Experimental study of CO$_2$ solubility in high concentration MEA solution for intensified solvent-based carbon capture

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Abstract. The solvent-based carbon capture process is the most matured and economical route for decarbonizing the power sector. In this process, aqueous monoethanolamine (MEA) is commonly used as the solvent for CO$_2$ scrubbing from power plant and industrial flue gases. Generally, aqueous MEA with 30 wt% (or less) concentration is considered the benchmark solvent. The CO$_2$ solubility data in aqueous MEA solution, used for modelling of the vapour-liquid equilibria (VLE) of CO$_2$ in MEA solutions, are widely published for 30 wt% (or less) concentration. Aqueous MEA with higher concentrations (from 40 to 100 wt%) is considered in solvent-based carbon capture designs with techniques involving process intensification (PI). PI techniques could improve the process economics and operability of solvent-based carbon capture. Developing PI for application in capture process requires CO$_2$ solubility data for concentrated MEA solutions. These data are however limited in literature. The modelling of the vapour-liquid equilibria (VLE) of CO$_2$ in MEA solutions for PI-based solvent capture techniques involving stronger MEA solution of about 80 wt% concentration requires solubility data at the concentration. In this study, the data for 80 wt% MEA is presented for 40, 60, 100 and 120$^\circ$C. The experimental technique and analytical procedure in this study were validated by comparing the measurements for 30 wt% MEA with data from the literature. The data from this study can be fitted to VLE models such as electrolyte NRTL, extended UNIQUAC etc. which is an important component of solvent-based capture model using MEA as the solvent. More accurate VLE models will improve the prediction accuracy of capture level, rich loading etc. using PI-based solvent-based capture model.

1 Introduction

Aqueous monoethanolamine (MEA) is an essential industrial solvent for CO$_2$ scrubbing from gas mixtures [1]. Generally, aqueous MEA with 30 wt% (or less) concentration is considered the benchmark solvent in CO$_2$ absorption processes. For example, Kerr-McGee/ABB Lummus Crest process and Fluor Daniel’s Econamine FG process, the oldest

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commercial solvent-based CO₂ capture processes, uses 20 and 30 wt% MEA solutions respectively as solvent [2]. The CO₂ solubility data in aqueous MEA solution, used for modelling the vapour-liquid equilibria (VLE) in MEA solutions [3], are widely published for 30 wt% (or less) concentration [3-5]. Aqueous MEA with higher concentrations (up to 100 wt%) are considered in solvent-based carbon capture designs with techniques involving process intensification (PI) such as rotating packed beds [6-9]. PI techniques could improve the process economics and operability [8-10]. The CO₂ solubility data for concentrated MEA solutions (> 30 wt%) are however limited in literature: Mason and Dodge [11] and Atadan [12] data covered up to 74 and 59 wt% MEA concentrations respectively. However, their measurements did not include regeneration temperature conditions (> 100°C). More extensive data covering up to 120°C and 60 wt% MEA concentration was reported in Aronu et al. [13]. More data covering similar temperature range as Aronu et al. [13] for higher concentration is necessary. The aim of this study is to experimentally obtain CO₂ solubility data for 80 wt% MEA solution at 40, 60, 80, 100 and 120°C to complement existing data for concentrated MEA solution.

2 Experiment

2.1 Materials

MEA (purity ≥ 99 wt%) was supplied by Aladdin Industrial Corporation and used without further purification. The gases used, CO₂ (>99.99 vol%) and N₂ (>99.99 vol%) and the various calibration gases (100 vol% N₂, 97 vol% N₂+3 vol% CO₂, 85 vol% N₂+15 vol% CO₂ and 50 vol% N₂+50 vol% CO₂), were supplied by Beijing Qianxi Gas Chemical Industry Co., Ltd. The 30 and 80 wt% MEA solutions were prepared using deionized water; a Mettle Toledo precision digital balance (ME103/M, accuracy ± 0.001 g) was used to weigh the MEA for the preparation of the solution.

2.2 Experimental setup

The solubility measurements at 40°C and 60°C were carried out in a low temperature thermostatic VLE reactor while measurements at 100°C and 120°C were carried out in a high temperature thermostatic VLE reactor shown in Fig 1. The reactors are similar to the ones in literature [14]. They consist of an electrically heated stainless steel cylindrical tank (400 mL) fitted with a magnetic stirrer at the top and inlet and outlet ports for the gas and liquid. The temperature was measured using calibrated thermometers, with an uncertainty of ± 0.1 K, inserted into the reactor. The pressure in the reactor and gas containers were measured using a calibrated pressure transducer with an uncertainty of ± 0.25%.

2.3 Experimental procedure

Each reactor was purged using N₂ gas before beginning the solubility experiment. This is to remove any gas left in the tank. About 80 mL of the prepared MEA solution was injected into the reactor through the liquid inlet valve and the temperature was adjusted to the desired value. The solution in the reactor was continuously stirred at 100 rpm to achieve equilibrium (i.e. when the liquid and vapour phase temperatures are equal). The initial pressure of the reactor was recorded as well as the temperature and pressure of CO₂ tank. CO₂ is then injected into the reactor. The amount of CO₂ injected into the tank was calculated through the pressure and temperature differences of the CO₂ container before and after injecting the CO₂ using Peng Robinson equation of state. New reactor pressure is
recorded each time (approximately 24hrs) when vapour-liquid equilibrium is reached in the reactor after CO₂ is injected into the reactor. The VLE data is obtained in the form of equilibrium partial pressure of CO₂ ($p_{CO₂}$) for the vapour phase and CO₂ loading for the liquid phase. The vapour phase was assumed to follow Dalton’s Law and as such the equilibrium partial pressure of CO₂ was simply taken as the difference between the total equilibrium pressure and the initial pressure of the reactor [14].

![Diagram of the thermostatic VLE stirred reactor](image)

**Fig. 1.** Schematic diagram of the thermostatic VLE stirred reactor.

The CO₂ loading in the liquid phase was obtained as follows:

$$\alpha_{CO₂} = \frac{n_{CO₂} - n_{CO₂}^g}{n_{MEA}}$$  

(1)

where:
- $n_{CO₂}$ = moles of CO₂ injected
- $n_{CO₂}^g$ = moles of CO₂ remaining in the vapour phase
- $n_{MEA}$ = moles of MEA in the liquid phase

The moles of CO₂ remaining in the vapour phase were determined as follows:

$$n_{CO₂}^g = \frac{V_e \cdot PCO₂}{Z_{CO₂} RT}$$  

(2)

where:
- $V_e$ = volume of gas phase
- $Z_{CO₂}$ = compressibility factor of CO₂ in the equilibrium reactor obtained using Peng-Robinson equation of state.

### 3 Results

The CO₂ solubility data for the system was first obtained at a condition, namely 30 wt% MEA solution at 40°C, for which data had previously been reported in literature to confirm the sampling and analytical procedure in this study and to validate the thermostatic VLE stirred reactor. The data, presented in the form of partial pressure as a function of the CO₂ loading, obtained at this condition were compared with existing data from literature [3,13]. The result from the comparison, shown in Fig. 2, indicate that the measurements using the procedure and reactor in this study agrees closely with the data from different sources in the literature. This indicates that the procedure can be relied on with confidence to obtain CO₂.
solubility data in an 80 wt% MEA solution at different temperature. The results of the measurements in the 80 wt% MEA solution at different temperature is presented in Table 3.

![Graph showing solubility of CO₂ in an 80 wt% MEA solution at different temperatures.](image)

**Fig. 2.** Solubility of CO₂ in a 30 wt% MEA solution at 40°C.

|        | 40°C |       | 60°C |       | 100°C |       | 120°C |       |
|--------|------|-------|------|-------|-------|-------|-------|-------|
| \( \alpha_{\text{CO}_2} \) | \( P_{\text{CO}_2} \) (kPa) | \( \alpha_{\text{CO}_2} \) | \( P_{\text{CO}_2} \) (kPa) | \( \alpha_{\text{CO}_2} \) | \( P_{\text{CO}_2} \) (kPa) | \( \alpha_{\text{CO}_2} \) | \( P_{\text{CO}_2} \) (kPa) |
| 0.15   | 0.46 | 0.03  | 0.18 | 0.08  | 1.81  | 0.04  | 1.07  |
| 0.17   | 0.93 | 0.05  | 0.52 | 0.09  | 2.59  | 0.05  | 3.07  |
| 0.19   | 1.14 | 0.09  | 1.00 | 0.10  | 3.15  | 0.08  | 9.44  |
| 0.21   | 1.3  | 0.11  | 1.42 | 0.11  | 3.14  | 0.09  | 13.87 |
| 0.24   | 1.61 | 0.13  | 1.48 | 0.13  | 3.56  | 0.10  | 18.73 |
| 0.26   | 1.43 | 0.15  | 1.58 | 0.14  | 3.95  | 0.12  | 27.46 |
| 0.28   | 1.05 | 0.17  | 1.38 | 0.15  | 3.78  | 0.14  | 31.91 |
| 0.30   | 1.4  | 0.21  | 1.36 | 0.16  | 4.19  | 0.16  | 33.46 |
| 0.32   | 1.76 | 0.23  | 1.8  | 0.18  | 4.59  | 0.17  | 34.02 |
| 0.35   | 1.82 | 0.28  | 2.11 | 0.19  | 5.09  | 0.18  | 37.28 |
| 0.37   | 2.14 | 0.32  | 2.16 | 0.21  | 5.11  | 0.20  | 39.17 |
| 0.41   | 2.8  | 0.34  | 2.42 | 0.22  | 5.48  | 0.23  | 49.08 |
| 0.44   | 3.15 | 0.36  | 3.54 | 0.24  | 6.2   | 0.24  | 56.92 |
| 0.46   | 5.44 | 0.38  | 4.01 | 0.25  | 6.59  | 0.25  | 62.62 |
| 0.47   | 8.38 | 0.42  | 5.75 | 0.26  | 7.67  | 0.26  | 67.52 |
| 0.49   | 18.53 | 0.43  | 7.8  | 0.27  | 8.82  | 0.27  | 76.33 |
| 0.50   | 28.05 | 0.44  | 11.51 | 0.29  | 9.81  | 0.28  | 75.97 |

**Table 3.** Solubility of CO₂ in an 80 wt% MEA solution.
4 Conclusions

A new VLE data for CO₂ absorption in 80 wt% MEA has been obtained from 40 to 120°C. The VLE data is useful for modelling and simulation of CO₂ absorption in 80 wt% MEA solution which have been found to be applicable in PI-based designs such as rotating packed beds. The experimental approach used in this study was first validated by taking VLE measurements at 30 wt% MEA concentration and comparing the result to data from different sources in literature. The result from the comparison showed good agreement with literature and demonstrated the reliability of the procedure and reactor.

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References
1. Oko, E., Wang, M. and Joel, A.S. Current status and future development of solvent-based carbon capture. *Int. J. Coal Sci. Technol.* (2017) 4(1), 5–14

2. Rao, A. B., Rubin, E.S. and Berkenpas, M., 2004. An integrated modelling framework for carbon management technologies, Volume 1 – Technical documentation: Amine-based CO2 capture and storage systems for fossil fuel power plant. Available at: https://www.cm.edu/epc/icem/documentation/tch_04.pdf [Accessed March, 2018].

3. Jou, F.-Y., Mather, A. E., Otto, F. D. The solubility of CO2 in a 30 mass percent monoethanolamine solution. *Can. J. Chem. Eng.* 73 (1995), 140-147.

4. Wagner, M., Harbou, I. Kim, J., Ermatchkova, I., Maurer, G. and Hasse, H. Solubility of carbon dioxide in aqueous solutions of monoethanolamine in the low and high gas loading regions. *J. Chem. Eng. Data* 58 (2013), 883–895.

5. Lee, J. I., Otto, F. D. and Mather, A. E. Equilibrium between carbon dioxide and aqueous monoethanolamine solutions. *J. Appl. Chem. Biotechnol.* 26 (1976), 541-549.

6. Oko, E., Ramshaw, C. and Wang, M. Study of absorber intercooling in solvent-based CO2 capture based on rotating packed bed technology. *Energy Procedia* 142 (2017) 3511–3516.

7. Chambers, H.H. and Wall, R.G. Some factors affecting the design of centrifugal gas absorbers. *Trans. Instn Chem. Engrs.* 32 (1954), 96-107.

8. Joel, A. S., Wang, M., Ramshaw, C., Oko, E. Process analysis of intensified absorber for post-combustion CO2 capture through modelling and simulation. *Journal of Greenhouse Gas Control*, 21 (2014), 91–100.

9. Jassim, M.S., Rochelle, G., Eimer, D., Ramshaw, C. (2007). Carbon dioxide absorption and desorption in aqueous monoethanolamine solutions in a rotating packed bed. *Industrial & Engineering Chemistry Research*, 46(9), 2823–2833.

10. Thiels, M., Wong, D. S. H., Yu, C.-H., Kang, J.-L., Jang, S. S., Tan, C.-S. (2016). Modelling and design of carbon dioxide absorption in rotating packed bed and packed column. In 11th IFAC Symposium on Dynamics and Control of Process Systems, *including Biosystems*. Trondheim, Norway.

11. Mason, J. W. and Dodge, B. F. Equilibrium absorption of carbon dioxide by solutions of the ethanolamines. *Trans. Amer. Inst. Chem. Eng.* 32 (1936), 27-48.

12. Atadan, E. M. (1954). Absorption of carbon dioxide by aqueous monoethanolamine solutions, *Ph.D. Thesis*, University of Tennessee, Knoxville, TN.

13. Aronu, U.E., Gondal, S., Hessen, E.T., Haug-Warberg, T., Hartono, A., Hoff, K.A. and Svendsen, H.F., 2011. Solubility of CO2 in 15, 30, 45 and 60 mass% MEA from 40 to 120 1C and model representation using the extended UNIQUAC framework. *Chemical Engineering Science*, 66, pp.6393–6406.

14. Luo, W., Yang, Q., Conway, W., Puxty, G., Feron, P., Chen, J. Evaluation and modelling of vapour–liquid equilibrium and CO2 absorption enthalpies of aqueous designer diamines for post combustion capture processes. *Environ. Sci. Technol.* 2017, 51, 7169–7177.