Carbon Dioxide CO₂ Capture Using Amino Acid Salt Solution

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Abstract. The concern of climate change and global warming has consecutively risen to progress research fields pledging to find the possible solutions. The use of fossil fuels for energy leads to an increase in CO₂ emission causing environmental problems like global warming and climate change. For industrial applications, aqueous solutions of amines are extensively used as chemical absorbent or solvent. However, amine reaction with CO₂ results in stable carbamate formation, which in turn leads to high energy usage for regeneration and promote additional corrosion problems. To overcome these restrictions, this study proposes a methodology to analyze the performance of new solvent namely amino acid salt solution. Evaluation of solvent performance in terms of CO₂ loading and designing of acid gas removal system, requires pressure solubility data and design properties like density, pH value and refractive index.

Keyword: CO₂ capture, absorption, thermophysical properties, solubility, loading capacity

1. Introduction

The increase of global carbon dioxide (CO₂) emission has arisen multiple concerns related to environmental science. The amount of CO₂ present in the atmosphere have increased significantly and will pose a much greater threat to climate change if no proper preventive actions are taken [1-3]. CO₂ emission started with the use of fossil fuel for steam engines after the industrial revolution. Fossil fuels still plays a major role in catering the world’s energy demands. Higher presence of CO₂ in natural gas decrease the octane number or heating value and also due to its acidic nature it creates corrosion problems in pipelines during the transmission and while processing it in the equipment’s [4]. Besides, the burning of natural gas further leads to increase in CO₂ emissions into the atmosphere. Carbon capture and storage (CCS) schemes embody a group of technologies for the capture of CO₂ from
power plants, followed by compression, transport, and permanent storage [5]. CCS enhance energy efficiency, shifting to low carbon concentrated fuels and more use of renewable resources which will counterpart the reduction of CO₂ emissions. A main concern is that the deployment of CCS technology is a complicated problem that requires investment, joint vision and worldwide collaborative efforts.

Absorption is commonly used in industry for CO₂ capture. There are two types of absorption: physical absorption and chemical absorption. In physical absorption, a liquid solvent physically absorbs a gas mixture or a part of it. In chemical absorption, the flue stream is treated with a selected solvent (amines) which form weakly bonded transition compound and then the solvent can be regenerated using the application of heat. The efficiency of chemical absorption is relatively higher than physical absorption [6-8]. For CO₂ capture mostly chemical absorption is adopted in industries with different solvents like monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), blends of amines piperazine (PZ), Lipophilic amine solvents like dipropylamine (DPA) and n,n-dimethylethanolamine (DMCA) and their blends [9,10].

A typical amine gas treating unit involves two stages; absorber unit and regeneration unit. In absorption unit, the upcoming flue gas stream comes into contact with the down-flowing amine solution which absorbs the acidic gas (mainly CO₂). Now the CO₂ rich amine solution is pumped to the regeneration unit, where the solvent is extracted with the application of heat and the lean amine solution is then again recycled back to the absorber unit for reuse. Typically, primary and secondary based amine solvents form carbamates upon reaction with CO₂. The rate of hydrolysis of these carbamates into bicarbonates depends upon the stability of the carbamate. Carbamate formation is main and fast reaction during absorption, makes this step the most decisive in finding the CO₂ absorption capacity as well as the CO₂ regeneration energy requirement [11,12]. The CO₂ loading capacity of tertiary amine is higher than that of primary and secondary amines because only a small part of carbamate molecules is hydrolyzed into hydrogen carbonates. However, tertiary amines have relatively low reactivity towards CO₂. The tertiary amines react according to base catalyzed reactions with the existence of water avoiding the formation of carbamate. Thus, minor amounts of primary and secondary amines are mixed together into tertiary amines in boosting the CO₂ absorption rates.

However, the regeneration of loaded solvent requires high amount of energy and causes corrosion problem and also oxidative degradation is a big concern. Therefore, new solvents with improved characteristics of lower heat of regeneration, high CO₂ loading capacity and fast reaction kinetics has been a topic for researchers [13]. There are some of disadvantages in dealing with the conventional alkanol amines used as absorbents like low capacity, low absorption rate, high regeneration cost and cause degradation and corrosion. A new proposed solvent, which is the amino acid salt solution, is subjected to have more advantages as compare to the conventional alkanol amine [14,15]. The features are fast reaction kinetics, high achievable cyclic loading, has good stability towards oxygen and has favorable binding energy.

Once CO₂ loading exceeds certain value, the solid precipitate is formed from the amino acid salt solution [16]. This precipitate is made up of either neutral amino acid molecule or bicarbonate salt. This condition causes the chemical reaction equilibria shifted along with the result, letting the equilibrium CO₂ pressure to remain constant as the loading keep on increasing. This implied that the driving force for the absorption can be moderated and maintained at higher level with respect to higher loading, improving the absorber performance. Besides, higher loading resulted in reduced energy consumption during regeneration. This finding leads to the design of specific absorption process based on precipitating amino acid [17].

Amino acid salts are obtained through neutralization of amino acid with base, for example, potassium hydroxide [18-20]. As pure amino acid (HOOC-R-NH₂) is dissolved in water, the related equilibria is derived. In the solution, the neutral molecule exists in dipole, due to the carboxylic group losing a proton while amine group is protonated. When amino acid reacts with potassium hydroxide, a proton is removed from –NH₃⁺ group resulted in formation of potassium salt. Potassium salt is the active components, reacts with CO₂ like usual amine thru NH₂ group, increasing the solubility due to the
neutralization. Later, the neutralized potassium salts of amino acids will react as following the same way of usual reaction between amines and CO₂; via formation of carbamate and bicarbonate. For carbamate hydrolysis, the reaction did not involve primary amine, so the major CO₂ absorption will be in the form of carbamate [21-23]. For each CO₂ molecule absorbed, it will form one molecule of carbamate and one protonated amine molecule. This indicates that two amino acid salts are needed in absorption of one molecule of CO₂.

Objectives of this proposed work are to assess the amino acid salt solvent performance in terms of CO₂ loading for wide variety of temperature and pressure conditions for industrial applications and to get optimized mixture concentration for effective CO₂ series. The thermophysical properties that includes density, pH value and refractive index was measured. The thermodynamic solubility data of the given solvents and conventional alkanol amines like MEA and MDEA was compared.

2. Materials
Several solvents will be used in this research work for CO₂ absorption process. Amino acid that used as solvents is glycine. All these solvents are ordered from Merck Sdn Bhd, Malaysia with a purity of 99% each and will be used without any further purification. The base used will be Sodium Hydroxide in pellet form, obtained from the Chemical Engineering Department Laboratory, UTP. The aqueous solutions of the above mentioned amino acids and base will be prepared on weight percentage using an analytical balance (model AS120S, Mettler Toledo) with a precision of ± 0.0001g and we considered the solution to be equimolar. The weight percentage of the solution used is 10%, 20% and 30%. For each of the solution prepared, 2% and 5% weight percentage of piperazine will be added. The aqueous solutions will be prepared using the distilled water, and measurements for each sample will be performed in duplicate. The basis of the solution is 100 grams for each of the solution prepared. Average values will be used in reporting. The purified gases such as carbon dioxide and nitrogen with a purity of 99.99% both respectively are also obtained from the laboratory.

3. Results and Discussions

3.1 Density Measurement
The density of the aqueous solutions of the amino acid salt is measured using a density meter (model DMA 5000, Anton Paar, Austria) at temperatures from 303.15 to 353.15 K with a built-in platinum resistance thermometer having an uncertainty of ± 0.01 K. The apparatus is calibrated by measuring the density of distilled water at regular intervals according to the supplier instructions and is compared with the water density bibliography given in the manual. A suitable solvent (volatile, capable to dissolve residue) i.e., acetone in this case, is injected several times in the measuring cell to avoid any contamination from the residues left behind by earlier samples. Later, dry air is blown through the measuring cell using a built-in air pump for approx. 5 minutes (as recommended in the manual).

The procedure of accurate density measurement is totally dependent on the measurement settings which includes equilibrium mode, viscosity correction and temperature scan steps. The settings for density measurement of all samples is adjusted to work at medium equilibrium mode with automatic viscosity correction method of <700 mPa.s and 5K step increment of temperature within the initial and final temperature range. The predefined quantity of the sample (approx. 2 mL) is filled in a syringe and slowly injected in U-tube measuring cell (0.7 mL) ensuring that there is no bubble in the cell by viewing through the optical glass window. The preset method is activated to start the density measurement and simultaneously recording the data in the equipment memory. Obtained results are shown in Tables 1-6.

| Temperature (°C) | Density (g/cm³) |
|-----------------|----------------|
| 30              | 1.0429         |
| 40              | 1.0387         |
Table 2: Density of 10% of sodium glycinate, 5% of piperazine, 85% of water

| Temperature (°C) | Density (g/cm³) |
|-----------------|----------------|
| 30              | 1.0448         |
| 40              | 1.0406         |
| 50              | 1.0358         |
| 60              | 1.0307         |

Table 3: Density of 20% of sodium glycinate, 2% of piperazine, 78% of water

| Temperature (°C) | Density (g/cm³) |
|-----------------|----------------|
| 30              | 1.0897         |
| 40              | 1.0849         |
| 50              | 1.0799         |
| 60              | 1.0744         |

Table 4: Density of 20% of sodium glycinate, 5% of piperazine, 75% of water

| Temperature (°C) | Density (g/cm³) |
|-----------------|----------------|
| 30              | 1.0919         |
| 40              | 1.087          |
| 50              | 1.0819         |
| 60              | 1.0764         |

Table 5: Density of 30% of sodium glycinate, 2% of piperazine, 68% of water

| Temperature (°C) | Density (g/cm³) |
|-----------------|----------------|
| 30              | 1.1395         |
| 40              | 1.1344         |
| 50              | 1.1288         |
| 60              | 1.1231         |

Table 6: Density of 30% of sodium glycinate, 5% of piperazine, 65% of water

| Temperature (°C) | Density (g/cm³) |
|-----------------|----------------|
| 30              | 1.1403         |
| 40              | 1.135          |
| 50              | 1.1294         |
| 60              | 1.1235         |

It is found that the density of the solution blend has higher density as compared to pure amino acid salt solution based on the collected data. This is due to the presence of both amino acid and amine in the solution that will induce greater density as compared to unique solution.

### 3.2 Refractive Index Measurement

The refractive index of the corresponding aqueous solutions of amino acid salt is measured using a digital refractometer (Atago, RX-5000 alpha). This refractometer covers a wide range of temperature from 298.15 K to 333.15 K and temperature is controlled within ± 0.05 K. The refractometer is calibrated before every sample measurement using distilled water and checked with pure liquids of
known refractive indices. The reported values will be the average of five measurements and are shown in Table 7.

Table 7: Refractive Index value testing result

| Sample                                           | RI Value |
|--------------------------------------------------|----------|
| 10% of sodium glycinate, 2% of piperazine, 88% of water | 1.3523   |
| 10% of sodium glycinate, 5% of piperazine, 85% of water | 1.3565   |
| 20% of sodium glycinate, 2% of piperazine, 78% of water | 1.3648   |
| 20% of sodium glycinate, 5% of piperazine, 75% of water | 1.3709   |
| 30% of sodium glycinate, 2% of piperazine, 68% of water | 1.3797   |
| 30% of sodium glycinate, 5% of piperazine, 65% of water | 1.3853   |

Refractive index of the proposed solution is greater as compared to the pure amino acid salt solution, as referred to the data collected. The presence of the mixture of both amino acid and amine will affect the RI value as observed.

3.3 pH Value Measurement

The pH value of each aqueous solution of amino acid salt solution is measured using pH meter. pH meter is operated at room temperature and calibrated using distilled water before each sample is tested. The reported values will be the average of three times measurements.

Table 8: pH value testing result

| Sample                                           | pH value |
|--------------------------------------------------|----------|
| 10% of sodium glycinate, 2% of piperazine, 88% of water | 12.14    |
| 10% of sodium glycinate, 5% of piperazine, 85% of water | 12.47    |
| 20% of sodium glycinate, 2% of piperazine, 78% of water | 12.01    |
| 20% of sodium glycinate, 5% of piperazine, 75% of water | 12.12    |
| 30% of sodium glycinate, 2% of piperazine, 68% of water | 11.97    |
| 30% of sodium glycinate, 5% of piperazine, 65% of water | 12.09    |

As per the data collected, it is found that the pH value of the proposed solution is less than the pure amino acid salt solution. This is due to the fact that the presence of piperazine, which is amine, has slightly acidic properties that will affect the pH value of the solution.

3.4 Solubility Measurement

The solubility of a gas is a thermodynamic property in which solvent and gas are brought in contact with each other under specific operating conditions of pressure and temperature which results in absorption of gas in the solvent [24]. This absorbed amount of gas in the solvent is termed as gas loading. The solubility of gas in aqueous solutions of amino acid salt solutions will be measured in a high-pressure solubility cell. The high-pressure solubility cell SOLTEQ Model: BP22 was fabricated and installed by Solution Engineering Sdn Bhd, Malaysia. This high-pressure solubility cell is proficient of measuring pressure up to 100 bars and temperature up to 353.15K. The cell comprises of three main units, namely (i) Gas supply unit, (ii) Gas solubility cell and (iii) data acquisition and logging system for data log and online monitoring of experiment.

The set up involves two vessels, first mixing vessel (3L) in which gas pressure is raised up to 6000kPa and other one is equilibrium cell (50mL) where solubility measurements are to be done. Initially both vessels are purged with nitrogen and then the mixing vessel is pressurized from 50kPa to 6000kPa so as to avoid any contamination in the vessels. The pressure of the system is measured using digital pressure indicator (Druck DPI 150) with a precision of ± 1.0kPa for a range of 0kPa to 10,000kPa. The temperature of the system is maintained by thermostat water bath Julabo with an uncertainty of ± 0.1°C and the inside temperature of the mixing vessel and equilibrium cell is measured by Yokogawa (7653) digital thermometer with an accuracy of ± 0.01°C. Originally vacuum is created inside equilibrium cell and 5 mL of aqueous solution is fed using metering pump. The
temperature of the cell is then adjusted to the required value and pressure is noted. At this point, solvent exists under its own vapor pressure $P_v$. The $CO_2$ is then transferred from mixing vessel to equilibrium cell with the stirrer on. The moles of $CO_2$ transferred can be calculated using pressure drop, volume of vessel and temperature by the following equation 1:

$$n_{CO_2} = \frac{V_f}{RT_a} \left( \frac{P_1 - P_2}{z_1 - z_2} \right)$$  \hspace{1cm} (1)

Here $V_f$ is the volume of the gas container i.e. mixing vessel, $z_1$ and $z_2$ are the compressibility factors for pressure’s $P_1$ and $P_2$, $R$ is the real gas constant and $T_a$ is the ambient temperature. The compressibility factors can be calculated using Peng Robinson equation of state (EOS). After almost 2-3hrs, when there is no change in pressure drop in the solubility cell, then we can assume that thermodynamic equilibrium has been achieved. Pressure value recorded at this time is termed equilibrium pressure ($P_{CO_2}$). It can also be calculated by following equation 2:

$$P_{CO_2} = P_f - P_v$$  \hspace{1cm} (2)

Here $P_f$ represents the total pressure and $P_v$ represents vapor pressure of solutions. The remaining moles of $CO_2$ in the gas phase $n^g$ can be calculated by equilibrium pressure ($P_{CO_2}$), temperature and overhead gas volume by using the following equation 3:

$$n^gCO_2 = \frac{V^gP_{CO_2}}{Z_{CO_2}RT}$$  \hspace{1cm} (3)

The solubility is then calculated as volume of $CO_2$, assuming the solution is equimolar, using the gas equation 4:

$$V_{CO_2} = \frac{RT}{P}$$  \hspace{1cm} (4)

In this work the solubility data was used to validate the data obtained from the thermophysical properties testing and be compared to the data for the alkanol amines available. The sample was tested at given condition specified tested pressure (5 bar, 10 bar, 15 bar) and tested temperature (30 °C, 40 °C, 50 °C) respectively. The Figure 1, 2 and 3 showed the graph of carbon dioxide absorbed at different pressure (5-15 bar) and different temperature (30-50 °C) for solubility testing. These solubility values were measured at different concentration of sodium glycinate with different concentration of piperazine at given pressure and temperature conditions.

![Graph of solubility testing at 30 °C](image)

**Figure 1:** Graph of solubility testing at 30 °C
From the solubility testing done, it is observed that the variation of different temperature and pressure gives different variation of the absorption or loading capacity. At 30°C, it is observed that the solution does not induce any positive loading capacity as desorption of CO₂ is happening at the moment. At 40°C and 50°C, some positive loading capacity is observed at certain composition of the solution used. Generally, it can be induced that the variation of different composition of the mixture give different loading capacity as the parameters: temperature and pressure are increased. This irregular trend observed is due to the presence of both amino acid and amine that has different reliability in performing absorption as proposed in the literature review research. The intrinsic properties of both chemicals are contradictory but at certain extent, it inhibits positive outcome.

4. Conclusion

It can be concluded that different composition of amino acid salt solution will give different loading capacity of CO₂. This is due to the sensitivity of the solution at different composition to tolerate the different variation of the temperature and pressure. In the experiment work done, the best condition, at composition of 10% sodium glycinate, 5% piperazine give the best loading capacity of the CO₂. To compare with the pure amino acid salt solution, the loading capacity will decrease as the temperature increases. The proposed solution has optimum loading capacity upon specific operating condition as this result show its significant over the available amino acid salt solution.
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