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Absorption of CO_2 in Aqueous Blends of Methyl-Diethanolamine (MDEA) and Diethanol Amine (DEA): 25wt% MDEA-25wt% DEA and 30wt% MDEA-20wt% DEA Concentrations

Khalid Osman[1], Coquelet Coquelet[2], Deresh Ramjugernath[1*]

[1]Thermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu Natal, 4041, Durban, South Africa

[2]Mines Paris-Tech Centre d'Énergétique et procédés, CEP/TEP, 35, rue Saint Honoré, 77305 Fontainebleau, France

* Corresponding author : E-mail: ramjuger@ukzn.ac.za; Tel: +27312603128; Fax: +2731260118

Abstract

This report contains CO_2 loading data for the solvent absorption of CO_2. Two amine blends were studied extensively using a static analytic apparatus described herein. The blends were 25wt%MDEA-25wt%DEA-50wt%H_2O and 30wt%MDEA-20wt%DEA-50wt%H_2O. A minor study was conducted on a 50wt%DEA-50wt%H_2O solvent as well. Different CO_2 partial pressures were studied, ranging from 0.05 to 1.05 MPa. Nitrogen gas was used for achieving desired system pressure. System pressures ranged from 0.5 to 1.5 MPa. Solvent absorption was studied at 363.15 and 413.15 K. The data is presented and discussed in this report, both tabulated, as solubility curves and partition coefficient curves. Conclusions drawn from the CO_2 liquid loading data are that increasing temperature greatly reduces the absorption capacity of the solvents studied. The amine blend of 25wt%MDEA-25wt%DEA-50wt%H_2O produced the best loading performance of all the solvents studied, as well as the literature data that was used for comparison. This proved that higher concentrations of DEA in the blend, is beneficial in increasing CO_2 liquid loading in relation to CO_2 partial pressure. The data was also compared to similar systems in literature, as well as in terms of partition coefficients, showing some contradictory and varying results. The literature data found also varied among sources. A wider and more standardised method of experimentation is required to confirm the results.

Introduction

The reduction of CO_2 emissions by industries is of utmost importance in an attempt to curb air pollution and global climate change. As of 2008, CO_2 concentrations in the atmosphere stood at 383.9 ppm (CDIAC 2007), a 37% increase since the beginning of the industrial revolution of the late 18th century. This is the likely cause of the acceleration of global warming and rapid climate change. CO_2 emitting industries include petroleum refineries, coal power plants, steelmaking and cement producing industries.

One solution to this problem is amine absorption. It is a CO_2 capture technique. It involves passing the flue gas emanating from various process industries through an absorber. An amine solvent is also passed through the absorber and is contacted with the flue gas. CO_2 is selectively absorbed into the solvent. One overriding issue however, is the choice of an applicable solvent that would provide a high absorption rate and absorption capacity.

There has been much research done in the application of single amines of different concentration. Mamun (2005) has done low pressure solubility and absorption rate measurements for monoethanolamine (MEA), 2-(butylamino)ethanol (BEA), *N*-methyldiethanolamine (MDEA), 2-(methylamino)ethanol (MMEA), 2-(ethylamino)ethanol (EMEA), 2-(2-aminoethyl-amino)ethanol (AEEA) and Piperazin PZ solvents of different solvent concentrations and CO_2 partial pressures. Coquelet and Richon (2007) measured solubilities of CO_2 of up to 0.3 MPa partial pressure in 50wt% MDEA at temperatures up to 393.15 K. Bouallou et al. (2007) considered MEA, MDEA and DEA solvents at 30wt% concentration. Oexmann et al. (2007) considered the use of potassium carbonate for absorption at 335.15 K. Nerula and Ashraf (1987) did a vast study on MEA, MDEA, DEA and K_2CO_3 solvents of different concentrations.

Another idea is to blend two or more amines in an attempt to ensure high absorption rate and absorption capacity. Primary amines such as MEA have high CO2 absorption rates but comparatively low absorption capacity and high corrosiveness. Tertiary amines such as MDEA have high absorption capacity but low absorption rate. Secondary amines vary in their performance, with absorption rate generally favoured over absorption capacity (IPCC (2005)).

There has been much research into this idea in recent years. Although it is still an emerging technique, there is substantial data available for comparison. Mamun et al. (2006) obtained solubility data for MDEA, BEA, AEEA and MEA blends. Bouallou et al. (2007) focussed on MEA-MDEA of different blend ratios and solvent concentrations. Oexmann et al. (2008) obtained loading data for Potassium Carbonate-PZ blends of different concentrations.

Therefore, further research into the use of blended solvents was undertaken. There is abundant information regarding the use of MEA-MDEA blends. Kaewsichen and Al-Bofersen (2001) have obtained solubility data for MDEA-MEA blends at 25-120°C and CO_2 partial pressures of 0.1-10 bar. Comparatively less data is available for MDEA-DEA blends, which are also of great interest. Data is typically limited in temperature range and often recorded for low CO_2 partial pressures. Kundu and Bandyopadhyay (2006) studied and obtained solubility data for MDEA-DEA blends in MDEA-DEA compositions of 1.5-28.5, 3-27, 4.5-25.5 (wt%), at CO_2 partial pressures of up to 1 bar and temperatures up to 50°C. Murrieta-Guivara et al. (1998) published solubility data for CO_2 in MDEA-DEA blends of ratios 15-10, 20-10, 10-20 and 35-10 (wt%) at temperatures from 30-120°C. CO_2 partial pressures ranged from 0.3-3 MPa.

One of the advantages stated regarding secondary and tertiary amines, was their relatively low corrosiveness. Many papers did not exploit this advantage and investigated solvent weight fractions of 30%. Murrieta-Guevara et al. (1998) was one of the few sources investigating solvent concentrations of up to 45wt%. This study focussed on solvent concentrations of 50wt%. Two solvent blend ratios were studied: 25wt% MDEA - 25wt% DEA – 50wt% Water, and 30wt% MDEA – 20wt% DEA – 50wt% water.

The reaction mechanism for systems involving CO_2, DEA (a secondary amine) and MDEA (a tertiary amine) is as follows (Mamun et al. (2005), and Austgen et al. (1991)):

1) $CO_2\ (g) \leftrightarrow CO_2\ (aq)$.....$CO_2$ phase change
2) $2H_2O \leftrightarrow OH^- + H_3O^+$.....Dissociation of H_2O
3) $2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^-$.....Dissociation of CO_2
4) $H_2O + HCO_3^- \leftrightarrow CO_3^{2-} + H_3O^+$.....Dissociation of Bicarbonate ion

Reactions 1) to 4) are common for all amines. Thereafter, the reaction mechanism differs between primary and secondary amines, which form zwitterions mechanisms, and tertiary amines which undergo alternative reactions. Reaction mechanisms for DEA and CO_2 are as follows:

5) $CO_2 + R^1R^2NH \leftrightarrow R^1R^2NH^+COO^-$.....Zwitterion formation
6) $R^1R^2NH^+COO^- + B \leftrightarrow R^1R^2NCOO^- + BH^+$.....Zwitterion deprotonation by a base

The mechanism for MDEA is different to DEA. Tertiary amines cannot react with CO_2 directly. The tertiary amine acts as a base for CO_2 to react with hydroxide in solution according to the following reaction mechanism (Mamun et al.(2005)):

7) $R^1R^2R^3N + H_2O \leftrightarrow R^1R^2R^3NH^+ + OH^-$.....Dissociation of Amine
8) $CO_2 + OH^- \leftrightarrow HCO_3^-$.....Hydroxide reaction
9) $CO_2 + R^1R^2R^3N + H_2O \leftrightarrow R^1R^2R^3NH^+ + HCO_3^-$.....Overall reaction (7) and 8) combined)

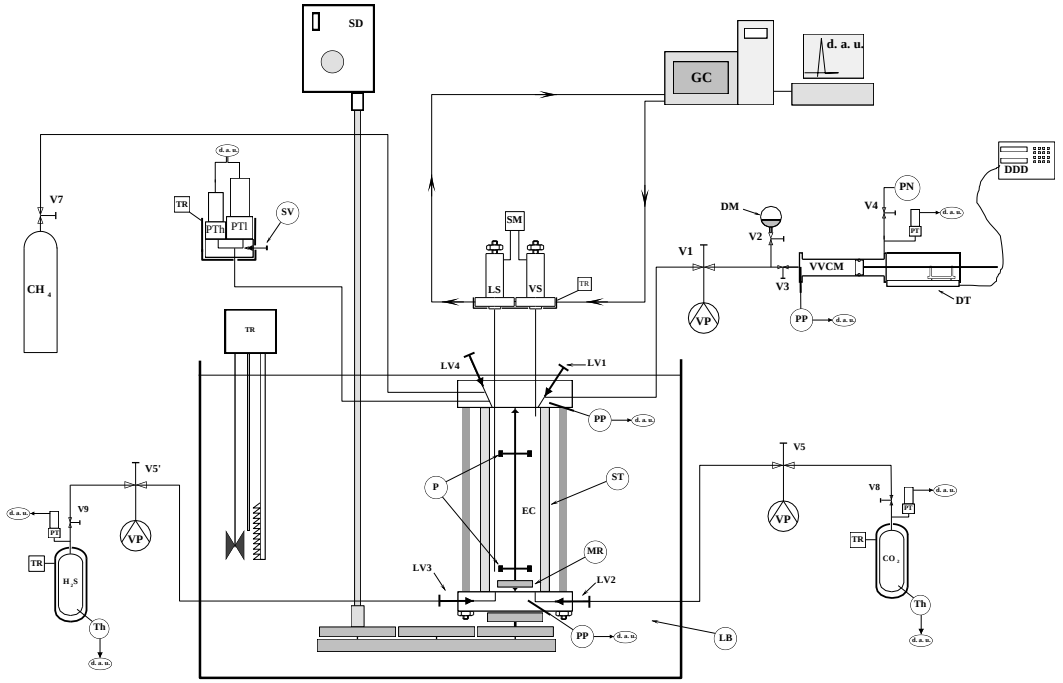
The solvents were studied at system temperatures of 363.15 and 413.15 K and at total pressures of 0.5 bar and 1.5 MPa.

A further minor study was done testing the performance of 50wt% DEA in H_2O, at 393.15 K and at 1.5 MPa system pressure.

Experimental Method

Apparatus used

A static analytic apparatus was used to determine the solubility of CO_2 and N_2 for the systems mentioned.



d. a. u. : Data Acquisition Unit ; DDD : Displacement Digital Display ; DM : Degassed Mixture ; DT : Displacement Transducer ; EC : Equilibrium Cell ; GC : Gas Chromatograph ; LB: Liquid Bath; LS : Liquid Sampler ; LVi : Loading Valve ; MR; Magnetic Rod; P: Propeller; PP : Platinum Probe ; PN : Pressurized Nitrogen ; PT: Pressure transducer; PTh: Pressure transducer for high pressure values; PTl: Pressure transducer for low pressure values; SD : Stirring Device ; SM: Sample Monitoring; ST : Sapphire Tube ; TR: Thermal Regulator; Th: Thermocouple Vi: Valve; VP: Vacuum Pump; VS: Vapor Sampler; VVCM: Variable Volume Cell for Mixture.

Figure 1: Static Analytic Apparatus

Figure 1 shows a diagram of the apparatus. The equilibrium cell (EC) is composed of a sapphire tube (ST) between two hastelloy flanges, which allows for system pressures of up to 10.0 MPa and operating temperatures up to 473.15 K. The internal diameter of the cell is 25 mm (±0.01mm) and the total volume is 34 cm^3 (±1x10-6 mm^3). The top flange has two non-rotating stem valves (LV1 and LV4) for gas or liquid loading. For this project, one valve was closed and inactive, while the other was used for N_2 pressurisation. The bottom flange has two non-rotating stem valves (LV2 and LV3), for which liquid solvent loading and CO_2 loading was used. Inside the equilibrium cell is a rotating axis holding a magnetic rod (MR) with two propellers (P) (one for liquid stirring and one for gas

stirring). The magnetic rod and the propellers are rotated by a stirring assembly and driven by a stirring motor (SD).

To control temperature and maintain system temperature, the cell is immersed in a Ultra-Kryomat Lauda constant temperature liquid bath (LB). The liquid that was used was silicone oil, which can be used as a heating medium for up to 553.15 K. Temperature is controlled to within 0.01 K. Temperature is monitored using PT100 thermometer devices connected to an HP Data Acquisition unit (HP34970A). There are two thermometers in the cell measuring liquid and vapour phase temperature to check for thermal gradients and determine thermal equilibrium. The temperature of CO_2 gas is also monitored at its cylinder, to ensure constant temperature while loading. The same monitoring exists for H_2S gas as well, but it is not used for this project. Calibration of the PT100 thermometers is done periodically against a 25Ω reference platinum resistance thermometer (Tinsley Precision Instruments). A second order calibration was achieved by Laboratoire National d'Essais (Paris) based on the 1990 International Temperature Scale. The uncertainty is ±0.01K in the range of 278.15 to 402.81K.

N_2 gas is used merely to achieve the desired total system pressure. Pressure is monitored by Druck pressure transducers. The equilibrium cell has two pressure transducers. One for accurate pressure measurement of pressures of 0-1 MPa and one for 0-10MPa. Pressure transducers are also present for measuring pressure in CO_2 and H_2S cylinders. All transducers are connected to an HP data acquisition unit (HP34970A). Transducers were calibrated using a Dead Weight Pressure Balance. (Desgranges & Huot 5202S, CP 0.3 to 40 MPa, Aubervilliers, France). The uncertainty was found to be ±0.0001MPa.

Vapour and liquid sampling is done using ROLSI™ samplers (LS and VS). Sampling is controlled and monitored using a sample monitoring device (SM). Samples are analysed by a Gas Chromatograph (PERICHROM model PR-2100). The thermal conductivity detector is sufficient for the purpose of this project. A "Porapak R80/100 mesh" (1.2m x 2mm ID Silicosteel) column was used in the GC.

The HP data acquisition unit is connected to a personal computer through one RS-232 interface. The sample monitoring device and gas chromatograph is also connected to the personal computer. WINILAB III software ver. 4 was used as the interface. Uncertainty in area determination and resultant composition measurement occurred due to manual integration of areas using the WINILAB III software. The uncertainty is estimated to be ±2% for both vapour and liquid samples.

The density of solvents was measured using an Anton Paar DMA 5000 density meter. Densities were measured over a range of 278.15-343.15 K (the upper and lower bounds of good performance of the measuring instrument). Thereafter, densities were extrapolated to 363.15 and 413.15 K (the

temperature of the systems studied). Measurements for each solvent were done twice to ensure repeatability of measurements.

Gases and Chemicals Used

The N_2 gas used was purchased from Air Liquide. Impurities included CO_2<1ppm v; CO < 1ppm v; H_2O <3ppm v; NO_x < 0.1ppm v and CN_{HM} <0.2ppm v. CO_2 was available 99+% purity.

MDEA at 99+% purity was available from ATOFINA Chemicals Inc., ALDRICH. DEA at 99% was available from SIGMA ALDRICH©. Distilled H_2O was obtained using a Millipore Direct-Q™ 5 water filter. Ethanol, used for cleaning the apparatus was available at 99% purity from Vitlab.

The total amount of CO_2 charged into the cell was measured by pressure and density difference of the CO_2 tank under constant temperature conditions. The uncertainty is ±0.0001 MPa.

The solvents were prepared by combining weighted amounts of DEA, MDEA and H_2O in a round bottom flask under vacuum. A Trivac D2-5E vacuum pump was used. 400g solvent mixtures were prepared each time.

Three solvents were prepared. Their exact composition in wt% is given in Table 1, along with uncertainties in its synthesis:

Table 1: Solvent Compositions and Uncertainties

	MDEA (wt%)	Uncertainty	DEA (wt%)	Uncertainty	Water (wt%)	Uncertainty
Mixture 1	24.9	0.4%	25.0	0.08%	50.1	0.02%
Mixture 2	30.0	0.3%	19.9	0.01%	50.1	0.02%
Mixture 3	-	-	50.0	0.03%	50.0	0.02%

Solvent was charged into the cell for each system run using a Variable Volume Cell (VVCM) attached to a displacement meter with an uncertainty of ±0.001mm. The volumes charged had an uncertainty of ±0.01 cm^3.

Results and Discussion

Refer to Appendix A for sample calculation to get the results shown.

Table 2: Measured Data					
System	Temperature (K)	System Pressure (MPa)	CO_2 Partial Pressure (MPa)	Loading (mol CO_2/mol (MDEA+DEA))	LnP_{CO2}
1. 25wt%MDEA-25wt% DEA	363.15	1.500	0.150	0.108	-1.897
		1.490	0.450	0.296	-0.799
		1.692	1.051	0.789	0.050
		0.497	0.351	0.297	-1.048
		0.465	0.061	0.043	-2.795
		0.488	0.149	0.101	-1.902
2. 25wt%MDEA-25wt% DEA	413.15	1.482	0.151	0.098	-1.891
		1.512	0.450	0.304	-0.799
		1.664	1.153	0.544	0.142
		0.539	0.049	0.042	-3.008
		0.687	0.160	0.102	-1.833
		0.534	0.351	0.200	-1.048
3. 30wt%MDEA-20wt% DEA	363.15	1.495	0.450	0.293	-0.799
		1.723	1.050	0.301	0.049
		0.996	0.152	0.117	-1.887
		0.505	0.057	0.046	-2.863
		0.496	0.351	0.344	-1.048
		0.511	0.152	0.148	-1.886
4. 30wt%MDEA-20wt% DEA	413.15	1.500	0.153	0.094	-1.881
		1.590	1.050	0.301	0.049
		1.556	0.450	0.236	-0.798
		0.499	0.052	0.043	-2.957
		0.531	0.152	0.155	-1.884
		0.522	0.352	0.209	-1.044
5. 50 wt% DEA	393.15	1.484	1.050	0.416	0.049
		1.500	0.450	0.281	-0.798
		1.497	0.150	0.092	-1.896

Table 2 shows the data obtained using the static analytic apparatus shown in Figure 1. The CO_2 liquid loading was calculated using equations and methods described in Appendix A.

For the purpose of this report, the performance of a solvent shall refer to the CO_2 liquid loading of the solvent in relation to its system conditions (ie. system pressure, system pressure and CO_2 partial pressure).

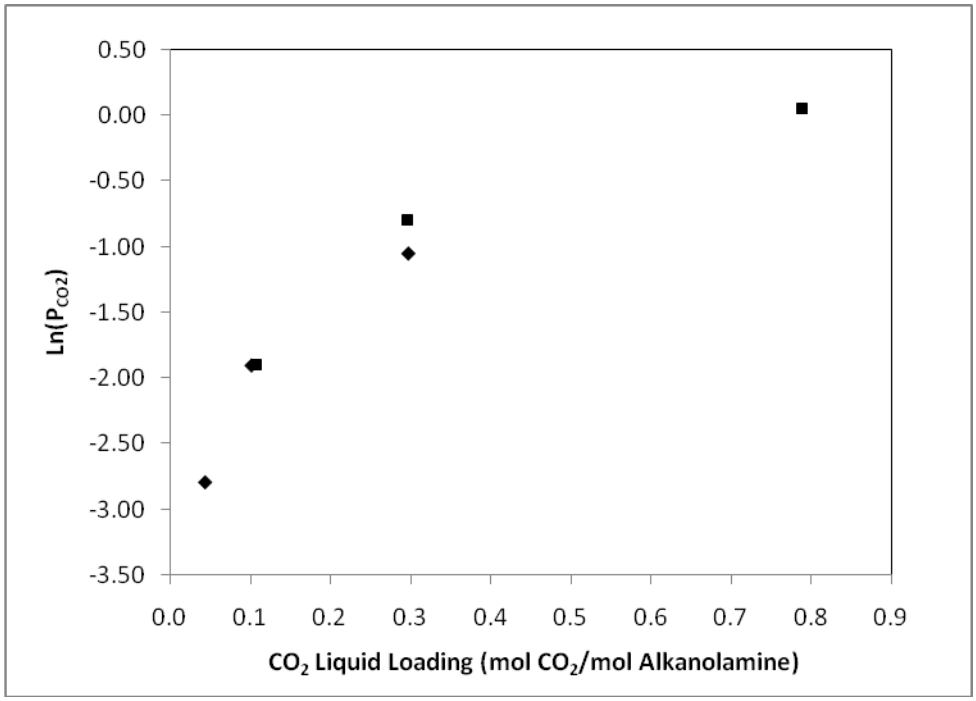


Figure 2: Ln(P_{CO2}) vs CO_2 Loading for System 1: 25wt% MDEA – 25wt% DEA – 50wt%H_2O, at 363.15 K. ♦ - 0.5 MPa System Pressure; ■ – 1.5 MPa System Pressure

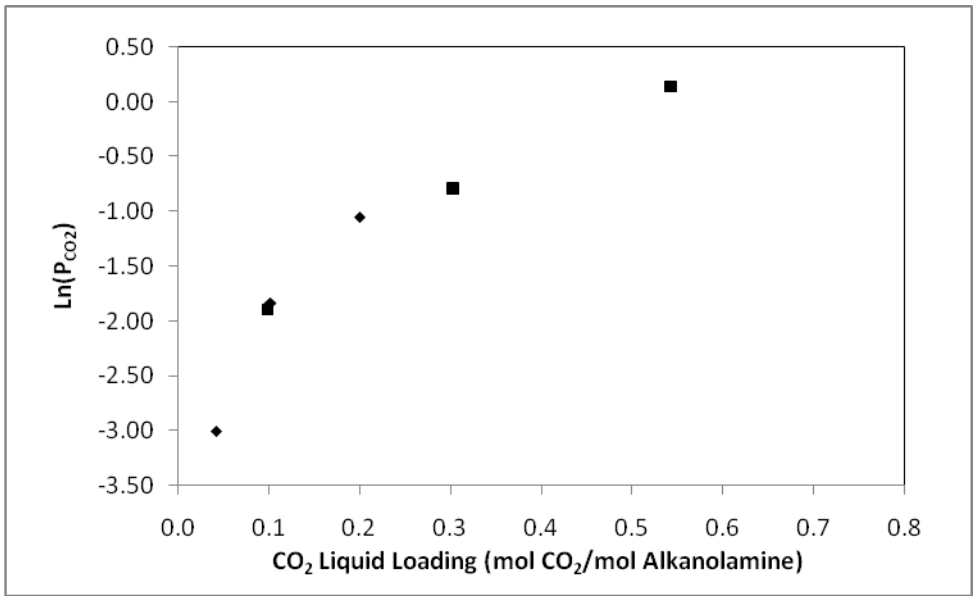


Figure 3: Ln(P_{CO2}) vs CO_2 Loading for System 2: 25wt% MDEA – 25wt% DEA – 50wt%H_2O, at 413.15 K. ♦ - 0.5 MPa System Pressure; ■ – 1.5 MPa System Pressure

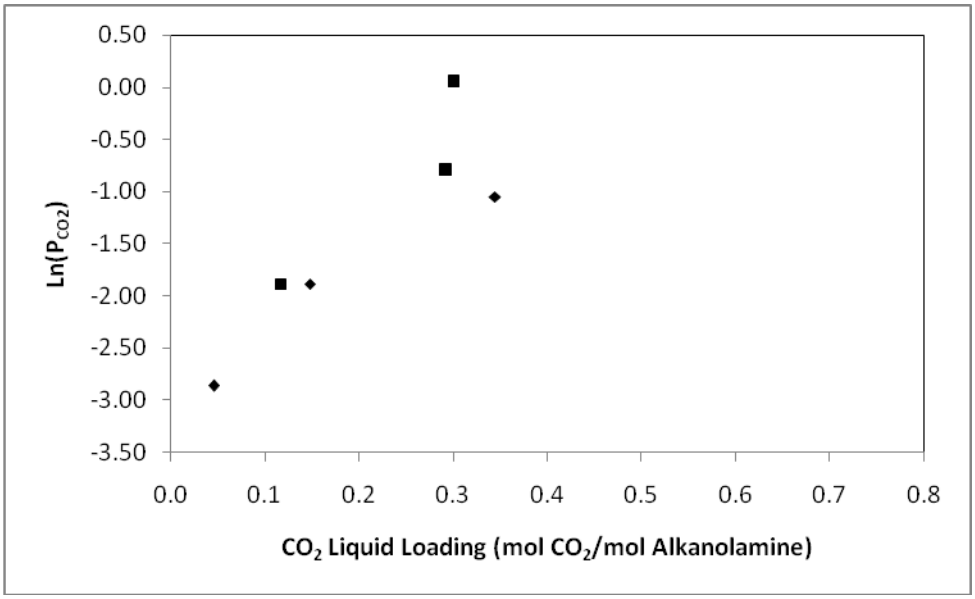


Figure 4: Ln(P_{CO2}) vs CO_2 Loading for System 3: 30wt% MDEA – 20wt% DEA – 50wt% H_2O, at 363.15 K. ♦ - 0.5 MPa System Pressure; ■ – 1.5 MPa System Pressure

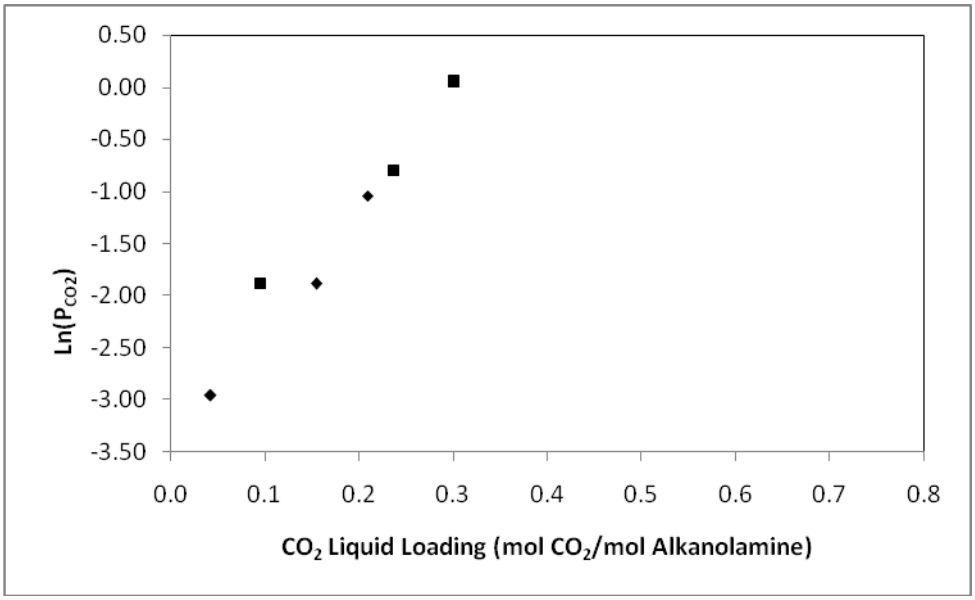


Figure 5: Ln(P_{CO2}) vs CO_2 Loading for System 4: 30wt% MDEA – 20wt% DEA – 50wt% H_2O, at 413.15 K. ♦ - 0.5 MPa System Pressure; ■ – 1.5 MPa System Pressure

One observation of Figures 2-5 is that the total system pressure has a substantial effect on the CO_2 loading in the solvent. In each case, both system pressures produced the same pattern of CO_2 loading in the solvent. However the CO_2 loading is more limited in the case of 5 bar system pressure. This is evident in the pattern of the data shown. The difference is not as significant as expected. Tripling the system pressure produced only minor variations in the data obtained.

This observation has no conclusions on the operation of this process on an industrial scale however, since this lack of effect of system pressure can be attributed to the fact that N_2 gas was used as the

pressurising gas. N_2 gas is practically insoluble in MDEA, DEA and H_2O. Another reason for the lack of difference in results due to total pressure, could be the relatively high rate of absorption of CO_2 and the high absorption capacity of the solvent. Table B1-1 to B4-1 of Appendix B show a consequence of low pressure however. At total pressures of 5 bar, there is increased H_2O composition in the vapour phase. This indicates that H_2O is being lost due to evaporation and entrainment. Industrially, this would be absolutely undesirable.

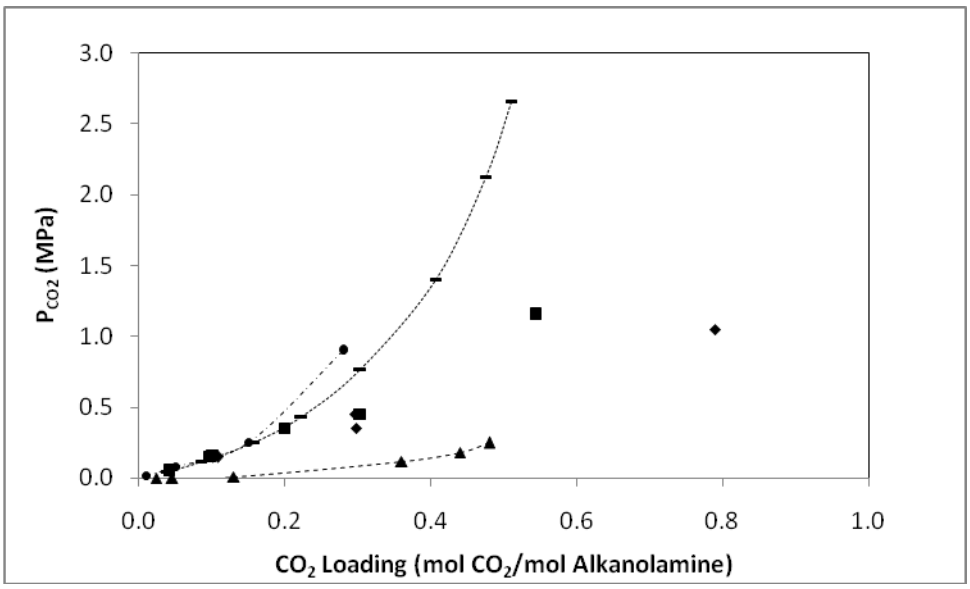


Figure 6: Comparison of System 1 and System 2, using 25wt% MDEA- 25wt% DEA, with other closely related literature data. ♦ - System 1 (363.15 K); ■ – System 2 (413.15 K); - - Guevara et al. (1998), 393.15 K, 20wt% MDEA, 10wt% DEA; ▲- Sulaiman et al. (1998), 353.15 K, 23wt% MDEA, 20wt% DEA; ●- Gabrielson et al. (2005), 393.15 K, 50wt% DEA.

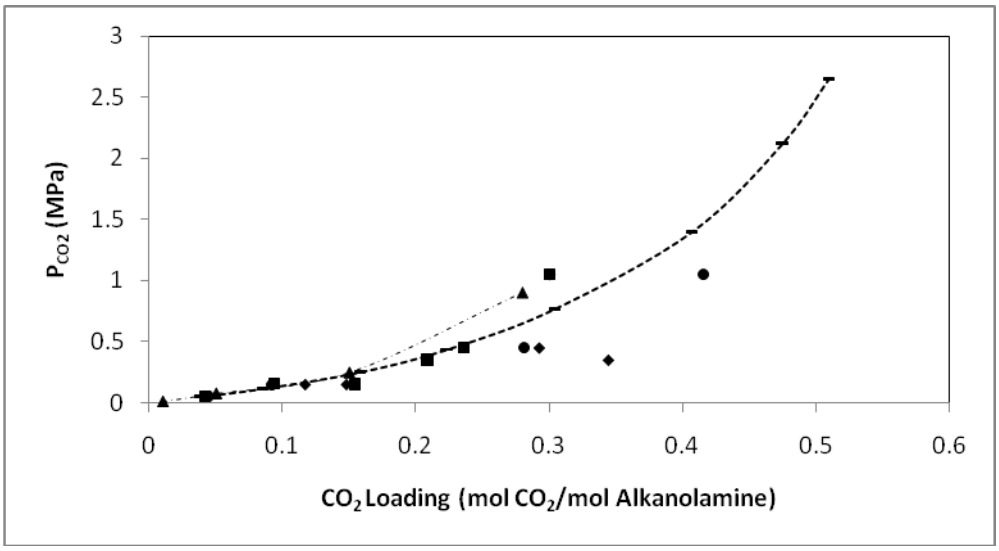


Figure 7: Comparison of System 1 and System 2, using 25wt% MDEA- 25wt% DEA, with other closely related literature data. System 5 (50wt% DEA) also shown. . ♦ - System 3 (363.15 K); ■ –

System 4 (413.15 K); ● - System 5 (393.15 K); - - Guevara et al. (1998), 393.15 K, 20wt% MDEA, 10wt% DEA; ▲- Gabrielson et al. (2005), 393.15 K, 50wt% MDEA.

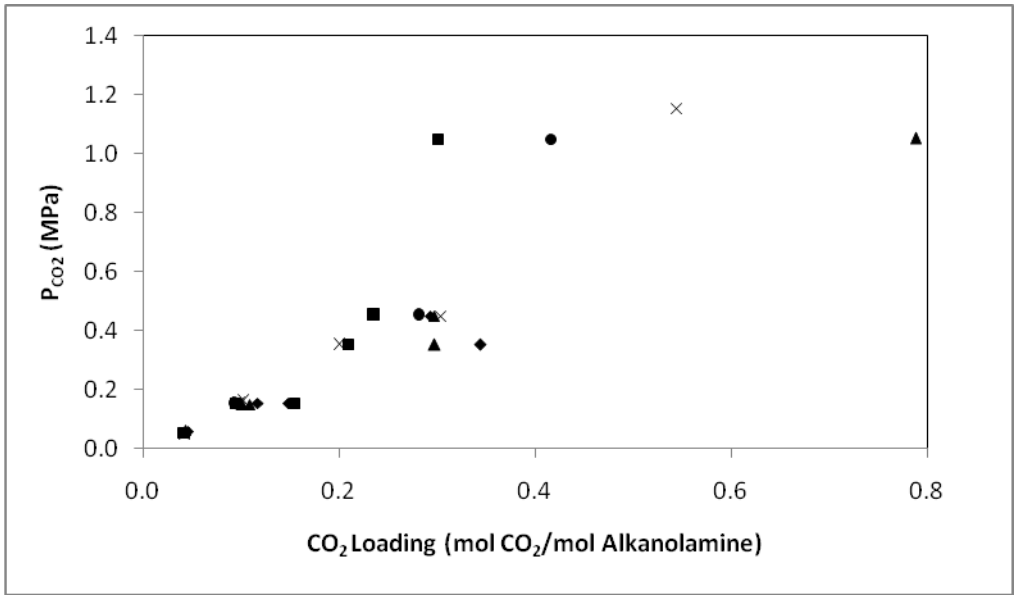


Figure 8: Comparison of all the measured systems. ▲- System 1 (363.15 K); x – System 2 (413.15 K); ♦ - System 3 (363.15 K); ■ – System 4 (413.15 K); ● - System 5 (393.15 K)

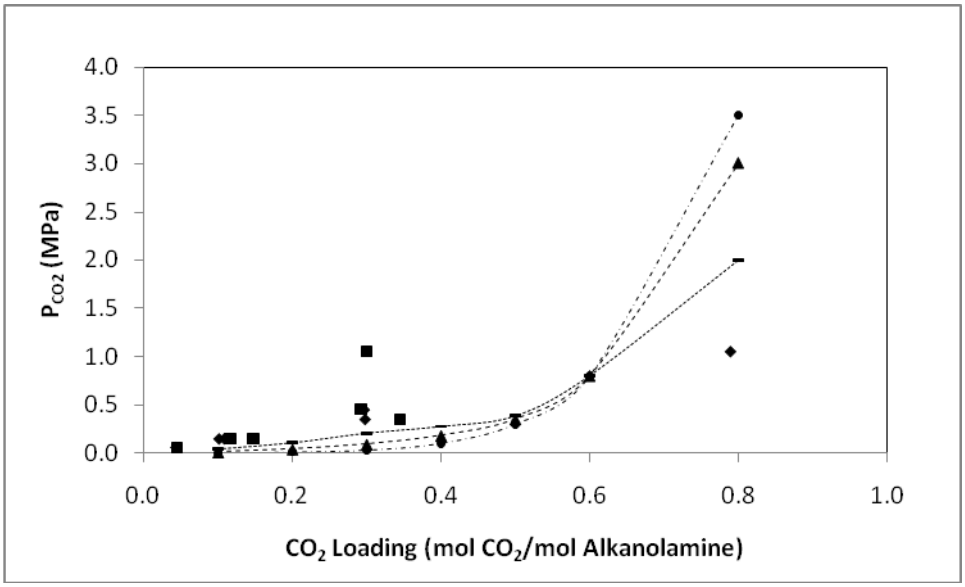


Figure 9: Comparison of System 1 and System 3, at 90°C System Temperature, with other closely related literature data. ♦ - System 1 (363.15 K); ■ – System 3 (363.15 K); - - Austgen and Rochelle (1991), 353.15 K, 45.2 wt% MDEA ; ▲- Austgen and Rochelle (1991), 353.15 K, 22.6 wt% MDEA, 19.9 wt% DEA; ●- Austgen and Rochelle (1991), 353.15 K, 39.8 wt% DEA.

In systems of high temperature (System 2 and 4), a sharp decrease in equilibrium CO_2 loading is clearly shown as compared with System 1 and 3. This is expected as reactive absorption occurs and the absorption reaction is exothermic, for both secondary and tertiary reaction mechanisms. Any increase in temperature would favour desorption. The difference in results between system operating at 363.15 and 413.14 K is very wide. Even with literature comparison, as shown in Figure 6 and 7, solvents with lower concentration achieved better loading performance, because they were used at lower system temperatures. The conclusion is that flue gases with temperatures exceeding 393.15 K, need to be cooled before undergoing CO_2 capture by solvent absorption, in order to achieve greater efficiency. Another consequence of high temperature is that the H_2O in the solvent mixture get evaporated and entrained at high temperatures. This is evident by comparing compositions at different temperatures of Table B1-1 to B4-1 in Appendix B.

From Figure 8, it can be observed that a solvent having 25wt% MDEA and 25wt% DEA (system 1 and 2) yielded higher CO_2 loading than the solvent with 30wt% MDEA and 20wt% DEA (system 3 and 4). This is true when the experiment was done at system temperatures of 363.15 and 413.14 K. This result is somewhat unexpected since a higher amount of MDEA, a tertiary amine, is expected to provide a relatively higher absorption capacity than a solvent having high secondary and primary amine composition.

The result obtained could be due to the very low absorption rate of MDEA. Each system took typically 12 hours to reach equilibrium, during which small changes in system pressure were observed. Thereafter only minuscule changes of system pressure are observed, indicating a very low rate of CO_2 absorption. The reason for the low absorption rate of CO_2 in MDEA, is because of the reaction mechanism that proceeds. With secondary amines such as DEA, CO_2 reacts directly with the amine (reaction 5 as described above), but with tertiary amines CO_2 undergoes a hydroxide reaction before reacting with the amine (reaction 7 and 8).

Three measurements were done using 50wt% DEA (System 5). This was done as a secondary check up for comparing such a solvent with similar solvents studied in the literature. Figure 7 shows the comparison. The data shows that system 5 has better performance than the literature data of 50wt% MDEA and 20wt% MDEA-10wt% DEA. However, the performance is not as good as the amine blends of System 1 to 4. This proves that while high quantities of MDEA are not recommended, a balance or low amount of MDEA does significantly increase CO_2 liquid loading capacity.

The data for System 5 shows a better performance of 50wt% DEA solvent when compared to the data of Murrieta-Guivara et al. (1998) and Gabrielsen et al. (2005) at the temperature of 393.15 K. This is evident in figure 7. By experimentation, it has been successfully proven that a solvent of 50wt% DEA produces better performance than blends which include MDEA, at the same temperature. The superior performance recorded by Sulaiman et al. (1998) were probably due to the decreased temperature.

All systems measured show either similar or better performance than that recorded by Murrieta-Guivara et al. (1998) and Gabrielsen et al. (2005). This is true even though some systems were measured at 413.15 K, higher than the temperature of literature measurements. This proves a significant increase in performance when higher amine concentrations are used in the solvent. It also further emphasises the benefit of blending tertiary amines such as MDEA to produce a solvent that is high in concentration and has low corrosiveness.

It is expected that system 1 and 3 have better loading performance as the temperature was lower. There is a blatant increase in performance. The recommendation is hence to cool the flue gas before applying solvent absorption in industrial applications. Knudsen et al. (2008) shows a pilot plant in Austria operating with a flue gas of 320.15 K, a low temperature which is expected to provide excellent efficiency and solvent performance. System 2 showed better performance than the literature data despite the higher temperature of 413.15 K. This clearly indicates the superiority of the solvent used in system 2 (25wt% MDEA- 25wt% DEA – 25wt% H_2O) over the solvents studied by Murrieta-Guivara et al. (1998) and Gabrielsen et al. (2005). This is evident in Figure 6.

Figure 6, Figure 7 and Figure 8 suggests that the solvent used in Systems 1 and 2 are a success in performance, surpassing those of other measured amine blends and also blends used in other literature sources in figure 8. However, this conclusion seems obscured by the data of figure 9, as the literature data seems to show better results than the results of the solvents studied here. The data by Austgen and Rochelle (1991) was however recorded at a lower system temperature of 353.15 K. Figure 9 thus confirms the important relationship between system temperature and CO_2 liquid loading.

Another observation worth noting is that depicted in Appendix C. The partition coefficients do not show much consistency with changes in solvent, system pressure and system temperature. This is possibly due to the complex reaction mechanism involved between CO_2 and both amines. Sidi-Boumedine et al. (2004) provided liquid and vapour mole fraction results for their study of 25.73wt% MDEA solvent at 313.13 K, with system pressures ranging from 0.5 to 4.3 MPa. The study found that Partition coefficient decreases with CO_2 liquid loading. While Figure C2 and C3 agree with this trend, Figure C1 and C4 do not. The discrepancy could be related to the fact that this study concerns blends of MDEA and DEA at conditions that are very different to Boumedine et al. (2004), and the presence of nitrogen in this study.

Conclusions

- Two solvents, one containing 25wt% MDEA-25wt% DEA and the other containing 30wt% MDEA-20wt% DEA were studied under system temperatures of 363.15 and 413.14 K and under system pressure of 0.5 MPa and 1.5 MPa. CO_2 liquid loadings for different CO_2 partial pressures were investigated and compared.
- CO_2 loading decreases substantially with increasing temperature. Industrially, flue gas will have to be cooled to at least below 393.15 K in order for efficient CO_2 capture to occur. System temperature is a very great influence on solvent performance, sometimes enabling lower amine concentrations to achieve higher CO_2 loading performance.
- System pressure affects CO_2 liquid loading but to a lesser degree than temperature. However, CO_2 partial pressure affects liquid loading greatly. The higher the CO_2 partial pressure, the higher the CO_2 loading.
- Between the two amine blends studied, 25wt%MDEA – 25wt%DEA resulted in higher CO_2 loadings for each CO_2 partial pressure. This was true for both temperatures: 363.15 and 413.14 K. This solvent also produced higher CO_2 liquid loadings than those studied in the literature. This confirms that higher concentrations of DEA are recommended for CO_2 absorption. This is expected as it is what the reaction mechanism suggests.
- The inclusion of MDEA is beneficial however, as MDEA increases the absorption capacity of the solvent. This is evident when comparing CO_2 loading in System 1 and 2 with System 5.
- The amine blend of 25wt% MDEA – 25wt% DEA also showed better performance in comparison with the literature, sometimes despite a lower temperature. Comparison with other literature sources studied in this paper however, confirms that lower temperature can certainly allow for lower amine concentrations in the solvent.
- The data varies substantially in some cases with literature. It was also found that the different literature sources vary widely with each other. A broader, more standardised programme of measurement is needed for MDEA-DEA blends, using a common flue gas composition and a common apparatus.

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Nomenclature

x_x : liquid mole fraction of component x

y_x : vapour mole fraction of component x

X_x : liquid mole fraction of component x in charged solvent

P : Total system pressure (MPa)

P_x : Partial pressure of component x (MPa)

T : System temperature (K)

ρ : solvent density (kg/m^3)

V_S : volume of solvent in the press (m^3)

V_{CO2} : volume of CO_2 in the CO_2 cylinder (m^3)

V : volume of the cell (m^3)

V^V : vapour volume in cell (m^3)

V^L: liquid volume in cell (m^3)

P_{CO2}^1 : Pressure of CO_2 cylinder before charging

P_{CO2}^2 : Pressure of CO_2 cylinder after charging

ρ_{CO2} : Density of CO_2 in cylinder (kg/m^3)

n_x : number of moles of component x

m_s : mass of charged solvent (kg)

x_x^m : mass fraction of component x in the charged solvent

M_x : Molar mass of component x (g/mol)

L_{CO2} : CO_2 loading in amine

v_x^V : molar volume of component x (m^3)

v_T^V : total molar volume (m^3)

Appendix A: CO_2 Loading Calculation Procedure

The quantities measured experimentally are the liquid and vapour mole fractions of CO_2, H_2O, N_2, MDEA and DEA. The system temperature (K) and pressure (MPa), the volume of the solvent charged (m^3) and the solvent density (kg/m^3) is also measured. Liquid mole fractions of components in the prepared solvent were also known by preparation.

Mass of charged solvent $m_s = \rho V_S$

Thus $n_{MDEA} = (x_{MDEA})(m_s)/(M_{MDEA})$

Similarly $n_{DEA} = (x_{DEA})(m_s)/(M_{DEA})$

$n_{H2O} = (x_{H2O})(m_s)/(M_{H2O})$

$n_{total} = n_{MDEA} + n_{DEA} + n_{H2O}$

$n_{amine} = n_{MDEA} + n_{DEA}$

The amount of CO_2 charged into the cell was controlled by pressure difference under constant temperature. The CO_2 tank was used according to pressure difference.

Initial CO_2 Pressure in tank (P_{CO2}^1) was measured using pressure transducer, at constant temperature T_{CO2}. Final CO_2 Pressure in tank (P_{CO2}^2) after charging was also measured.

ρ_{CO2}^1 of CO_2 in tank before charging was obtained using ALLPROPS. (Taken at P_{CO2}^1 , T_{CO2})

ρ_{CO2}^2 of CO_2 in tank after charging was obtained using ALLPROPS (Taken at P_{CO2}^2, T_{CO2})

$\Delta\rho_{CO2} = \rho_{CO2}^1 - \rho_{CO2}^2$

The total volume of the CO_2 tank (V_{CO2}) was 101.692 $x10^{-6}$ m^3

Thus moles taken from the CO_2 tank and loaded into the cell $n_{CO2} = \Delta\rho_{CO2}\ [\frac{mol}{dm^3}] \times V_{CO2}\,[dm^3]$

Total moles dissolved in solvent = $n_{MDEA} \times \frac{x_{CO2}}{x_{MDEA}}$

$V = V^L + V^V$

Hence $V^V = V - V^L$

For CO_2, the molar balance is as follows:

$n_{CO2} = n_{CO2}^L + n_{CO2}^V$

In the vapor phase, the mole number of CO_2 is calculated considering the vapor phase composition.

$$n_{CO2}^{V} = \frac{V^{V}}{v_{T}^{V}} y_{CO2}$$

The molar volumes (v_i^v) of pure gases were used at T, and P to calculate molar volumes (v_T^v). The ALLPROPS Property Package (developed by the Centre of Applied Thermodynamic Studies, University of Idaho, Moscow) was used to obtain molar volumes at the system temperature system pressure.

$$v_{T}^{V} \approx \sum_{i} y_i v_i^{V} = (y_{CO2})(v_{CO2}{}^{V}) + (y_{N2})(v_{N2}{}^{V}) + (y_{H2O})(v_{H2O}{}^{V})$$

Thus

$$n_{CO2}^{V} = \frac{V^{V}}{v_{T}^{V}} y_{CO2}$$

Finally, liquid loadings for CO_2 can be defined as

$$L_{CO_2} = \frac{n_{CO_2} - n_{CO_2}^{V}}{nMDEA + nDEA} = [mol\ CO_2 / mol\ \ a\min e]$$

Appendix B: Measured Vapour and Liquid Compositions and System Data

Table B1-1: 25wt% MDEA - 25wt% DEA - 50wt% H_2O - 90°C									
Measurement	P_{CO2} (MPa)	y_{N2}	y_{CO2}	y_{H2O}	x_{N2} ($x10^6$)	x_{CO2}	x_{H2O}	x_{DEA}	x_{MDEA}
1	0	0.979	0.000	0.021	1.149	0.000	0.861	0.074	0.065
2	0	0.936	0.000	0.064	1.285	0.000	0.861	0.074	0.065
3	0	0.924	0.000	0.076	1.344	0.000	0.861	0.074	0.065
4	0.15	0.951	0.008	0.041	2.342	0.009	0.853	0.073	0.065
5	0.0611	0.881	0.006	0.114	1.444	0.003	0.858	0.074	0.065
6	0.1492	0.923	0.026	0.051	1.562	0.005	0.856	0.074	0.065
7	0.4496	0.901	0.079	0.020	0.988	0.028	0.837	0.072	0.063
8	0.3508	0.704	0.233	0.063	0.996	0.025	0.839	0.072	0.064
9	1.051	0.175	0.760	0.065	1.485	0.054	0.815	0.070	0.062

Table B1-2 : 25wt% MDEA - 25wt% DEA - 50wt% H_2O - 90°C							
Measurement	Average Temp. (K)	Average Pressure (MPa)	Density of Solvent ρ_m (kg/m^3) at 90°C	Measured Volume of Solvent (m^3)	Amount of CO_2 Charged (mol)	CO_2 Liquid Loading (mol CO_2/mol DEA+MDEA)	Partition coefficient
1	361.69	1.497	1042.30	1.41E-05	0.000	0	0
2	362.17	0.984	1042.30	1.42E-05	0.000	0	0
3	362.19	0.491	1042.30	1.42E-05	0.000	0	0
4	362.17	1.500	1042.30	1.42E-05	0.007	0.107	0.976
5	362.14	0.465	1042.30	1.42E-05	0.003	0.043	1.988
6	362.22	0.488	1042.30	1.42E-05	0.007	0.101	4.995
7	362.15	1.490	1042.30	1.42E-05	0.020	0.285	2.875
8	362.16	0.497	1042.30	1.56E-05	0.022	0.287	9.256
9	362.14	1.692	1042.30	1.42E-05	0.058	0.730	14.064

Table B2-1: 25wt% MDEA - 25wt% DEA - 50wt% H_2O - 140°C									
Measurement	P_{CO2} (MPa)	y_{N2}	y_{CO2}	y_{H2O}	x_{N2} ($x10^6$)	x_{CO2}	x_{H2O}	x_{DEA}	x_{MDEA}
10	0	0.725	0.000	0.275	1.000	0.000	0.861	0.074	0.065
11	0.0494	0.365	0.045	0.591	1.041	0.001	0.860	0.074	0.065
12	0.1509	0.644	0.097	0.259	1.429	0.007	0.855	0.073	0.065
13	0.45	0.778	0.179	0.044	1.907	0.020	0.844	0.072	0.064
14	0.16	0.268	0.172	0.559	1.064	0.010	0.853	0.073	0.065
15	0	0.004	0.000	0.996	1.152	0.000	0.861	0.074	0.065
16	1.1529	0.186	0.076	0.737	1.039	0.025	0.839	0.072	0.064
17	0.3506	0.004	0.368	0.628	1.628	0.014	0.849	0.073	0.064

Table B2-2 : 25wt% MDEA - 25wt% DEA - 50wt% H_2O - 140°C							
Measurement	Average Temp. (K)	Average Pressure (MPa)	Density of Solvent ρ_m (kg/m^3) at 140°C	Measured Volume of Solvent (m^3)	Amount of CO_2 Charged (mol)	CO_2 Loading (mol CO_2/mol DEA+MDEA)	Partition coefficient
10	412.13	1.524	1039.21	1.42E-05	0.000	0	0
11	412.18	0.539	1039.21	1.42E-05	0.003	0.042	36.481
12	412.15	1.482	1039.21	1.42E-05	0.007	0.097	13.690
13	412.17	1.512	1039.21	1.42E-05	0.021	0.294	9.558
14	412.16	0.687	1039.21	1.42E-05	0.007	0.100	18.136
15	411.01	0.502	1039.21	1.42E-05	0.000	0	0
16	412.13	1.664	1039.21	1.42E-05	0.036	0.524	3.009
17	412.17	0.534	1039.21	1.42E-05	0.014	0.196	26.043

Table B3-1: 30wt% MDEA - 20wt% DEA - 50wt% H_2O - 90°C									
Measurement	P_{CO2} (MPa)	y_{N2}	y_{CO2}	y_{H2O}	x_{N2} (x10^6)	x_{CO2}	x_{H2O}	x_{DEA}	x_{MDEA}
18	0.0571	0.952	0.008	0.039	1.412	0.004	0.859	0.059	0.078
19	0.1516	0.487	0.023	0.507	1.384	0.008	0.856	0.059	0.078
20	1.0502	0.284	0.047	0.023	1.261	0.050	0.819	0.056	0.075
21	0.45	0.855	0.051	0.047	1.753	0.026	0.840	0.058	0.076
22	0.3508	0.635	0.051	0.051	1.752	0.022	0.843	0.058	0.077
23	0.1517	0.914	0.020	0.051	1.163	0.009	0.854	0.059	0.078
24	0	0.980	0.028	0.020	1.058	0.000	0.862	0.059	0.079
25	0	0.972	0.000	0.028	1.664	0.000	0.862	0.059	0.079

Table B3-2 : 30wt% MDEA - 20wt% DEA - 50wt% H_2O - 90°C							
Measurement	Average Temp. (K)	Average Pressure (MPa)	Density of Solvent ρ_m (kg/m^3) at 90°C	Measured Volume of Solvent (m^3)	Amount of CO_2 Charged (mol)	CO_2 Loading (mol CO_2/mol DEA+MDEA)	Partition coefficient
18	361.59	0.505	1041.50	1.42E-05	0.003	0.045	1.780
19	361.96	0.996	1041.50	1.42E-05	0.008	0.116	2.963
20	361.89	1.723	1041.50	1.42E-05	0.044	0.548	0.937
21	362.07	1.495	1041.50	1.42E-05	0.020	0.282	1.948
22	362.08	0.496	1041.50	1.42E-05	0.023	0.334	2.321
23	362.15	0.511	1041.50	1.42E-05	0.010	0.146	2.160
24	361.62	0.543	1041.50	1.42E-05	0.000	0	0
25	361.94	1.496	1041.50	1.42E-05	0.000	0	0

Table B4-1: 30wt% MDEA - 20wt% DEA - 50wt% H_2O - 140°C									
Measurement	P_{CO2} (MPa)	y_{N2}	y_{CO2}	y_{H2O}	x_{N2} (x10^6)	x_{CO2}	x_{H2O}	x_{DEA}	x_{MDEA}
26	0.052	0.418	0.002	0.580	1.913	0.003	0.860	0.059	0.078
27	0.1525	0.674	0.149	0.177	1.062	0.005	0.858	0.059	0.078
28	1.05	0.188	0.616	0.196	1.150	0.014	0.850	0.058	0.077
29	0.152	0.004	0.003	0.996	1.655	0.005	0.858	0.059	0.078
30	0	0.198	0.000	0.802	1.702	0.000	0.862	0.059	0.079
31	0	0.646	0.000	0.354	1.174	0.000	0.862	0.059	0.079
32	0.352	0.214	0.294	0.492	1.315	0.007	0.857	0.059	0.078
33	0.4503	0.621	0.290	0.089	1.911	0.008	0.856	0.059	0.078

Table B4-2 : 30wt% MDEA - 20wt% DEA - 50wt% H_2O - 140^oC							
Measurement	Average Temp. (K)	Average Pressure (MPa)	Density of Solvent ρ_m (kg/m^3) at 140^oC	Measured Volume of Solvent (m^3)	Amount of CO_2 Charged (mol)	CO_2 Loading (mol CO_2/mol DEA+MDEA)	Partition coefficient
26	412.11	0.499	1038.41	1.42E-05	0.003	0.042	0.793
27	412.16	1.500	1038.41	1.42E-05	0.008	0.094	27.085
28	412.17	1.590	1038.41	1.42E-05	0.026	0.301	43.147
29	412.08	0.531	1038.41	1.42E-05	0.010	0.155	0.604
30	412.15	0.520	1038.41	1.42E-05	0.000	0.000	0.000
31	412.14	1.493	1038.41	1.42E-05	0.000	0.000	0.000
32	412.12	0.522	1038.41	1.42E-05	0.015	0.209	45.156
33	412.13	1.556	1038.41	1.42E-05	0.018	0.236	37.268

Table B5-1: 50wt% DEA - 50wt% H_2O - 120^oC									
Measurement	P_{CO2} (MPa)	y_{N2}	y_{CO2}	y_{H2O}	x_{N2} (x10^6)	x_{CO2}	x_{H2O}	x_{DEA}	x_{MDEA}
34	1.0501	0.120	0.829	0.051	1.334	0.039	0.820	0.141	0.000
35	0.4504	0.719	0.148	0.133	1.820	0.021	0.835	0.143	0.000
36	0.1501	0.912	0.018	0.070	1.021	0.007	0.848	0.145	0.000

Table B5-2 : 50wt% DEA - 50wt% H_2O - 120^oC							
Measurement	Average Temp. (K)	Average Pressure (MPa)	Density of Solvent ρ_m (kg/m^3) at 120^oC	Measured Volume of Solvent (m^3)	Amount of CO_2 Charged (mol)	CO_2 Loading (mol CO_2/mol DEA+MDEA)	Partition coefficient
34	392.11	1.484	1053.66	1.42E-05	0.036	0.394	21.241
35	392.13	1.500	1053.66	1.42E-05	0.021	0.273	6.911
36	392.13	1.497	1053.66	1.42E-05	0.007	0.091	2.735

NB.: In each case y_{MDEA} and y_{DEA} is negligible due to system temperature being significantly lower than solvent boiling point temperature.

Appendix C: Partition Coefficient Graphs

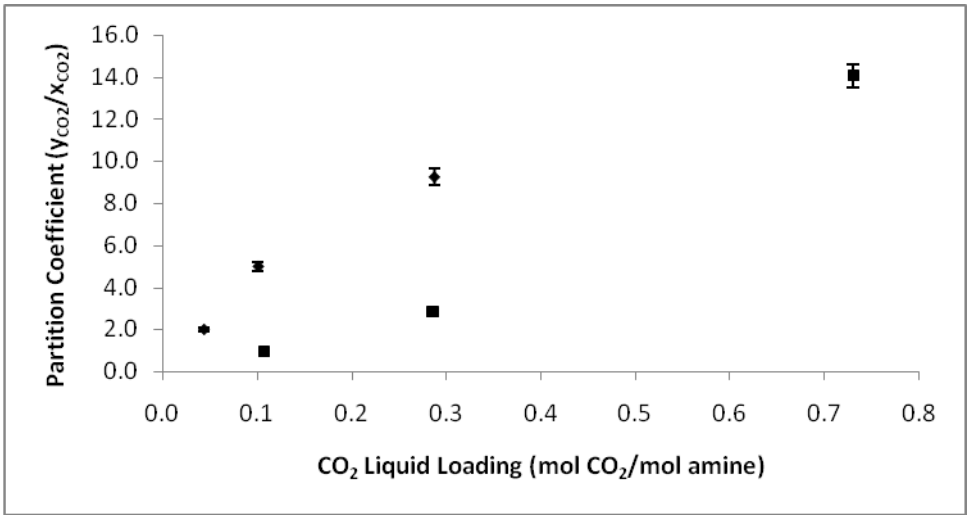

Figure C1: Partition Coefficient vs CO_2 Liquid Loading for System 1: 25wt% MDEA – 25wt% DEA – 50wt% H_2O, 363.15 K. ■ – 1.5 MPa pressure; ♦ - 0.5 MPa pressure

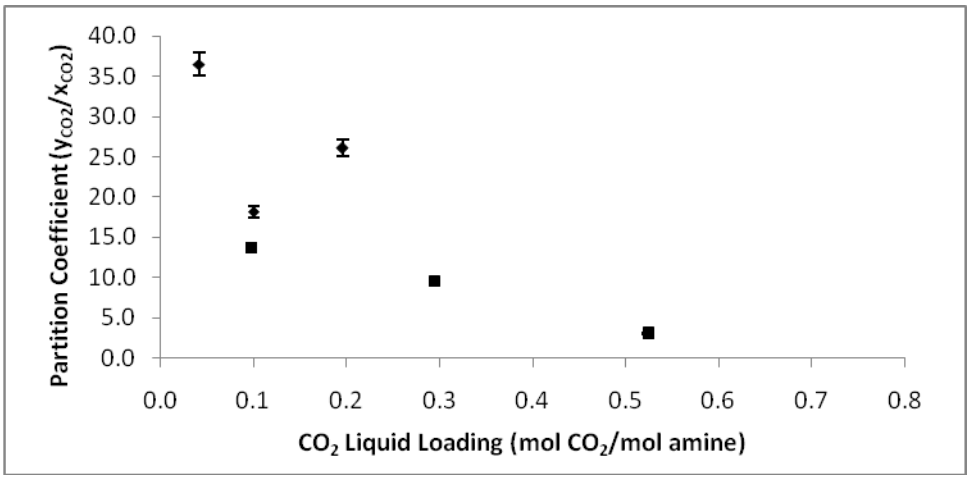

Figure C2: Partition Coefficient vs CO_2 Liquid Loading for System 1: 25wt% MDEA – 25wt% DEA – 50wt% H_2O, 413.15 K. ■ – 1.5 MPa pressure; ♦ - 0.5 MPa pressure

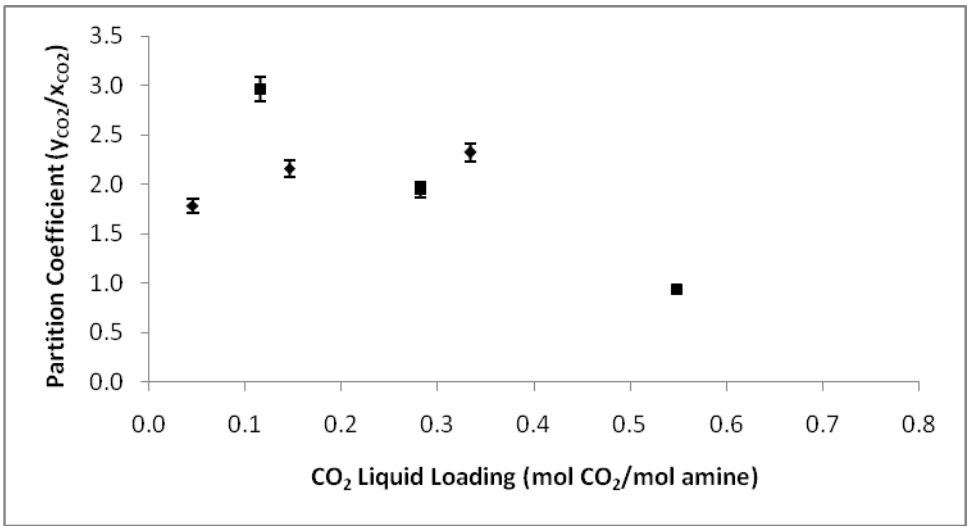

Figure C3: Partition Coefficient vs CO_2 Liquid Loading for System 1: 30wt% MDEA – 20wt% DEA – 50wt% H_2O, 363.16 K. ■ – 1.5 MPa pressure; ♦ - 0.5 MPa pressure

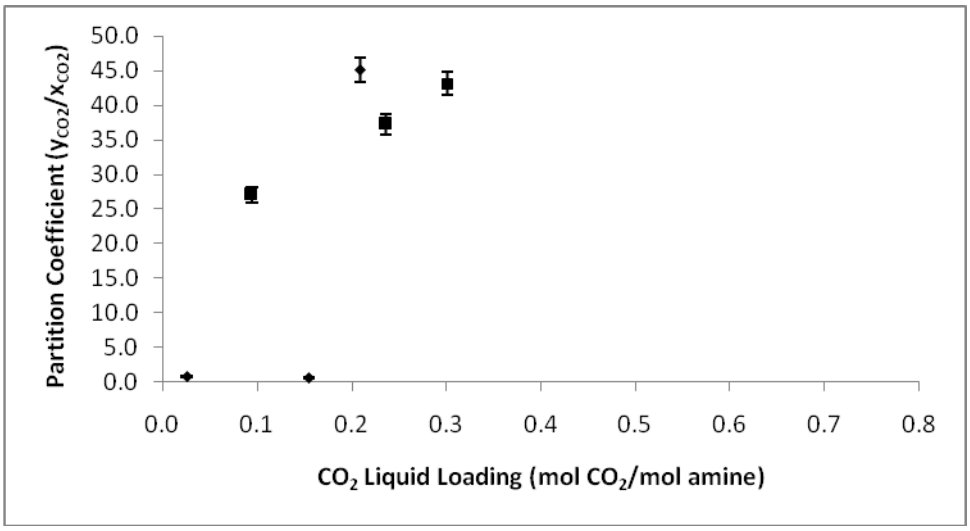

Figure C4: Partition Coefficient vs CO_2 Liquid Loading for System 1: 25wt% MDEA – 25wt% DEA – 50wt% H_2O, 413.15 K. ■ – 1.5 MPa pressure; ♦ - 0.5 MPa pressure