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°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 CO_2 capture processes, uses 20 and 30 wt% MEA solutions respectively as solvent [2]. The CO_2 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 CO_2 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 (> 100ºC). More extensive data covering up to 120ºC 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 CO_2 solubility data for 80wt% MEA solution at 40, 60, 80, 100 and 120ºC 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, CO_2 (>99.99 vol%) and N_2 (>99.99 vol%) and the various calibration gases (100 vol% N_2, 97 vol% N_2+3 vol% CO_2, 85 vol% N_2+15 vol% CO_2 and 50 vol% N_2+50 vol% CO_2), 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 $\pm$ 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 $\pm$ 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 $\pm$ 0.25%.

2.3 Experimental procedure

Each reactor was purged using N_2 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 CO_2 tank. CO_2 is then injected into the reactor. The amount of CO_2 injected into the tank was calculated through the pressure and temperature differences of the CO_2 container before and after injecting the CO_2 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 CO_2 is injected into the reactor. The VLE data is obtained in the form of equilibrium partial pressure of CO_2 (p_{CO_2}) for the vapour phase and CO_2 loading for the liquid phase. The vapour phase was assumed to follow Dalton's Law and as such the equilibrium partial pressure of CO_2 was simply taken as the difference between the total equilibrium pressure and the initial pressure of the reactor [14].
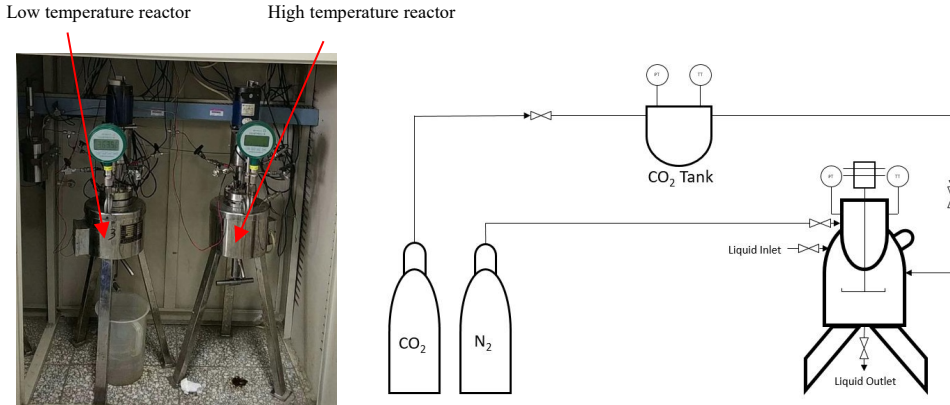

Fig. 1. Schematic diagram of the thermostatic VLE stirred reactor.

The CO_2 loading in the liquid phase was obtained as follows:

$$\alpha_{CO_2} = \frac{n_{CO_2} - n_{CO_2}^g}{n_{MEA}} \qquad (1)$$

where:

n_{CO_2} = moles of CO_2 injected

$n_{CO_2}^g$ = moles of CO_2 remaining in the vapour phase

n_{MEA} = moles of MEA in the liquid phase

The moles of CO_2 remaining in the vapour phase were determined as follows:

$$n_{CO_2}^g = \frac{V_c^g \, PCO_2}{Z_{CO_2} RT} \qquad (2)$$

where:

V_c^g = volume of gas phase

Z_{CO_2} = compressibility factor of CO_2 in the equilibrium reactor obtained using Peng-Robinson equation of state.

3 Results

The CO_2 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 CO_2 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 CO_2

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.
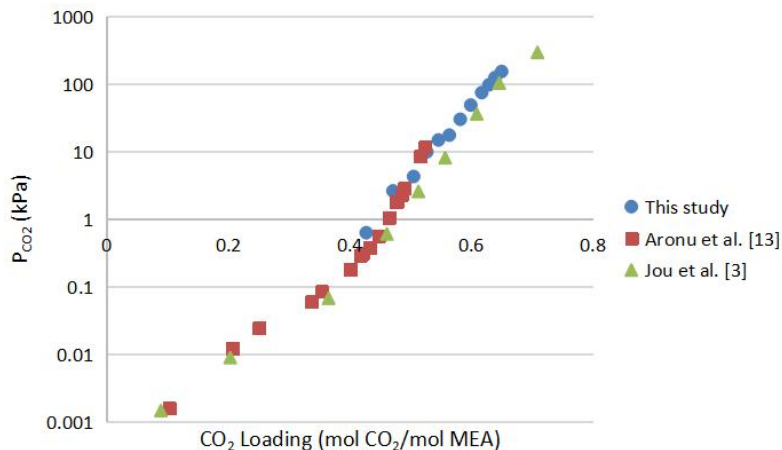

Fig. 2. Solubility of CO_2 in a 30 wt% MEA solution at 40°C.

Table 3. Solubility of CO_2 in an 80 wt% MEA solution.

40°C		60°C		100°C		120°C	
α_{CO_2}	P_{CO_2}(kPa)	α_{CO_2}	P_{CO_2}(kPa)	α_{CO_2}	P_{CO_2}(kPa)	α_{CO_2}	P_{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

0.51	47.42	0.46	14.12	0.30	11.51	0.30	80.82
0.51	71.03	0.47	22.57	0.31	11.32	0.31	85.68
0.52	103.64	0.48	29.38	0.32	13.44	0.32	90.43
0.53	122.25	0.48	40.63	0.33	16.81	0.34	103.44
0.53	141.48	0.49	59.39	0.34	16.19	0.34	106.62
0.54	172.03	0.50	99.76	0.35	18.19	0.35	123.02
0.54	192.56	0.50	131	0.36	21.41	0.36	138.84
0.54	208.08	0.51	173.52	0.37	24.39	0.37	153.73
0.55	245.62			0.38	30.5	0.37	160.15
				0.39	39.85	0.38	170.61
				0.40	50.44	0.38	180.81
				0.41	60.5	0.39	182.67
				0.42	69.99	0.39	190.29
				0.43	95.37	0.40	204.04
				0.44	116.1	0.40	210.34
				0.45	136.29	0.41	229.87
				0.45	160.3		
				0.45	185.16		
				0.46	209.01		
				0.46	229.6		
				0.47	264.68		

4 Conclusions

A new VLE data for CO_2 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.

Acknowledgments

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