K. The influence of increasing the temperature from 298 K to 313 K and then to 323 K was studied at 7 m in the case of MEA and the potassium salts of taurine, glycine, L-alanine, L-proline, and 3.5 m in the case of the

potassium salt of L-lysine. The concentrations, for the study of the influence of temperature on the CO₂ solubility, were selected according to the reasoning, that the solutions all have the same number of amine groups per kg of water, as the benchmark solution of 7 m MEA, forming ground for a direct comparison between the amines (see Chapter 5 Section 5.4).

CO₂ solubility is usually expressed as loading (α), mol CO₂ · (mol amine)⁻¹, a unit which is independent of the concentration of the solution. It can also be expressed as capacity, a quantity defined in terms of the amount of solution, either per volume, mol CO₂ · (dm solvent)⁻³ or weight, mol CO₂ · (kg solvent)⁻¹. The capacity gives valuable insight into the amount of solvent, which needs to be circulated in the CO₂ capture plant. A very dilute solution of a given amine can have a high loading, but the capacity of such a solution is low. In this work both quantities are considered, thus the results are presented in term of loading (α), and capacity, mol CO₂ · (kg solvent)⁻¹ (Cap.).

6.3. Phase equilibrium data in literature.

Despite the increasing interest in amino acid salt solutions for CO₂ capture, few phase equilibrium data on these systems are presently available in literature. One of the first works was performed by Hook [1], as part of his study of the relationship between the structure of different amines and their function in CO₂ absorption. The study included CO₂ absorption into a number of different sterically and non-sterically hindered aqueous alkanolamines and amino acid salts (including the potassium salts of glycine, alanine and 2-methyl alanine).

Absorption from atmospheres with various levels of CO₂ was measured in a 2.5 M aqueous solution of each amine at 295 K. It was found, that the amino acids react with comparable CO₂ absorption rate and CO₂ solubility to alkanolamines of a similar class. The study established that, for the amines in general, introduction of steric-hindrance to the amine group (in the form of methyl groups on the α -carbon) results in higher loading, but lower absorption rates. For some of the amino acids salts, but not the alkanolamines, precipitations was encountered, and it was found that methyl group substitution on the α -carbon reduces the level of CO₂ that can be absorbed into an amino acid salt solution prior to precipitation. This was illustrated by comparing the CO₂ absorption in a 100 kPa gas atmosphere of glycine (no α -carbon methyl, no precipitation), alanine (one α -carbon methyl, precipitation at a loading of 0.94) and 2-methyl alanine (two α -carbon methyl groups, precipitation at a loading of 0.32). On the other hand, Hook [1] found that methyl substitution on the amine group (i.e., secondary amine), reduces the chance of precipitation.

Muñoz et al. [2] also examined the structure/function relationship of different amino acid salt solutions in CO₂ capture. Their study included CO₂ absorption into 1 M solutions of the potassium salts of the amino acids: glycine, taurine, proline, threonine, serine, histidine, arginine and ornithine. From absorption experiments performed at 293 K and 100 kPa partial pressure of CO₂, it was found that the amino acid salt solutions have absorption abilities similar to MEA. However, arginine and ornithine, which both have an extra amine group in their

side chain with a strong alkaline character as revealed by the pKa values (12.48 for arginine and 10.53 for ornitine), showed significant improvement in absorption when compared to MEA [2].

Amino acids which have been subjected to more detailed phase equilibrium studies include proline, taurine and glycine.

In a recent work Majchrowicz and Brilman [3] studied the solubility of CO₂ in aqueous solutions of potassium L-prolinate, with various concentrations between 0.5 M and 3 M, at temperatures ranging from 285 K to 323 K and partial pressures up to 70 kPa. The authors report that for a given partial pressure and temperature, increasing the initial L-prolinate concentration from 0.5 M to 3 M results in a reduction of the CO₂ loading by an average of 27 %. On the other hand, increasing the CO₂ partial pressure increases the CO₂ loading; e.g. at 298 K a change of CO₂ partial pressure from 2 kPa to 15 kPa results in an increase of CO₂ loading of approx. 20 % for all the studied concentrations. Precipitation was observed with a 3 M solution at 285 K and CO₂ partial pressures above 6 kPa, with the precipitation leading to a significant increase in the CO₂ absorption by the solution [3].

Kumar et al. [4] examined the CO₂ solubility in aqueous potassium taurate solutions, with concentrations between 0.5 M and 4 M, at 298 K and 313 K and CO₂ partial pressures from 0.1 kPa to 6 kPa. At 298 K, precipitation was observed

at the higher end of the examined CO₂ partial pressure range for a 2 M solution, but for the 3 M and 4 M solutions, the authors observed precipitation even at pressures as low as 0.1 kPa; in all cases, the solid formation markedly increased the CO₂ absorption.

Portugal et al. [5] examined CO₂ absorption in aqueous solutions of potassium glycinate, and potassium threonate. The CO₂ loading of potassium threonate was investigated at 1.0 M and 313 K, whereas the loading of potassium glycinate was studied over a concentration range of 0.1 M to 3.0 M, at temperatures from 293 K to 351 K. Experiments were carried out at CO₂ partial pressures up to 60 kPa. The authors report that the tested amino acid salt solutions show absorption abilities in the same order of magnitude as MEA, but no precipitations was observed in the experiments. The CO₂ loading decreases with increasing potassium glycinate concentration. As CO₂ absorption is exothermic in nature, an increase in temperature should decrease the extent of absorption in accordance with Le Chatelier's principle. Interestingly, Portugal et al. [5] report that there is no significant difference in the loading of potassium glycinate solutions between 293 K and 323 K, but increasing the temperature to 351 K resulted in a considerably decrease in the CO₂ loading .

Song et al. [6] studied CO₂ absorption in aqueous solutions of 10 wt%, 20 wt%, and 30 wt% sodium glycinate at 303 K, 313 K, and 323 K over a CO₂ partial pressure range from 0.1 kPa to 200 kPa. These authors found many of the same

tendencies observed by Majchrowicz and Brilman [3], as well as by Portugal et al. [5]. The study showed a decrease in loading with an increase in amino acid salt concentration. The loading increases, with an increase in CO₂ partial pressure, however no precipitation was reported. Increasing the temperature led to a decrease in loading, but depending on the partial pressure of CO₂ and the initial amino acid salt concentrations the effect of changing the temperature in the range of 303 K to 323 K could be small [6].

Zhao et al. [7] and Zang et al. [8] investigated the absorption of CO₂ in aqueous solutions of sodium glycinate and potassium glycinate respectively. The authors present CO₂ capacities, which they defined as mol CO₂ absorbed per volume of solvent (mol CO₂) · dm⁻³. The authors report an increase in capacity with increase in initial amino acid salt concentration [7,8]. This is expected, as more concentrated solutions have more amino acid salt, and thus will bind more CO₂.

From the above description of phase equilibrium data from literature on CO₂ + amino acid salt + H₂O systems, some trends are observed. Generally, higher partial pressure of CO₂, lower temperature and lower initial concentration of the amino acid salt will lead to higher CO₂ loading. Precipitation happens especially at higher amino acid salt concentrations and higher loadings, the solid formation can increase the absorption by the solution; the conditions at which a system changes from a non-precipitating to a precipitating system vary depending on the particular amino acid salt solution.

6.4. Materials and methods

The data obtained in this work were produced, using the apparatus, described in Chapter 4. With the setup being operated at a partial pressure of CO₂ of 10 kPa and temperatures varying from 298 K to 353 K, it covers the possible conditions of CO₂ absorption from a coal fired power plant [9,10]. The experimental procedure follows the description in Chapter 4, and will not be repeated here. A note should be made concerning the precision of the results, given in Chapter 4 as equal to 2.4 %. In the case of large amounts of precipitation in the experiments with the amino acid salt solutions, a small decrease in precision is expected. The chemicals and the procedures for preparation of the solutions follow Chapter 5 (Section 5.3.1) in the case of the amino acid salts, and Chapter 4 (Section 4.4.2) in the case of MEA.

6.5. Results and discussions

This work concerns the influence on the CO₂ solubility of increasing the amino acid salt concentration between 2 m and 8 m, and increasing the temperature from 298 K to 313 K and then to 323 K. Tables 6.1 to 6.5 present the results obtained in this work with the amino acid salt solutions; each table presents data obtained at 313 K with amino acid salt concentrations of 2 m, 3.5 m, 4.5 m, 6 m, 7 m and 8 m. As the influence of increasing the temperature, was studied at 7 m in the case of the potassium salts of taurine, glycine, L-alanine and L-proline, and 3.5 m in the case of the potassium salt of L-lysine, each table contain additional values obtained at 298 K and 323 K for these concentrations. Table 6.6 presents similar

data obtained with solutions of MEA, with the influence of temperature on the CO₂ solubility being examined at 7 m. Some of the experiments with the CO₂ + MEA + H₂O system were performed as part of the validation study presented in Chapter 4; in Table 6.6 it is indicated when the data are reproduced from Table 4.1. Tables 6.1 to 6.6 list the conditions of each experiment, together with the obtained CO₂ solubility presented as loading (α), and as capacity (Cap.). The loading is given by the total amount of moles CO₂ absorbed divided by the total amount of moles amine examined, while the capacity is calculated from the total amount of moles CO₂ absorbed divided by the weight (kg) of solvent examined. In some of the experiments with the amino acid salts, precipitation occurred, which is indicated by P in the tables.

Table 6.1: Phase equilibrium data of the CO₂ + potassium taurate + H₂O system obtained in this work, with amino acid salt concentrations from 2 m to 8 m, CO₂ partial pressure of 10 kPa and total pressure equal to the atmospheric pressure.

m	p_{Total}	p_{CO_2}	T	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	kPa	kPa	K	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
2.00	100.26	9.6	312.9	0.51	0.77
3.50^P	100.81	9.6	312.8	0.51	1.14
4.50^P	101.46	9.7	312.8	0.54	1.40
6.00^P	100.50	9.6	312.9	0.53	1.61
7.00^P	100.57	9.6	297.5	0.54	1.75
7.00^P	101.53	9.7	312.8	0.54	1.78
6.99^P	102.22	9.8	321.1	0.51	1.66
8.00^P	100.97	9.7	313.1	0.58	2.03

P: Precipitation occurred in the experiment

Table 6.2: Phase equilibrium data of the CO₂ + potassium glycinate + H₂O system obtained in this work, with amino acid salt concentrations from 2 m to 8 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure.

m	p_{Total}	$p\text{CO}_2$	T	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	kPa	kPa	K	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
2.00	102.21	10.1	312.9	0.62	1.02
3.50	101.62	9.7	312.9	0.57	1.43
4.50	100.47	9.6	312.9	0.56	1.67
6.00	99.68	9.4	313.0	0.56	2.02
7.00 ^P	100.57	9.6	297.5	0.71	2.78
7.00 ^P	102.78	9.9	313.0	0.58	2.27
7.00	101.22	9.6	321.8	0.55	2.15
8.00 ^P	101.77	9.8	312.9	0.59	2.46

P: Precipitation occurred in the experiment

Table 6.3: Phase equilibrium data of the CO₂ + potassium L-alaninate + H₂O system obtained in this work, with amino acid salt concentrations from 2 m to 8 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure.

m	p_{Total}	$p\text{CO}_2$	T	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	kPa	kPa	K	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
2.00	99.87	9.5	313.4	0.66	1.04
3.50 ^P	101.48	9.6	311.8	0.63	1.52
4.51 ^P	99.55	9.3	312.5	0.63	1.81
6.01 ^P	100.29	9.4	312.3	0.66	2.25
7.00 ^P	100.96	9.5	298.1	0.75	2.79
7.00 ^P	99.17	9.3	313.0	0.70	2.61
7.00 ^P	99.80	9.4	322.8	0.57	2.13
8.00 ^P	99.73	9.4	311.7	0.80	3.19

P: Precipitation occurred in the experiment

Table 6.4: Phase equilibrium data of the CO₂ + potassium L-prolinate + H₂O system obtained in this work, with amino acid salt concentrations from 2 m to 8 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure.

m	p_{Total}	$p\text{CO}_2$	T	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	kPa	kPa	K	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
2.00	101.25	9.6	312.8	0.67	1.03
3.50	101.19	9.7	312.7	0.63	1.44
4.50	101.44	9.7	312.9	0.62	1.64
6.00 ^P	101.24	9.6	312.9	0.59	1.85
7.05 ^P	100.28	9.5	297.6	0.62	2.12
7.00 ^P	101.17	9.7	312.9	0.63	2.11
7.05	101.09	9.6	322.0	0.57	1.93
8.00 ^P	101.17	9.6	313.0	0.62	2.23

P: Precipitation occurred in the experiment

Table 6.5: Phase equilibrium data of the CO₂ + potassium L-lysinate + H₂O system obtained in this work, with amino acid salt concentrations from 2 m to 8 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure.

m	p_{Total}	$p\text{CO}_2$	T	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	kPa	kPa	K	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
2.00	100.41	9.6	312.9	1.31	1.91
3.50	101.12	9.6	297.3	1.24	2.66
3.50	99.71	9.4	312.4	1.02	2.28
3.50	100.31	9.5	322.6	0.96	2.14
4.50	100.80	9.5	312.2	1.05	2.58
6.00 ^P	100.27	9.5	312.2	1.05	3.01
7.00 ^P	100.10	9.4	310.6	0.98	2.99
7.99 ^P	100.75	9.5	310.1	1.02	3.29

P: Precipitation occurred in the experiment

Table 6.6: Phase equilibrium data of the CO₂ + MEA+ H₂O system obtained in this work, with MEA concentrations from 2 m to 8 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure.

m	p_{Total}	p_{CO_2}	T	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	kPa	kPa	K	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
2.00*	100.37	9.5	313.0	0.56	1.00
3.50	99.32	9.4	312.5	0.55	1.58
4.50	101.17	9.7	313.0	0.53	1.87
6.00	100.67	9.6	312.9	0.53	2.31
7.00*	101.12	9.8	297.6	0.54	2.64
7.00*	102.44	9.8	311.7	0.52	2.51
7.00*	101.82	9.8	321.4	0.50	2.45
8.00	100.81	9.6	312.90	0.52	2.77

*The data are reproduced from Table 4.1.

6.5.1. Comparison to literature data

As mentioned in Section 6.3, the number of phase equilibrium data available in literature regarding CO₂ + amino acid salt + H₂O systems are very limited. Figure 6.1 presents a comparison of the CO₂ solubility values obtained in this work at 313 K with solutions of 2 m and 3.5 m potassium glycinate to data obtained by Portugal et al. [5], at 313 K with 1 M and 3 M potassium glycinate solutions and CO₂ partial pressures up to 60 kPa. In order to properly compare the results; the molar concentrations of Portugal et al. [5] were converted to molality, using the densities determined by Portugal et al. [11] for 1 M and 3 M potassium glycinate solutions at 313 K. It was found that 3 M corresponds to 3.7 m, and 1 M corresponds to 1.1 m. From Figure 6.1, it is seen that the loading obtained in this work for 3.5 m fits well with the data obtained by Portugal et al. [5] at 3.7 m. The

loading obtained in this work at 2 m is well in line with Portugal et al. [5], as it is between the values obtained by the authors at 1.1 m and 3.7 m, hereby agreeing with the decrease in CO₂ loading, with increase in initial amine concentration, which is typical for CO₂ + amine + H₂O system (see Section 6.3) [5]. In conclusion, Figure 6.1 shows that there is good agreement between the presented results from our work and data from literature.

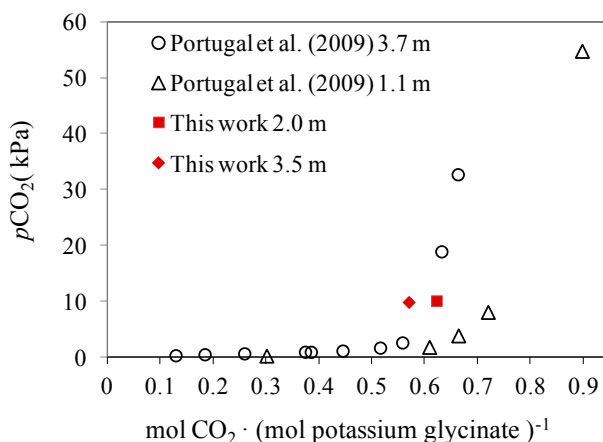


Figure 6.1: Results for the system CO₂ + potassium glycinate + H₂O obtained in this work at 313 K with 2 m and 3.5 m potassium glycinate solutions, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure; compared with data obtained by Portugal et al. [5] for the same system at 313 K, with 1.1 m and 3.7 m potassium glycinate solutions, over a comparable pressure range.

6.5.2. Influence of concentration

The influence of increasing the initial amino acid salt concentration on the CO_2 solubility was examined at 313 K. The concentration was increased as follows: 2 m, 3.5 m, 4.5 m, 6 m, 7 m and 8 m. The results are listed in Tables 6.1 to 6.5. Similar data were obtained with solutions of MEA; these data are listed in Table 6.6. The data of the tables are represented in the Figures 6.2 to 6.4. Figure 6.2 shows the CO_2 loading, as a function of initial amine concentration for the aqueous solutions of MEA and the potassium salts of taurine, glycine, L-alanine and L-proline. Because of the much higher CO_2 solubility in solutions of the potassium salt of L-Lysine, the corresponding representation for this amino acid is given separately in Figure 6.3.

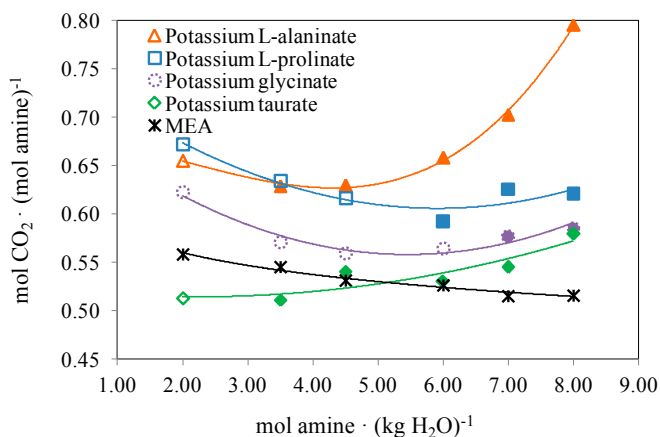


Figure 6.2: Results showing the loading as function of the initial amine concentration for four CO_2 + amino acid salt + H_2O systems and the CO_2 + MEA + H_2O system, obtained in this work around 313 K, with amine concentrations between 2 m and 8 m, 10 kPa CO_2 partial pressure and total pressure equal to the atmospheric pressure. In the case of the systems with the amino acid salts, a filled point means that precipitation occurred in the experiment. The lines in the plot are given for eye guidance.

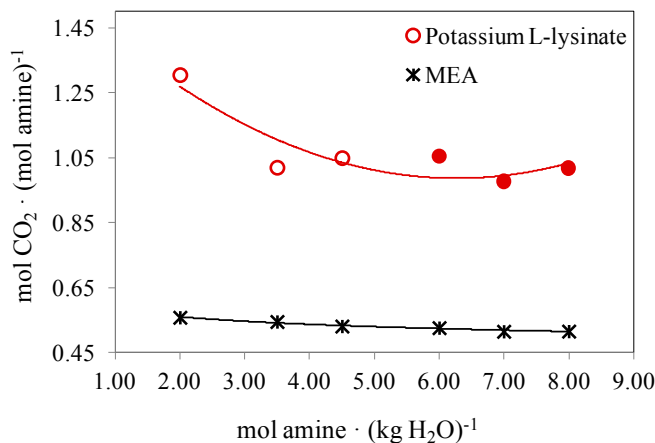


Figure 6.3: Results showing the loading as function of the initial amine concentration for the CO₂ + potassium L-lysinate + H₂O system and the CO₂ + MEA + H₂O system obtained in this work around 313 K, with amine concentrations between 2 m and 8 m, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure. The lines in the plot are given for eye guidance.

From Figures 6.2 and 6.3 it can be seen that the amino acid salt solutions absorb with similar or higher loading, compared to MEA. Interestingly, Figure 6.3 shows that L-lysine exhibits approximately the double loading compared to MEA, this very high loading of L-lysine can be explained mainly by its two active amines groups, one of which has a high base strength, as given by its pK_a value of 10.67 [12]. The high loading of potassium L-lysinate fits well with results of Muñoz et al. [2]. As mentioned in Section 6.3, Muñoz et al. [2] found that the potassium salts of arginine and ornitine, which like lysine both have an extra amine group with strong alkaline character, showed significant improvement in absorption compared to MEA.

The observation of a higher loading for L-alanine compared to taurine, glycine and MEA can also be explained by a structure function relationship. Taurine,

glycine and MEA are all non-sterically hindered amines with the base strength of their amine group being in the same range, as given by the pKa's; taurine: 9.06 glycine: 9.58, and MEA: 9.50. In contrast, L-alanine is a sterically hindered amine, with its amine group having a pKa value of 9.71. [12] As explained in Chapter 3, sterically hindrance makes the formed carbamate prone to hydrolysis, liberating the amine, which can then react with another molecule of CO₂, thereby increasing CO₂ absorption [1].

The amine group of L-proline is part of a ring structure, making the molecule a cyclical amine, as well as a secondary amine. According to da Silva and Svendsen [13], cyclical amines form stable carbamates. The fairly high loading of L-proline, can be assigned to the high base strength of its amine group (pKa = 10.47), which increases the formation of bicarbonate (according to Reaction 3.4 + 3.5 and 3.6) and thus the CO₂ absorption [12].

In conclusion the results obtained follow the trends of literature, and show that CO₂ loading is increased when the solvent molecule have more than one amine group, when the amine group(s) is sterically hindered and/or has high base strength. Interestingly L-lysine with its two active amine groups possesses all of these qualities at the same time.

Figures 6.2 and 6.3 show that the loading of the MEA solutions decrease steadily with increase of the initial amine concentration. As described in Section 6.3, this is a common tendency for CO₂ + amine + H₂O systems [5]. For the tested amino acid salt solutions, the decrease in loading, with increasing initial concentration of the amino acid salt, seems to be counteracted by the effect of precipitation, and for

taurine and L-alanine, the loading even increases above the value found at lower initial concentrations of the amino acid salt. These observations are in agreement with literature [4,14,15], as outlined in Chapter 3.

As seen in Figures 6.2 and 6.3, the concentration boundary for where the system changes from a non-precipitating to a precipitating system deviates between the solutions: The potassium salts of taurine and L-alanine already form precipitation at an initial concentration of 3.5 m, whereas the change to a precipitating system in the case of the potassium salts of L-proline and L-lysine is at 6 m, and for potassium glycinate the solid formation is not observed until an initial concentration of 7 m. Glycine and taurine are both non-sterically hindered amines, thus according to the observations by Hook [1] they would be expected to have a low tendency to precipitate, however it seems that the sulfonic acid group of taurine increases the tendency for precipitation, as it was also observed by Kumar et al. [16] that the potassium salt of this amino acid forms precipitation easily, even at low loadings. [4,16]. The high tendency of L-alanine for precipitation is in agreement with Hook [1], whom observed that sterically hindered amines (like alanine) are prone to precipitation. L-proline has a ring structure giving rise to the secondary amine functionally, which according to Hook [1] reduces the change of precipitation. The precipitation behavior of amino acid like L-lysine, containing two active amine groups, has not previously been addressed in literature.

In order to minimize the energy consumption of the capture plant, it is important to limit the pump power for circulating the solution and the heat requirement in the regeneration step. In order to accomplish this, it is necessary to use somewhat concentrated amine solutions, with a high CO₂ capacity, thus the capacity can be a better measure than the loading for describing the actual effectiveness of a given solvent. Figure 6.4 shows the capacity as a function of initial amine concentration, for the aqueous solutions of MEA and the potassium salts of taurine, glycine, L-alanine, L-proline and L-lysine. The capacity increases with initial amine concentration for all the tested solutions, which is expected, as a solution containing more amine also will absorb more CO₂. Interestingly, Figure 6.4 shows that solutions of potassium L-lysinate exhibit higher capacity compared to MEA in the whole concentration range. As a 7 m solution of MEA is the benchmark solution for which new solvents is to be evaluated, it is interesting to compare the capacities at 7 m; it is seen that MEA has higher capacity, than the solutions of the potassium salts of taurine, glycine and L-proline, whereas potassium L-alaninate exhibits similar capacity and L-lysine exhibits higher capacity than MEA.

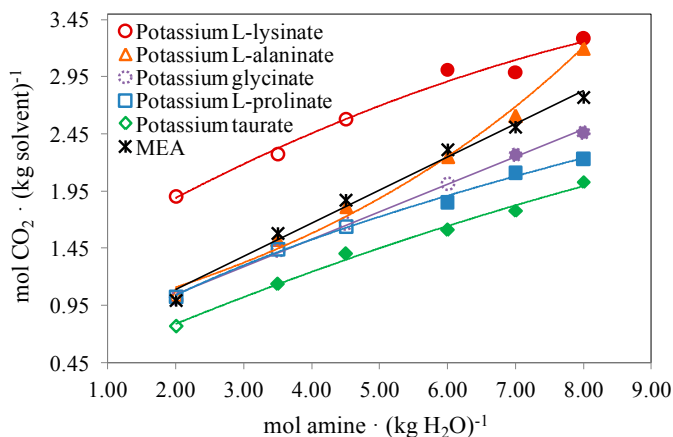


Figure 6.4: Results showing the capacity as function of the initial amine concentration, for five systems CO_2 + amino acid salt + H_2O and the system CO_2 + MEA + H_2O obtained in this work around 313 K, with amine concentrations between 2 m and 8 m, 10 kPa CO_2 partial pressure and total pressure equal to the atmospheric pressure. In the case of the systems with the amino acid salts, a filled point means that precipitation occurred in the experiment. The lines in the plot are given for eye guidance.

The capacity of a solvent molecule is affected by the relation of its active amine groups to its molecular weight. Meaning, large molecules with high molecular weight will lower the capacity, whereas more than one active amine group will increase the capacity. The molecular weights of the examined amines increase as follows: MEA < glycine < L-alanine < L-proline < taurine < L-lysine. Interestingly, potassium L-lysinate solutions having concentrations of 3.5 m to 4.5 m exhibit capacities in similar range to that of 7 m MEA, and at the experimental conditions used in this work, there are no precipitations in these solutions; this opens up for the possibility of using potassium L-lysinate in a non-precipitation CO_2 capture process, exhibiting the same capacity as 7 m MEA.

6.5.3. Influence of temperature

The influence of increasing the temperature on the CO₂ solubility was examined in 7 m solutions of the potassium salts of taurine, glycine, L-alanine, L-proline and 3.5 m solutions of the potassium salt of L-lysine. Experiments were performed at 298 K, 313 K and 323 K. The phase equilibrium results of the experiments are listed in Tables 6.1 to 6.5. Similar data were obtained with 7 m solutions of MEA; these data are given in Table 6.6. The data of the tables are represented in the Figures 6.5 to 6.7. Figure 6.5 shows the CO₂ loading, as a function of temperature for solutions of the potassium salts of taurine, glycine, L-alanine and L-proline compared with MEA. Because of the much higher CO₂ solubility in solutions of the potassium salt of L-Lysine, the corresponding representation for this amino acid is given separately in Figure 6.6.

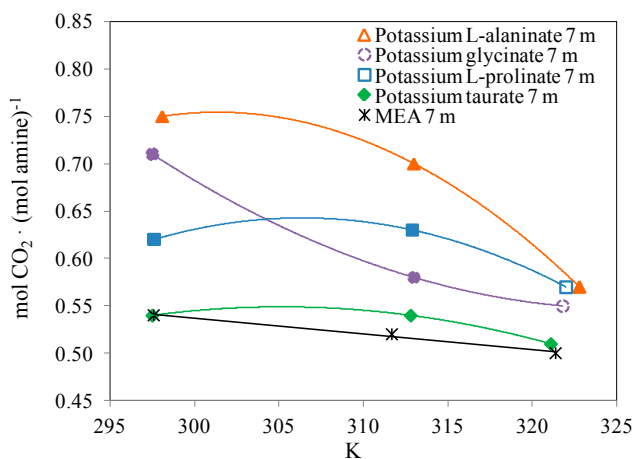


Figure 6.5: Results showing the loading as function of temperature for four CO₂ + amino acid salt + H₂O systems and the CO₂ + MEA + H₂O system obtained in this work around 298 K, 313 K, and 353 K with 7 m solutions of the amines, 10 kPa CO₂ partial pressure and total pressure equal to the atmospheric pressure. In the case of the systems with the amino acid salts, a filled point means that precipitation occurred in the experiment. The lines in the plot are given for eye guidance.

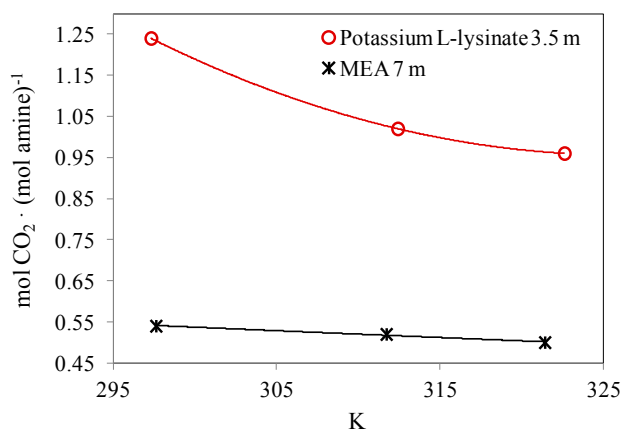


Figure 6.6: Results showing the loading as function of temperature for the system $\text{CO}_2 + \text{potassium L-lysinate} + \text{H}_2\text{O}$ and the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work around 298 K, 313 K and 323 K, with concentrations of 3.5 m potassium L-lysinate and 7 m MEA, 10 kPa CO_2 partial pressure and total pressure equal to the atmospheric pressure. The lines in the plot are given for eye guidance.

Figure 6.7 presents the capacity, as a function of temperature, including data of the five amino acid salts, as well as MEA.

The decrease in CO_2 solubility is most significant for the potassium salt of glycine, L-alanine and L-lysine, which decrease around 20 % in CO_2 loading as well as capacity, over the temperature interval from 298 K to 323 K. For the solutions of potassium taurate, and L-proline the decrease in CO_2 solubility is in the same range as for MEA, which decreases about 7 % over the studied temperature interval. The larger the decrease in solubility with increased temperature the better, as it promises lower energy consumption for the regeneration step. For the solutions of L-proline and glycinate the system changes from a precipitating to a non-precipitating system, by increasing the temperature from 313 K to 323 K. Data at higher temperatures will be very

important to know which temperatures are needed in order to obtain efficient desorption of the CO_2 ; this issue is addressed in Chapter 7 for solutions of the potassium salts of L-lysine and L-proline.

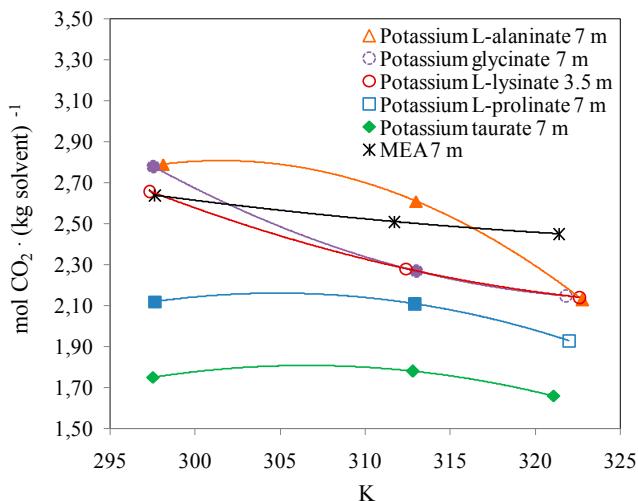


Figure 6.7: Results showing the capacity as function of temperature for five CO_2 + amino acid salt + H_2O systems and the system CO_2 + MEA + H_2O obtained in this work around 298 K, 313 K, and 353 K with 7 m solutions of the amines, except for potassium L-lysinate which was examined at 3.5 m. The experiments were performed at 10 kPa CO_2 partial pressure and total pressure equal to the atmospheric pressure. In the case of the systems with the amino acid salts, a filled point means that precipitation occurred in the experiment. The lines in the plot are given for eye guidance.

6.6. Conclusions

In this work the solubility of CO_2 , in aqueous solutions of MEA and the potassium salts of five amino acids; taurine, glycine, L-alanine, L-proline and L-lysine, was examined. Experiments were carried out with amine concentrations between 2 m and 8 m, temperatures ranging from 298 K to 323 K, 10 kPa CO_2 partial pressure and a total pressure equal to the atmospheric pressure. The

obtained data provide a unique insight into the phase equilibrium behaviour of the selected CO_2 + amino acid salt + H_2O systems, compared to the corresponding system with MEA. This information is necessary for understanding the operation conditions of these potential new solvents in the chemical absorption of CO_2 from flue gas. The results of this work show, that all the tested amino acid salt have the potential for use in CO_2 capture. However, the potassium salt of L-lysine distinguishes itself, by having much higher loadings than MEA. Interestingly, it was found that 3.5 m and 4.5 m solutions of the potassium salt of L-lysine exhibit capacities, in the same range as 7 m MEA with no precipitation occurring, as a result of the CO_2 absorption. For the other tested amino acids salt solutions a similar high capacity involves a precipitating system. This result opens up for the possibility of using the potassium salt of L-lysine in a non precipitating CO_2 capture system. The CO_2 solubility decreased as a result of increasing the temperature from 298 to 323 K, in the case of solutions of MEA and the amino acid salts. Interestingly, a 3.5 m solution of potassium L-lysinate was among the amino acid salts solutions that showed pronounced decrease in CO_2 solubility with increased temperature compared to MEA; this indicates a high temperature dependence of the equilibrium constants involved in CO_2 absorption, promising low energy requirements for the regeneration process using a solution of this amino acid salt as the solvent.

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Chapter 7

CO₂ solubility studies using a synthetic method

7.1. Abstract

This chapter describes a study of CO₂ solubility in aqueous solutions of the potassium salts of L-lysine and L-proline with concentrations of 3.5 m and 7 m respectively. Using an experimental setup based on a synthetic method experiments were performed at CO₂ partial pressures up to around 760 kPa, and temperatures around 313 K, 333 K and 353 K. CO₂ solubility in 7 m solutions of MEA were examined at CO₂ partial pressures up to about 2.3 MPa and temperatures around 313 K, 333 K and 353 K .

7.2. Introduction

Before starting the experiments with the amino acids salt solutions, the experimental setup was validated with solutions of 7 m MEA. In addition to validation of the set-up, the obtained data are used for comparing to the results with the amino acid salt solutions.

A 3.5 m solution of potassium L-lysinate was selected for the present study, based on our results presented in Chapter 6, where it was found that a 3.5 m solution of the potassium salt of L-lysine, offers similar capacity to 7 m MEA, without the occurrence of precipitation. A 7 m solution of potassium L-prolinate was selected for the present study, based on the fact that this amino acid has been found to react fast with CO₂ (faster than MEA) [1-3]. As mentioned in Chapter 2, a high reaction kinetic is desirable, as it allows for limiting the height of the absorber column. The concentrations of the solutions were selected based on the same reasoning, as given in Chapter 5, Section 5.4. As L-proline has one amine group and L-lysine has two amine groups, the studied solutions have the same number of amine groups per kg of water, as a 7 m solution of MEA, forming ground for a direct comparison between the amines.

CO₂ solubility experiments were performed at temperatures spanning from absorber conditions to 353 K (80 °C). Complete desorption usually needs temperatures around 393 K (120 °C), but due to equipment limitations, the maximum operating temperature in our experiments was 353 K.

This study also addresses the issue of degradability of the amino acid salt solutions at CO₂ capture conditions, by measuring their ability to absorb CO₂ after

repeated heating; these measurements involved longer experiments, with temperature cycles between 313 K and 353 K.

7.3. Materials and methods

7.3.1. Chemicals and preparation of solutions

The chemicals and the procedure for preparation of the solutions follow Chapter 5 (Section 5.3.1) in the case of the amino acid salts, and Chapter 4 (Section 4.4.2) in the case of MEA. Although in this case L-proline was acquired from Merck, having a mass fraction superior to 0.99 and milli Q water was used instead of the deionised water. The CO₂ gas with a purity of 99.995 mol % was obtained from AGA, Denmark.

7.3.2. Experimental setup

According to Fonseca et al. [4], there are two fundamental different classes of phase equilibrium methods, analytical and synthetic, referring to the way the equilibrium composition is determined. The apparatus used in the present work, is based on a synthetic method. A synthetic method involves indirect determination of the composition of the phases at equilibrium, by measuring phase volumes and densities, and subsequently using these properties in calculations of material balances. The experimental setup used in the present work is presented in Figures 7.1 and 7.2. The apparatus was developed by Fonseca [5], where a detailed description is found. Here a brief description of the apparatus and its operational procedure is given.

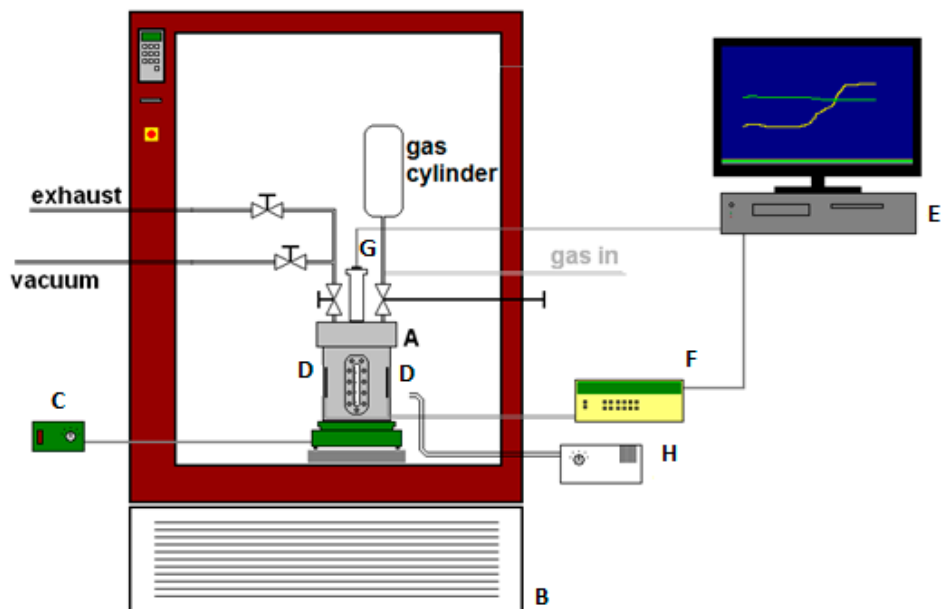


Figure 7.1: Schematic representation of the experimental setup for the measurement of phase equilibria at high pressures. **A:** High pressure cell with two parallel sapphire windows. **B:** Temperature chamber. **C:** Remote control for the magnetic stirrer **D:** Platinum resistance thermometers Pt100. **E:** Computer. **F:** Data logger. **G:** Temperature compensated high precision pressure sensors **H:** Cold light source with optical fiber. The figure is reproduced (with small changes) from the thesis by Fonseca [5].



Photo: Christian Ove Carlsson

Figure 7.2: Image of the high-pressure equilibrium cell together with the gas cylinder, pressure sensors and other parts, inside the temperature chamber.

A few adjustments were made to the apparatus of Fonseca [5] before starting this work. The experimental setup was originally suitable for measurements at temperatures ranging from 233 K to 353 K, and at pressures up to 20 MPa, using a pressure transducer; Keller 33X (KELLER AG für Druckmesstechnik, Switzerland), with an accuracy of 20 kPa. As our measurements concentrate on studying CO₂ absorption at moderate pressures, an additional transducer, EJX310A (Yokogawa, Japan) absolute pressure transducer was installed, having a

range of 300 kPa with an accuracy of ± 0.1 kPa. Due to technical problems during the experimental trials, the pressure transducer from KELLER was exchanged with a 26.600 G, pressure transducer (BD sensors, Germany), having a range of 4000 kPa, with an accuracy of ± 20 kPa.

Another adjustment is the way the liquid volume in the cell is measured; the apparatus developed by Fonseca [5] used a camera inside the temperature chamber connected to a monitor outside the chamber. The camera was facing the window of the cell, which had a scale for the reading of the liquid volume via the monitor. We changed this procedure, and have instead used a cathetometer (Precision Tools & Instruments Co. LTD., Surrey, England), shown in Figure 7.3.



Photo: Christian Ove Carlsson

Figure 7.3: Image of the cathetometer used to determine the liquid volume inside the equilibrium cell.

Essentially a cathetometer consists of a telescope, which can slide up and down a vertical rigid column with an attached vernier scale. In measuring the liquid volume, the vertical distance between the bottom of the window of the cell and the top of the liquid level is found, by first adjusting the crosshair in the eyepiece of the telescope to coincide with the bottom of the window, and then note the position of the telescope, using the vernier scale. The cross hair is then brought to coincide with the top liquid level and the new position of the telescope is noted. The difference in cm between these readings corresponds to a certain volume (cm^3) of liquid, according to a correlation found by a previous calibration with water. This calibration of the readings of the cathetometer was performed by transferring a known weight of pure water at the temperature of 298 K to the cell. The cathetometer was then used to measure the vertical distance between the bottom of the window of the cell and the top of the water level. By repeating this procedure for different amounts of water, and knowing the density of water at 298 K and atmospheric pressure, a correlation between the distance reading of the cathetometer (cm) and the volume (cm^3) was obtained. The results are presented in the plot of Figure 7.4. The linearity of the graph is a consequence of the cylinder shaped cell.

For the phase equilibrium experiments, the volume of the liquid phase at equilibrium can then be calculated from the distance readings of the cathetometer through Equation 7.1:

$$V / \text{cm}^3 = 50.193 \cdot (\text{cm}) + 19.24 \quad (7.1)$$

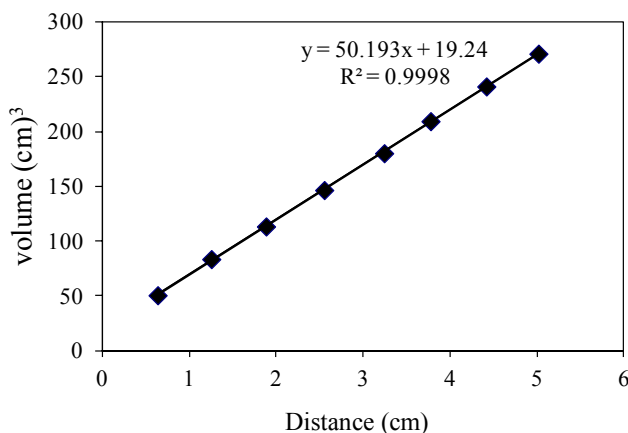


Figure 7.4: Results obtained during the calibration of the readings of the cathetometer.

Another calibration which has to be performed before starting the experiments is the total volume of the system (cell + gas cylinder). This calibration was performed without a condensed phase in the cell. The gas cylinder was charged with a precisely known amount of nitrogen gas (special calibration grate), and subsequently connected to cell. With the valve between the gas cylinder and the cell closed, the cell was evacuated; where after the same valve was opened, allowing the gas from the cylinder to fill the system. Once the temperature and pressure was stable, the volume of the system was calculated using the density of the gas at the equilibrium pressure and temperature, obtained through the NIST standard reference data base [6]. By repeating this procedure for different pressures (different amounts of nitrogen gas), it resulted in a value of $742 \pm 1 \text{ cm}^3$ for the total volume of the cell and the gas cylinder.

7.3.3. Principle of experimental procedure

The central part of the apparatus (Figure 7.1) is the high pressure stainless steel equilibrium cell (A), equipped with two parallel sapphire windows, placed inside a temperature chamber (B). The temperature stability of the cell is ± 0.01 K. The experimental procedure starts by setting the temperature chamber (B) to 313 K (40°C). Then a known amount of solvent is placed in the cell via a syringe; an empty and dry syringe is filled with solution and weighed, using an analytical balance with a precision of 0.001 g, the solution is then transferred to the cell, and the syringe, now containing small amounts of remaining solution, is weighed again, using the same analytical balance, for the exact determination of the weight of solution placed in the cell. The amount of solution transferred to the cell is checked, by leaving the system at 313 K, then using the cathetometer (Figure 7.3) to read the liquid volume; the reading of the cathetometer is then compared to the volume inferred from the grams of solution placed in the cell and the density of the solution measured at 313 K (using a densitometer, Anton Paar, DMA 4100). It was found that the difference in volumes obtained by the two methods is negligible (± 0.5 %). After introducing the solution to the cell, the gas cylinder is filled with a known amount of CO₂; the cylinder is first evacuated and then weighed, using the analytical balance mentioned before with a precision of 0.001 g. It is then charged with CO₂ and weighed once more with the same balance, for the exact determination of the mass of gas inside. The cylinder is then attached to the cell, and with the valve between the cell and cylinder closed, controlled vacuum is applied to the cell in order to evacuate dissolved gases from the

solution and the cell prior to the experiment. With the temperature chamber still at 313 K, the experiment is started by opening the valve between the gas cylinder and the cell, thereby letting the CO₂ in contact with the solution. Mixing of the gas with liquid is obtained by magnetic stirring of the liquid phase (C). The temperature is measured in opposite sides of the cell, by means of platinum resistance thermometers (D) placed inside the walls of the cell. The two temperature compensated pressure sensors (G) mentioned previously and the thermometers are connected to a computer (E) through a data logger (F), for monitoring and recording of the pressure and temperature inside the cell throughout the experiment. The data are recorded by the computer at 30 sec intervals. The system has reached equilibrium when the pressure and temperature has stabilized. At equilibrium the cell is illuminated, using the cold light source (H), and the liquid phase volume¹ is measured, using the cathetometer. The volume of the liquid phase is used to infer the volume of the gas phase, knowing the total volume of the system (cell + gas cylinder) previously calibrated. The partial pressure of CO₂ at equilibrium is obtained by subtraction the vapor pressure of the solution from the measured equilibrium pressure. By assuming ideality, the amount of CO₂ in the gas phase at equilibrium is obtained through the gas density values, collected from NIST standard reference database [6] at equilibrium conditions of CO₂ partial pressure and temperature. Knowing the amount of CO₂ charged into the cylinder, the amount of CO₂ absorbed by the solution at 313 K is obtained. After measuring phase equilibrium data at 313 K,

¹In some of the experiments with the amino acid salt solutions precipitation occurred. In these cases the liquid + solid volume was determined.

the chamber is set first to 333 K and then to 353 K, obtaining phase equilibrium data at these temperatures. Afterwards, a new round of experiments are performed, with a different amount of CO₂ transferred to the cylinder; this way, the obtained phase equilibrium data form isotherms. The vapor pressures used in the above described calculation were measured for the two amino acid salt solutions and the MEA solution at 313 K, 333 K, and 353 K, using the same set up and procedure, but without adding any CO₂.

7.4. Results and discussions

The results obtained in this work are given in Tables 7.1 to 7.5. In some of the experiments with the amino acid salts, precipitation occurred, which is indicated by P in the tables. The CO₂ solubility is presented as both loading (α), mol CO₂ · (mol amine)⁻¹ and capacity (Cap.), mol CO₂ · (kg solvent)⁻¹. Table 7.1 concerns data obtained with solutions of MEA at concentrations around 7 m, temperatures around 313 K, 333 K and 353 K, and CO₂ partial pressures up to about 2.3 MPa. Tables 7.2 and 7.3 respectively present data obtained with solutions of the potassium salt of L-proline and L-lysine, at temperatures around 313 K, 333 K and 353 K, and CO₂ partial pressures up to 760 kPa; the potassium salt of L-proline was studied at concentrations around 7 m, whereas the potassium salt of L-lysine was studied at concentrations around 3.5 m. Table 7.4 and 7.5 presents data of the experiments concerning the temperature cycles between 313 K and 353 K for a solution of the potassium salt of L-proline at 7.00 m (Table 7.4) and a solution of the potassium salt of L-lysine at 3.52 m (Table 7.5)

Table 7.1: Phase equilibrium data of the system CO₂ + MEA + H₂O, obtained in this work at temperatures around 313 K, 333 K and 353 K, with a MEA concentration of 7 m.

m	<i>T</i>	<i>p</i> CO ₂	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	K	kPa · 10 ³	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
7.00	314.28	0.0399	0.57	2.81
7.00	314.59	0.193	0.64	2.86
7.00	314.45	0.476	0.72	3.54
7.00	314.26	1.834	0.86	4.21
7.00	333.52	0.0708	0.55	2.72
7.00	333.52	0.268	0.61	2.98
7.00	333.37	0.587	0.68	3.34
7.00	333.09	2.094	0.78	3.84
7.00	352.51	0.1132	0.53	2.61
7.00	352.41	0.333	0.58	2.86
7.00	352.60	0.701	0.64	3.15
7.00	352.26	2.323	0.74	3.63

Accuracy of the pressure measurements are ± 0.1 kPa up to 300 kPa and ± 20 kPa above 300 kPa.

Table 7.2: Phase equilibrium data of the system CO₂ + potassium L-prolinate + H₂O, obtained in this work at temperatures around 313 K, 333 K and 353 K, with a potassium L-prolinate concentration around 7 m.

m	<i>T</i>	<i>p</i> CO ₂	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	K	kPa · 10 ³	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
7.00	314.47	0.0004	0.46	1.57
7.00 ^P	314.77	0.0204	0.67	2.28
7.00 ^P	314.48	0.0666	0.80	2.72
7.03 ^P	314.69	0.540	0.93	3.16
7.00	333.57	0.0006	0.46	1.57
7.00	333.72	0.0625	0.64	2.18
7.00 ^P	333.66	0.1473	0.75	2.54
7.03 ^P	333.70	0.616	0.91	3.08
7.00	352.65	0.0025	0.46	1.56
7.00	352.73	0.0929	0.63	2.12
7.00	352.82	0.2404	0.69	2.35
7.03 ^P	352.59	0.759	0.84	2.863

Accuracy of the pressure measurements are ± 0.1 kPa up to 300 kPa and ± 20 kPa above 300 kPa. P: Precipitation occurred in the experiment.

Table 7.3: Phase equilibrium data of the system CO₂ + potassium L-lysinate + H₂O obtained in this work at temperatures around 313 K, 333 K and 353 K, with a potassium L-lysinate concentration around 3.5 m.

m	<i>T</i>	<i>p</i> CO ₂	α	Cap.
mol amine · (kg H ₂ O) ⁻¹	K	kPa · 10 ³	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
3.52	314.59	0.0503	1.29	2.75
3.50	313.98	0.1909	1.49	3.16
3.50	314.84	0.363	1.61	3.42
3.50 ^P	314.50	0.566	1.69	3.59
3.52	333.54	0.0857	1.25	2.67
3.50	333.39	0.2532	1.40	2.98
3.50	333.55	0.440	1.52	3.23
3.50	333.84	0.674	1.57	3.34
3.52	352.56	0.1345	1.20	2.57
3.50	352.33	0.2891	1.37	2.91
3.50	352.95	0.513	1.45	3.08
3.50	352.56	0.752	1.51	3.22

Accuracy of the pressure measurements are ± 0.1 kPa up to 300 kPa and ± 20 kPa above 300 kPa. P: Precipitation occurred in the experiment

Table 7.4: Phase equilibrium data of the system CO₂ + potassium L-prolinate + H₂O, obtained in this work at temperature cycles between 313 K and 353 K, with a potassium L-prolinate concentration of 7.00 m.

Temperature Cycles	<i>T</i>	<i>p</i> CO ₂	α	Cap.
	K	kPa · 10 ³	mol CO ₂ · (mol amine) ⁻¹	mol CO ₂ · (kg solvent) ⁻¹
Cycle 1	314.76	0.0004	0.46	1.57
	333.57	0.0006	0.46	1.57
	352.65	0.0025	0.46	1.56
Cycle 2	314.47	0.0004	0.46	1.57
	333.98	0.0010	0.46	1.57
	352.90	0.0028	0.46	1.56
Cycle 3	314.58	0.0004	0.46	1.57
	333.49	0.0005	0.46	1.57
	352.87	0.0031	0.46	1.56
Cycle 4	314.74	0.0006	0.46	1.57
	333.50	0.0007	0.46	1.57
	352.50	0.0029	0.46	1.56

Accuracy of the pressure measurements are ± 0.1 kPa.

Table 7.5: Phase equilibrium data of the system CO₂ + potassium L-lysinate + H₂O, obtained in this work at temperature cycles between 313 K and 353 K, with a potassium L-lysinate concentration of 3.52 m.

Temperature Cycles	T K	$p\text{CO}_2$ kPa·10 ³	α mol CO ₂ · (mol amine) ⁻¹	Cap. mol CO ₂ · (kg solvent) ⁻¹
Cycle 1	314.59	0.0503	1.29	2.75
	333.54	0.0857	1.25	2.67
	352.56	0.1345	1.20	2.57
Cycle 2	315.02	0.0489	1.29	2.75
	333.34	0.0836	1.25	2.67
	352.74	0.1349	1.20	2.56
Cycle 3	314.38	0.0471	1.29	2.76
	333.61	0.0832	1.25	2.68
	352.55	0.1329	1.20	2.57
Cycle4	314.39	0.0463	1.29	2.76
	333.41	0.0819	1.25	2.68
	352.55	0.1322	1.20	2.57

Accuracy of the pressure measurements are ± 0.1 kPa.

7.4.1. Validation of the experimental setup

Before starting the experiments with the amino acid salt solutions the experimental setup was validated by studying phase equilibria of the CO₂ + MEA + H₂O system, with solutions of 7 m MEA, around 313 K, 333 K and 353 K and pressures up to about 2.3 MPa. The results of the validation study are given in Table 7.1. Figures 7.5 to 7.7 present the data of the table, compared with data of Shen and Li [7], Lee et al. [8,9], and Jou et al. [10]. The figures present the partial pressure of CO₂ as a function of loading.

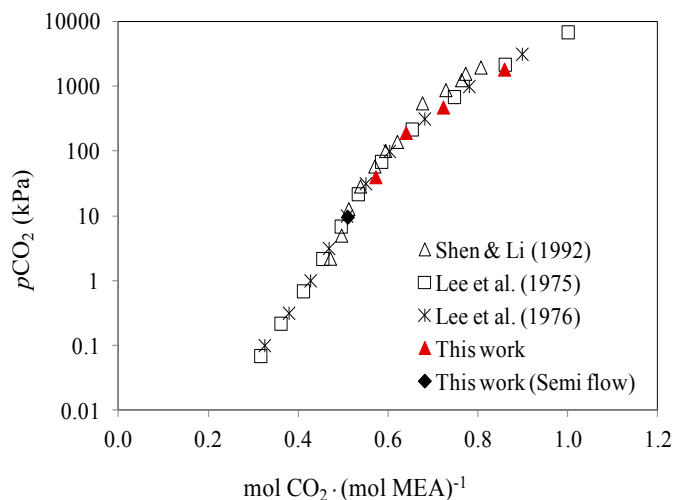


Figure 7.5: Results of the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work with 7 m MEA at 313 K, compared with data from literature [7-9] at the same MEA concentration and temperature over a comparable pressure range. Shown is also the value obtained in this work with the semi-flow method for the same system.

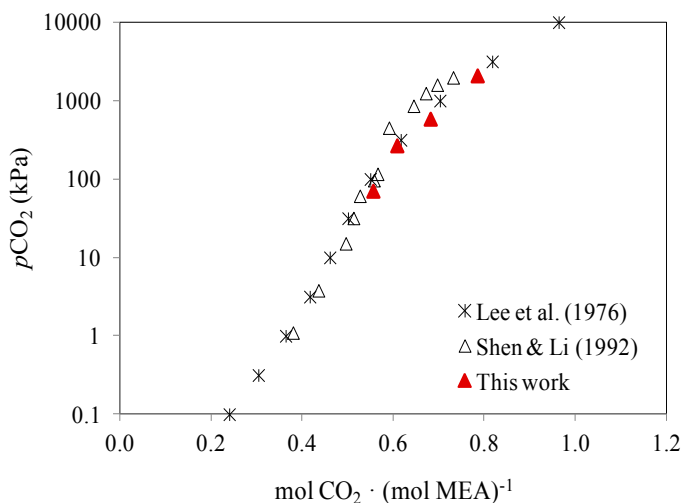


Figure 7.6: Results of the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work with 7 m MEA at 333 K, compared with data from literature [7,8] at the same MEA concentration and temperature over a comparable pressure range.

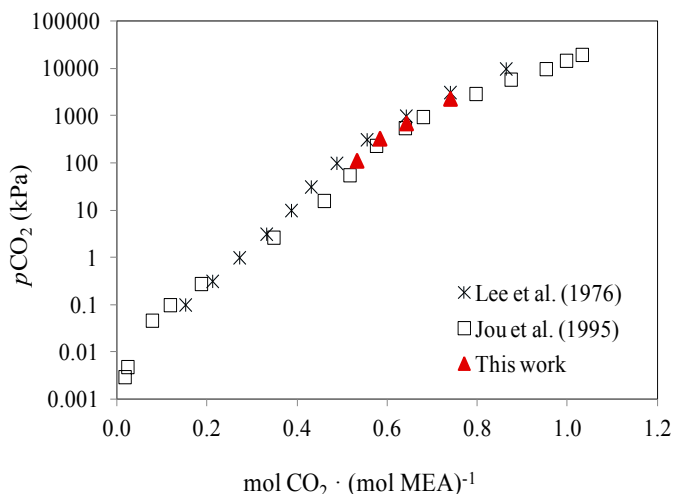


Figure 7.7: Results of the system CO₂ + MEA + H₂O obtained in this work with 7 m MEA at 353 K, compared with data from literature [8,10] at the same MEA concentration and temperature over a comparable pressure range.

As seen in Figures 7.5 to 7.7, there is very good agreement between data obtained in this work for the CO₂ + MEA + H₂O system and literature data of the same system. This confirms the validity of the apparatus, and its ability for the attainment of high quality data. Data for the CO₂ + MEA + H₂O system obtained in this work using the semi-flow method (Chapter 4) are in very good agreement with data of the same system, obtained with the synthetic method (Figure 7.5); further strengthening the quality of the two experimental setups, and their ability to complement each other.

7.4.2. Phase equilibrium data (Loading)

After its validation, the experimental setup was used to study phase equilibria of the two systems, $\text{CO}_2 + \text{potassium L-proline} + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{potassium L-lysinate} + \text{H}_2\text{O}$, at amino acid salt concentrations of 7 m and 3.5 m respectively. The experiments were performed at 313 K, 333 K and 353 K, and pressures up to about 760 kPa. As pointed out in previous chapters, there exists no literature data on CO_2 absorption using potassium L-lysinate, and for potassium L-proline there are only few literature sources available, none of which are focusing on the concentration, temperature and pressure range of this study.

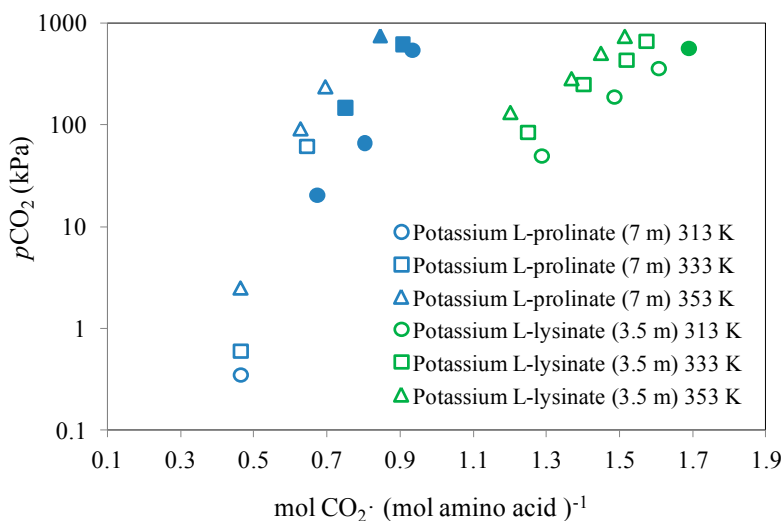


Figure 7.8: Results of the systems $\text{CO}_2 + \text{potassium L-proline} + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{potassium L-lysinate} + \text{H}_2\text{O}$ obtained in this work at 313 K, 333 K and 353 K. Concentrations are 7 m for potassium L-proline, and 3.5 m for potassium L-lysinate. A filled point means precipitation occurred in the experiment.

Figure 7.8 is a graphic representation of the data given in Tables 7.2 and 7.3, presenting the partial pressure of CO₂ as a function of the loading. Figure 7.8 shows that at a given CO₂ partial pressure and temperature, a 3.5 m solution of the potassium salt of L-lysine has higher loading than a 7 m solution of the potassium salt of L-proline. For both solutions, the loading increases with lower temperature, and higher CO₂ partial pressure. The observed effect of temperature and CO₂ partial pressure on the CO₂ solubility follows the trends reported in literature for CO₂ + amino acid salt + H₂O systems, described in Chapter 6 (Section 6.3). Figure 7.8 shows the difference in precipitation tendencies between the two amino acid salt solutions. In agreement with our findings given in Chapter 6, a 7 m solution of potassium L-prolinate has a higher tendency for precipitation than a 3.5 m solution of potassium L-lysinate. It is seen that the tendency for precipitation increases at lower temperature and higher CO₂ partial pressure; these observations are also in agreement with observations by other authors, as described in Chapter 6 (Section 6.3).

Figures 7.9 to 7.11 inspect the data of Tables 7.2 and 7.3 in more detail and present the partial pressure of CO₂ as a function of loading, at 313 K, 333 K and 353 K individually. In order to compare the results to a known reference system, the figures include the data for the CO₂ + MEA + H₂O system given in Figures 7.5 to 7.7.

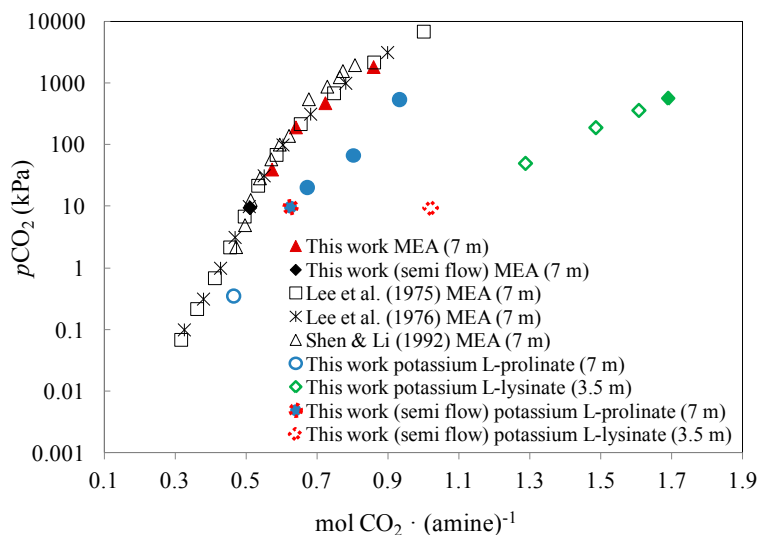


Figure 7.9: Results of the systems $\text{CO}_2 + \text{potassium L-proline} + \text{H}_2\text{O}$, $\text{CO}_2 + \text{potassium L-lysinate} + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work at 313 K. Concentrations are 7 m for MEA and potassium L-proline, and 3.5 m for potassium L-lysinate. Values for the same systems, obtained in this work using the semi-flow method are also presented. For systems with amino acid salts, a filled point means precipitation occurred in the experiment. For the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$, the obtained data are compared with literature data [7-9].

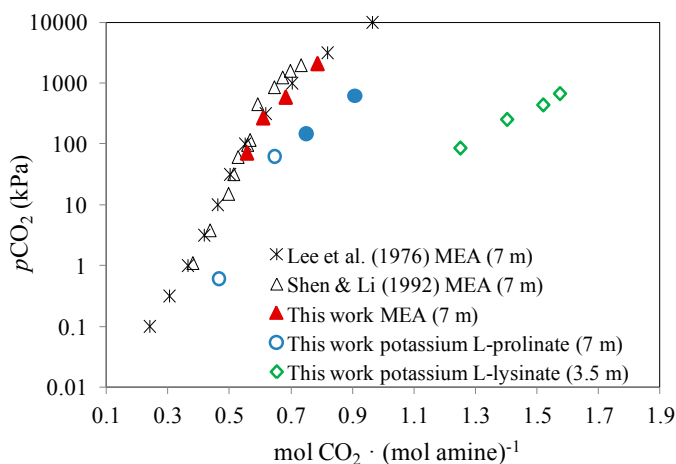


Figure 7.10: Results of the systems $\text{CO}_2 + \text{potassium L-proline} + \text{H}_2\text{O}$, $\text{CO}_2 + \text{potassium L-lysinate} + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work at 333 K. Concentrations are 7 m for MEA and potassium L-proline and 3.5 m for potassium L-lysinate. For systems with amino acid salts, a filled point means precipitation occurred in the experiment. For the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$, the obtained data are compared with literature data [7,8].

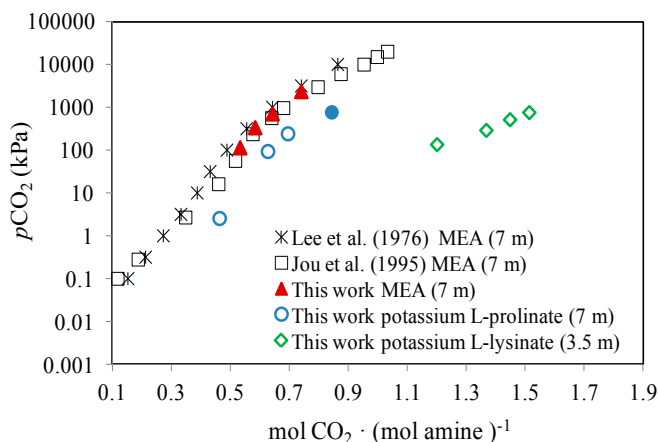


Figure 7.11: Results of the systems CO_2 + potassium L-prolinate + H_2O , CO_2 + potassium L-lysinate + H_2O and CO_2 + MEA + H_2O obtained in this work at 353 K. Concentrations are 7 m for MEA and potassium L-prolinate, and 3.5 m for potassium L-lysinate. For systems with amino acid salts, a filled point means precipitation occurred in the experiment. For the system CO_2 + MEA + H_2O , the obtained data are compared with literature data [8,10].

Figure 7.9 includes values for the three systems, obtained using the semi-flow method (Tables 6.4, 6.5 and 6.6); it is seen that there is good agreement between data obtained with the synthetic method and the semi-flow method. Figure 7.9 shows that for a given partial pressure of CO_2 , a 7 m solution of potassium L-prolinate and a 3.5 m solution of potassium L-lysinate have higher loading, than a 7 m solution of MEA, with the solution of potassium L-lysinate having approximately double loading of MEA; this is in agreement with the results obtained in this work with the semi-flow method, presented in Chapter 6 (Figures 6.2 and 6.3). The same tendency is observed at 333 K (Figure 7.10) and 353 K (Figure 7.11).

7.4.3. Phase equilibrium data (Capacity)

As mentioned in Chapter 6; expressing the CO₂ solubility as capacity provides valuable insight into the amount of solvent, which actually needs to be circulated in the capture system.

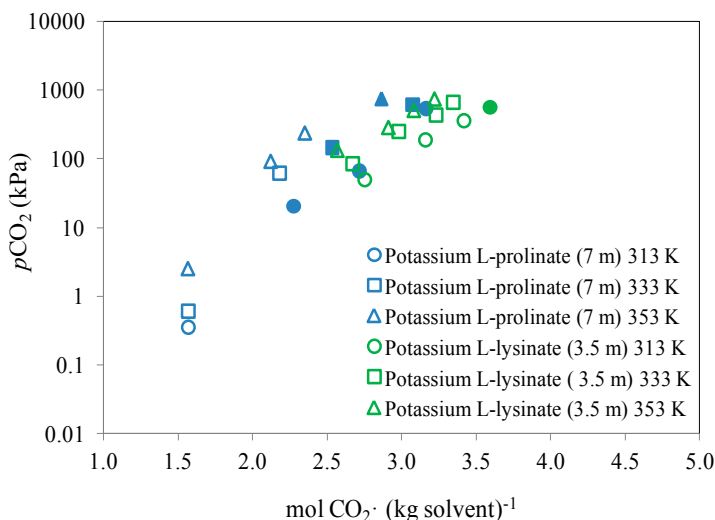


Figure 7.12: Results showing the partial pressure of CO₂ as function of capacity for the systems CO₂ + potassium L-prolinate + H₂O and CO₂ + potassium L-lysinate + H₂O obtained in this work at 313 K, 333 K and 353 K. Concentrations are 7 m for potassium L-prolinate, and 3.5 m for potassium L-lysinate. A filled point means precipitation occurred in the experiment.

Figure 7.12 is a graphic representation of the data given in Tables 7.2 and 7.3, presenting the partial pressure of CO₂, as a function of capacity. Figure 7.12 shows that at a given partial pressure of CO₂ a 3.5 m solution of potassium L-lysinate has higher capacity than a 7 m solution of potassium L-prolinate, and for both amino acid salt solutions, the capacity decrease with increasing temperature.

Figures 7.13 to 7.15 inspect the data of Tables 7.2 to 7.3 in more detail and present the partial pressure of CO_2 as a function of capacity, at 313 K, 333 K and 353 K individually. In order to compare with a known reference system, the figures include data for the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$, obtained in this work (Table 7.1).

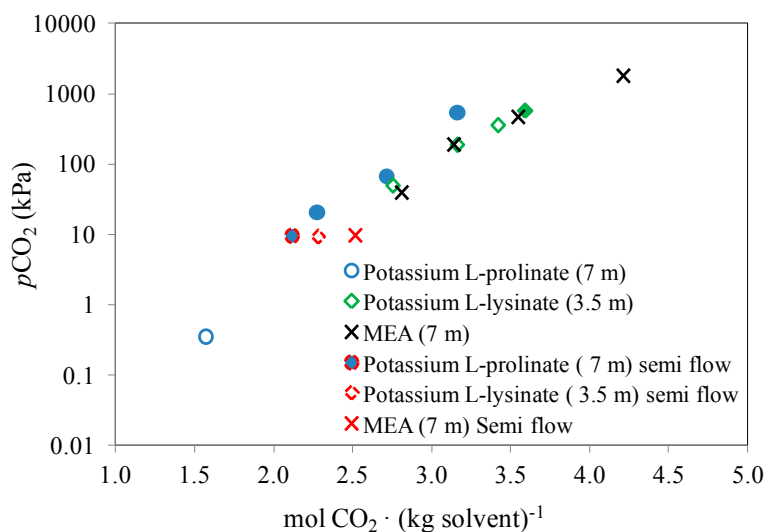


Figure 7.13: Results showing CO_2 partial pressure as function of capacity for the systems $\text{CO}_2 + \text{potassium L-prolinate} + \text{H}_2\text{O}$, $\text{CO}_2 + \text{potassium L-lysinate} + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ obtained in this work, at 313 K. Values for the same systems obtained in this work using the semi-flow method are also presented. Concentrations are 7 m for MEA and potassium L-prolinate, and 3.5 m for potassium L-lysinate. For systems with amino acid salts a filled point means precipitation occurred in the experiment.

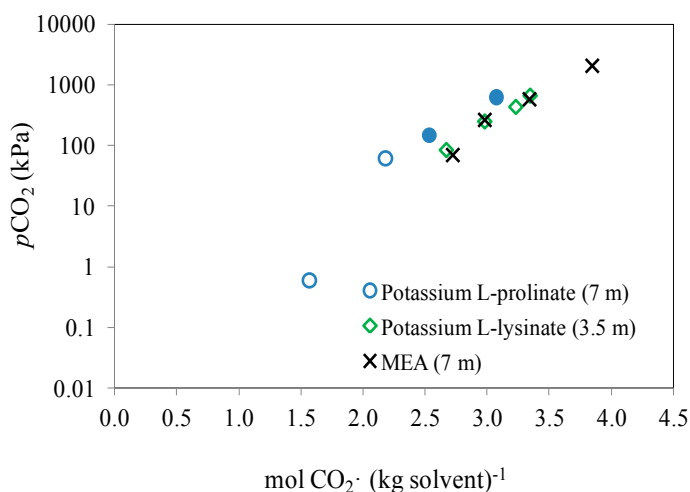


Figure 7.14: Results showing CO_2 partial pressure as function of capacity for the systems CO_2 + potassium L-prolinate + H_2O , CO_2 + potassium L-lysinate + H_2O and CO_2 + MEA + H_2O obtained in this work at 333 K. Concentrations are 7 m for MEA and potassium L-prolinate, and 3.5 m for potassium L-lysinate. For systems with amino acid salts, a filled point means precipitation occurred in the experiment.

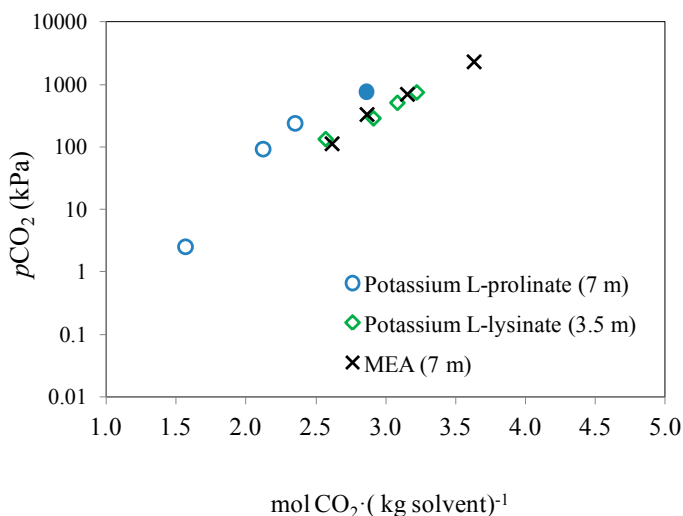


Figure 7.15: Results showing CO_2 partial pressure as function of capacity for the systems CO_2 + potassium L-prolinate + H_2O , CO_2 + potassium L-lysinate + H_2O and CO_2 + MEA + H_2O obtained in this work at 353 K. Concentrations are 7 m for MEA and potassium L-prolinate, and 3.5 m for potassium L-lysinate. For systems with amino acid salts, a filled point means precipitation occurred in the experiment.

Figure 7.13 includes values for the three systems, obtained using the semi-flow method (Tables 6.4, 6.5 and 6.6); it is seen that there is very good agreement between data obtained with the synthetic and the semi-flow method. Figure 7.13 show that at a given partial pressure of CO₂ a 3.5 m solution of potassium L-lysinate has similar capacity to 7 m MEA; however, a solution of 7 m potassium L-prolinate has lower capacity than 7 m MEA. This fits well with the results obtained in this work, using the semi-flow method presented in Chapter 6 (Figure 6.4). The same tendency is observed at 333 K (Figure 7.14) and 353 K (Figure 7.15).

7.4.4. Solubility and precipitation

As seen from Figures 7.8 to 7.15 precipitations occur in the case of the amino acid salt solutions, and in accordance with literatures, the solid formation is more pronounced at higher partial pressure of CO₂ and at lower temperatures (Chapter 6 Section 6.3). As discussed previously (Chapter 3) precipitation in amino acid salt solutions offers advantages, which are explained by the fact that precipitation of the reaction product(s) in an equilibrium limited reaction shifts the reaction towards the formation of more products [11-13]. It has been shown that as a result of precipitation, higher absorption ability at lower CO₂ partial pressures can be achieved; which can be noticed as a decrease in the slope of the equilibrium curve with the onset of precipitation [12-14]. In our experiments, the effect of precipitation is observed most profoundly for the 7 m solution of potassium L-

prolinate at 333 K; this is illustrated in Figures 7.16 and 7.17, showing the CO_2 partial pressure as function of loading and capacity respectively.

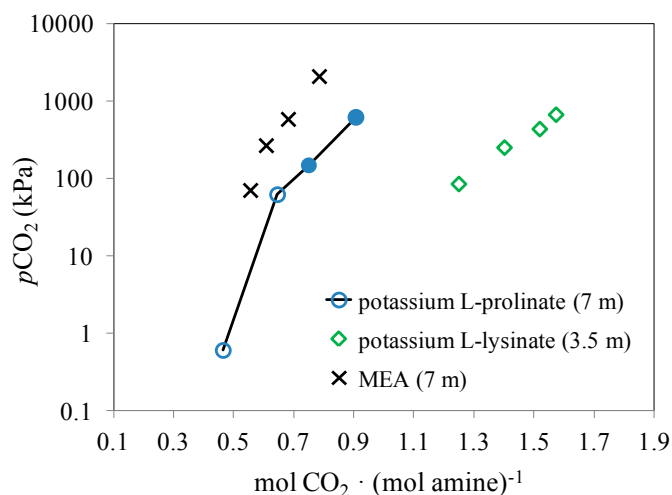


Figure 7.16: Results showing CO_2 partial pressure as function of loading for the systems CO_2 + potassium L-prolinate + H_2O , CO_2 + potassium L-lysinate + H_2O and CO_2 + MEA + H_2O obtained in this work at 333 K. Concentrations are 7 m for MEA and potassium L-prolinate, and 3.5 m for potassium L-lysinate. For systems with amino acid salts, a filled point means precipitation occurred in the experiment. The line through the data of potassium L-prolinate shows the change of slope, caused by precipitation.

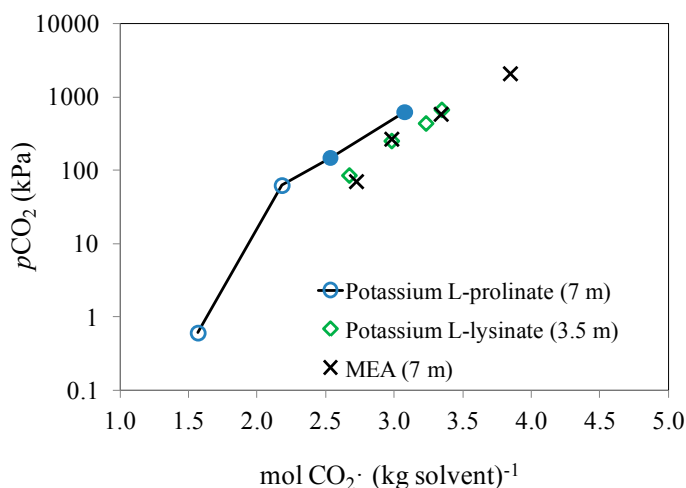


Figure 7.17: Results showing CO₂ partial pressure as function of capacity for the systems CO₂ + potassium L-prolinate + H₂O, CO₂ + potassium L-lysinate + H₂O and CO₂ + MEA + H₂O obtained in this work at 333 K. Concentrations are 7 m for MEA and potassium L-prolinate, and 3.5 m for potassium L-lysinate. For systems with amino acid salts, a filled point means precipitation occurred in the experiment. The line through the data of potassium L-prolinate shows the change of slope, caused by precipitation.

Majchrowicz and Brilman [14] also studied the solubility of CO₂ in aqueous solutions of potassium L-prolinate. The authors report precipitation with a 3 M solution at 285 K and CO₂ partial pressures above 6 kPa, with the chemical nature of the solid being potassium bicarbonate. The precipitation significantly increased the CO₂ absorption by the solution, as seen by a decrease in the slope of the equilibrium curve [14]. This result by Majchrowicz and Brilman [14] fits well with our observations (Figures 7.16 and 7.17), with the difference in conditions (p, T) for the onset of precipitation, attributed to difference in the initial concentration of the amino acid salt.

7.4.5. Stability of the amino acid salt solutions

As mentioned in the introduction to this chapter the experiments also involved temperature cycles between 313 K and 353 K, in order to determine the degradability of the 7 m potassium L-prolinate and 3.5 m potassium L-lysinate solutions under CO₂ capture conditions. In these experiments the solution was kept in the equilibrium cell for four cycles, with the CO₂ absorption measured at 313 K, 333 K and 353 K in each cycle. The loadings of all 12 experiments were calculated, and the change in absorption ability from cycle to cycle was examined. The results are reported in Tables 7.4 and 7.5, and illustrated in Figures 7.18 and 7.19.

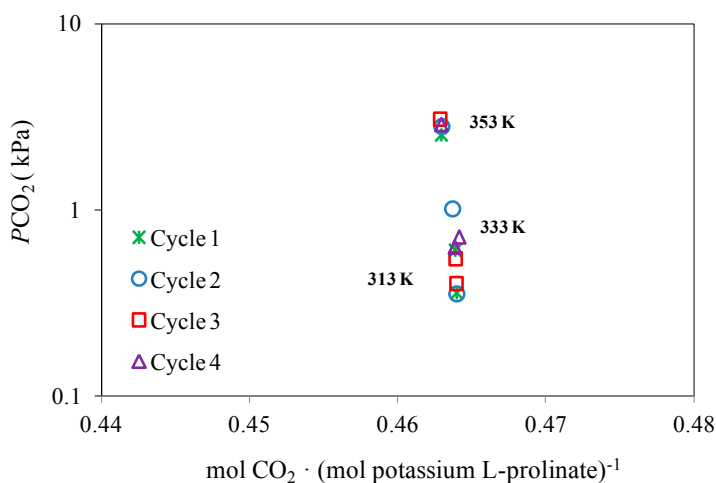


Figure 7.18: Results showing the partial pressure of CO₂ as a function of loading of four temperature cycles between 313 K and 353 K, for the system CO₂ + potassium L-prolinate + H₂O obtained in this work with a potassium L-prolinate concentration of 7.00 m.

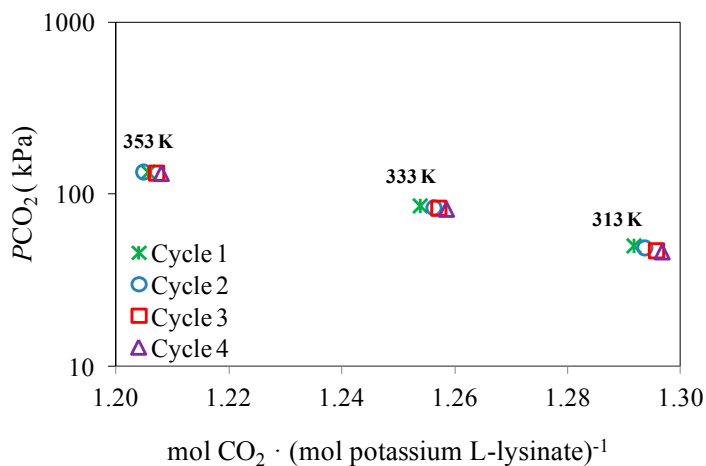


Figure 7.19: Results showing the partial pressure of CO₂ as a function of loading of four temperature cycles between 313 K and 353 K for the system CO₂ + potassium L-lysinate + H₂O obtained in this work with a potassium L-lysinate concentration of 3.52 m.

For both solutions, little difference was observed between the loadings of each cycle, which indicates good stability of the solutions, although much longer experiments at higher temperatures (393 K, 120 °C) are needed in order to accurately determine the stability of the solutions at realistic conditions. Interestingly, the solution of potassium L-prolinate seems to have the same loading at all three temperatures. This is possibly caused by the system being at conditions, where the counteracting effect of increasing both pressure and temperature on the loading is canceling each other out. Increased temperature leads to release of CO₂ from the solution, which in the closed system will result in a rise of pressure, promoting increased CO₂ uptake by the solution. From Figure 7.8 it is seen, that this effect is not appearing at higher pressures.

7.5. Conclusions

Using a synthetic method, CO₂ solubility in aqueous solutions of 7 m potassium L-prolinate and 3.5 m potassium L-lysinate were examined at 313 K, 333 K and 353 K and CO₂ partial pressures up to about 760 kPa. In order to validate the experimental setup, as well as directly compare the results for the amino acid salt solutions with a known reference, CO₂ solubility in solutions of 7 m MEA were also performed at the same temperatures and CO₂ partial pressures up to about 2.3 MPa. There is very good agreement between data obtained in this work for the CO₂ + MEA + H₂O system and literature data of the same system, attesting the quality of the experimental setup. In addition, there is good accordance between data obtained using the synthetic and the semi-flow method, confirming the value and reliability of the data presented in this thesis.

For all three temperatures, both amino acid salt solutions were found to have higher loading than 7 m MEA, with the potassium L-lysinate solution having approximately double loading of MEA. For all three temperatures, the capacity of the potassium L-prolinate solution was lower than 7 m MEA; however, the capacity of the potassium L-lysinate solution was similar to that of the MEA solution. The CO₂ absorption ability as well as the tendency for precipitation of the two amino acid salt solutions increases with higher partial pressure of CO₂ and lower temperature. The solution of the potassium salt of L-proline has much higher tendency for precipitation, than the solution of the potassium salt of L-lysine, which only precipitated in one of the experiments at the highest loading. In the case of potassium L-prolinate, it seems that there is an increase in CO₂

absorption as a consequence of precipitation, as illustrated by the decrease in the slope of the equilibrium curve (most pronounced at 333 K). The low tendency for the solution of potassium L-lysinate to form precipitation, even at fairly high loadings, strengthens the observation made in Chapter 6, regarding the possibility of a CO₂ capture process with a non-precipitating system involving this amino acid salt.

Some degree of desorption of the captured CO₂ occurs, upon heating to 353 K (80°C) in the case of both amino acid salt solutions, however experiments at higher temperatures probably up to 393K (120° C) are necessary in order to determine the amount of energy required to sufficiently desorb the CO₂. In order to test the degradability of the amino acid salt solutions at CO₂ capture conditions, temperature cycles between 313 K and 353 K were performed. For both solutions, little difference was observed between the loadings of each cycle, which indicates good stability of the solutions.

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Chapter 8

Conclusions and future work

The purpose of this project was to investigate the use of amino acid salt solutions in CO₂ capture from flue gas of coal fired power plants. The work focused on the experimental study of phase equilibrium behavior of five CO₂ + amino acid salt + H₂O systems.

Two different experimental apparatuses were used. One was designed and assembled as part of this project, and is based on an analytical semi-flow method. The other is based on a synthetic method and was recently constructed as part of another project (JMS Fonseca, PhD Thesis 2010). The semi flow method was used for measurements at a 10 kPa partial pressure of CO₂, total pressure equal to the atmospheric pressure and temperatures of 298 K, 313 K and 323 K. These conditions cover the absorber part of the capture process. The apparatus based on the synthetic method was used in order to obtain data at different pressures and temperatures up to 353 K (80 °C), which is the maximum operation temperature of some of the components in the apparatus. Ideally, measurements in the full temperature range for desorption, which usually needs approximately 393 K (120 °C), would be desirable. An important task for future work is thus to obtain equipment suitable for measurements at higher temperatures.

For the purpose of validating the experimental apparatuses, as well as obtaining data of a known reference system, for which to compare the results obtained with the amino acid salt solutions, phase equilibrium data of the system $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$ were obtained. In the case of both apparatuses, it was found that there is very good concordance between results of the validation study and data from literature of the same system, attesting their ability to produce high quality data. In addition, the agreement between data obtained with the two apparatuses is very good, supporting the ability of the two methods to complement each other.

The experimental work with the amino acid salt solutions started out by studying the chemical nature of the precipitations, which occurs upon CO_2 absorption into solutions of the potassium salts of taurine, glycine, L-alanine and L-proline at 7 m and the potassium salt of L-lysine at 4.5 m. Using the apparatus based on the semi-flow method, the solutions were saturated with CO_2 at 298 K. All five solutions formed precipitation upon CO_2 absorption; the chemical compositions of the precipitations were determined by XRD. The solids consisted of either the pure zwitterion form of the amino acid, pure potassium bicarbonate or a mixture of the two. These findings are in agreement with the results published by other authors for similar systems. Importantly, despite the differences in experimental conditions of this work to those of other authors, there seem to be a tendency for a given amino acid salt to form precipitations with a certain chemical composition. Our results imply a relation between the bicarbonate contents of the formed solids and increased alkalinity of the system, with the solutions of L-proline and L-

lysine, having the highest base strengths, and forming precipitates consisting of pure potassium bicarbonate. In the case of precipitation consisting of pure bicarbonate, there is the opportunity to temporarily store the CO_2 , opening new possibilities for the capture process. The formation of solids is known to increase the CO_2 absorption by the solution, and possibly lower the heat requirements for regeneration. However, any type of solid formation demands some adaptations of the equipment design; the absorber needs to be able to handle slurry formation, and in order to take advantage of the possible lower heat requirements for regeneration further adjustments are required. In this context, it is important to examine the conditions for which a system of interest changes from a non-precipitating to a precipitating system, the next step of our work addressed this issue.

Using the apparatus based on the semi-flow method, CO_2 solubility in aqueous solutions of MEA and the potassium salts of taurine, glycine, L-alanine, L-proline and L-lysine was examined at concentrations between 2 m and 8 m at 313 K. The amino acid salt solutions were found to have similar or better loadings, compared to MEA at equal concentrations. L-lysine exhibited approximately the double loading, compared to MEA. Our results follow the trends of literature, and show that CO_2 loading is increased, when the solvent molecule has more than one amine group, when the amine group is sterically hindered and has high base strength. Interestingly L-lysine, with its 2 active amine groups, possesses all of these qualities at the same time, which accounts for its high CO_2 loading.

Increasing the initial amine concentration, resulted in a decrease in CO₂ loading for all the systems, this is a tendency, commonly observed for CO₂ + amine + H₂O systems. However, for the amino acid salts, precipitations at higher concentrations, counteracted the decrease in CO₂ loading, and for some systems even increased it above values found at lower initial concentrations. The precipitation tendency of the amino acid salt solutions was as follows; taurine and L-alanine (precipitation at 3.5 m, L-proline and L-lysine (precipitation at 6 m) and glycine (precipitation at 7 m). Looking at the same data, comparing capacities at 7 m, it is found that the solutions of the potassium salts of taurine, glycine, and L-proline have lower capacities than MEA, whereas the potassium salt of L-alanine has similar capacity and the potassium salt of L-lysine has higher capacity than MEA. Interestingly, a solution of potassium L-lysinate around 3.5 m can provide a capacity close to 7 m MEA, with no precipitation occurring, as a result of the CO₂ absorption. For the other tested amino acids salt solutions, a similar high capacity involves a precipitating system. This result opens up for the possibility of using the potassium salt of L-lysine in a non-precipitating CO₂ capture system. A high capacity is important in order to lower the energy penalty of the capture system; as it prevents unnecessary pumping of large amounts of water, as well as minimise the amount of energy needed for heating of water in the desorption step.

Using the apparatus based on the semi-flow method, the influence of increasing the temperature between 298 K and 323 K on the CO₂ solubility was examined with 7 m solutions of MEA and the potassium salts of taurine, glycine, L-alanine

and L-proline, and 3.5 m solutions of the potassium salt of L-lysine. It was found that the CO₂ solubility decreased, as a result of increased temperature in all cases. Interestingly a 3.5 m solution of potassium L-lysinate was among the amino acid salts showing pronounced decrease in loading, which indicates a high temperature dependence of the equilibrium constants involved in the CO₂ absorption, promising low energy requirements for the regeneration process.

The apparatus based on the synthetic method was used to study CO₂ solubility in aqueous solutions of 7 m MEA, 7 m potassium L-prolinate and 3.5 m potassium L-lysinate, at temperatures of 313 K, 333 K and 353 K and with CO₂ partial pressures up to approximately 760 kPa in the case of the amino acid salt solutions and around 2.3 MPa in the case of MEA. CO₂ solubility (as well as the tendency for precipitation, in the case of the amino acid salt solutions) increases with higher CO₂ partial pressure and lower temperature. For a given CO₂ partial pressure, the amino acid salt solutions were found to have higher loadings than the MEA solution, at all three temperatures, with the solution of potassium L-lysinate having approximately double loading of the MEA solution. For a given CO₂ partial pressure, the capacity of the solution of potassium L-prolinate was lower than the capacity of the MEA solution; however, the capacity of potassium L-lysinate was similar to MEA, these tendencies were observed at all three temperatures. In the case of potassium L-prolinate, it seems that there is an increase in CO₂ absorption, as a consequence of precipitation, as indicated by a change of slope of the equilibrium curve, at the initiation of precipitation.

Interestingly, the solution of potassium L-lysine showed very little tendency for precipitation, even at fairly high loadings, supporting the idea of using this amino acid salt in a non-precipitating CO₂ capture system.

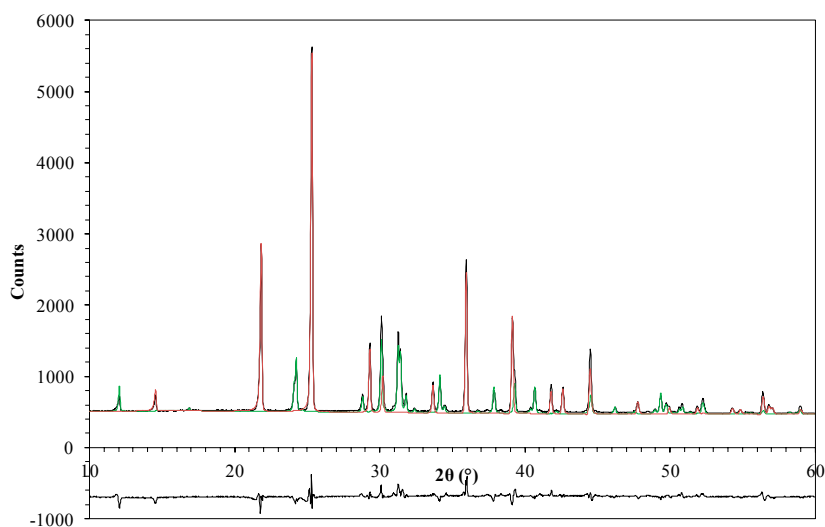
In order to test the degradability of the 7 m potassium L-prolinate and 3.5 m potassium L-lysinate solutions, temperature cycles between 313 K and 353 K were performed, using the apparatus based on the synthetic method. For both solutions, little difference was observed between the loadings of each cycle, indicating good stability of the solutions. However, in order to correctly determine the degradability of the amino acid salt solution under CO₂ capture conditions, much longer heating periods at higher temperatures are needed.

During this project, we have also looked at directly determining the degree of amino acid degraded as a consequence of heating, using amino acid analysis, which is a biochemical technique for determining the amount of a certain amino acids in a protein sample. By analyzing unheated and heated samples of the five amino acid salt solutions that had not been exposed to CO₂, and comparing the results, the degree of degradation was found. Even though these experiments were preliminary and are not presented in the thesis, the data indicated a good heat stability of potassium L-lysinate, compared to the other four amino acid salts included in this project. However more detailed experiments are needed, to determine the validity of this observation. The use of the technique amino acid analysis for this purpose is new, and has to our knowledge not been used for such studies before.

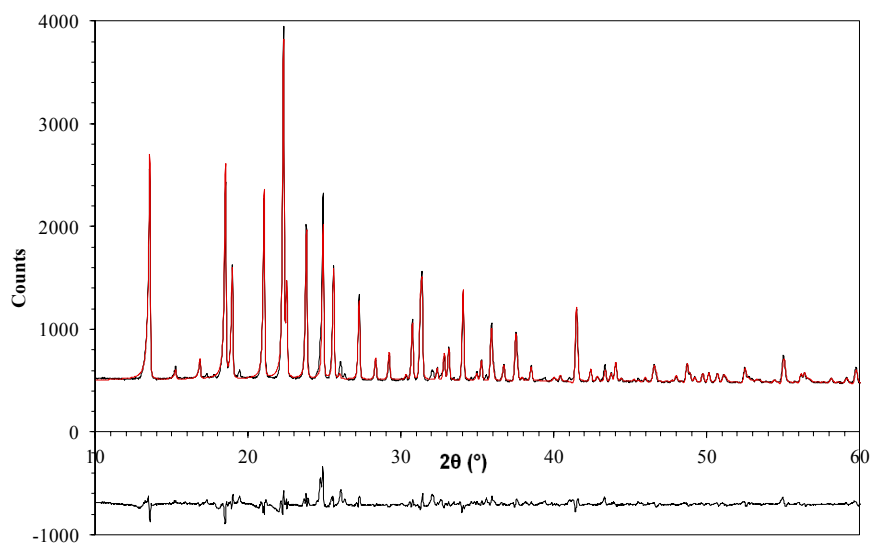
The data obtained in this project provides a unique insight into the phase equilibrium behaviour of the studied CO_2 + amino acid salt + H_2O systems, compared to the corresponding systems with MEA. All the tested amino acid salt solutions have the ability to capture CO_2 , with the potassium salt of L-lysine showing the best properties. Thus future work should concentrate on obtaining further phase equilibrium data of the system CO_2 + potassium L-lysinate + H_2O , especially important are experiments at desorption temperatures. In addition the kinetics of CO_2 absorption into potassium L-lysinate solutions has to be addressed, and further experiments regarding the stability of potassium L-lysinate solutions under CO_2 capture conditions should be performed.

Appendix

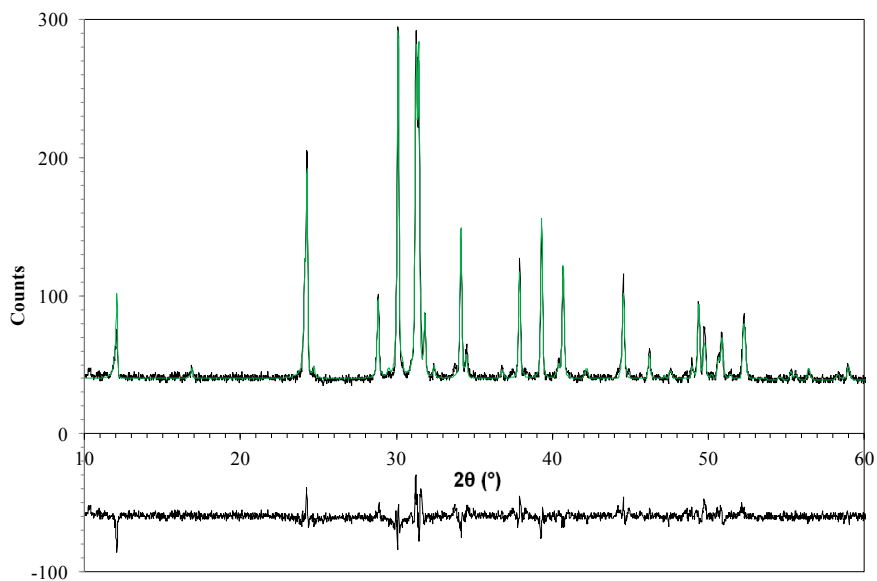
Rietveld fits



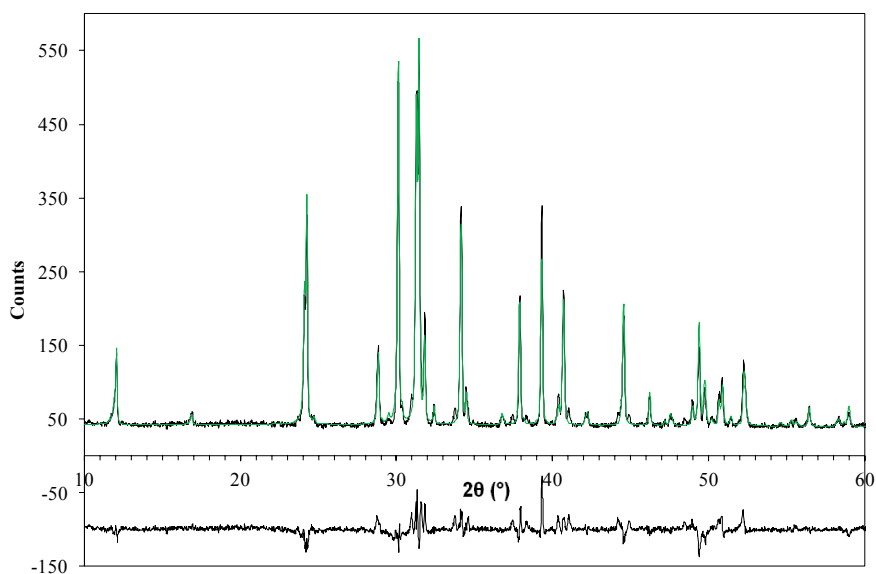
A1: Rietveld XRD fit of glycine and potassium bicarbonate to the powder pattern of the precipitation occurring in case of CO_2 absorption into a 7 m solution of the potassium salt of glycine. Powder patterns, Black (top): Observed pattern; Black (bottom): Difference between observed and fitted pattern; Green: Potassium bicarbonate; Red: glycine.



A2: Rietveld XRD fit of taurine to the powder pattern of the precipitation occurring in case of CO_2 absorption into a 7 m solution of the potassium salt of taurine. Powder patterns, Black (top): Observed pattern; Black (bottom): Difference between observed and fitted pattern; Red: Taurine.



A3: Rietveld XRD fit of potassium bicarbonate to the powder pattern of the precipitation, occurring in case of CO₂ absorption into a 7 m solution of the potassium salt of L-proline. Powder patterns, Black (top): Observed pattern; Black (bottom): Difference between observed and fitted pattern; Green: Potassium bicarbonate.



A4: Rietveld XRD fit of potassium bicarbonate to the powder pattern of the precipitation, occurring in case of CO_2 absorption into a 4.5 m solution of the potassium salt of L-lysine. Powder patterns, Black (top): Observed pattern; Black (bottom): Difference between observed and fitted pattern; Green: Potassium bicarbonate.

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