

Master Thesis Report

CRYSTALLIZATION IN THE POST-COMBUSTION CO₂ CAPTURE

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Abstract

Post combustion CO₂ capture is the process to capture CO₂, typically using solvent through the chemical absorption, from the flue gas stream in a power plant. Previous studies showed that crystallization may occur in the CO₂ capture system utilizing high concentration of certain amino acetate. This condition gives the disadvantage because of slurry formation in the absorption system. However, this crystallization offers the opportunity of higher CO₂ capturing capacity.

In this thesis, an aqueous sodium taurate solution was chosen as the solvent. Experimental works were carried out in order to define the solubility of taurine in aqueous sodium taurate solution at different pH. Data from these experiments are important to define at which conditions crystallization occurs when the solvent captures CO₂. Other experiments using *Crystalline* equipment were done to define the regime/zone (taurate solution concentration and temperature) at which taurine crystallization may occur during CO₂ capture. The crystallization process and when it starts can be observed during the experiment. The experiment results show that the higher solution concentration and lower temperature give a better chance for crystallization.

A set of thermodynamic models were built based on the experimental data in order to understand the effect of crystallization on the CO₂ capture process. These were the models of: solubility of taurine in the NaOH solution; the starting point of crystallization during CO₂ capture process; and the end point of CO₂ capture at which no more CO₂ can be absorbed by the solution. The modeling results show that a higher CO₂ loading can be achieved when the crystallization occurs during the CO₂ capture.

Keywords: amino acid, sodium taurate, CO₂ captures, crystallization.

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INTRODUCTION

Carbon dioxide (CO_2) has been indicated as one of contributors to the global warming as being a widespread public concern recently. One of the sectors that give significant contribution to the CO_2 emission to the environment is the electrical power generation. Consequently, in order to reduce the CO_2 emission, carbon capture and storage (CCS) in the power plants (i.e.: coal fired power plant and gas turbine power plant) becomes an issue and the important thing to be considered.

The CO_2 capture process in a power plant has a purpose to capture CO_2 from the flue gas stream and then to concentrate the CO_2 stream, which can be further easily transported to a storage site. The main reason is the direct injection of low concentration of CO_2 gas stream to underground is impractical, although in principle, it is possible. The concentrated CO_2 stream allows the reasonable energy usage and operational cost for injection of the gas. Therefore, it is essential to produce a nearly pure CO_2 stream for transportation and storage.

In the industrial field, CO_2 separation is already in large scale operation today, such as in natural gas treatment plant and ammonia production facility. However, there is no application of CO_2 capture for the large power plant up to now [1].

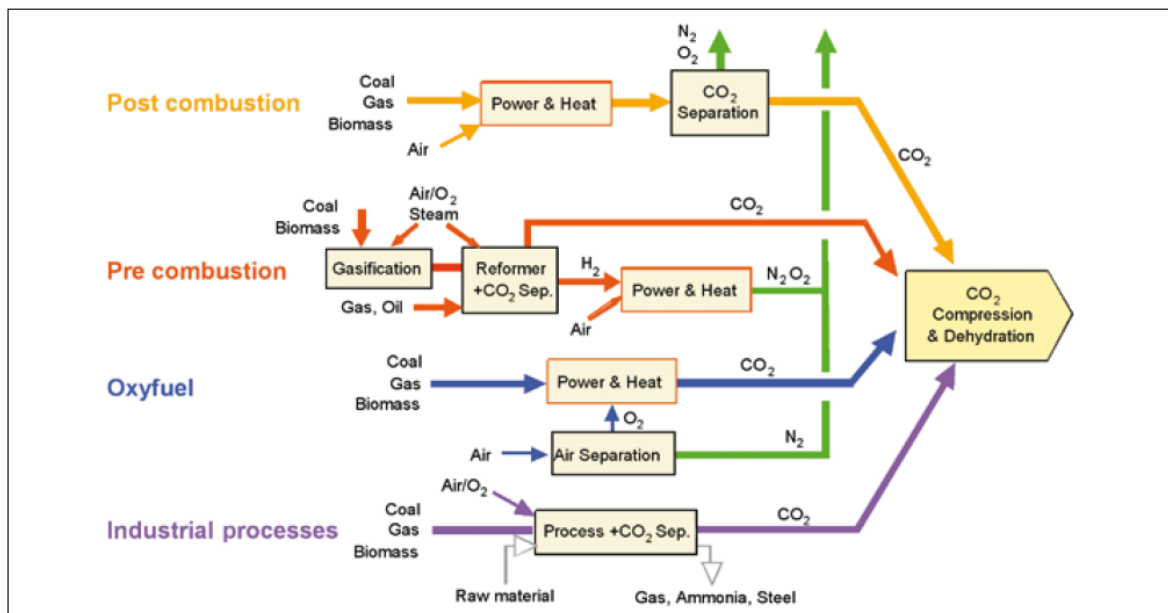


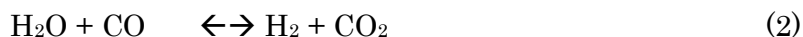
Figure 1.1. Overview of CO_2 captures processes and systems.

(IPCC Special Report, 2005, *Carbon Dioxide Capture and Storage: Technical Summary*, Cambridge university press)

Recently, the following CO₂ capture approaches have been studied and have been developed for the power generations that use primary fossil fuel (coal, oil or natural gas), biomass or the mix fueled (biomass-fuel oil) power plant. Figure 1.1 describes the schematic processes of those approaches.

1. Pre-combustion capture

Pre-combustion capture is to be used in the power plants that utilize Integrated Gasification Combined Cycle (IGCC). In this system, the primary fuel is converted into hydrogen through a three-stage process. Firstly, as described in the reactions (1) and (2) below, the fuel which is rich of methane is reacted with steam and air (or oxygen) at high pressure and temperature to produce a gas mixture mainly contains CO and H₂ (called as “synthesis gas”). In the second stage, CO is reacted with water using a water-gas shift reactor to form additional H₂ and CO₂. At last, H₂ and CO₂ are separated into H₂ gas stream and CO₂ gas stream prior to combustion.



The advantage of this pre-combustion capture system is that the CO₂ concentration in the gas stream is high and has elevated pressure. This condition reduces the energy capture penalty of the process [2]. The other advantage is that this system produces a hydrogen-rich fuel that can be used for fuel stock to be used in fuel cell for power generation.

2. Post-combustion capture

The flue gas exiting combustion chamber (furnace) contains CO₂ as one of products of fossil fuel combustion. The CO₂ is to be separated before the flue gas leaving the plant through its stack. The post-combustion capture typically uses a solvent to chemically absorb the CO₂ from this flue gas.

3. Oxyfuel combustion

Nearly pure oxygen instead of air is used for combustion of primary fuel so that the resulted flue gas mainly contains water vapor and CO₂ in high concentration. The water vapor is removed from the stream using compression and condensation method. As combustion using pure oxygen produces very high temperature, part of the flue gas is recirculated to the furnace in order to maintain combustion temperature at an optimum level.

The pure oxygen is produced by air separation unit that extracts oxygen from the air at cryogenic temperature.

1.1. Post-Combustion CO₂ Capture

The method used in post-combustion CO₂ capture is the most mature method in the CO₂ capture. It has the advantage that one can add the additional equipment and process on the existing power plant without doing dramatic modification to the whole plant.

Figure 1.2 depicts a sequential absorption and desorption process in this approach. The lean solvent captures CO₂ in an absorber (absorption column), and the CO₂-rich solvent resulted from this process is transferred to a stripper to release CO₂ from the solvent by introducing heat into it. The heat is supplied by reboiler that is attached to the bottom of stripper. The concentrated CO₂ gas is collected from the top of stripper and being compressed prior to be transferred to the storage. The CO₂-lean solvent is to be recirculated again to the absorber. To optimize the heat usage, a heat exchanger is placed between both column to transfer the heat between CO₂-rich solvent and CO₂-lean solvent.

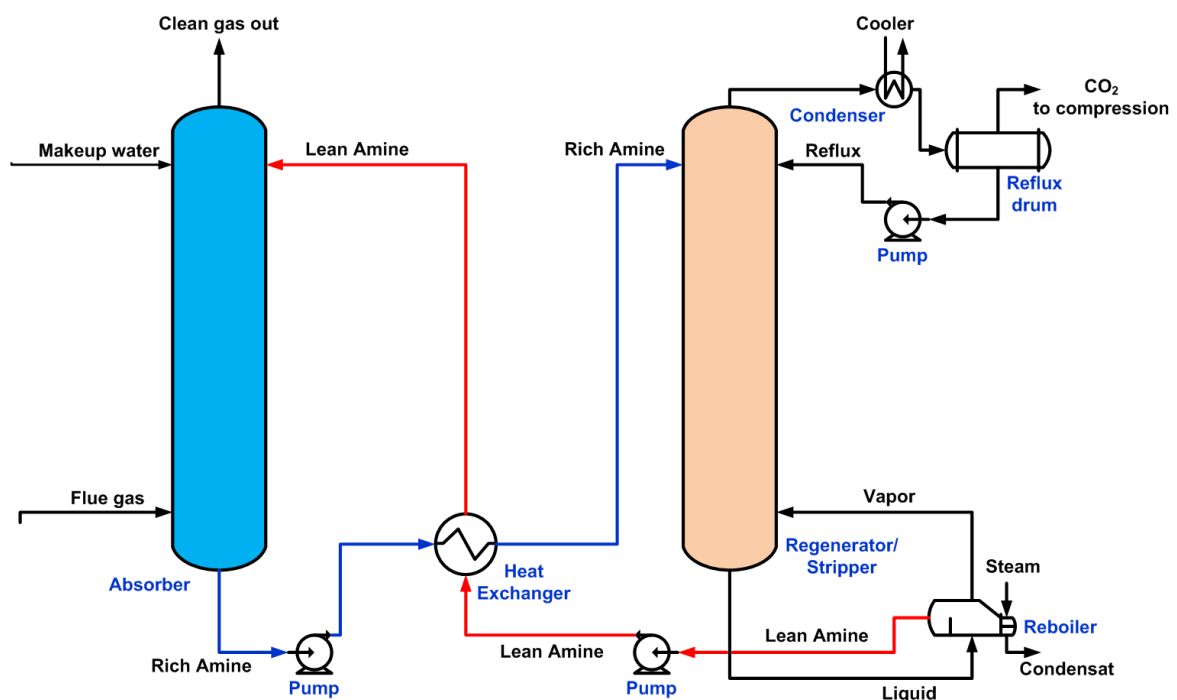


Figure 1.2. Post-combustion CO₂ capture basic process

In this scheme, the solvent selection becomes the important issue because it relates to the absorption performance and heat consumption, and eventually to the operational cost. As the result, the main line of reseaches is on the development of reactive solvents for CO₂ capture.

The use of chemical solvent of alkanolamines are well known and already applied in the power plants' post-combustion CO₂ capture, while carbonates (such as: K₂CO₃) are already mature in the oil and gas industry for CO₂ capture from pressurized well gases but not yet for the power plant [2].

Monoethanolamine (MEA) is a primary amine used in the CO₂ capture. Nevertheless, D'Alessandro et al. defined that this MEA (typically 25-30% wt) has several drawbacks in the application such as: high energy required for regeneration; necessary use of inhibitors to control corrosion and oxidative degradation due to residual oxygen in the flue stream; sensitivity of solvent to chemical degradation from other products. These drawbacks lead to efficiency reduction and increase the cost for electricity production.

The diethanolamine (DEA) is considered as secondary amine. Compared to that of primary amine, DEA has the lower heat of reaction and the lower stability of the carbamate formed upon CO₂ absorption, therefore, it gives rise to a more economical regeneration step.

For what concerns of energy usage in the regeneration step, the thermodynamic minimum energy penalty for capturing 90% of the volume from the flue gas of a typical coal-fired power plant is approximately 3.5% (assuming a flue gas containing 12–15% CO₂ at 40 °C), and by comparison, conventional CO₂ capture using amine scrubbers will increase the energy requirements of a plant by 25–40%, that it is predicted to increase the cost of 6 cent USD/kWh electricity [2].

This condition consequently stimulates the need to discover or to improve the methods of CO₂ capture that will reduce the demanded energy and at the end the cost of operation.

1.2. Thesis Background

One of the interests on the development of reactive solvents as well as CO₂ capturing methods is on the CO₂ capture that utilizes the benefit of precipitation/crystallization of one or more compounds during absorption and or regeneration process. The basic principle is that the precipitation shifts the reaction equilibrium and it may give an advantage in CO₂ absorption or desorption.

DECAB process is the absorption-desorption process of CO₂ that allows the crystallization to occur in the absorption process. This process was patented by Versteeg et al. [3]. This method was developed based on the principle that the reaction equilibrium can be shifted by removing one of the components in the reaction. In case of CO₂ capture, the shifting enhances the CO₂ absorption. In the patent, it is described that acid gas in the gas mixture is absorbed by contacting it to the liquid that has high concentration of amino acids or its salts. The amino acid or one of the reaction products crystallizes after chemical reaction. The more detail process and reaction is explained in the next chapter.

The advantage of this method is that application of higher concentration of amino acid is possible so that the high amount of CO₂ absorption (namely loading) can be achieved. The drawback is on the material handling and equipment design. As the reaction produces crystals, the slurry is formed so that the absorption column design is limited to the packing-free type column or column with packing that able to handle slurries.

The regeneration step can be carried out by direct regeneration of slurry. The slurry temperature is increased so that CO₂ is released and the slurry becomes a solution again. This method is preferable if the precipitate contains bicarbonate or carbonate compounds. The other alternative is by separating the slurry into liquid fraction containing CO₂ and thickened liquid containing amino acid. The regeneration then can be carried out with a smaller amount of liquid so that the energy usage will be lower. This method is suitable if the precipitate consists essentially of precipitated amino acid.

For what concerns of energy usage, DECAB process offers the lower energy requirement compared to that of CO₂ capture using alkanolamines (Monoethanolamine (MEA)) base process that is previously applied and more mature in technology. Brouwer et al. did a feasibility study for capturing 90% of the CO₂ emission from a 500 MW pulverised coal fired power plant and 465 MW natural gas fired combined cycle and yielded the result as shown in Table 1.1. The study claimed that the DECAB process need about 45% less thermal energy usage compared to that of MEA [4].

That interesting feature of DECAB process motivates this master thesis to investigate phenomena related to crystallization in the CO₂ capture and its benefit.

Table 1.1: Technical comparison of MEA and DECAB processes – consumption per ton CO₂ removal at a 500MW pulverized coal fired power station [4].

	MEA based process	DECAB process
Thermal energy (GJ)	4.2	2.3
Electricity (kWh)	69	41
Cooling water (m ³)	73	37
Chemicals (kg)	1.0	0.1

1.3. Thesis Questions

Some studies regarding DECAB process have been published. Among other authors, Kumar et al. [5] reported the experimental works (using double-walled stirred reactor with the capacity of 1660 cm³) on CO₂ capture using potassium taurate solution at 298 K. In this study, the crystallization of a reaction product was observed and the critical

CO₂ loading (the loading at which crystallization starts) was measured for various concentrations of amino acid salt. A relation between initial amino acid solution, the critical CO₂ loading and solubility of the amino acid in water was established.

In the second part of the publication of Kumar et al.[6], the thermodynamic model was discussed. The model was built based on the Vapor-Liquid Equilibrium data obtained from the experiments. Unfortunately, the model did not provide the prediction on the benefit of crystallization on the CO₂ capture by comparing with and without crystal formation during CO₂ capture.

Departing from that point, the main thesis questions are:

1. how does crystallization occur and in what condition during CO₂ capture?
2. how do experimental works and the models explain the capture and crystallization processes?
3. how does crystallization give a benefit to the CO₂ capture and how do the models predict that benefit?

1.4. Scope of Master Thesis

1.4.1. Experimental Work

In this scope, the solubility of taurine in the NaOH solution was investigated in order to establish the relation between temperature, initial taurine solution and the pH at which crystallization occurs. The experimental works were done using *Crystal16* equipment.

Other experiments were carried out using *Crystalline* equipment to define the region (solution concentration and temperature) at which crystallization occurs during CO₂ capture. The formed crystals were investigated using RAMAN spectroscopy equipment.

1.4.2. Thermodynamic Modeling

In this scope, the solubility model, critical CO₂ loading model and the end point of CO₂ capture model were built. The data from the experimental works as well as some data from literatures were used in the calculation. These models were built in order to explain the benefit of crystallization in the CO₂ capture.

The basic method to capture CO₂ in a post-combustion system using a common absorption-desorption process has been discussed in Chapter 1. In this method, solvent selection becomes the important thing to be considered, hence, it becomes an interesting topic to be studied and discussed by some researchers.

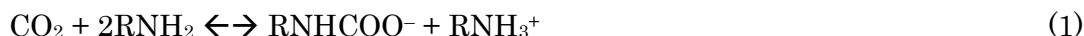
2.1. CO₂ Capture Using Alkanolamines

Aqueous Monoethanolamine (MEA) is the well-known solvent used in the post combustion CO₂ capture. Rochelle reported that hundreds of plants currently remove CO₂ from the gases with low oxygen [7]. At least four coal-fired power plants with output of 6 to 30 MW separate CO₂ from flue gas using 20% MEA and more than 20 plants use 30% MEA on gases with substantial oxygen content, including a gas fired power plant that has flue gas rate equivalent to that of a 40 MW coal fired power plant that produces flue gas with 15% CO₂.

MEA has some advantages in its high reactivity, low solvent cost, ease of reclamation and low absorption of hydrocarbons [8]. Moreover, it has reasonable thermal stability and low molecular weight and thus high absorbing capacity on a mass basis [9]. Beside its advantages, the MEA has several backdraws such as: high enthalpy of reaction with CO₂ that leads to higher desorber/ regeneration energy consumption; the formation of a stable carbamate and also the formation of degradation products with carbon oxysulfide (oxygen bearing gas); vaporization losses because of high vapor pressure; and higher corrosiveness than that of many other alkanolamines so that it needs inhibitors to control corrosion and oxidative degradation due to residual oxygen in the flue stream [2][9].

Diethanolamine (DEA) is the other amine, considered as the secondary amine, has the lower heat of reaction and lower stability of carbamate.

For what concern of maximum CO₂ can be absorbed by the solvent, namely CO₂ loading, MEA and DEA share the same limitation by stoichiometry to 0.5 mole of CO₂ per mol of amine when carbamate formation is the only reaction, according to the following reaction:



At high partial pressure carbamates may hydrolyze and generate free amine which can react with traditional CO₂, so that the CO₂ loading may exceed 0.5 [10].

Abu-Zahra [11] summarized that the absorption of CO₂ by aqueous MEA solution is based on a complex system of parallel and consecutive reaction in liquid phase. Generally, by simplify the reaction mechanism that actually occurs, the capturing process is carried out by the following reaction:



For the Methyldiethanolamine (MDEA) that is considered as the tertiary amine, a different limiting behavior is shown, which is unable to form carbamate.



Aqueous tertiary amine reaction with CO₂ leads to formation of the bicarbonate and stoichiometric absorption of CO₂ can now reach 1.0 mol CO₂ per mol of amine [12].

2.2. CO₂ Capture Using Amino Acids and DECAB process

Despite the popularity and proven technology usage of MEA, the disadvantage of this amine, especially for the high energy usage, motivates the interest to find another type of solvents and capturing methods that utilizes the lower energy.

One of the interests is on the usage of amino acids as the solvent. Amino acid salt solutions provide an interesting alternative to conventional amine based solution for CO₂ capture from flue gas. These amino acids have some features of: fast reaction kinetics; high achievable cyclic loadings; good stability towards oxygen; and favorable binding energy [4].

As previously discussed in Chapter 1, Versteeg et al. patented a CO₂ capture method that utilize amino acids as the solvent and this so called DECAB process take an advantage on the crystallization that may occurs in the CO₂ capture process. The invention comprises a method for absorbing acid gases from a gas mixture by contacting this gas mixture with a liquid that has so high concentration of an amino acid. The use of higher concentration amino acid allows the higher loading of the absorption. The amino acid or one of the reaction products crystallizes after reaction with the acid component. Based on the principle that the selective removal of reaction product from the reaction mixture will shift the equilibrium toward product side, it is expected that the crystallization of the component during CO₂ capture increases the CO₂ loading because of the reaction equilibrium shift.

Versteeg et al. suggested the use of the amino acids without hindrance. The advantage of amino acids is that they have a lower binding energy for CO₂ thus easier to regenerate. Examples of non-sterically hindered amino acids according to the invention are: taurine, methyl taurine, methyl- α -aminopropionic acid, N-(β -ethoxy) taurine and N-(β -aminoethyl) taurine. The preferred solutions for the invention are

solutions of amino salts rather than the corresponding amino acid. Amino salts are more soluble at a higher concentration, so that it is possible to use the high concentration to have high loading of absorption as previously discussed. The amino salts are preferably salts with potassium or sodium.

The schematic DECAB process is described in Figure 2.1, adapted from the study of Brouwer et al.[4]. In this scheme, the flue gas passes through the absorber and the CO₂ gas is to be absorbed by solvent through chemical reactions. Precipitation occurs as the effect of CO₂ absorption so that slurry forms at the bottom of absorber. This slurry, that has rich content of CO₂, is transferred to the stripper via a heat exchanger to be heated up to change its form to liquid. The stripper has integrated heat exchanger in it and utilized by a reboiler at the bottom and a condenser at the top. In the stripper, the CO₂ contained in liquid is stripped out and is collected at the top of reactor. The gas is condensed and compressed before it is transferred to the storage site. The lean solvent at the bottom of stripper is recirculated to the absorber again and being cooled down before it enters the absorber.

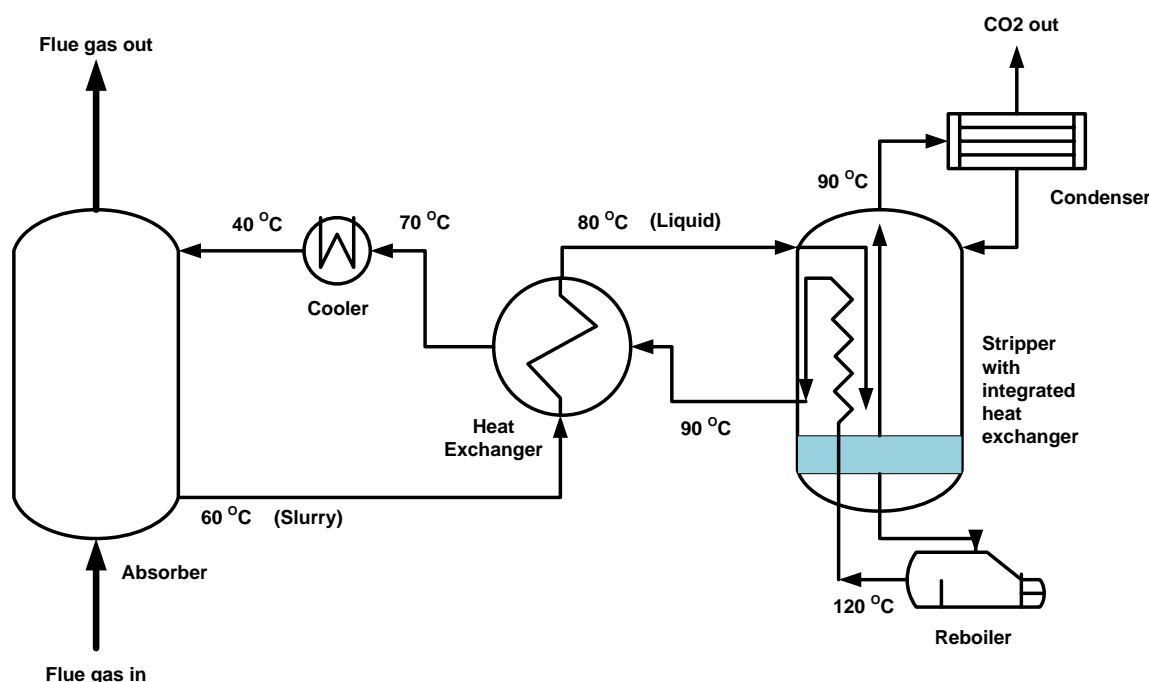


Figure 2.1. Schematic representation of the DECAB process.

2.3. Crystallization in the CO₂ Capture

In a research with an objective to improve the efficiency of carbon dioxide cycling process and to reduce amine emissions, Hook [13] investigated a series of non-volatile amino acid salts to determine their potential as direct replacements for monoethanolamine (MEA). The author utilized 2.5 M amino acid salts solutions that absorbed pure CO₂ from a constant-pressure (100 kPa) gas reservoir in a batch

experimental setup. It was reported that some amino acid salts undergo crystallization at various values of CO₂ loading, with the carbonate salt was confirmed as the precipitated compound. The precipitation of the reaction product was an undesirable result at that time and it would likely to prohibit the use of those amino acids as a direct replacement for MEA.

Kumar et al. [5][6] studied CO₂ capture using taurine-KOH-water solution with the main purpose to investigate the equilibrium solubility of CO₂ in aqueous potassium taurate. The study was based on the opportunities that were shown by the previous work of Hook. The opportunities are related to the fact that the crystallization of reaction product(s) results in an increase of the equilibrium CO₂ loading capacity (usually expressed in terms of moles of CO₂ per mole of amine) over a situation where no crystallization of the reaction product(s) occurs. In this study, crystallization of a reaction product was observed during the absorption of CO₂. The ¹³C-NMR spectroscopy analysis of the crystallized solid product showed that it was the protonated amine (the zwitterionic form of taurine), which is one of the reaction products. An experimental study was carried out at near-ambient conditions (298 K) with the objective to predict process parameters that control the onset of crystallization and to identify the nature of the solids formed. The thermodynamic model was built to fit the Vapor-Liquid Equilibrium data obtained from the experiments.

Majchrowicz et al.[14] investigated some amino acids of: α-aminoisobutyric acid, taurine, l-alanine and 6-aminohexanoic acid with the same concern to what Hook did. The main purpose of the study is to define the solid products precipitating upon a reactive absorption of CO₂ in aqueous solutions of the potassium, sodium and lithium salts. This subject is important for example from the slurry handling point of view and for mechanistic considerations. Moreover, different precipitate compositions will probably lead to different absorption behavior that may affect absorption capacities and regeneration conditions. It was found that in a potassium or sodium salts of taurine the solid was amino acid itself, while in potassium or sodium salts of α-aminoisobutyric acid, l-alanine and 6-aminohexanoic the solid contains CO₂ species.

Further in the next work, Majchrowicz et al. [15] investigated the precipitation regime for selected amino acid salts for CO₂ capture from flue gases. The tendency of potassium, sodium and lithium salts of taurine, β-alanine, sarcosine and L-proline to form precipitates in various operational conditions of CO₂ absorption was investigated with the purpose to determine the regime at which precipitation occurs. The knowledge from this study is important in designing a new regenerative gas separation process for CO₂ removal utilizing the features of either precipitating or non-precipitating amino acid salts solutions.

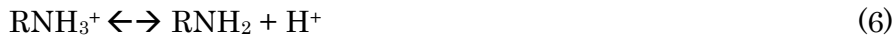
2.4. Reaction Scheme in CO₂ Capture Using Aqueous Amino Acids

In water, amino acids exist as zwitterions or dipolar ions with the amino group completely protonated. These zwitterions are considered as electrically neutral because they have the equal number of positive and negative charges. Addition of a base to the zwitterionic amino acid solution removes a proton from the ammonium group, leaving the molecule with a net negative charge (anion). This anion with a deprotonated amino group can react with acid gases such as CO₂ and H₂S [5][6]. The reactions to be considered in this scheme are:

Dissociation of water:



Dissociation of protonated amine:



R is the non reacting part of the amino acid anion.

For the CO₂ capture system, reaction of amino acids or amino salts in solution with the passed-through CO₂ proceeds according to the similar reaction of alkanolamines (reaction (1)). The reactions that occur in the liquid phase are as follows:

Carbamate formation:



At sufficiently high concentration of amino acid salt solution, the [RNH₃⁺] will crystallize.

Hydrolysis of Carbamate:



Hydrolysis of carbon dioxide:



Dissociation of bicarbonate:



Dissociation of protonated amine:



Dissociation of water



The following remarks apply for amino acid salt systems:

- (1) the deprotonated amino acid $[RNH_2]$ that reacts with CO_2 is an anion with a single negative charge.
- (2) The protonated amino acid $[RNH_3^+]$ is a zwitterion and was considered to be electrically neutral, as for molecular species.
- (3) The concentration of the cation of the amino acid salt is the same as the initial amino acid salt concentration ($[RNH_2]_0$).
- (4) The carbamate anion of the amino acid salt $[RNHCOO^-]$ has a charge of -2 .

2.5. Equilibrium Model Equations

The equilibrium constant associated with the above reactions can be expressed thermodynamically in term of activities of the reacting species [6]:

$$K_{CO_2} = \frac{[HCO_3^-][H^+]}{[CO_2]} \cdot \frac{\gamma_{HCO_3^-} \gamma_{H^+}}{\gamma_{CO_2}} \quad (13)$$

$$K_{HCO_3^-} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \cdot \frac{\gamma_{CO_3^{2-}} \gamma_{H^+}}{\gamma_{HCO_3^-}} \quad (14)$$

$$K_W = [H^+][OH^-] \frac{\gamma_{H^+} \gamma_{OH^-}}{a_w} \quad (15)$$

$$K_{Carbamate} = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]} \cdot \frac{\gamma_{RNH_2} \gamma_{HCO_3^-}}{a_w \gamma_{RNHCOO^-}} \quad (16)$$

$$K_{Tau} = \frac{[RNH_2][H^+]}{[RNH_3^+]} \cdot \frac{\gamma_{RNH_2} \gamma_{H^+}}{\gamma_{RNH_3^+}} \quad (17)$$

γ is the activity coefficient and a_w is the activity of water. γ of each species is defined by:

$$\ln \gamma_i = \frac{-2.303 A z_i^2 I^{0.5}}{1 + B a I^{0.5}} + 2 \sum_{j \neq w} \beta_{ij} [j] \quad (18)$$

where $A = 1.825 \times 10^6 (\text{CT})^{-3/2}$ and $B = 50.3 (\text{CT})^{-1/2}$. z is the charge number of the ion, a is an adjustable parameter with units of angstrom, I is the ionic strength, and β is the binary interaction parameter.

The ionic strength is defined by:

$$I = \frac{1}{2} \sum_j [j] z_j^2 \quad (19)$$

EXPERIMENTAL METHODOLOGY

3.1. Materials and Instrumentations

The following materials are used in the experiments:

- Distilled water
- Taurine (2-aminoethanesulfonic acid assay $\geq 99\%$) from Sigma-Aldrich
- Sodium Hydroxide (NaOH) pellets with reagent grade
- CO₂ gas from Linde Gas with $\geq 99\%$ purity

The first three were used in both of taurine solubility in NaOH solution measurement and crystallization experiment, while CO₂ gas was only used in the crystallization experiment. The samples were prepared on the molarity unit (mol/liter) basis, which refers to the mol of taurine per liter of solution.

The main instrumentations in the following were utilized to obtain the experimental data:

- Crystal16 (of Avantium, Amsterdam) was utilized in the measurement of taurine solubility in the NaOH solution. It has 16 reactors that hold 1.5 ml vial in each reactor, with 1 ml of sample in every vial.
- Crystalline (of Avantium, Amsterdam) was utilized in the crystallization experiments. It has 8 reactors with 4 of them have the insitu camera. A 3 ml sample in an 8 ml vial was prepared in every reactor in the experiment.
- A Hololab series 5000 RAMAN spectroscopy (Kaiser Optical System, Inc.) was used to measure the Raman spectra to identify the product species.

3.2. Solubility Measurement of Taurine in a NaOH Solution Using *Crystal16*

A series of experiments using *Crystal16* were carried out for four sodium taurate molarities (1M, 2M, 3M, and 4M) to measure the solubility of taurine at different acidities (pH). In order to obtain the different pH, NaOH compositions in the solution were varied from 0 to 100%. A 0% NaOH refers to the condition where there is no NaOH added into the solution or it is Taurine-water solution only, while 100% NaOH refers to the equimolar composition of NaOH-Taurine in the solution.

3.2.1. Sample Preparation

The sodium taurate solution was prepared by weighing the solid NaOH and taurine for an expected concentration and put them into the 1.5 ml vials. A calculated volume of distilled water was added into the vial to have a 1 ml of total volume.

Along with the molecular weights, the densities of NaOH and taurine were taken into consideration in the calculation during sample preparation to have an exact final volume.

The chemical compositions can be calculated using the following relation:

- Component mass (gram) =
$$\frac{\text{Molarity} \left(\frac{\text{mol}}{\text{liter}} \right) * \text{Molecular weight of component} \left(\frac{\text{gram}}{\text{mol}} \right) * \text{volume (ml)}}{1000 \left(\frac{\text{ml}}{\text{liter}} \right)}$$
- Component volume (ml) =
$$\frac{\text{Component mass (gram)}}{\text{Component density} \left(\frac{\text{gram}}{\text{ml}} \right)}$$
- Water volume (ml) = final volume – (total volume of components)

As an example, using the above data and equations, to obtain 1 ml of 1 Molar sodium taurate solution it needs:

- Taurine mass (gram) =
$$\frac{1 \left(\frac{\text{mol}}{\text{liter}} \right) * 124.15 \left(\frac{\text{gram}}{\text{mol}} \right) * 1 \text{ (ml)}}{1000 \left(\frac{\text{ml}}{\text{liter}} \right)} = 0.124 \text{ gram}$$
- Taurine volume (ml) =
$$\frac{0.124 \text{ (gram)}}{1.734 \left(\frac{\text{gram}}{\text{ml}} \right)} = 0.072 \text{ ml}$$
- NaOH mass (gram) =
$$\frac{1 \left(\frac{\text{mol}}{\text{liter}} \right) * 40 \left(\frac{\text{gram}}{\text{mol}} \right) * 1 \text{ (ml)}}{1000 \left(\frac{\text{ml}}{\text{liter}} \right)} = 0.04 \text{ gram}$$
- NaOH volume (ml) =
$$\frac{0.04 \text{ (gram)}}{2.13 \left(\frac{\text{gram}}{\text{ml}} \right)} = 0.019 \text{ ml}$$
- Added water volume (ml) =
$$1 - (0.071 + 0.019) = 0.910 \text{ ml}$$

The composition of compounds in the 1 ml samples are presented in Table 3.1.

Table 3.1. Composition of compounds in the samples.

Molar (mol/liter)											
1 M			2 M			3 M			4 M		
Taurine (gram)	NaOH (gram)	Water (ml)	Taurine (gram)	NaOH (gram)	Water (ml)	Taurine (gram)	NaOH (gram)	Water (ml)	Taurine (gram)	NaOH (gram)	Water (ml)
0.124	0.040	0.910	0.248	0.080	0.819	0.372	0.120	0.729	0.497	0.160	0.638

The concentration (molarity) of taurine was used as a base for the composition calculation, hence, for the different portion of NaOH, the amount of taurine and water

were set to be equal to the amount at 100%NaOH composition. In other words, the variation was only applied to the NaOH portion. The NaOH percentage variations in the experiment were calculated from the NaOH portion (in mass) resulted from the above calculation method (100% NaOH).

The samples were prepared for 1M, 2M, 3M and 4M concentrations, with the eight NaOH portion variations of 0%, 20%, 35%, 50%, 62.5%, 75%, 87.5% and 100%, respectively. These compositions were chosen by considering the coverage of experiments (from 0% to 100% NaOH) and the capacity of *Crystal16* equipment which has 16 reactors, so that the equipment was used efficiently. The detail composition of each component in solution can be found in Appendix A.

3.2.2. Experimental Method

Crystal16 was used to determine the solubility of a compound in a solute, based on turbidity. During the measurement, a solution is first heated and then cooled at certain temperature with a defined heating and cooling rate (see Figure 3.2). A point at which suspended solid materials disappears from solution (100% transmissivity) is taken as the saturation temperature of the compound in solution. Also the point at which solid material first appear in a solution from which crystal is being carried out is considered as the cloud point. The clear point represents saturation temperature, or in the other words, it is the solubility of compound in solution at a certain temperature.

The experimental set up is depicted in the Figure 3.1. The system comprises of: *Crystal16* unit, thermostat bath, control unit and computer unit.

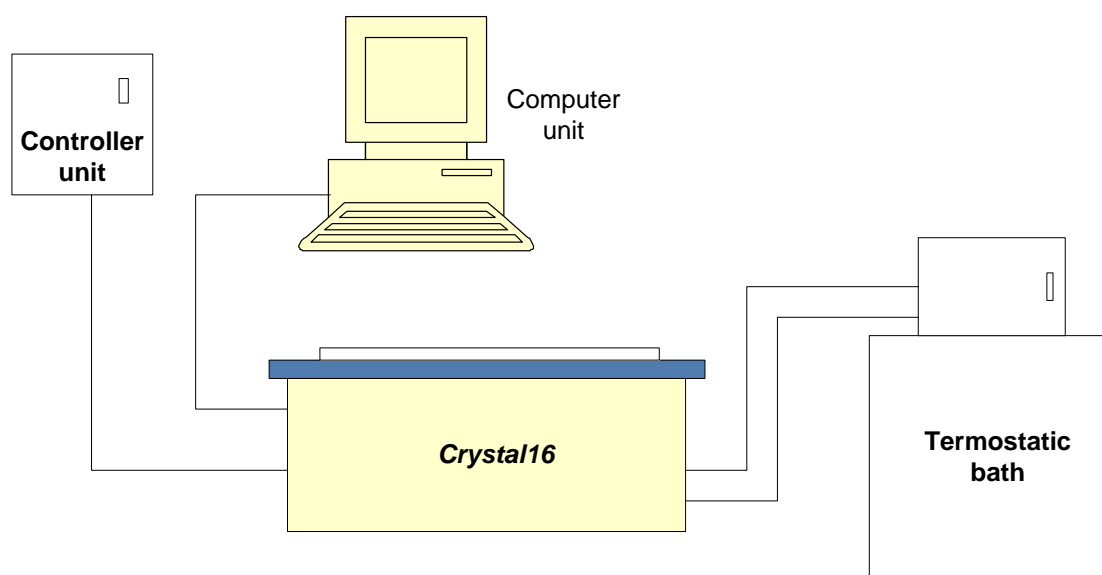


Figure 3.1. Schematic diagram of *Crystal16* equipment set up.

The following heating-cooling cycle was used in the experimental works:

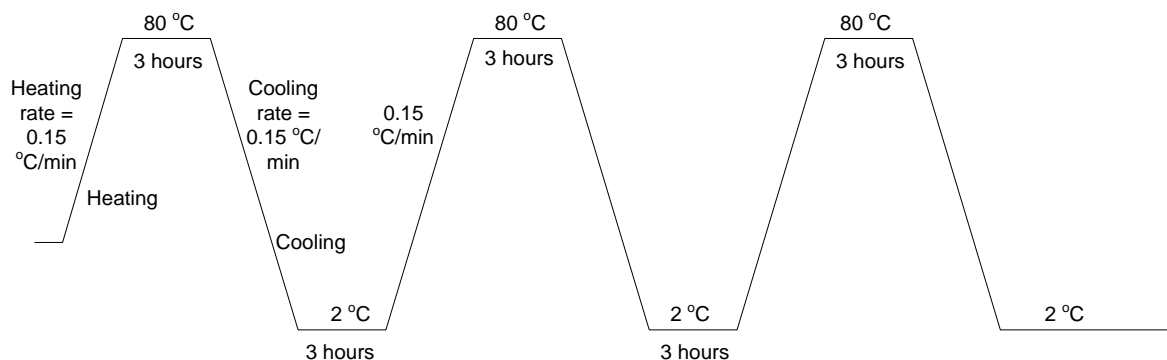


Figure 3.2. Temperature profile set up for *Crystal16*.

The samples were heated up with the heating rate of 0.15 °C/minute up to 80 °C and to be held at that point for 3 hours. Next, they were cooled down with the cooling rate of 0.15 °C/minute to 2 °C and to be held for 3 hours at that point. The samples were stirred with a control stirring speed of 700 rpm using magnetic stirring bars. This cycle was repeated for 3 times as depicted in Figure 3.2. This repetition was carried out to get the reliable data.

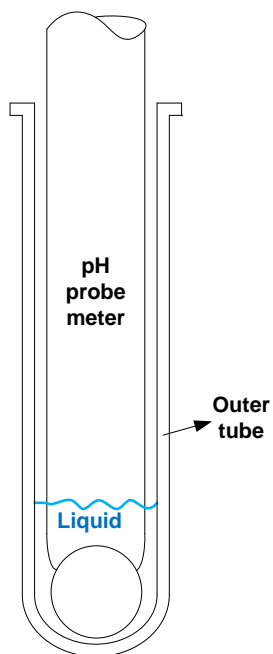


Figure 3.3. pH measurement

pH measurement:

The pH data of samples were analyzed after the solubility measurement. The samples were placed in a tube which inner diameter was little bigger than that of the pH probe meter. As shown in Figure 3.3, the sample was allowed to wet the probe surface to approximate the good measurement in a bulky liquid.

3.3. Crystallization Experiments

The crystallization experiments using *Crystalline* were carried out to observe the precipitation/crystallization due to CO₂ absorption at a certain temperature. The solution concentrations of samples, ranging from 1M to 4M, were placed into the 8 ml vials. The CO₂ gas can be purged into the solution via evaporative cap of the *Crystalline*. During the experiment, the temperature was kept constant. The inside-vial view can be observed using insitu camera available in the *Crystalline* unit.

3.3.1. Sample Preparation

The liquid samples were prepared in a bulk amount with the highest concentration (4 Molar). To have the lower concentration for other experiment, the rich concentration was diluted with distilled water into the other concentration, for example to 1M, 2M and 3M, respectively.

A 3 ml of liquid sample was put in a 8 ml vial in each experiment. During the experiment, the sodium taurate concentrations of 1M, 2M, 3M and 4M were used as the main references. However, in order to have a better crystallization map, the molarity numbers in between these concentrations were also examined when it was needed. It was a condition where the crystallization may or may not occur at the temperature set up. For example, for the solution concentration between 1M and 2 M and between 2M and 3M, crystallization may occur at the lower temperature (exp. 25 °C) and that is not the case at the higher temperature (exp. at 50 °C).

3.3.2. Experimental Method

The experimental set up is depicted in Figure 3.4 and 3.5. The set up comprises with: *Crystalline* unit, thermostatic bath, controller unit, computer unit and CO₂ gas vessel that supplies CO₂ through gas inlet port in *Crystalline* unit.

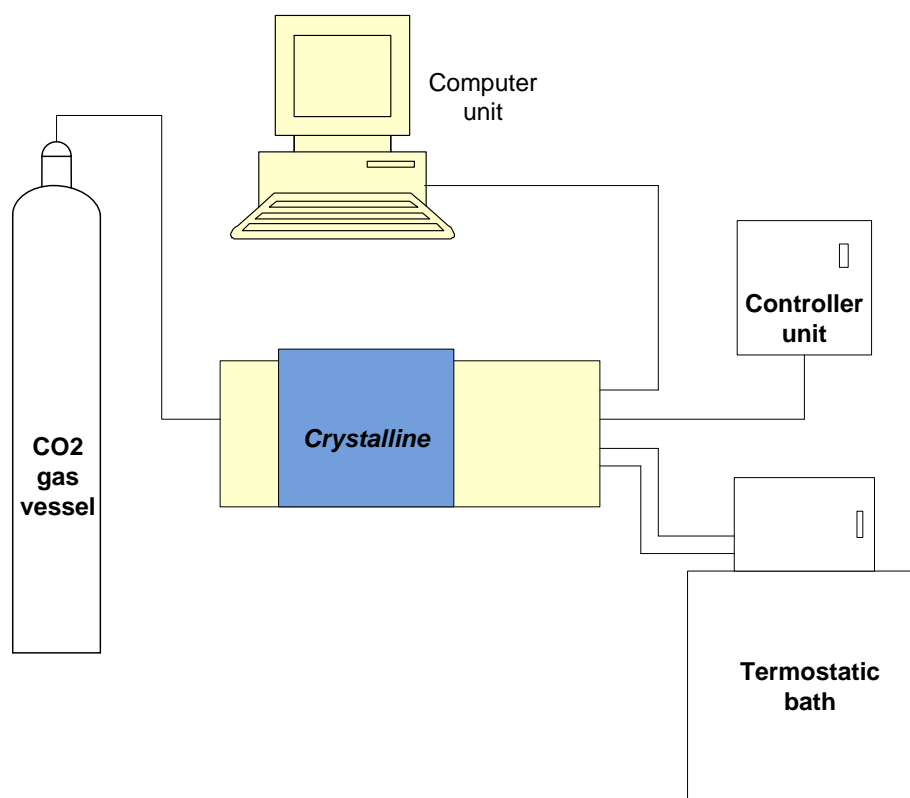


Figure 3.4. Schematic *Crystalline* equipment set up

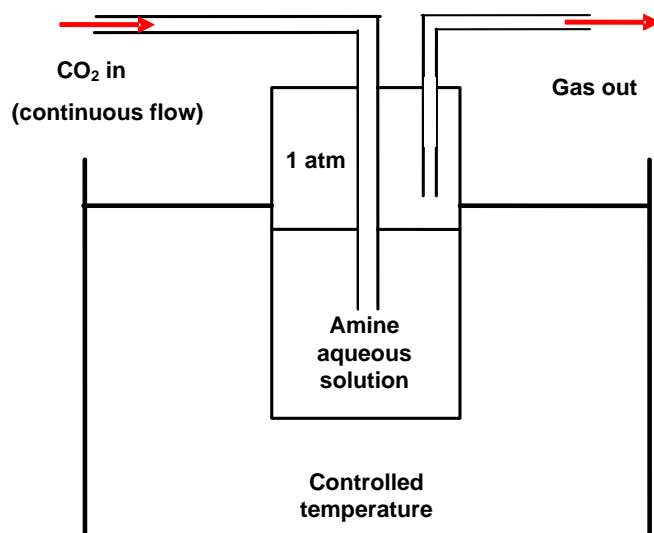


Figure 3.5. Schematic CO₂ purging system and the vial arrangement

A special arrangement was applied to the vial as can be seen in Figure 3.5. A transparent rubber tube was attached to allow the CO₂ gas purged at the bottom of vial in order to have the best contact between gas and solution. A magnetic stirrer was put in the vial to provide a well-mixing during experimental process.

The CO₂ was purged continuously into the solution at a constant temperature. The CO₂ purging was performed for a period of 1 hour, to have an approximated equilibrium condition. The purging was carried out at a temperature ranging from 25 °C to 60 °C. The process was observed by insitu camera to identify the solid precipitation which may occur during the experiment.

The precipitated solid was filtered using 0.025 µm mesh and was dried in the oven at 80 °C for 24 hours. The dried solid was examined using RAMAN spectroscopy to define its compound(s) and to be compared to the standard taurine spectrum.

EXPERIMENTAL RESULTS

4.1. Taurine Solubility in NaOH Solution

The clear and cloud points of each sample data can be obtained from the *Crystal16* experiments. The clear point represents the solubility of compound in solution at a certain temperature. By combining the *Crystal16* experimental results and pH measurement data, the solubility of taurine in a solution concentration (Molar) can be performed as function of temperature and pH as shown in Figure 4.1. It is shown that the higher concentration of sodium taurate has a higher pH. The solubility of taurine is affected by the pH as well as the temperature. For example, at temperature of 40 °C, a 4 Molar solution with the pH of 10.2 has solid taurine in it while at pH of 10.4 the taurine dissolves completely, or, at the same pH (10.2), when the temperature is raised to 60 °C the taurine will dissolve completely. The area at the left of the solubility lines represents a region at which no clear solution condition can be achieved (supersaturated region), while the right hand side area represents a region at which all of the taurine is soluble (undersaturated region).

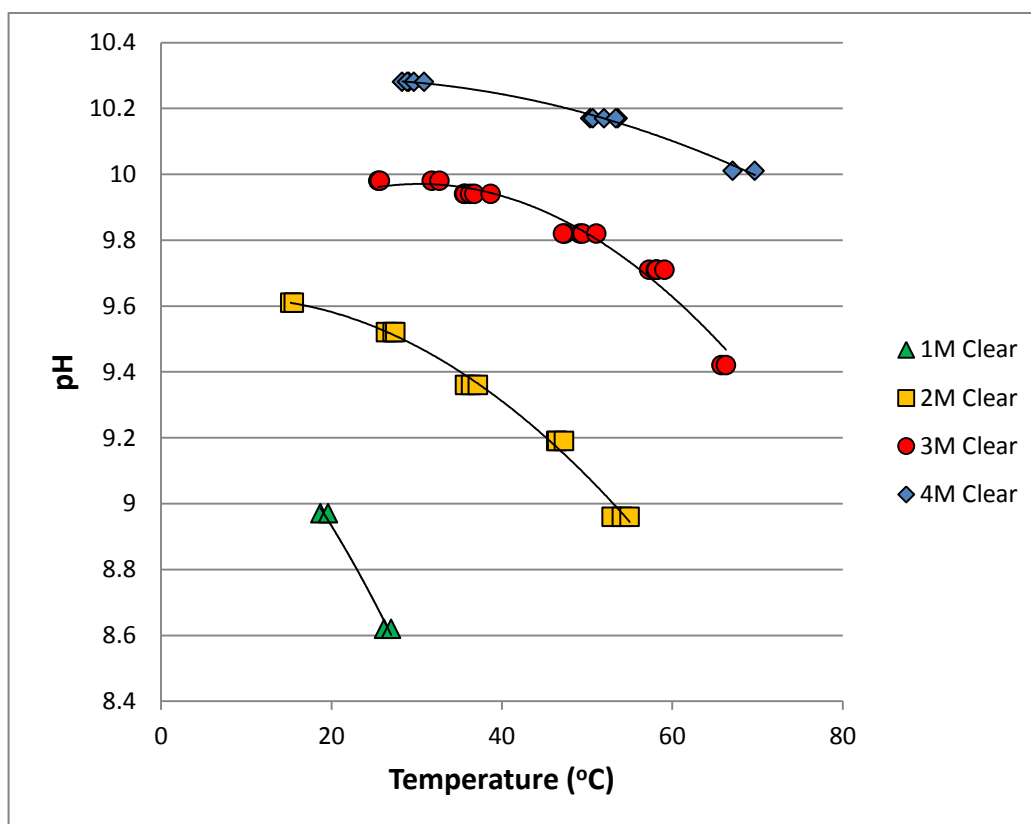


Figure 4.1. Solubility lines of taurine in the different molarities of Sodium Taurate solution.

Usually, the absorption process of a compound using gas as the absorbant is designed at a constant temperature. In the experiments, pH variation was resulted from %NaOH composition in the samples, while the solubility temperature was obtained from the clear point temperature measured by *Crystal16*. In order to have the basic data for modeling, the solubility line of taurine as a function of concentration (Molar) and pH (or %NaOH) at constant temperature should be established. Therefore, in this thesis, the experimental data were rearranged in order to have a relation between the variables (which were solution concentration (Molar), %NaOH and pH) of the experiment at the constant temperature.

The MS Excel linear regression is chosen to define the equations for Molarity as function of temperature at each %NaOH composition as shown in Figure 4.2. Using these equations, the Molarity of solution for a certain constant temperature can be calculated as presented in Table 4.1.

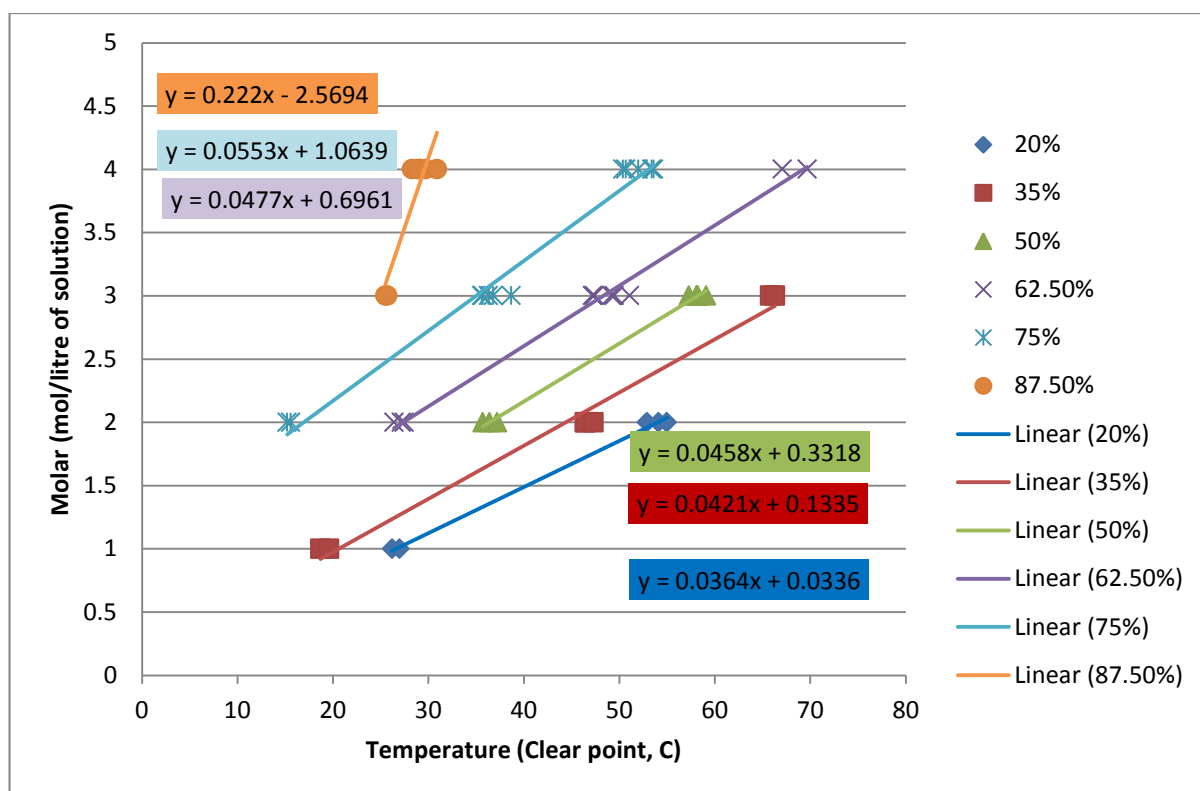


Figure 4.2. Solubility temperature vs Molarity of solution for various %NaOH compositions.

Table 4.1. Molarity of solution calculation at constant temperatures.

Formula	%NaOH	T (°C)			
		30	40	50	60
	(y-axis)	Molarity (x-axis)			
From the reference [16]	0	0.9900	1.3400	1.7500	2.1800
$y = 0.0364x + 0.0336$	20	1.1256	1.4896	1.8536	2.2176
$y = 0.0421x + 0.1335$	35	1.3965	1.8175	2.2385	2.6595
$y = 0.0458x + 0.3318$	50	1.7058	2.1638	2.6218	3.0798
$y = 0.0477x + 0.6961$	62.5	2.1271	2.6041	3.0811	3.5581
$y = 0.0553x + 1.0639$	75	2.7229	3.2759	3.8289	4.3819
$y = 0.222x - 2.5694$	87.5	4.0906			

From the calculated data in Table 4.1, the solubility line at constant temperatures can be defined as shown in Figure 4.3. The 3rd order polynomial regression is used to define the continuous constant temperature lines. Figure 4.3 shows that at a higher temperature, the solubility line occurs at a higher solution concentration. It indicates that when the higher temperature process is chosen, the higher solution concentration should be utilized to make crystallization possible. Figure 4.3 also shows that the more basic solution is needed when the lower temperature is chosen in a system with the same solution concentration. It indicates that at a lower temperature, the process needs less absorption of acid gas (CO₂) in order to start crystallization.

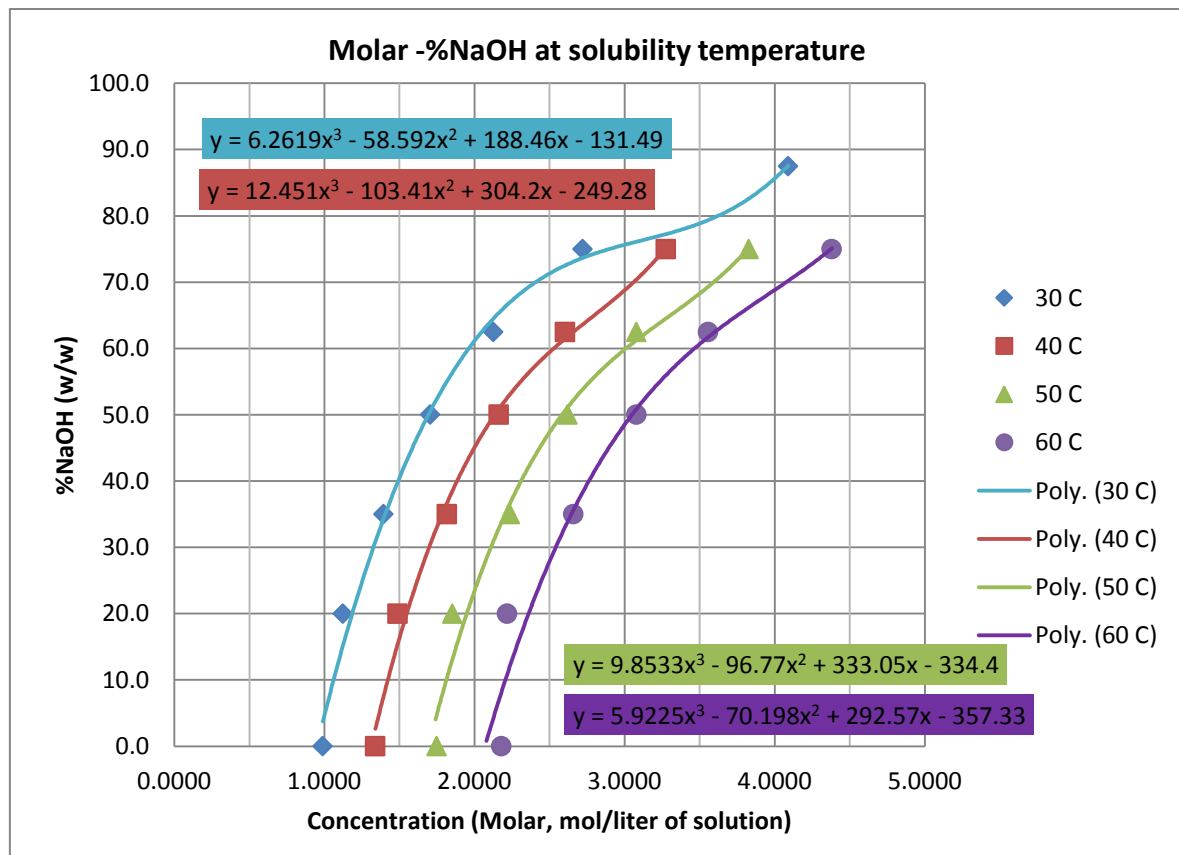


Figure 4.3. Molarity vs. %NaOH composition of solution at the constant temperatures.

The %NaOH composition in the Figure 4.3 should be corresponded to the pH data from measurement in order to be used as input in the thermodynamic model because the output of the model is the pH, therefore, the model calculation and the experimental result can be connected or compared. Figure 4.4 shows the pH data as a function of %NaOH composition in the certain solution concentrations obtained from the measurement. The detail of pH measurement data at %NaOH composition can be found in the Appendix A.3. The 3rd order polynomial regression is chosen to have the equations that reflect the relation between %NaOH composition and pH at constant solution concentrations.

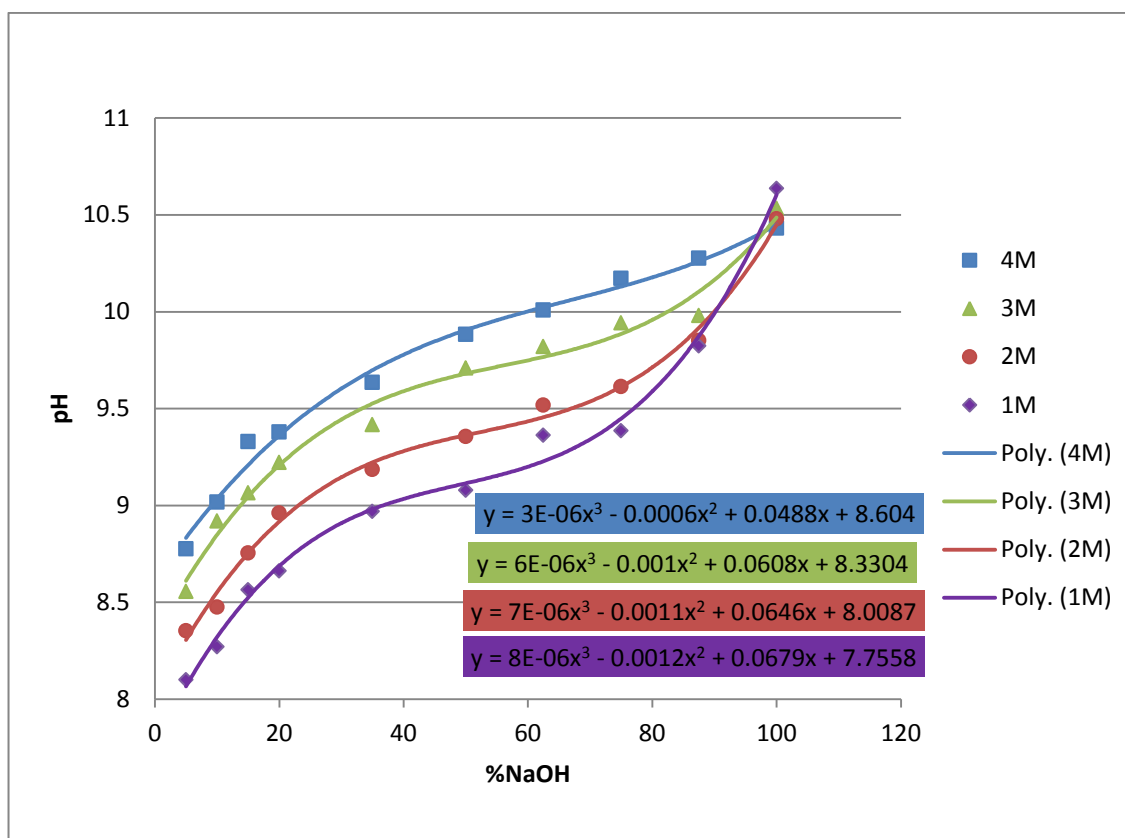


Figure 4.4. %NaOH and pH correlation for different solution concentration of taurine obtained from the measurement.

4.2. Crystallization Experiment

Figure 4.5 shows the sequential view of the crystallization process during CO₂ absorption in the 2 M sodium taurate solution at a constant temperature of 25 °C. The first figure is the initial condition where the CO₂ gas not yet been purged into the solution. In the second figure, it is shown that the CO₂ gas start to be purged. The continuous CO₂ purging eventually causes the crystals to form at about 21 minutes from the first purge, starting from the small sizes and then they grow as the process continues.

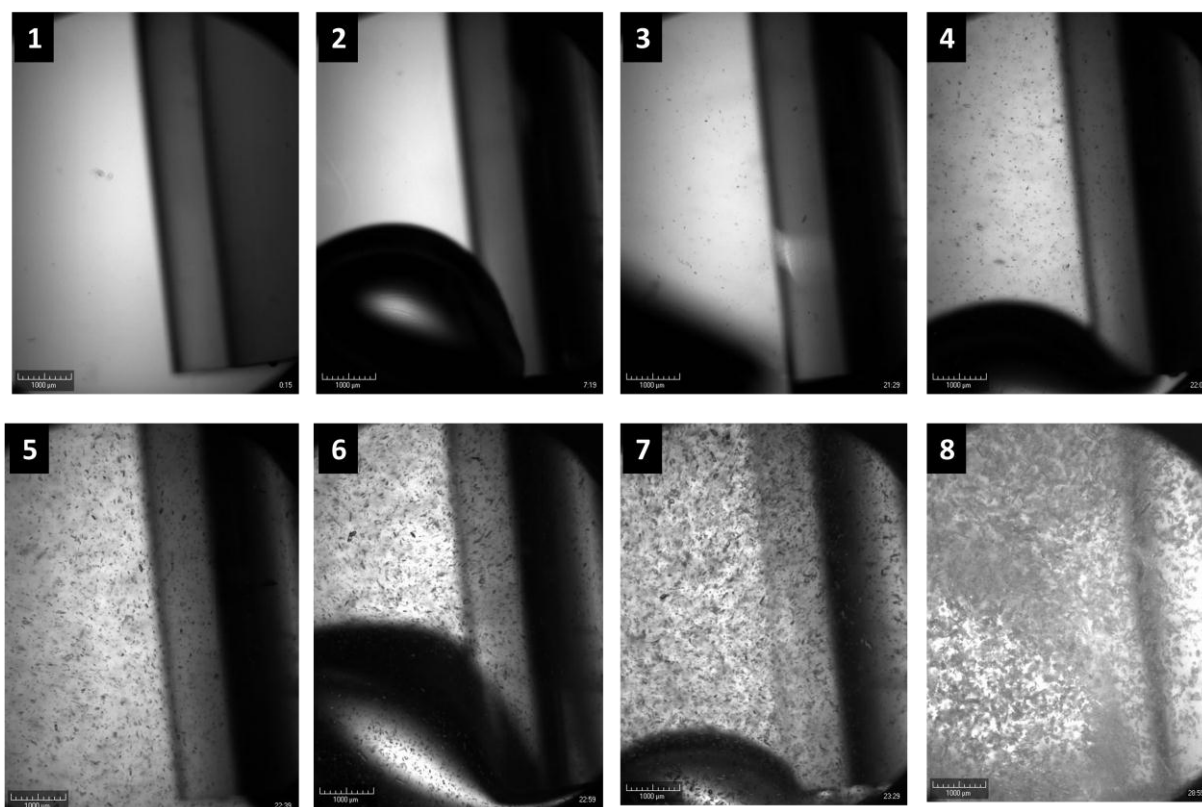


Figure 4.5. The sequential view of crystallization process during CO₂ capture in the 2M sodium taurate solution at 25 °C.

Using a series of *Crystalline* experiment with the solution concentration between 1M and 4M and temperature between 25 °C and 60 °C, a map of crystallization zone can be obtained as shown in Figure 4.6. It is shown that both solution concentration and temperature affect the possibility of crystallization during CO₂ capture process. The high solution concentration and relatively low temperature give the better chance of crystallization.

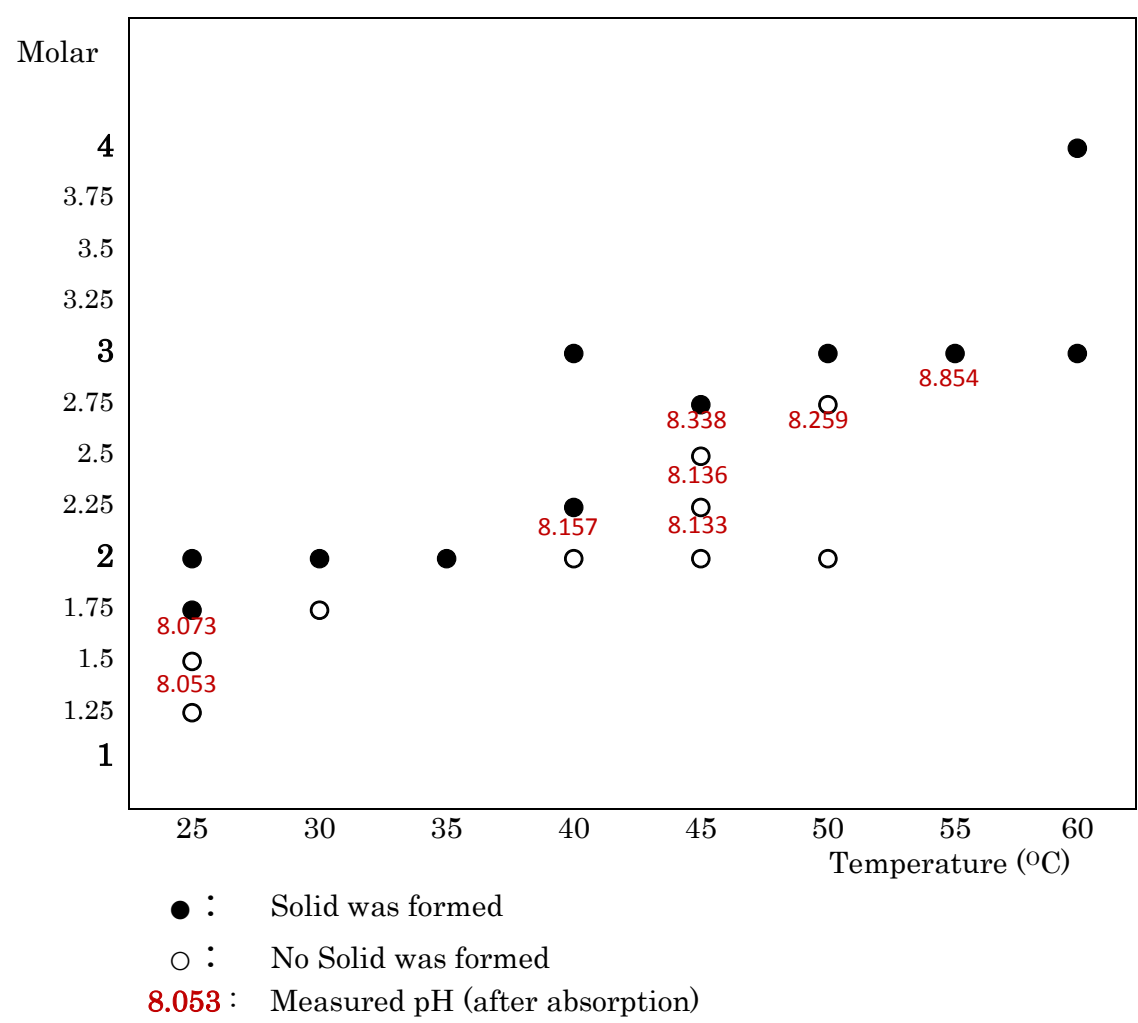


Figure 4.6. Crystallization zone for the sodium taurate solution during CO₂ absorption.

RAMAN spectroscopy result as shown in Figure 4.7 confirms that the precipitated solid resulted from the CO₂ capture is identical to that of standard taurine. It agrees with that was reported by Majchrowicz et al. [14][15] and Kumar et al [5][6]. It was reported that in the potassium and sodium salts of taurine, the precipitated solid formed during the CO₂ capture is the taurine and the solid did not contain CO₂ species.

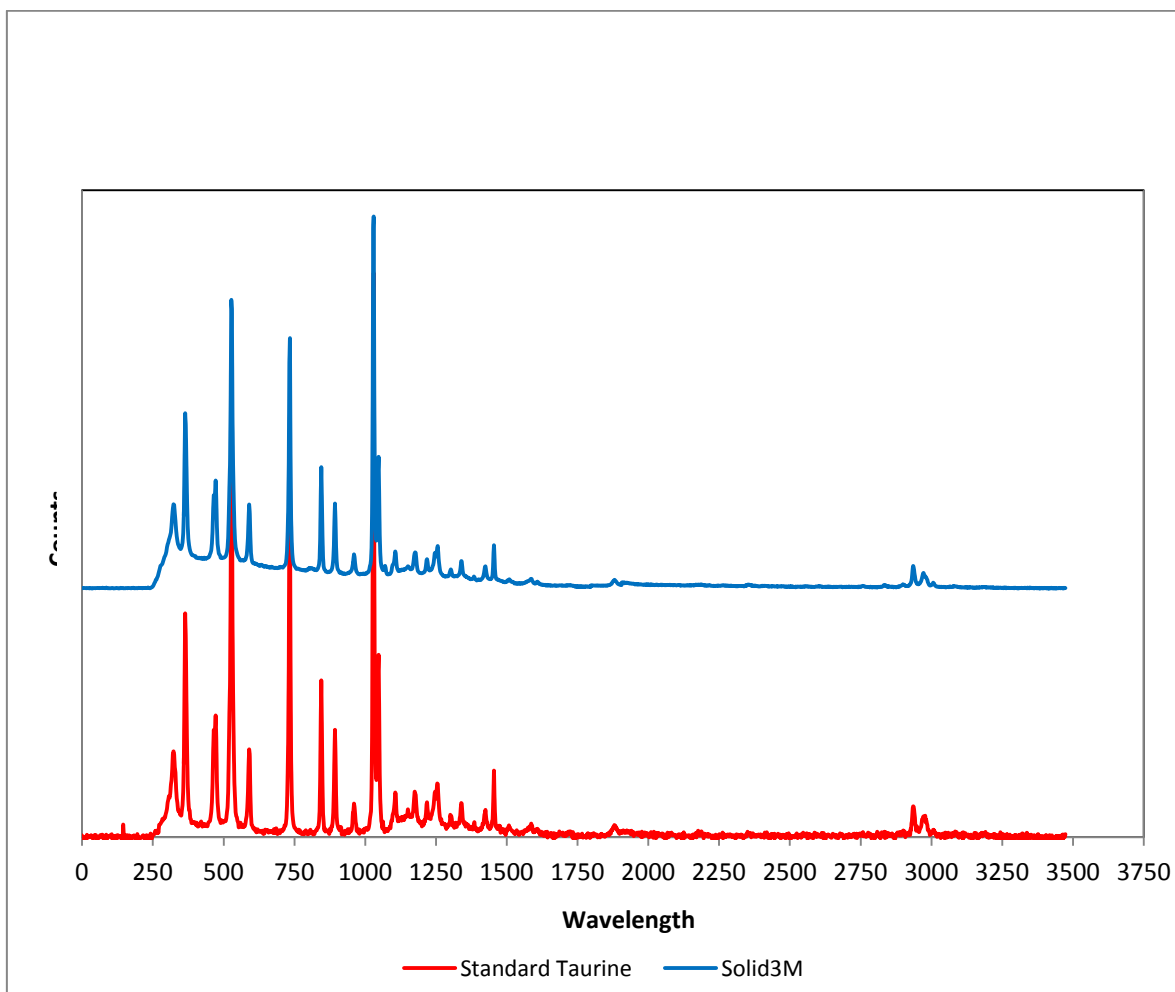


Figure 4.8. RAMAN Spectroscopy for standard taurine and the solid precipitated from 3M sodium taurate solution during CO₂ absorption

THERMODYNAMIC MODELING

The first purpose of these models is to understand the CO₂ capture process and the crystallization within it, based on the experimental data. The models predict the conditions that could not be obtained from the experimental works using *Crystalline* equipment, such as: the critical CO₂ loading at which crystallization starts; the composition of compounds at the equilibrium; and the final equilibrium of the reaction.

The second purpose is to investigate the benefit of crystallization to the CO₂ capture, especially to the amount of CO₂ can be absorbed in the solution (CO₂ loading) if the crystallization occurs. As previously explained in Chapter 2, it is expected that the crystallization of taurine from the solution during CO₂ capture increases the CO₂ loading because of the reaction equilibrium shift. The higher CO₂ loading allows the less amount of solvent to be used in the capture process so that it leads to the less energy usage for the CO₂ capture in the end.

The experimental works as discussed in Chapter 3 and Chapter 4 provided the data that can be used to develop the models to predict/explain the CO₂ capture process, especially at the equilibrium condition. Those data were used as the inputs as well as the constraint in calculation. The MATHCAD software was chosen to build the models by considering that this software is able to solve the non-linear problem with all positive roots. Hence, this software is appropriate to determine species in the equilibrium condition.

In this study, there are three important conditions to be defined: the solubility of taurine in the NaOH solution; the starting point of crystallization during CO₂ capture process; and the end point of CO₂ capture at which no more CO₂ can be absorbed by the solution.

Figure 5.1 depicts the main flowchart of the models. The experimental data (%NaOH and pH) as well as K-value (equilibrium constant) of Taurine are used as the inputs for the solubility model. The outputs of solubility model are used as the inputs in the starting point of crystallization model and the end point model.

To fit in with the experimental results, the models were built at the constant CO₂ pressure (1 bar). The temperature of process is to be chosen between 25 °C and 70 °C. This is the range in which the solubility of taurine was measured. In this work, the constant temperature of 30 °C was chosen. The reason was that at this constant temperature, all of investigated solution molarities (1M, 2M, 3M, and 4M) have the solubility point data. The only thing to be changed when the other temperature will be used in calculation is the equation to define the correlation between the solution

molarity and %NaOH at solubility line. Other than 30 °C, the available equations are for 40 °C, 50 °C and 60 °C.

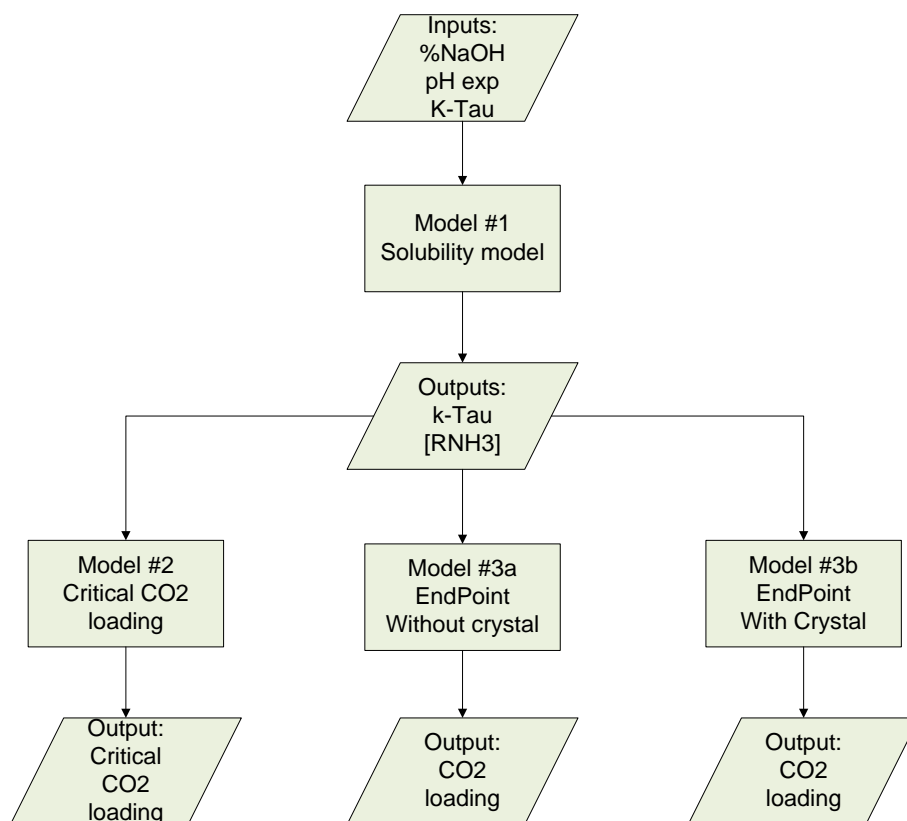


Figure 5.1. Flow chart of the equilibrium models.

5.1. The Models

To solve calculations in the models, the ideal solution approach was used. This approach was chosen with the following considerations:

- This approach makes the models to be simple and executable. The limitation in data availability (both experimental and literature) brings the consequence that the liquid phase non-ideality approach as proposed by Kumar et al. [6], which considers the activity coefficient of the components to define the equilibrium constant, could not be solved in this work.
- In the Kumar et al. work range, which is comparable to this work range, the change in ionic strength of the loaded amino acid salt is insignificant and the interaction parameters are neglected. Hence, the activity coefficients can be set to 1.

- c. The ideal solution approach (applied in the Kent-Eisenberg model) gives a well-fitted result in the CO₂ loading range of 0.2 – 0.7 mol CO₂ / mol amine. This CO₂ loading range is comparable to that of the range in this work.

As the effect of this ideality approach, the equations presented in Chapter 2 were modified to the equations as written in this section.

5.1.1. Solubility Model

The solubility model of taurine in the NaOH solution was developed in order to define the species in solution at the solubility point. It is important to define the amount of crystallizable species at this point in order to provide the calculation constrain in the next models. The other purpose is to determine the equilibrium dissociation constant of the protonated amine that was also used as the input in the next model.

The model utilized the reaction scheme as previously discussed in Chapter 2, as well as molar balance and charge balance as follows:

(1) Dissociation of water:

$$K_W = [H^+][OH^-] \quad (5.1)$$

(2) Dissociation of protonated amine:

$$K_{Tau} = \frac{[RNH_2][H^+]}{[RNH_3^+]} \quad (5.2)$$

(3) Charge balance:

$$[RNH_2] + [OH^-] = [H^+] + [Na^+] \quad (5.3)$$

(4) Taurine balance:

$$Total\ Taurine\ Molar = [RNH_2] + [RNH_3^+] \quad (5.4)$$

(5) Sodium species:

$$[Na^+] = \%NaOH * Total\ Taurine\ Molar \quad (5.5)$$

Therefore, there are 5 unknown variables:

$$[RNH_2], [RNH_3^+], [OH^-], [H^+], [Na^+] \quad (5.6)$$

As determined by Kumar et al., $[RNH_2]$ is the deprotonated amine, an anion with single negative charge. This component reacts with CO₂. Meanwhile, $[RNH_3^+]$ is the protonated amino acid. It is a zwitterion and is considered as electrically neutral. This compound is the species that can be precipitated from the solution.

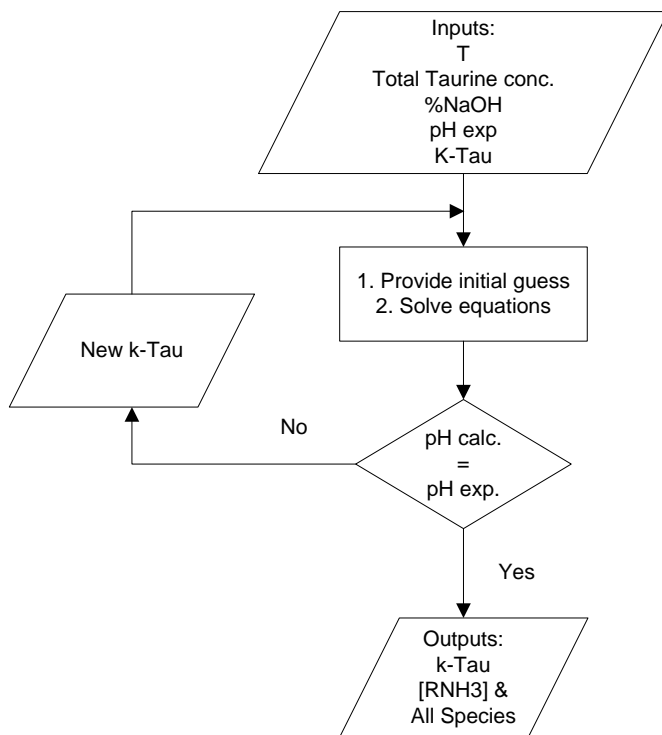


Figure 5.2. Flowchart of the solubility model.

The modeling flowchart as shown in Figure 5.2 describes the calculation procedure.

Inputs of this model are the total taurine concentration, the chosen temperature, %NaOH of the solubility point and the related pH, and the K-value (equilibrium constant of Taurine, K_{Tau}). %NaOH and pH is defined based on the data from the experimental works while K_{Tau} is determined arbitrarily for initial guess.

The final K_{Tau} is to be defined in the program loop based on the condition that the pH resulted from the calculation is equal to that of experimental result.

Amount of the protonated amine $[RNH_3^+]$ resulted from this model is the amount of this species in solubility point, or in other words, it is the maximum amount to be exist before precipitation occurs.

The MATHCAD listing of this model can be found in the Appendix B.

5.1.2. Critical CO₂ Loading Model

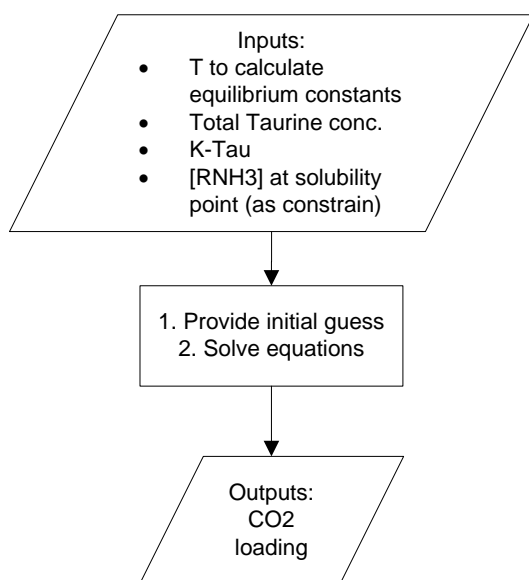


Figure 5.3. Flowchart of the critical CO₂ loading model

This model was built with the purpose to determine the critical CO₂ loading at which the precipitation/ crystallization starts. The result from this model is important to predict whether or not the crystallization occurs in the CO₂ capture using a certain molarity of sodium taurate at a certain temperature.

The K_{Tau} and $[RNH_3^+]$ that were resulted from the solubility model become the input for this model. $[RNH_3^+]$ becomes the constraint in the calculation.

Output of this model is the critical CO₂ loading which is calculated as total absorbed CO₂ (in any forms) divided by total taurine molarity (mol CO₂ / mol taurine).

The model is relatively a straight forward calculation with the flowchart as shown in Figure.5.3.

Chemical reactions utilized in this model are as the same as reactions presented in Chapter 2. The additional equations are molar balance of taurine and CO₂ and charge balance of species.

K-value for carbon hydroxide hydrolysis, bicarbonate dissociation and water dissociation are calculated from the empirical expressions given by Kent-Eisenberg as reported by Chakma et al. [17].

$$K_{CO_2} = \exp\left(-241.818 + \frac{298.253 * 10^3}{T} - \frac{148.528 * 10^6}{T^2} + \frac{332.648 * 10^8}{T^3} - \frac{282.394 * 10^{10}}{T^4}\right) \quad (5.7)$$

$$K_{HCO_3^-} = \exp\left(-294.74 + \frac{364.385 * 10^3}{T} - \frac{184.158 * 10^6}{T^2} + \frac{415.793 * 10^8}{T^3} - \frac{354.291 * 10^{10}}{T^4}\right) \quad (5.8)$$

$$K_W = \exp\left(39.5554 - \frac{987.9 * 10^2}{T} + \frac{568.828 * 10^5}{T^2} - \frac{146.451 * 10^8}{T^3} + \frac{136.146 * 10^{10}}{T^4}\right) \quad (5.9)$$

The Henry constant (in SI Unit = Pa.m³/mol) is calculated from:

$$K_H = \frac{\exp\left(22.2819 - \frac{138.306 * 10^2}{T} + \frac{691.346 * 10^4}{T^2} - \frac{155.895 * 10^7}{T^3} + \frac{120.037 * 10^9}{T^4}\right)}{7.50061} \quad (5.10)$$

The equilibrium constant for carbamate reaction is left out from the reaction scheme [6].

Equations (from the reaction):

(1)Carbon dioxide hydrolysis:

$$K_{CO_2} = \frac{[HCO_3^-][H^+]}{[CO_2]} \quad (5.11)$$

(2)Dissociation of bicarbonate:

$$K_{HCO_3^-} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (5.12)$$

(3) Dissociation of water:

$$K_W = [H^+][OH^-] \quad (5.13)$$

(4) Carbamate hydrolysis:

$$K_{Carbamate} = \frac{[RNH_2][HCO_3^-]}{[RNHCOO^-]} \quad (5.14)$$

(5) Dissociation of protonated amine:

$$K_{Tau} = \frac{[RNH_2][H^+]}{[RNH_3^+]} \quad (5.15)$$

(6) Amine balance:

$$[RNH_2]_{0,total} = [RNH_2] + [RNH_3^+] + [RNHCOO^-] \quad (5.16)$$

(7) CO₂ balance:

$$[CO_2]_{total} = [RNH_2]_{0,total} * [CO_2]_{Crit.Loading} = [CO_2] + [HCO_3^-] + [CO_3^{2-}] + [RNHCOO^-] \quad (5.17)$$

(8) Charge balance:

$$[Na^+] + [H^+] = [RNH_2] + [OH^-] + [HCO_3^-] + 2 * [RNHCOO^-] + 2 * [CO_3^{2-}] \quad (5.18)$$

According to Kumar et al.: [RNHCOO⁻] has two negative charges; the concentration of [Na⁺] is as the same as original concentration of taurine; [RNH₂] has a single negative charge; and [RNH₃⁺] is electrically neutral.

As the CO₂ pressure is constant at 1 bar, this pressure variable is not included as the unknown one. Hence, there are 8 unknowns left:

$$[CO_2], [H^+], [RNH_2], [OH^-], [HCO_3^-], [RNHCOO^-], [CO_3^{2-}], [CO_2]_{Loading}$$

The MATHCAD listing of this model can be found in Appendix B.

5.1.3. End Point Model

The end point model is intended to predict the equilibrium condition at which no more CO₂ can be absorbed (saturation). To what concerns of crystallization, there are two possibilities for the end point: no crystallization occurs or there is the crystal formed. Two models were built regarding these possibilities: the one that assumes that there is no crystallization and the other one that considers the crystallization. The benefit of crystallization during CO₂ capture process, which is represented by the maximum amount of CO₂ can be absorber, can be investigated using both models as well.

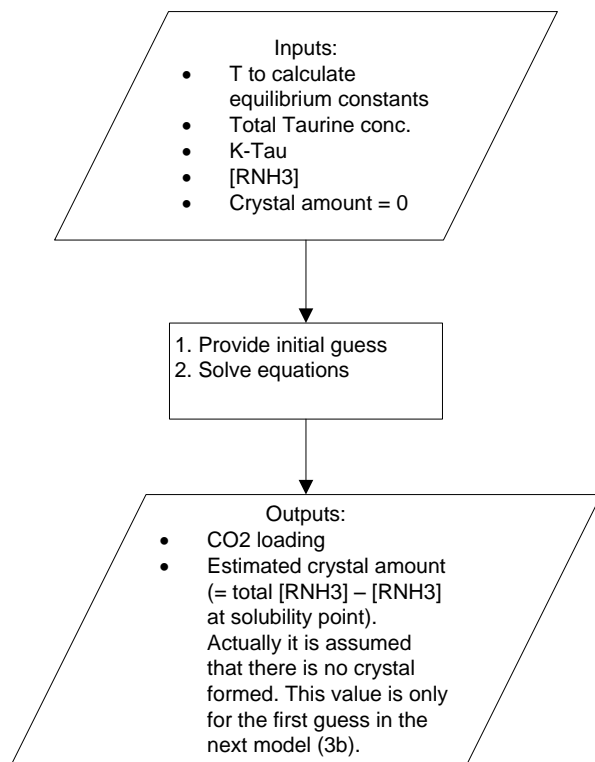


Figure.5.4. Flowchart of the end point model without crystallization

In the first end point model (without crystallization), the utilized equations are as the same as in critical CO₂ loading model. The differences are: the [RNH₃⁺] is not to be used as constraint but rather as one of species to be calculated; and the total amount of absorbed CO₂ is not a function of critical loading but rather the summation of all forms of CO₂ species in the solution.

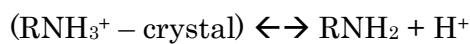
The partial pressure of CO₂ equation is as a function of Henry constant and CO₂ (liquid) concentration is also utilized.

The inputs are: temperature, total taurine molarity, K_{Tau} , and [RNH₃⁺]. The crystal amount is set to be zero, however, the dissociation protonated amine equation is already modified by including crystal amount into it.

The significant outputs are total CO₂ loading and estimated crystal amount that will be used as the first guess for the second model (with crystallization).

The modeling flowchart is shown in Figure 5.4. and the MATHCAD listing of this model can be found in Appendix B.

In the second model (with crystallization), the utilized equations are similar to that of the first model. The modification is on the dissociation of protonated amine equation as follow:



Hence, equation (5.11) should be modified as follow:

$$K_{Tau} = \frac{[\text{RNH}_2][\text{H}^+]}{[\text{RNH}_3^+ - [\text{Crystal}]]} \quad (5.19)$$

The other thing to do in this second model is giving the amount of crystal as initial guess iteratively. The given number of crystal should be equal to that of calculation result. Figure 5.5 shows the flowchart of this end point modeling. The significant outputs are total CO₂ loading and formed crystal amount.

The MATHCAD listing of this model can be found in Appendix B.

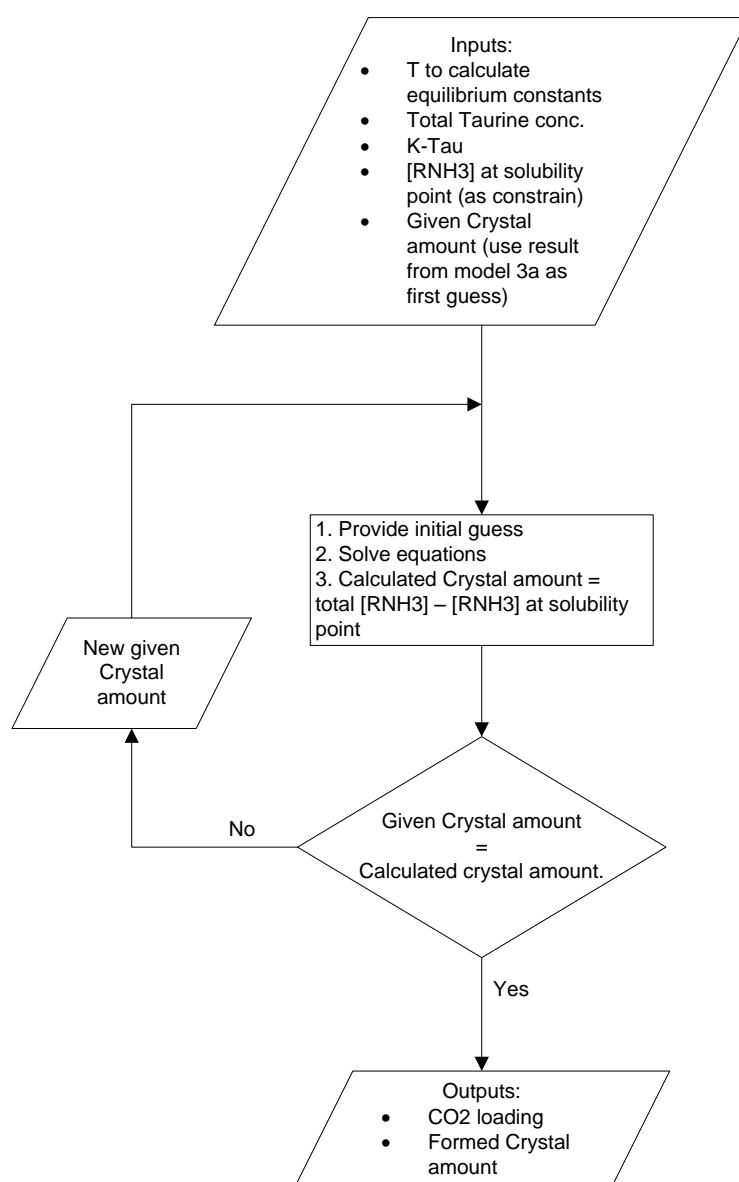


Figure.5.5. Flowchart of the end point model with crystallization

5.2. Modeling Result and Discussion

The models were performed for the investigated sodium taurate concentrations, which are 1M, 2M, 3M and 4M. The prediction on whether or not crystallization occurs is based on the amount of $[\text{RNH}_3^+]$ could be formed when the solution absorbed CO_2 . Crystallization is predicted to occur when the amount of $[\text{RNH}_3^+]$ at the end of the absorption process is higher than that of at solubility line.

Based on the results that are presented in the following subsections, it was predicted that there is no crystallization at 1M, while at 2M the crystallization occurs. Hence,

other than the calculation on 1M, 2M, 3M and 4M solution concentrations, the exact concentration at which crystallization starts was investigated as well. As there are no experimental works on the solution concentrations between 1M and 2M, the data from 1M concentration was used for the concentration close to 1M and data from 2M concentration was used for the concentration close to 2M.

In this study, the solution concentrations of 1.25M and 1.75M were investigated and the result was that the crystallization occurs for the minimum solution concentration of 1.25M. This result is different with that of crystallization experiment using *Crystalline* as discussed in Chapter 4, which is at 30 °C the minimum solution concentration that allows crystallization is 2M. This difference may be caused by the calculation method that used the closest concentration experimental data because the data at the same concentration were not available.

5.2.1. Solubility of Taurine in the NaOH Solution

Model calculations result in equilibrium constant for taurine at the different molarities. At 30 °C, the constants are in the range of 3.22×10^{-10} and 4.95×10^{-10} as shown in Figure 5.6. For the comparison, in potassium taurate solution, Kumar et al. [6] provided the value from the equilibrium data fitting of 1.18×10^{-9} (mol/liter) for 1M solution and 9.05×10^{-10} (mol/liter) for 2 M solution at 298 K (25 °C).

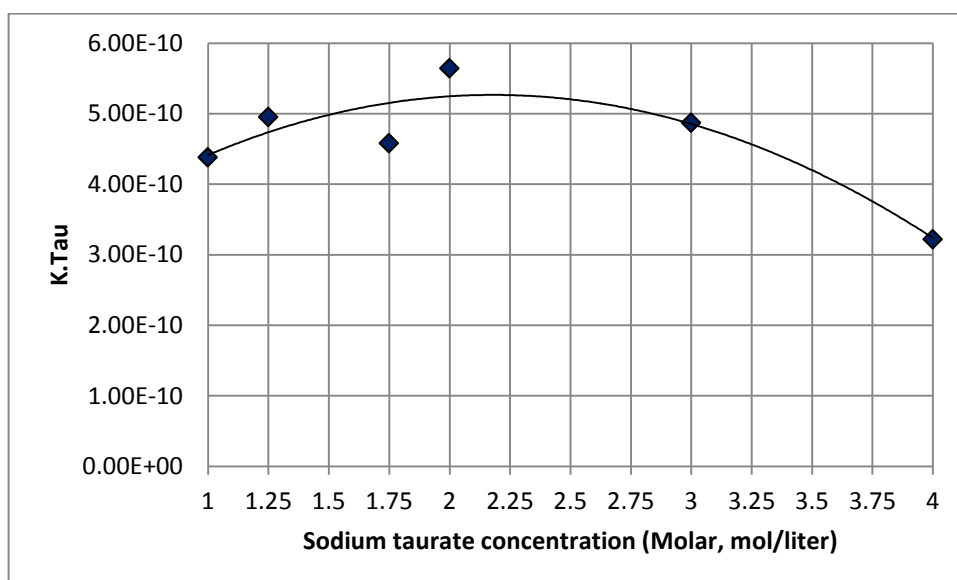


Figure.5.6. Taurine equilibrium constant (K_{Tau}) in sodium taurate solution. (the continuous line is the regressed trend of data)

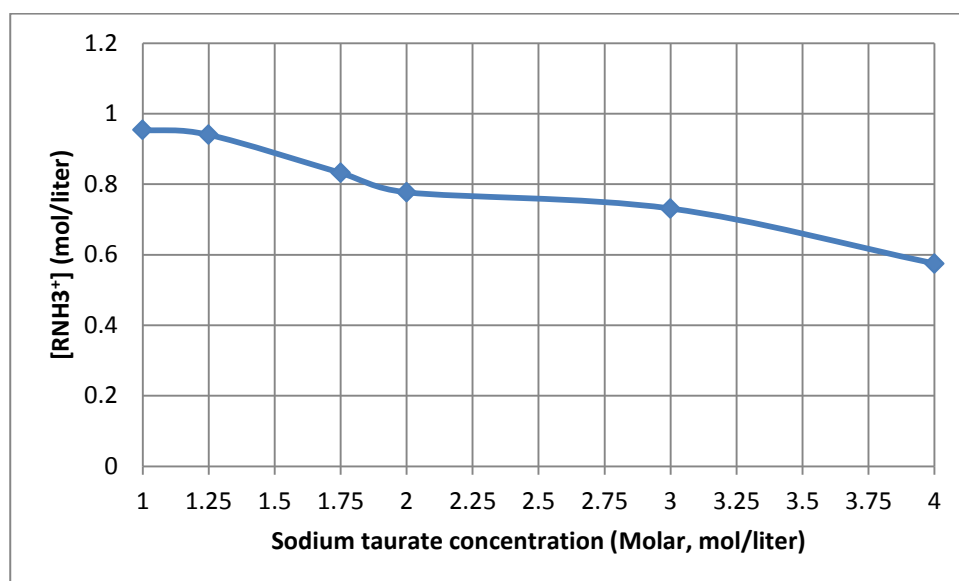


Figure.5.7. [RNH₃⁺] content (mol/liter) at solubility line for various concentration of sodium taurate solution.

Figure 5.7. shows the solubility line of taurine in sodium taurate solution that is represented by the amount of [RNH₃⁺]. This graph reflects that in the higher concentration solution, crystallization seemed to be started earlier as it needs the lower amount of protonated taurine to be formed. This statement is to be proved by the critical CO₂ loading model.

5.2.2. Critical CO₂ Loading

As shown in Figure 5.8, the crystallization occurs at the lower CO₂ loading for the higher solution concentration. It means that the crystallization start earlier for the higher solution concentration. The graph is started from 1.25M, the lowest solution concentration at which crystallization occurs based on the model calculation. Although these results are not exactly the same, they are comparable to that of Kumar et al. [5] (as shown in Figure 5.9) that presented the similar patterns (that the higher solution concentration needs the lower CO₂ loading to start crystallization). As shown in Figure 5.9, the 1.98 mol/liter solution starts crystallization at CO₂ loading of 0.45 mol CO₂/mol amino acid, while the 2.88 mol/liter solution starts crystallization at CO₂ loading of 0.3 mol CO₂/mol amino acid.

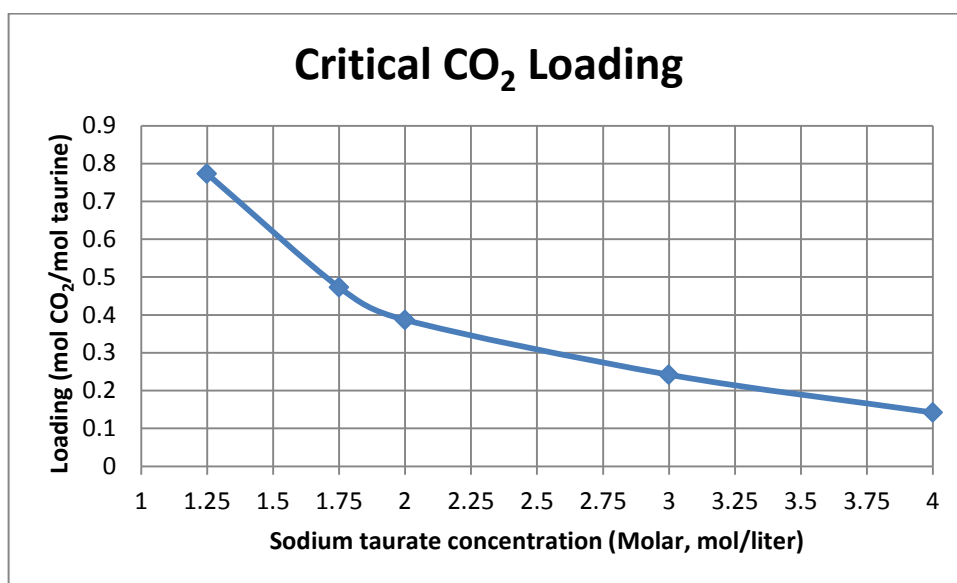


Figure.5.8. Critical CO₂ loading for the different sodium taurate concentrations.

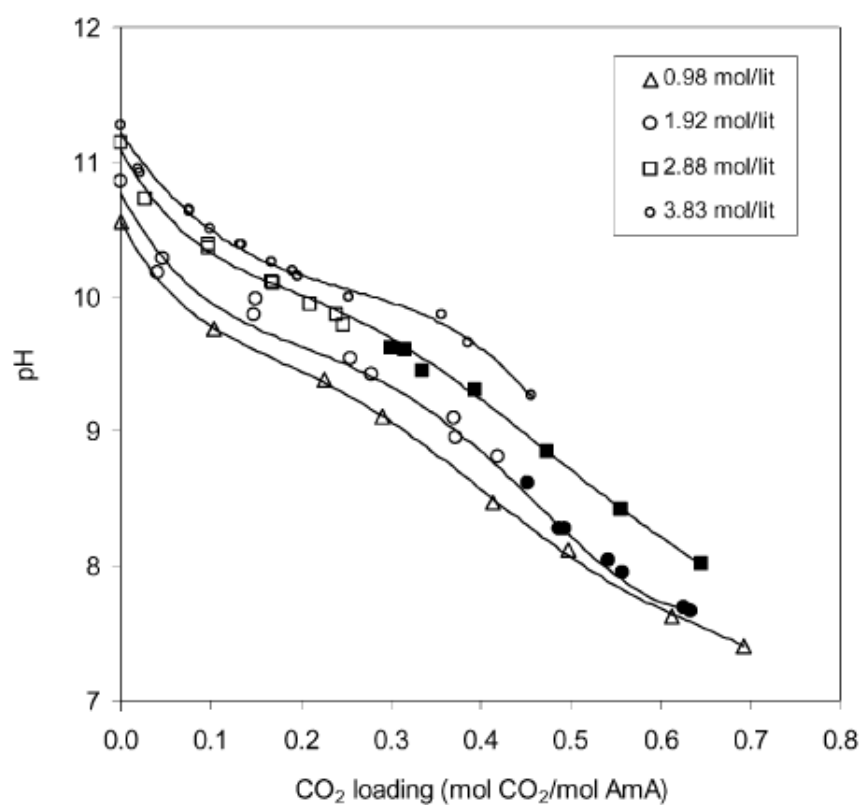


Figure.5.9. Effect of CO₂ loading on the pH of the aqueous potassium salt of taurine (at 298 K). The dark points in the figure denote the presence of solids in the solution [5]

5.2.3. End Point of CO₂ Capture

In this end point model, two conditions of with and without crystallization were applied to investigate the maximum CO₂ loading can be achieved at the end of process (final equilibrium) in both assumptions. Figure 5.10 shows that by considering crystallization during CO₂ capture, the maximum CO₂ loading is higher than that without considering crystallization. The CO₂ loading difference is about 6.6% for 2M solution concentration and it goes up to 10.9% for 3 M and 17.2% for 4M. These numbers reflect that the better benefit of crystallization is obtained at higher concentration, in the CO₂ loading point of view. This result supports the previous studies of Hook [13] as well as Kumar et al.[5][6], and the DECAB patent by Versteeg et al. [3] as discussed in Chapter 2. These authors predicted the benefit of this crystallization based on the principle that the selective removal of reaction product from the reaction mixture will shift the equilibrium toward product side, which is in this case, the crystallization of protonated taurine during CO₂ capture makes more CO₂ can be absorbed.

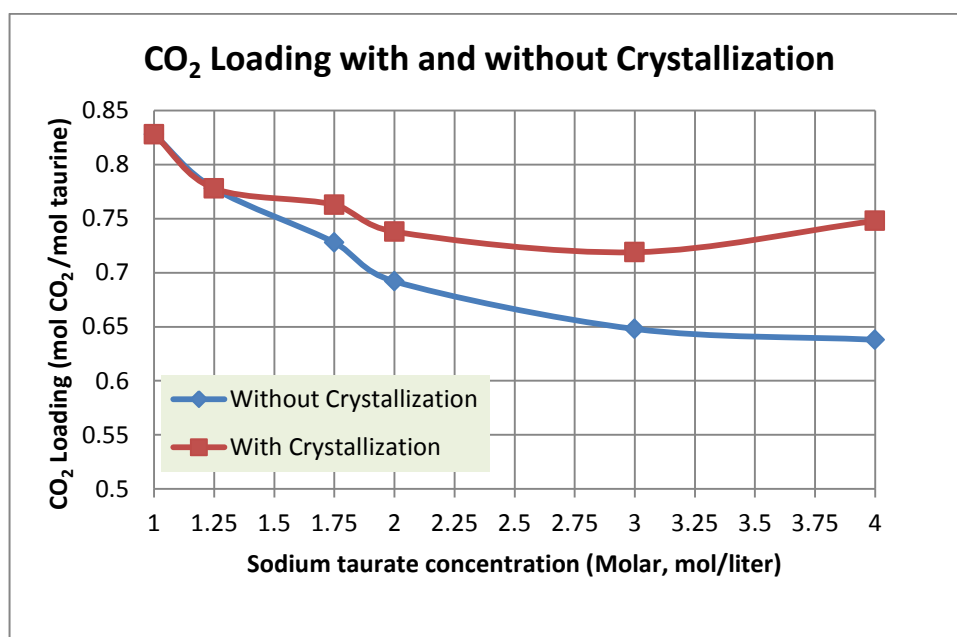


Figure 5.10. End point CO₂ loading with and without considering crystallization occurrence during CO₂ capture.

5.3. Cohesiveness between the Experiment Results and the Thermodynamic Models

The solubility of taurine in NaOH solution data obtained from the experiment have been used to understand the CO₂ capture process through the thermodynamic models. These data, especially the pH, help the models to define a constraint so that they can

determine the important variables (equilibrium constants, compound species) and to produce the reasonable results compared to that of previous work (Kumar et al.'s work).

Crystallization experiment confirmed that the crystallization during CO₂ capture using sodium taurate solution is likely to occur at a relatively high solution concentration and lower temperature. This condition was found in the modeling result as well. Even though the crystallization occurs at lower solution concentration compared to that of *Crystalline* result, they showed the same pattern that the higher solution concentration gives a better chance for crystallization. It is reflected by the lower CO₂ loading needed to start the crystallization.

RAMAN spectroscopy measurement, which showed that taurine is the precipitated solid from the CO₂ capture, assured that this species is the only one to be considered as crystal product in the models.

From the explanation above, it can be concluded that the experimental works provide the sufficient data and support to the thermodynamic models in this study.

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The experimental works has provided the data of taurine solubility in a taurine-NaOH-water solution and the crystal formation zone (solution concentration and temperature) during CO₂ absorption in that solution. These data were used to build the models that help one to understand the CO₂ capture process, the crystallization phenomena during the process, and to investigate the benefit of crystallization in this capturing process.

The following conclusions can be drawn from the both of experimental works and the models in this thesis:

1. In a system of Taurine–NaOH–water, a decrease in pH due to less NaOH portion decreases the solubility of Taurine in the solution.
2. CO₂ absorption by sodium taurate solution decreases the pH and increases the amount of [RNH₃⁺] in the solution. The crystallization of taurine occurs when the amount of [RNH₃⁺] exceeds its maximum point of solubility.
3. Crystallization occurs at a relatively high molarity of sodium taurate. The higher the molarity, the lower the CO₂ loading needed for precipitation to occur.
4. The temperature during capturing process affects the crystallization, especially for a lower solution concentration. For example, for 2 M solution that did not experience crystallization at 40 °C during CO₂ capture, the lower temperature (35 °C) allows the crystallization to occur. It is because of lower taurine solubility at a lower temperature.
5. RAMAN spectroscopy showed that the precipitated solid was taurine. This is consistent with the result of previous study by Kumar et al. and Majchrowics et al.
6. Crystallization of taurine during the CO₂ capture process increases the CO₂ loading, because crystallization shifts the reaction to the product side so that more CO₂ needs to be reacted with the deprotonated amine. It is a benefit for the process because fewer amounts (mass) of material should be circulated in the system. This condition leads to lower energy usage and lower operational cost.

6.2. Recommendations

The experimental works and the models have given some results as presented in the previous chapters and has been concluded above. Some recommendations are given hereunder for the improvement in the future works regarding CO₂ capture using sodium taurate or any related subject.

1. The experimental works and the models of this thesis show that crystallization occurs at a relatively high solution concentration and low temperature. According to the model results as well as to the works of some authors mentioned in this report, this crystallization results in the higher CO₂ absorption. Regarding this benefit, using the experimental method and the models of this thesis, the subject of the study can be extended to the investigation on the optimum solution concentration and temperature for the CO₂ capture using sodium taurate.
2. The use of 1M, 2M, 3M and 4M samples in the solubility experiments in this work was sufficient to provide the data to develop the thermodynamic model. However, for one who will need to carry out the similar works, it is recommended to do the experiment with the narrower difference of molarity to have a better accuracy. A more precise experimental data will help one to get the more accurate modeling result.
3. Study on the CO₂ capture using the real flue gas rather than pure CO₂ gas will be so challenging but worth to do in order to have the almost-real situation. This kind of set will help one to understand the benefit of crystallization in the real post combustion CO₂ capture.

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APPENDIX A

EXPERIMENTAL RESULTS

A.1. Sample Preparation Calculation for *Crystal16* Experiment

Note: Taurine and NaOH units are in gram, water unit is in cm³.

Reactor	Molar	vial#											
		1			2			3			4		
		Taurine	NaOH 100%	water	Taurine	NaOH 87.5%	water	Taurine	NaOH 75%	water	Taurine	NaOH 62.5%	water
A	4	0.497	0.160	0.638	0.497	0.140	0.638	0.497	0.120	0.638	0.497	0.100	0.638
		Taurine	NaOH 50%	water	Taurine	NaOH 35%	water	Taurine	NaOH 20%	water	Taurine	NaOH 0%	water
B	4	0.497	0.080	0.638	0.497	0.056	0.638	0.497	0.032	0.638	0.497	0.000	0.638
		Taurine	NaOH 100%	water	Taurine	NaOH 87.5%	water	Taurine	NaOH 75%	water	Taurine	NaOH 62.5%	water
C	3	0.372	0.120	0.729	0.372	0.105	0.729	0.372	0.090	0.729	0.372	0.075	0.729
		Taurine	NaOH 50%	water	Taurine	NaOH 35%	water	Taurine	NaOH 20%	water	Taurine	NaOH 0%	water
D	3	0.372	0.060	0.729	0.372	0.042	0.729	0.372	0.024	0.729	0.372	0.000	0.729
		Taurine	NaOH 100%	water	Taurine	NaOH 87.5%	water	Taurine	NaOH 75%	water	Taurine	NaOH 62.5%	water
A	2	0.248	0.080	0.819	0.248	0.070	0.819	0.248	0.060	0.819	0.248	0.050	0.819
		Taurine	NaOH 50%	water	Taurine	NaOH 35%	water	Taurine	NaOH 20%	water	Taurine	NaOH 0%	water
B	2	0.248	0.040	0.819	0.248	0.028	0.819	0.248	0.016	0.819	0.248	0.000	0.819
		Taurine	NaOH 100%	water	Taurine	NaOH 87.5%	water	Taurine	NaOH 75%	water	Taurine	NaOH 62.5%	water
C	1	0.124	0.040	0.910	0.124	0.035	0.910	0.124	0.030	0.910	0.124	0.025	0.910
		Taurine	NaOH 50%	water	Taurine	NaOH 35%	water	Taurine	NaOH 20%	water	Taurine	NaOH 0%	water
D	1	0.124	0.020	0.910	0.124	0.014	0.910	0.124	0.008	0.910	0.124	0.000	0.910

A.2. Clear Point of Taurine-NaOH-water solution at NaOH composition variation
(Crystal16 experiment)

Experiment Name	Molarity	NaOH %	pH	Temperature [°C]
NaTauratePHeffect1MD	1	20	8.62	26.2
NaTauratePHeffect1MD	1	20	8.62	27
NaTauratePHeffect1MD	1	35	8.97	18.7
NaTauratePHeffect1MD	1	35	8.97	19.6
NaTauratePHeffect2MB	2	20	8.96	52.9
NaTauratePHeffect2MB	2	20	8.96	54.1
NaTauratePHeffect2MB	2	20	8.96	55
NaTauratePHeffect2MB	2	35	9.19	46.4
NaTauratePHeffect2MB	2	35	9.19	46.5
NaTauratePHeffect2MB	2	35	9.19	47.3
NaTauratePHeffect2MB	2	50	9.36	35.7
NaTauratePHeffect2MB	2	50	9.36	36.4
NaTauratePHeffect2MB	2	50	9.36	37.2
NaTauratePHeffect2MA	2	62.5	9.52	26.4
NaTauratePHeffect2MA	2	62.5	9.52	27.2
NaTauratePHeffect2MA	2	62.5	9.52	27.5
NaTauratePHeffect2MA	2	75	9.61	15.2
NaTauratePHeffect2MA	2	75	9.61	15.6
NaTauratePHeffect3MD-2	3	35	9.42	65.8
NaTauratePHeffect3MD-2	3	35	9.42	66.3
NaTauratePHeffect3MD	3	50	9.71	57.3
NaTauratePHeffect3MD	3	50	9.71	58.2
NaTauratePHeffect3MD-2	3	50	9.71	58.1
NaTauratePHeffect3MD-2	3	50	9.71	58.2
NaTauratePHeffect3MD-2	3	50	9.71	59.1
NaTauratePHeffect3MC	3	62.5	9.82	47.4
NaTauratePHeffect3MC	3	62.5	9.82	49.2
NaTauratePHeffect3MC-2	3	62.5	9.82	47.2
NaTauratePHeffect3MC-2	3	62.5	9.82	49.5
NaTauratePHeffect3MC-2	3	62.5	9.82	51.1
NaTauratePHeffect3MC	3	75	9.94	35.6
NaTauratePHeffect3MC	3	75	9.94	35.7
NaTauratePHeffect3MC-2	3	75	9.94	36.3
NaTauratePHeffect3MC-2	3	75	9.94	36.8
NaTauratePHeffect3MC-2	3	75	9.94	38.7
NaTauratePHeffect3MC	3	87.5	9.98	25.5
NaTauratePHeffect3MC	3	87.5	9.98	25.7
NaTauratePHeffect3MC-2	3	87.5	9.98	31.8
NaTauratePHeffect3MC-2	3	87.5	9.98	32.7
NaTauratePHeffect4MA-2	4	62.5	10.01	67.1
NaTauratePHeffect4MA-2	4	62.5	10.01	69.7
NaTauratePHeffect4MA	4	75	10.17	50.4
NaTauratePHeffect4MA	4	75	10.17	53.6
NaTauratePHeffect4MA-2	4	75	10.17	50.7
NaTauratePHeffect4MA-2	4	75	10.17	52
NaTauratePHeffect4MA-2	4	75	10.17	53.4
NaTauratePHeffect4MA	4	87.5	10.28	28.3
NaTauratePHeffect4MA	4	87.5	10.28	29.1

NaTauratePHeffect4MA-2	4	87.5	10.28	28.9
NaTauratePHeffect4MA-2	4	87.5	10.28	29.7
NaTauratePHeffect4MA-2	4	87.5	10.28	30.9

A.3. pH Measurement of *Crystal16* Samples

Experiment Molarity	Vial	NaOH % *	pH
4	A 1	100	10.431
4	A 2	87.5	10.276
4	A 3	75	10.172
4	A 4	62.5	10.009
4	B 1	50	9.883
4	B 2	35	9.635
4	B 3	20	9.379
4	N/ A	15	9.329
4	N/ A	10	9.017
4	N/ A	5	8.775
4	B 4	0	4.923
3	C 1	100	10.534
3	C 2	87.5	9.981
3	C 3	75	9.942
3	C 4	62.5	9.82
3	D 1	50	9.709
3	D 2	35	9.416
3	D 3	20	9.222
3	N/ A	15	9.064
3	N/ A	10	8.919
3	N/ A	5	8.556
3	D 4	0	5.428

Experiment Molarity	Vial	NaOH % *	pH
2	A 1	100	10.48
2	A 2	87.5	9.851
2	A 3	75	9.614
2	A 4	62.5	9.517
2	B 1	50	9.356
2	B 2	35	9.186
2	B 3	20	8.961
2	N/ A	15	8.754
2	N/ A	10	8.474
2	N/ A	5	8.353
2	B 4	0	5.851
1	C 1	100	10.636
1	C 2	87.5	9.824
1	C 3	75	9.386
1	C 4	62.5	9.362
1	D 1	50	9.077
1	D 2	35	8.968
1	D 3	20	8.662
1	N/ A	15	8.563
1	N/ A	10	8.269
1	N/ A	5	8.099
1	D 4	0	6.241

APPENDIX B

THERMODYNAMIC MODELS

This Appendix B contains the calculation results summary and MATHCAD code listings. Considering the concision of this report and that all molarities have the similar models, only the listing of 2 Molar's models and the models to define the minimum molarity where crystallization may occur are presented in this report.

B.1. Calculation results summary.

Absorption Pressure: 1 bar

Temperature: 30 °C (303 K)

A. Solubility Model Calculation Result (NaOH-Taurine-Water system)

Note: 1.25M calculation is based on 1 M experimental data
1.75M calculation is based on 2 M experimental data

Molar (M)	1	1.25	1.75	2	3	4
K.Taurine	4.38E-10	4.95E-10	4.58E-10	5.64E-10	4.87E-10	3.22E-10
pH	8.046	8.823	9.381	9.446	9.804	10.267
Species (mol/liter):						
[RNH ₂]	0.046	0.31	0.918	1.223	2.269	3.425
[RNH ₃ ⁺]	0.954	0.94	0.832	0.777	0.731	0.575
[OH ⁻]	1.65E-06	9.86E-06	3.57E-05	4.14E-05	9.45E-05	2.74E-04
[H ⁺]	9.00E-09	1.50E-09	4.16E-10	3.58E-10	1.57E-10	5.40E-11
[Na ⁺]	0.046	0.31	0.918	1.223	2.269	3.426

B. Critical CO₂ Loading Model Calculation Result

Molar (M)	1	1.25	1.75	2	3	4
Species (mol/liter):						
[RNH ₃ ⁺]	0.954	0.94	0.832	0.777	0.731	0.575
[CO ₂]	0.331	0.028	4.56E-04	1.10E-04	9.76E-06	1.19E-06
[HCO ₃ ⁻]	0.91	0.648	0.14	0.065	0.021	9.20E-03
[CO ₃ ²⁻]	2.62E-04	1.55E-03	4.49E-03	4.02E-03	4.92E-03	7.45E-03
[RNH ₂]	2.31E-03	0.021	0.235	0.519	1.569	2.874
[RNHCOO ⁻]	0.044	0.289	0.683	0.704	0.7	0.551
[OH ⁻]	8.18E-08	6.81E-07	9.13E-06	1.76E-05	6.54E-05	2.30E-04
[H ⁺]	1.81E-07	2.18E-08	1.62E-09	8.44E-10	2.27E-10	6.44E-11
Loading	1.285	0.773	0.473	0.387	0.242	0.142
P.CO2	1.00E+05	1.00E+05	1.00E+05	1.00E+05	1.00E+05	1.00E+05
Total CO2	1.285	0.973	0.828	0.773	0.726	0.567

[RNH₃⁺] is the calculation constrain and it is the fixed value in the calculation.

B.1. Calculation results summary (continue).

C. End Point Model Calculation Result

a. Without crystallization

Molar	1	1.25	1.75	2	3	4
Species (mol/liter):						
[CO ₂]	0.03	0.03	0.03	0.03	0.03	0.03
[HCO ₃ ⁻]	0.612	0.657	0.767	0.748	0.883	1.108
[CO ₃ ²⁻]	1.33E-03	1.53E-03	2.08E-03	1.98E-03	2.76E-03	4.34E-03
[RNH ₂]	0.015	0.021	0.03	0.039	0.056	0.061
[RNH ₃ ⁺]	0.8	0.944	1.246	1.357	1.916	2.528
[RNHCOO ⁻]	0.185	0.285	0.474	0.605	1.028	1.411
[OH ⁻]	6.15E-07	6.60E-07	7.71E-07	7.52E-07	8.88E-07	1.11E-06
[H ⁺]	2.41E-08	2.25E-08	1.92E-08	1.97E-08	1.67E-08	1.33E-08
Total CO ₂	0.828	0.973	1.273	1.384	1.943	2.553
CO ₂ loading	0.828	0.778	0.728	0.692	0.648	0.638

b. With crystallization

Molar	1	1.25	1.75	2	3	4
RNH ₃ constrain	0.954	0.94	0.832	0.777	0.731	0.575
Species (mol/liter):						
[CO ₂]	0.03	0.03	0.03	0.03	0.03	0.03
[HCO ₃ ⁻]	0.612	0.657	0.883	0.919	1.288	1.952
[CO ₃ ²⁻]	1.33E-03	1.53E-03	2.76E-03	2.99E-03	5.87E-03	0.013
[RNH ₂]	0.015	0.021	0.023	0.027	0.031	0.025
[RNH ₃ ⁺] _{tot}	0.8	0.944	1.308	1.449	2.134	2.977
[RNHCOO ⁻]	0.185	0.285	0.419	0.524	0.835	0.998
[OH ⁻]	6.15E-07	6.60E-07	8.88E-07	9.25E-07	1.30E-06	1.96E-06
[H ⁺]	2.41E-08	2.25E-08	1.67E-08	1.60E-08	1.15E-08	7.55E-09
Total CO ₂	0.828	0.973	1.335	1.476	2.158	2.994
CO ₂ loading	0.828	0.778	0.763	0.738	0.719	0.748

based on "without crystal" because [RNH₃⁺] total =< [RNH₃⁺] constrain

B.2. Solubility model for 2 Molar NaOH-Taurine water system at 30 °C.

Solubility Model

2 Molar at 30 C

Na Taurate equilibrium calculations

$$T := 30 \text{ [K]}$$

[mol/l] Equilibrium constant of water dissociation

$$k_{H_2O} := \exp \left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4} \right) = 1.482 \times 10^{-14}$$

$$k_{AmA} := 5.64 \cdot 10^{-10} \quad \text{[mol/l] Equilibrium constant of Taurine deprotonation (to be fixed)}$$

Manipulating variables

$$y := 2 \quad \text{[mol/l] Initial Taurine Concentration}$$

$$xNa := 6.2619y^3 - 58.592y^2 + 188.46y - 131.49 = 61.157 \quad \text{\%NaOH from solubility profile}$$

$$pHControl := 7 \cdot 10^{-6} \cdot xNa^3 - 0.0011xNa^2 + 0.0646xNa + 8.0087 = 9.446 \quad \text{pH from Measurement}$$

Initial values variables (mol/l)

$$RNH_2 := 0.001y = 2 \times 10^{-3} \quad RNH_3 := 0.5y = 1$$

$$OH := 1 \times 10^{-7} \quad Hplus := 1 \times 10^{-7}$$

$$Na := y$$

Given

$$\log(k_{H_2O}) = \log(Hplus) + \log(OH)$$

$$\log(k_{AmA}) + \log(RNH_3) = \log(RNH_2) + \log(Hplus)$$

$$\log(RNH_2 + OH) = \log(Hplus + Na)$$

$$\log(RNH_2 + RNH_3) = \log(y)$$

$$\log(Na) = \log\left(\frac{xNa}{100}\right) + \log(y)$$

$\text{sol} := \text{Find}(\text{RNH}_2, \text{RNH}_3, \text{OH}, \text{Hplus}, \text{Na})$

sol =

	0
0	1.223
1	0.777
2	$4.138 \cdot 10^{-5}$
3	$3.582 \cdot 10^{-10}$
4	1.223

RNH2

~~~~~

RNH3

~~~~~

OH

~~~~~

Hplus

~~~~~

Na

~~~~~

:= sol

$\text{pH} := -\log(\text{Hplus})$

$\text{pH} = 9.446$  [Calculation result]

$\text{pOH} := -\log(\text{OH}) = 4.383$

$\text{pKw} := \text{pH} + \text{pOH} = 13.829$

B.3. Solubility model to define the minimum crystallization molar based on 2 Molar NaOH-Taurine water system at 30 °C.

### Solubility Model

To find ? Molar at 30 C, based on 2M data

Na Taurate equilibrium calculations

$$T := 30 \text{ [K]}$$

[mol/l] Equilibrium constant of water dissociation

$$k_{H_2O} := \exp \left( 39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4} \right) = 1.482 \times 10^{-14}$$

$$k_{AmA} := 4.58 \cdot 10^{-10} \quad \text{[mol/l] Equilibrium constant of Taurine deprotonation (to be fixed)}$$

Manipulating variables

$$y := 1.7 \quad \text{[mol/l] Initial Taurine Concentration}$$

$$xNa := 6.2619y^3 - 58.592y^2 + 188.46y - 131.49 = 52.437 \quad \text{\%NaOH from solubility profile}$$

$$pHControl := 7 \cdot 10^{-6} \cdot xNa^3 - 0.0011xNa^2 + 0.0646xNa + 8.0087 = 9.381 \quad \text{pH from Measurement (from 2M)}$$

Initial values variables (mol/l)

$$RNH_2 := 0.003y = 3.5 \times 10^{-3} \quad RNH_3 := 0.5y = 0.875$$

$$OH := 1 \times 10^{-7} \quad Hplus := 1 \times 10^{-7}$$

$$Na := y$$

Given

$$\log(k_{H_2O}) = \log(Hplus) + \log(OH)$$

$$\log(k_{AmA}) + \log(RNH_3) = \log(RNH_2) + \log(Hplus)$$

$$\log(RNH_2 + OH) = \log(Hplus + Na)$$

$$\log(RNH_2 + RNH_3) = \log(y)$$

$$\log(Na) = \log\left(\frac{xNa}{100}\right) + \log(y)$$



$$\text{sol} := \text{Find}(\text{RNH}_2, \text{RNH}_3, \text{OH}, \text{Hplus}, \text{Na})$$

sol =

|   |                        |
|---|------------------------|
|   | 0                      |
| 0 | 0.918                  |
| 1 | 0.832                  |
| 2 | $3.568 \cdot 10^{-5}$  |
| 3 | $4.155 \cdot 10^{-10}$ |
| 4 | 0.918                  |

RNH2

~~~~~

RNH3

~~~~~

OH

~~~~~

Hplus

~~~~~

Na

~~~~~

:= sol

$$\text{pH} := -\log(\text{Hplus})$$

$$\text{pH} = 9.381 \qquad \text{[Calculation result]}$$

$$\text{pOH} := -\log(\text{OH}) = 4.448$$

$$\text{pKw} := \text{pH} + \text{pOH} = 13.829$$

B.4. Critical CO₂ loading model for 2 Molar sodium taurate solution at 30 °C.

Critical CO₂ loading model

2 Molar at 30 C

$$T := 30 \text{ [K]}$$

Based on Kent-Eisenberg henry constant and equilibrium constants equations

Henry constant [Pa.m³/mol]

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \text{ [Pa.m}^3\text{/mol]}$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \text{ [Pa.l/mol]}$$

[mol/l] Equilibrium constant of CO₂ and H₂O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \text{ [mol/l] Equilibrium constant of carbamate hydrolysis (from Kumar et al.)}$$

$$k_5 := 5.64 \times 10^{-10} \text{ [mol/l] Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 2$ [mol/l] Added Taurine species

$Na := y = 2$ [mol/l] Added Na

$RNH3 := 0.77$

Initial values variables (mol/l)

$CO2 := 1 \cdot 10^{-5}$ $CO3 := 1 \cdot 10^{-6}$ $HCO3 := 1 \cdot 10^{-7}$

$RNH2 := y = 2$ $RNHCOO := 0.1 \cdot y = 0.2$

$OH := 1 \times 10^{-7}$ $Hplus := 1 \times 10^{-7}$

$P_{CO2} := 10^5$ $Loading := 0.2$ [molCO2/molTaurine]

Given

$$\log(P_{CO2}) = \log(CO2) + \log(k_H)$$

$$\log(k_1) + \log(CO2) = \log(HCO3) + \log(Hplus)$$

$$\log(k_2) + \log(HCO3) = \log(CO3) + \log(Hplus)$$

$$\log(k_3) = \log(Hplus) + \log(OH)$$

$$\log(k_4) + \log(RNHCOO) = \log(RNH2) + \log(HCO3)$$

$$\log(k_5) + \log(RNH3) = \log(RNH2) + \log(Hplus)$$

$$\log(CO2 + HCO3 + CO3 + RNHCOO) = \log(y \cdot Loading)$$

$$\log(RNH2 + RNH3 + RNHCOO) = \log(y)$$

$$\log(RNH2 + HCO3 + 2 \cdot CO3 + 2 \cdot RNHCOO + OH) = \log(Hplus + Na)$$

```
sol := Find(CO2,HCO3,CO3,RNH2,RNHCOO,OH,Hplus>Loading)
```

sol =

	0
0	1.104·10 ⁻⁴
1	0.065
2	4.022·10 ⁻³
3	0.519
4	0.704
5	1.756·10 ⁻⁵
6	8.441·10 ⁻¹⁰
7	0.387

CO2

HCO3

CO3

RNH2

RNHCOO

OH

Hplus

Loading

:= sol

RNH3 = 0.777

pH := -log(Hplus)

pH = 9.074

pOH := -log(OH) = 4.755

pKw := pH + pOH = 13.829

$P_{CO2} = 1 \times 10^5$

[Pa]

CO2sum:= CO2+ HCO3+ CO3+ RNHCOO= 0.773

TaurineSum:= RNH2+ RNH3+ RNHCOO= 2

B.5. Critical CO₂ loading model to define the minimum crystallization molar based on 2 Molar sodium taurate solution at 30 °C.

Critical CO₂ loading model

To find ? Molar at 30 C, based on 2M data

$$T := 30 \text{ [K]}$$

Based on Kent-Eisenberg henry constant and equilibrium constants equations

Henry constant [Pa.m³/mol]

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \text{ [Pa.m}^3\text{/mol]}$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \text{ [Pa.l/mol]}$$

[mol/l] Equilibrium constant of CO₂ and H₂O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \text{ [mol/l] Equilibrium constant of carbamate hydrolysis (from Kumat et al.)}$$

$$k_5 := 4.58 \times 10^{-10} \text{ [mol/l] Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 1.75$ [mol/l] Added Taurine species

$Na := y = 1.75$ [mol/l] Added Na

$RNH3 := 0.83$

Initial values variables (mol/l)

$CO2 := 1 \cdot 10^{-4}$ $CO3 := 1 \cdot 10^{-6}$ $HCO3 := 1 \cdot 10^{-7}$

$RNH2 := y = 1.75$ $RNHCOO := 0.1y = 0.175$

$OH := 1 \times 10^{-7}$ $Hplus := 1 \times 10^{-7}$

$P_{CO2} := 10^5$ $Loading := 0.2$ [molCO2/molTaurine]

Given

$$\log(P_{CO2}) = \log(CO2) + \log(k_H)$$

$$\log(k_1) + \log(CO2) = \log(HCO3) + \log(Hplus)$$

$$\log(k_2) + \log(HCO3) = \log(CO3) + \log(Hplus)$$

$$\log(k_3) = \log(Hplus) + \log(OH)$$

$$\log(k_4) + \log(RNHCOO) = \log(RNH2) + \log(HCO3)$$

$$\log(k_5) + \log(RNH3) = \log(RNH2) + \log(Hplus)$$

$$\log(CO2 + HCO3 + CO3 + RNHCOO) = \log(y \cdot Loading)$$

$$\log(RNH2 + RNH3 + RNHCOO) = \log(y)$$

$$\log(RNH2 + HCO3 + 2 \cdot CO3 + 2 \cdot RNHCOO + OH) = \log(Hplus + Na)$$

```
sol := Find(CO2,HCO3,CO3,RNH2,RNHCOO,OH,Hplus,Loading)
```

sol =

	0
0	$4.558 \cdot 10^{-4}$
1	0.14
2	$4.49 \cdot 10^{-3}$
3	0.235
4	0.683
5	$9.132 \cdot 10^{-6}$
6	$1.623 \cdot 10^{-9}$
7	0.473

CO2

HCO3

CO3

RNH2

RNHCOO

OH

Hplus

Loading

:= sol

RNH3 = 0.832

pH := -log(Hplus)

pH = 8.79

pOH := -log(OH) = 5.039

pKw := pH + pOH = 13.829

$P_{CO2} = 1 \times 10^5$ [Pa]

CO2sum:= CO2+ HCO3+ CO3+ RNHCOO= 0.828

TaurineSum:= RNH2+ RNH3+ RNHCOO= 1.75

B.6. End point model (without crystallization) for 2 Molar sodium taurate solution
at 30 °C.

End Point Model (without crystallization)

2 Molar at 30 C

$$T := 30 \text{ [K]}$$

Based on Kent-Eisenberg Henry constant and equilibrium constants equations

Henry constant

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \text{ [Pa.m}^3\text{/mol]}$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \text{ [Pa.l/mol]}$$

[mol/l] Equilibrium constant of CO2 and H2O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \text{ [mol/l] Equilibrium constant of carbamate hydrolysis (from Kumat et al.)}$$

$$k_5 := 5.64 \times 10^{-10} \text{ [mol/l] Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 2$ [mol/l] Initial Taurine Concentration

$Na := y = 2$ [mol/l] Na Concentration (from NaOH)

$P_{CO2} := 10^5$ [Pa] Partial pressure CO2

Initial values variables [mol/l]

$CO2 := 1 \cdot 10^{-5}$ $CO3 := 1 \cdot 10^{-5}$ $HCO3 := 1 \cdot 10^{-6}$
 $RNH2 := y = 2$ $RNH3 := 0.23y = 0.46$ $RNHCOO := 0.1y = 0.2$
 $OH := 1 \cdot 10^{-7}$ $Hplus := 1 \times 10^{-7}$
 $x := 0.4$ [mol/l] Total Soluble CO2

Varied variable

Crystal := 0.0 (mol/l)

Given

$\log(P_{CO2}) = \log(CO2) + \log(k_H)$
 $\log(k_1) + \log(CO2) = \log(HCO3) + \log(Hplus)$
 $\log(k_2) + \log(HCO3) = \log(CO3) + \log(Hplus)$
 $\log(k_3) = \log(Hplus) + \log(OH)$
 $\log(k_4) + \log(RNHCOO) = \log(RNH2) + \log(HCO3)$
 $\log(k_5) + \log(RNH3 - Crystal) = \log(RNH2) + \log(Hplus)$
 $\log(CO2 + HCO3 + CO3 + RNHCOO) = \log(x)$
 $\log(RNH2 + RNH3 + RNHCOO) = \log(y)$
 $\log(RNH2 + HCO3 + 2 \cdot CO3 + 2 \cdot RNHCOO + OH) = \log(Hplus + Na)$

$\text{sol} := \text{Find}(\text{CO}_2, \text{HCO}_3, \text{CO}_3, \text{RNH}_2, \text{RNH}_3, \text{RNHCOOH}, \text{Hplus}, x)$

	0	
0	0.03	
1	0.748	
2	$1.979 \cdot 10^{-3}$	
3	0.039	
4	1.357	
5	0.605	
6	$7.52 \cdot 10^{-7}$	
7	$1.971 \cdot 10^{-8}$	
8	1.384	

 $\text{sol} =$

CO_2
HCO_3
CO_3
RNH_2
RNH_3
RNHCOO
OH
Hplus
x

 $:= \text{sol}$

$\text{pH} := -\log(\text{Hplus})$

$\text{pH} = 7.705$

$\text{pOH} := -\log(\text{OH}) = 6.124$

$\text{pKw} := \text{pH} + \text{pOH} = 13.829$

$\text{CO}_2\text{sum} := \text{CO}_2 + \text{HCO}_3 + \text{CO}_3 + \text{RNHCOO} = 1.384$

$\text{TaurineSum} := \text{RNH}_2 + \text{RNH}_3 + \text{RNHCOO} = 2$

$x = 1.384$ [mol/l] Total Soluble CO_2

$\text{Loading} := \frac{x}{\text{TaurineSum}} = 0.692$ [mol CO_2 /molTaurine]

$\text{RNH}_3\text{sol} := 0.77$

$\text{RNH}_3\text{cryst} := \text{RNH}_3 - \text{RNH}_3\text{sol}$

$\text{RNH}_3\text{cryst} = 0.58$ (Estimated, if there is crystallization)

B.7. End point model (without crystallization) for to define the minimum crystallization molar based on 1 Molar sodium taurate solution at 30 °C.

End Point Model (without crystallization)

? Molar at 30 C based on 1M data

$$T := 30 \text{ [K]}$$

Based on Kent-Eisenberg henry constant and equilibrium constants equations

Henry constant

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \text{ [Pa.m3/mol]}$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \text{ [Pa.l/mol]}$$

[mol/l] Equilibrium constant of CO2 and H2O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \text{ [mol/l] Equilibrium constant of carbamate hydrolysis (from Kumar et al.)}$$

$$k_5 := 4.95 \times 10^{-10} \text{ [mol/l] Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 1.2^4$ [mol/l] Initial Taurine Concentration

$Na := y = 1.25$ [mol/l] Na Concentration (from NaOH)

$P_{CO2} := 10^5$ [Pa] Partial pressure CO2

Initial values variables [mol/l]

$CO2 := 1 \cdot 10^{-5}$

$CO3 := 1 \cdot 10^{-5}$

$HCO3 := 1 \cdot 10^{-6}$

$RNH2 := y = 1.25$

$RNH3 := 0.23y = 0.288$

$RNHCOO := 0.1y = 0.125$

$OH := 1 \cdot 10^{-7}$

$Hplus := 1 \times 10^{-7}$

$x := 0.4$ [mol/l] Total Soluble CO2

Varied variable

Crystal := 0.0 (mol/l)

Given

$$\log(P_{CO2}) = \log(CO2) + \log(k_H)$$

$$\log(k_1) + \log(CO2) = \log(HCO3) + \log(Hplus)$$

$$\log(k_2) + \log(HCO3) = \log(CO3) + \log(Hplus)$$

$$\log(k_3) = \log(Hplus) + \log(OH)$$

$$\log(k_4) + \log(RNHCOO) = \log(RNH2) + \log(HCO3)$$

$$\log(k_5) + \log(RNH3 - \text{Crystal}) = \log(RNH2) + \log(Hplus)$$

$$\log(CO2 + HCO3 + CO3 + RNHCOO) = \log(x)$$

$$\log(RNH2 + RNH3 + RNHCOO) = \log(y)$$

$$\log(RNH2 + HCO3 + 2 \cdot CO3 + 2 \cdot RNHCOO + OH) = \log(Hplus + Na)$$

sol := Find(CO2, HCO3, CO3, RNH2, RNH3, RNHCOOH, Hplus, x)

	0	
0	0.03	
1	0.657	
2	$1.525 \cdot 10^{-3}$	
3	0.021	
4	0.944	
5	0.285	
6	$6.602 \cdot 10^{-7}$	
7	$2.246 \cdot 10^{-8}$	
8	0.973	

$$\begin{pmatrix} \text{CO}_2 \\ \text{HCO}_3 \\ \text{CO}_3 \\ \text{RNH}_2 \\ \text{RNH}_3 \\ \text{RNHCOOH} \\ \text{OH} \\ \text{Hplus} \\ x \end{pmatrix} := \text{sol}$$

pH := -log(Hplus)

pH = 7.649

pOH := -log(OH) = 6.18

pKw := pH + pOH = 13.829

CO2sum := CO2 + HCO3 + CO3 + RNHCOOH = 0.973

TaurineSum := RNH2 + RNH3 + RNHCOOH = 1.25

x = 0.973 [mol/l] Total Soluble CO2

Loading := $\frac{x}{\text{TaurineSum}}$ = 0.778 [molCO2/molTaurine]

RNH3sol := 0.954

RNH3cryst := RNH3 - RNH3sol

RNH3cryst = -9.592×10^{-3} (Estimated)

B.8. End point model (without crystallization) for to define the minimum crystallization molar based on 2 Molar sodium taurate solution at 30 °C.

End Point Model (without crystallization)

? Molar at 30 C based on 2M data

$$T := 30 \text{ [K]}$$

Based on Kent-Eisenberg henry constant and equilibrium constants equations

Henry constant

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \text{ [Pa.m}^3\text{/mol]}$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \text{ [Pa.l/mol]}$$

[mol/l] Equilibrium constant of CO2 and H2O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \text{ [mol/l] Equilibrium constant of carbamate hydrolysis (from Kumar et al.)}$$

$$k_5 := 4.58 \times 10^{-10} \text{ [mol/l] Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 1.75$ [mol/l] Initial Taurine Concentration
 $Na := y = 1.75$ [mol/l] Na Concentration (from NaOH)
 $P_{CO2} := 10^5$ [Pa] Partial pressure CO2

Initial values variables [mol/l]

$CO2 := 1 \cdot 10^{-5}$ $CO3 := 1 \cdot 10^{-5}$ $HCO3 := 1 \cdot 10^{-6}$
 $RNH2 := y = 1.75$ $RNH3 := 0.23y = 0.403$ $RNHCOO := 0.1y = 0.175$
 $OH := 1 \cdot 10^{-7}$ $Hplus := 1 \times 10^{-7}$
 $x := 0.4$ [mol/l] Total Soluble CO2

Varied variable

Crystal := 0.0 (mol/l)

Given

$\log(P_{CO2}) = \log(CO2) + \log(k_H)$
 $\log(k_1) + \log(CO2) = \log(HCO3) + \log(Hplus)$
 $\log(k_2) + \log(HCO3) = \log(CO3) + \log(Hplus)$
 $\log(k_3) = \log(Hplus) + \log(OH)$
 $\log(k_4) + \log(RNHCOO) = \log(RNH2) + \log(HCO3)$
 $\log(k_5) + \log(RNH3 - Crystal) = \log(RNH2) + \log(Hplus)$
 $\log(CO2 + HCO3 + CO3 + RNHCOO) = \log(x)$
 $\log(RNH2 + RNH3 + RNHCOO) = \log(y)$
 $\log(RNH2 + HCO3 + 2 \cdot CO3 + 2 \cdot RNHCOO + OH) = \log(Hplus + Na)$

$\text{sol} := \text{Find}(\text{CO}_2, \text{HCO}_3, \text{CO}_3, \text{RNH}_2, \text{RNH}_3, \text{RNHCOOH}, \text{Hplus}, x)$

	0	
0	0.03	
1	0.767	
2	$2.082 \cdot 10^{-3}$	
3	0.03	
4	1.246	
5	0.474	
6	$7.714 \cdot 10^{-7}$	
7	$1.922 \cdot 10^{-8}$	
8	1.273	

$\left(\begin{array}{c} \text{CO}_2 \\ \text{HCO}_3 \\ \text{CO}_3 \\ \text{RNH}_2 \\ \text{RNH}_3 \\ \text{RNHCOOH} \\ \text{OH} \\ \text{Hplus} \\ x \end{array} \right) := \text{sol}$

$\text{pH} := -\log(\text{Hplus})$

$\text{pH} = 7.716$

$\text{pOH} := -\log(\text{OH}) = 6.113$

$\text{pKw} := \text{pH} + \text{pOH} = 13.829$

$\text{CO}_2\text{sum} := \text{CO}_2 + \text{HCO}_3 + \text{CO}_3 + \text{RNHCOOH} = 1.273$

$\text{TaurineSum} := \text{RNH}_2 + \text{RNH}_3 + \text{RNHCOOH} = 1.75$

$x = 1.273$ [mol/l] Total Soluble CO_2

$\text{Loading} := \frac{x}{\text{TaurineSum}} = 0.728$ [mol CO_2 /molTaurine]

$\text{RNH}_3\text{sol} := 0.83$

$\text{RNH}_3\text{cryst} := \text{RNH}_3 - \text{RNH}_3\text{sol}$

$\text{RNH}_3\text{cryst} = 0.414$ (Estimated, if there is crystallization)

B.9. End point model (with crystallization) for 2 Molar sodium taurate solution at 30 °C.

End point model (with crystallization)

2 Molar at 30 C

$$T := 30 \text{ [K]}$$

Based on Kent-Eisenberg Henry constant and equilibrium constants equations

Henry constant

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \text{ [Pa.m}^3\text{/mol]}$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \text{ [Pa.l/mol]}$$

[mol/l] Equilibrium constant of CO2 and H2O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \text{ [mol/l] Equilibrium constant of carbamate hydrolysis (from Kumar et al.)}$$

$$k_5 := 5.64 \times 10^{-10} \text{ [mol/l] Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 2$ [mol/l] Initial Taurine Concentration
 $Na := y = 2$ [mol/l] Na Concentration (from NaOH)
 $P_{CO2} := 10^5$ [Pa] Partial pressure CO2
 $R_{NH3} := 0.77$

Initial values variables [mol/l]

$CO2 := 1 \cdot 10^{-5}$ $CO3 := 1 \cdot 10^{-5}$ $HCO3 := 1 \cdot 10^{-5}$
 $R_{NH2} := y = 2$ $R_{NH3tot} := 1.2$ $R_{NHCOO} := 0.1y = 0.2$
 $OH := 1 \cdot 10^{-7}$ $H_{plus} := 1 \times 10^{-7}$
 $x := 0.4$ [mol/l] Total Soluble CO2

Varied variable

Crystal := 0.67% (mol/l) **To be defined / iterated**

Given

$\log(P_{CO2}) = \log(CO2) + \log(k_H)$
 $\log(k_1) + \log(CO2) = \log(HCO3) + \log(H_{plus})$
 $\log(k_2) + \log(HCO3) = \log(CO3) + \log(H_{plus})$
 $\log(k_3) = \log(H_{plus}) + \log(OH)$
 $\log(k_4) + \log(R_{NHCOO}) = \log(R_{NH2}) + \log(HCO3)$
 $\log(k_5) + \log(R_{NH3tot} - Crystal) = \log(R_{NH2}) + \log(H_{plus})$
 $\log(CO2 + HCO3 + CO3 + R_{NHCOO}) = \log(x)$
 $\log(R_{NH2} + R_{NH3tot} + R_{NHCOO}) = \log(y)$
 $\log(R_{NH2} + HCO3 + 2 \cdot CO3 + 2 \cdot R_{NHCOO} + OH) = \log(H_{plus} + Na)$

$\text{sol} := \text{Find}(\text{CO}_2, \text{HCO}_3, \text{CO}_3, \text{RNH}_2, \text{RNH}_3\text{tot}, \text{RNHCOOH}, \text{Hplus}, x)$

	0		
0	0.03		
1	0.919		
2	$2.991 \cdot 10^{-3}$		
3	0.027		
4	1.449		
5	0.524		
6	$9.246 \cdot 10^{-7}$		
7	$1.603 \cdot 10^{-8}$		
8	1.476		

$\left(\begin{array}{c} \text{CO}_2 \\ \text{HCO}_3 \\ \text{CO}_3 \\ \text{RNH}_2 \\ \text{RNH}_3\text{tot} \\ \text{RNHCOO} \\ \text{OH} \\ \text{Hplus} \\ x \end{array} \right)$	$:= \text{sol}$	$\text{RNH}_3 = 0.777$
---	-----------------	------------------------

$\text{pH} := -\log(\text{Hplus})$

$\text{pH} = 7.795$

$\text{pOH} := -\log(\text{OH}) = 6.034$

$\text{pKw} := \text{pH} + \text{pOH} = 13.829$

$\text{CO}_2\text{sum} := \text{CO}_2 + \text{HCO}_3 + \text{CO}_3 + \text{RNHCOO} = 1.476$

$\text{TaurineSum} := \text{RNH}_2 + \text{RNH}_3\text{tot} + \text{RNHCOO} = 2$

$x = 1.476$ [mol/l] Total Soluble CO₂

$\text{Loading} := \frac{x}{\text{TaurineSum}} = 0.738$ [molCO₂/molTaurine]

$\text{RNH}_3\text{sol} := 0.777$

$\text{RNH}_3\text{cryst} := \text{RNH}_3\text{tot} - \text{RNH}_3\text{sol}$

$\text{RNH}_3\text{cryst} = 0.672$

B.10. End point model (without crystallization) for to define the minimum crystallization molar based on 2 Molar sodium taurate solution at 30 °C.

End point model (with crystallization)

To find ? Molar at 30 C crystal may occur, based on 2M data

$$T := 30 \quad [\text{K}]$$

Based on Kent-Eisenberg henry constant and equilibrium constants equations

Henry constant

$$k_{\text{HSI}} := \frac{\exp\left(22.2819 - \frac{138.30610^2}{T} + \frac{691.34610^4}{T^2} - \frac{155.89510^7}{T^3} + \frac{120.03710^9}{T^4}\right)}{7.50061} = 3.376 \times 10^3 \quad [\text{Pa.m}^3/\text{mol}]$$

$$k_{\text{H}} := k_{\text{HSI}} 10^3 = 3.376 \times 10^6 \quad [\text{Pa.l/mol}]$$

[mol/l] Equilibrium constant of CO2 and H2O forming bicarbonate

$$k_1 := \exp\left(-241.818 + \frac{298.25310^3}{T} - \frac{148.52810^6}{T^2} + \frac{332.64810^8}{T^3} - \frac{282.39410^{10}}{T^4}\right) = 4.977 \times 10^{-7}$$

[mol/l] Equilibrium constant of bicarbonate carbonate dissociation

$$k_2 := \exp\left(-294.74 + \frac{364.38510^3}{T} - \frac{184.15810^6}{T^2} + \frac{415.79310^8}{T^3} - \frac{354.29110^{10}}{T^4}\right) = 5.217 \times 10^{-11}$$

[mol/l] Equilibrium constant of water dissociation

$$k_3 := \exp\left(39.5554 - \frac{987.910^2}{T} + \frac{568.82810^5}{T^2} - \frac{146.45110^8}{T^3} + \frac{136.14610^{10}}{T^4}\right) = 1.482 \times 10^{-14}$$

$$k_4 := 0.04 \quad [\text{mol/l}] \text{ Equilibrium constant of carbamate hydrolysis (from Kumar et al.)}$$

$$k_5 := 4.58 \times 10^{-10} \quad [\text{mol/l}] \text{ Equilibrium constant of Taurine deprotonation (from solubility model)}$$

Manipulating variables

$y := 1.75$ [mol/l] Initial Taurine Concentration

$Na := y = 1.75$ [mol/l] Na Concentration (from NaOH)

$P_{CO2} := 10^5$ [Pa] Partial pressure CO2

$R_{NH3} := 0.83$

Initial values variables [mol/l]

$CO2 := 1 \cdot 10^{-5}$

$CO3 := 1 \cdot 10^{-5}$

$HCO3 := 1 \cdot 10^{-6}$

$R_{NH2} := y = 1.75$

$R_{NH3tot} := 1.2$

$R_{NHCOO} := 0.1y = 0.175$

$OH := 1 \cdot 10^{-7}$

$H_{plus} := 1 \times 10^{-7}$

$x := 0.4$ [mol/l] Total Soluble CO2

Varied variable

$Crystal := 0.47$ (mol/l) **To be defined / iterated**

Given

$$\log(P_{CO2}) = \log(CO2) + \log(k_H)$$

$$\log(k_1) + \log(CO2) = \log(HCO3) + \log(H_{plus})$$

$$\log(k_2) + \log(HCO3) = \log(CO3) + \log(H_{plus})$$

$$\log(k_3) = \log(H_{plus}) + \log(OH)$$

$$\log(k_4) + \log(R_{NHCOO}) = \log(R_{NH2}) + \log(HCO3)$$

$$\log(k_5) + \log(R_{NH3tot} - Crystal) = \log(R_{NH2}) + \log(H_{plus})$$

$$\log(CO2 + HCO3 + CO3 + R_{NHCOO}) = \log(x)$$

$$\log(R_{NH2} + R_{NH3tot} + R_{NHCOO}) = \log(y)$$

$$\log(R_{NH2} + HCO3 + 2 \cdot CO3 + 2 \cdot R_{NHCOO} + OH) = \log(H_{plus} + Na)$$

$\text{sol} := \text{Find}(\text{CO}_2, \text{HCO}_3, \text{CO}_3, \text{RNH}_2, \text{RNH}_3\text{tot}, \text{RNHCOOH}, \text{Hplus}, x)$

$\text{sol} =$

	0
0	0.03
1	0.883
2	$2.757 \cdot 10^{-3}$
3	0.023
4	1.308
5	0.419
6	$8.876 \cdot 10^{-7}$
7	$1.67 \cdot 10^{-8}$
8	1.335

$$\begin{pmatrix} \text{CO}_2 \\ \text{HCO}_3 \\ \text{CO}_3 \\ \text{RNH}_2 \\ \text{RNH}_3\text{tot} \\ \text{RNHCOO} \\ \text{OH} \\ \text{Hplus} \\ x \end{pmatrix} := \text{sol}$$

$$\text{RNH}_3 = 0.832$$

$$\text{pH} := -\log(\text{Hplus})$$

$$\text{pH} = 7.777$$

$$\text{pOH} := -\log(\text{OH}) = 6.052$$

$$\text{pKw} := \text{pH} + \text{pOH} = 13.829$$

$$\text{CO}_2\text{sum} := \text{CO}_2 + \text{HCO}_3 + \text{CO}_3 + \text{RNHCOO} = 1.335$$

$$\text{TaurineSum} := \text{RNH}_2 + \text{RNH}_3\text{tot} + \text{RNHCOO} = 1.75$$

$$x = 1.335 \quad [\text{mol/l}] \text{ Total Soluble CO}_2$$

$$\text{Loading} := \frac{x}{\text{TaurineSum}} = 0.763 \quad [\text{molCO}_2/\text{molTaurine}]$$

$$\text{RNH}_3\text{sol} := 0.83$$

$$\text{RNH}_3\text{cryst} := \text{RNH}_3\text{tot} - \text{RNH}_3\text{sol}$$

$$\text{RNH}_3\text{cryst} = 0.476$$