CO₂ removal via promoted potassium carbonate with glycine: solubility measurement at elevated pressure

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Abstract. Potassium carbonate promoted with glycine is considered as potential candidates for CO₂ removal process as it demonstrated less energy usage during the regeneration process. Hence, in order to model the process at upscale condition, the loading of CO₂ into the promoted solvent is measured at temperature (30 - 60 °C) over the elevated pressure (10 bar) using high pressure solubility cell. The equilibrium solubility data is measured for 15wt% potassium carbonate + 3wt% glycine and 20wt% potassium carbonate + 5wt% glycine. This work aims to study the solubility of CO₂ into the promoted solvent at higher operating pressure, thus the vapor liquid equilibrium (VLE) can be derived and further facilitate the development of simulation for CO₂ absorption process at the upscale condition. Results show that the CO₂ is less favor to absorb into the promoted solvent at high temperature since the process is exothermic, thus increasing temperature would decrease the tendency of the absorption process. The comparative analysis also showed that solubility is improved at higher pressure as greater force assist to alleviate the surface stress of the solution.

1. Introduction
In natural gas treatment, CO₂ is one of the major contaminants that highly affected the gas quality standard. Thus, the various effort has been introduced to remove CO₂ before they can be transferred into the pipeline. The most commonly matured process is chemical absorption via a conventional fast reacting solution such as MEA, DEA. Nonetheless, the high regeneration energy that will severely increase the uptake of electricity up to 70-80 % [1] has led to many global researches to explore another potential solvent. Aside from amine based solvent, potassium carbonate has also long been studied as chemical absorption and their drawback in a slow kinetic reaction has been eliminated with the addition of various promoter. One of such promoters is amino acids and in the recent year, there has been renewed interest in using glycine as it has the same functional group as amine which leads to same reaction rate as amine but resistance to oxidative degradation, non-volatile and less toxicity [2].

Previous studies [2, 3] have reported various kind of finding related to CO₂ removal using promoted potassium carbonate but mostly focused on experimental works that emphasized on removal efficiency, rate enhancement and solubility. Realizing that the possibility of CO₂ removal using promoted potassium carbonate required a lot of trial and error to find the optimum condition, thus modelling and simulation is a must. Hence, in order to establish an accurate simulation model, a correct physical property and vapor Liquid Equilibrium (VLE) data are very necessary.
In Mondal et al. [4], a new VLE data in aqueous sodium glycinate (5-25 %) is measured and then correlated using Kent Eisenberg model. Hence, a carbamate hydrolysis equilibrium constant and amine deprotonation equilibrium constant are regressed. Even though, a model successfully predicted the experimental data but the operating condition is only up to medium pressure (2-6 bar). Another study [5] have also conducted VLE study for the absorption of CO₂ into a glycine promoted potassium carbonate solution over a range of temperatures and in this work ENRTL model has been used to model the data. The comparison between promoted potassium carbonate and pure potassium carbonate indicated that glycine can improve the CO₂ absorption but still the data is only suitable for post combustion process only. When designing or simulating an absorption column associated with chemical reaction, certain key data is required such as physical, thermal and transport properties, vapor liquid equilibrium (VLE) and reaction rate data. Unlike amine-based solvent, the information related with promoted potassium carbonate with glycine is not widely presented and available in the literature. Hence, a few studies have attempted to investigate the physical properties of this solvent but still the data are limited to post combustion operating condition. Hence, this study aims to study the solubility of the promoted solvent at higher operating pressure, thus the CO₂ absorption process at the upscale condition can be model and simulate accurately.

2. Research methodology

2.1 Chemical reaction

Understanding the chemical reaction in the of CO₂ in promoted potassium carbonate is very necessary before any process can be developed or modelled. The chemical absorption in the process can be divided into two main mechanisms. The solvent mechanism and promoter mechanism that taking at parallel reaction in the same time. The common solvent mechanism is listed from (R1) until (R5), the hydrolysis of potassium carbonate is defined in (R1) and (R2) shows the water ionization. Then, bicarbonate formation and carbonate formation are defined in (R3) and (R4). Then, the overall reaction is represented in (R5). The precipitation of potassium salt might occur at high concentration and considered as hydrated potassium carbonate (K₂CO₃, 1.5H₂O) is listed in (R6) but considered negligible in this reaction.

\[
K_2CO_3 + H_2O \leftrightarrow 2K^+ + HCO_3^- + OH^- \quad (R1)
\]
\[
2H_2O \leftrightarrow H_3O^+ + OH^- \quad (R2)
\]
\[
CO_2 + OH^- \leftrightarrow +HCO_3^- \quad (R3)
\]
\[
HCO_3^- + OH^- \leftrightarrow H_2O + CO_3^{2-} \quad (R4)
\]
\[
K_2CO_3 + H_2O + CO_2 \leftrightarrow 2KHCO_3 \quad (R5)
\]
\[
K_2CO_3, 1.5H_2O \leftrightarrow 2K^+ + CO_3^{2-} + 1.5H_2O \quad (R6)
\]

The promoter reaction is defined from (R7) - (R9). Based on the observation in Lee et al. [5], glycine is not only enhancing the kinetic reaction of the solvent but the glycine itself is capable to capture CO₂ to form glycine carbamate. In aqueous solution, glycine may present in term of protonated, anionic and zwitterionic.

\[
-Gly + H_3O^+ \leftrightarrow -Gly^+ + H_2O \quad (R7)
\]
\[
-Gly + CO_2 + H_2O \leftrightarrow -GlyCOO^- + H_3O^+ \quad (R8)
\]
\[
-GlyCOO^- + H_2O \leftrightarrow Gly + HCO_3^- \quad (R9)
\]

2.2 CO₂ solubility measurement

Potassium carbonate and glycine with purity (99%) are obtained from Sigma Aldrich. Two different concentration of samples are prepared based on the following ratio; PC:Gly, 15wt% : 3wt% and 20wt%: 5wt%. The solvent concentration as suggested in literature must be less than 40 wt% as higher concentrations will lead to precipitation in the column [6]. The experiments for solubility measurement are carried out at temperature (30-60 °C) at 10 bar using pressure solubility cell (SOLTEQ BP-22). The equilibrium cell consists of 2 mixing vessel that labelled as EC 1 and EC 2 with a volume of 50mL. Initially, N₂ purged and the vacuum condition is formed before 7 mL of sample is injected into the
equilibrium cell via a metering pump. The temperature is adjusted at the required condition and maintained until it stabilized. Then, the initial pressure reading in the equilibrium cells are recorded. Then, CO$_2$ gas is compressed into a pressure vessel (PV) until the desired operating pressure is achieved. Once the temperature in the cell maintained and pressure is stable, the valve is fully open and CO$_2$ is transferred to the mixing cell. The pressure will be rapidly increased and the valve will be fully closed once there is no change is observed after 5s. Sudden pressure drop is observed and the attainment of equilibrium is confirmed when there is no further change of pressure at least 2 h in equilibrium cell at a constant temperature. This procedure is repeated for each sample at different temperature. The simplified diagram of solubility cell is shown in figure 1.

Figure 1. High pressure gas solubility cell (SOLTEX).

Based on [7], mole of CO$_2$ is obtained using equation (1).

$$n_{CO_2} = \frac{V_T}{RT} \left( \frac{P_i}{Z_1} - \frac{P_f}{Z_2} \right)$$

(1)

$V_T$ denotes the volume of mixing cell, $Z$ are the compressibility factor that calculated using Peng rebingson equation of State (PR-EOS) while $R$ is the real gas constant and $T$ is referred to the operating temperature. The loading ($\alpha$) is calculated as mole of CO$_2$ per mole of promoted solvent using equation (2) The number of moles for the promoted potassium carboante and glycine is calculated using equation (3).

$$\alpha = \frac{n_{CO_2}}{n_{PC+Gly}}$$

(2)

$$n_{PC+Gly} = \frac{\rho V m_{PC+Gly}}{M_{PC+Gly}}$$

(3)
\( \rho \) denotes the density of solvent, \( V_l \) as the liquid volume in cell, \( m_{PC+Gly} \) is the mass fraction of the solvent and \( M_{PC+Gly} \) is the molecular weight.

3. Results and discussions

Figure 2 shows the pressure reduction for both solvents concentrations at different temperatures (30-60 °C). The pressure reduction is continued until the promoted solvent is saturated with CO\(_2\) gas and the equilibrium pressure is attained once no further reduction of pressure is observed after 2 hours of operation. According to Mondal et al. [4], the equilibrium pressure is described as a difference of total pressure and vapor pressure while the equilibrium is achieved for at least 1 hour at the constant temperature. However, this study has extended the equilibrium attainment time to ensure the accuracy is improved. It is interesting to note that the attainment time is different for each set of concentration and operating condition but the record is not presented in this paper as the main aim only to observe the loading value.

Pressure decay is recorded as it can give the overview of CO\(_2\) loading and based on the early observation, the CO\(_2\) is not favored to absorb into this promoted solvent at high temperature and this is true based on the Le Chatlier principle [8]. As in nature, CO\(_2\) absorption process is exothermic, thus increasing temperature would decrease the tendency of the absorption process. Besides, it is noticed that higher concentration of solvent (20 wt% PC + 5 wt% Gly) leads to higher pressure drop as the amount of active solvent is higher thus increase the tendency of the absorption process. Initially, the absorption is very vigorous once CO\(_2\) gas is introduced to the equilibrium cell and after sometimes, the absorption process is slowing down until it reached the steady state.

![Figure 2. Pressure reduction of CO\(_2\) against temperature](image)

The loading of mole CO\(_2\) over mole promoted solvent is calculated via measuring the difference between initial and final pressures (equilibrium pressure) as shown in figure 3.

At constant elevated pressure (10bar), the results manifested that the loading is decreased with the rise of temperature. The comparative analysis in table 1 shows that similar trend is also observed in [7] at same operating pressure but the solubility test is conducted using a pure potassium carbonate solution.

| Temperature (°C) | 15 wt% PC + 3 wt% Gly | 20 wt% PC + 5 wt% Gly | 20 wt% PC (1)  |
|-----------------|-----------------------|-----------------------|----------------|
| 30              | 0.75                  | 0.96                  | nil            |
| 40              | 0.62                  | 0.94                  | 1.25           |
| 50              | 0.52                  | 0.75                  | 0.93           |
| 60              | 0.53                  | 0.44                  | 0.79           |
The higher the concentration of potassium carbonate and glycine used (20wt% PC + 5 wt% Gly), the greater CO$_2$ loading is observed. This is expected as more active solvent present in the solution, the absorption will be improved, thus the loading calculation is also increased. The aim value for loading is 1 as it demonstrated that one mole of CO$_2$ is absorbed by one mole of solvent. The loading value for 15wt% PC + 3 wt% Gly has also shown a promising value but the calculated value is not able to reach the aim of the experiment.

Based on the literature [7], a pure K$_2$CO$_3$ yield a better solubility based on loading calculation but the time taken to reach the equilibrium during the solubility test is much longer than the current promoted solvent. Hence, the addition of promoter is helpful to compensate for the difference in term of mass transfer rate. This is true as [5] has also agreed that using the promoter itself will greatly enhance the reaction kinetic but blended solvent between potassium carbonate and glycine may provide a mean of balancing kinetics and capacity against the solvent cost.

4. Conclusions
The promoted potassium carbonate has good potential for CO$_2$ absorption. Nevertheless, further investigation at higher operating pressure at various concentration is an essential before the accurate VLE model can be derived. Hence, a scale up condition for the overall process can be designed and simulated at wider operating range.

Acknowledgements
The authors are thankful to Universiti Teknologi PETRONAS and research grant (FRGS-015MA0-036) for financial and technical support in the completion of this research study.

References
[1] Li X, Wang S, Chen C 2013 Experimental study of energy requirement of CO$_2$ desorption from rich solvent Energy Procedia, 37 1836-43
[2] Thee H, Suryaputradinata Y A, Mumford K A, Smith KH, da Silva G and Kentish SE 2012 A kinetic and process modelling study of CO$_2$ capture with MEA-promoted potassium carbonate solutions Chemical Engineering Journal 210 271-9
[3] Smith K, Lee A, Mumford K, Li S, Thanumurthy N and Temple N 2015 Pilot plant results for a precipitating potassium carbonate solvent absorption process promoted with glycine for enhanced CO$_2$ capture Fuel Processing Technology 135 60-5
[4] Mondal B K, Bandyopadhyay S S and Samanta A N 2015 VLE of CO$_2$ in aqueous sodium glycinate solution—New data and modeling using Kent–Eisenberg model. International Journal of Greenhouse Gas Control 36 153-60
[5] Lee A, Mumford K A, Wu Y, Nicholas N and Stevens G W 2016 Understanding the vapour–liquid equilibrium of CO$_2$ in mixed solutions of potassium carbonate and potassium glycinate. International Journal of Greenhouse Gas Control 47 303-9
[6] Haghtalab A and Gholami V 2019 Carbon dioxide solubility in the aqueous mixtures of diisopropanolamine+ l-arginine and diethanolamine+ l-arginine at high pressures Journal of Molecular Liquids 111064

[7] Bohloul M, Sadeghabadi M A, Peyghambarzadeh S and Dehghani M 2017 CO₂ absorption using aqueous solution of potassium carbonate: Experimental measurement and thermodynamic modeling Fluid Phase Equilibria 447 132-41

[8] Shaikh M S, Azmi M S, Bustam M A and Murshid G 2014 Study of CO₂ solubility in aqueous blend of potassium carbonate promoted with glycine Applied Mechanics and Materials 19-23.