

**PHYSICAL PROPERTIES OF GUANIDINIUM
TRIFLUOROMETHANESULFONATE-
METHYLDIETHANOLAMINE AQUEOUS MIXTURES
AND THEIR CO₂ ABSORPTION CAPACITIES**

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ABSTRACT

In this work, the physical properties *i.e.* density, viscosity and CO₂ solubility studies were conducted on the aqueous systems of *N*-methyldiethanolamine (MDEA) and guanidinium trifluoromethanesulfonate [gua][OTf]. The studies were carried out at various concentration of MDEA (1 – 4 M) and [gua][OTf] (0.1 – 2 M). The temperature and pressure were also varied depending on the study involved.

The studies on densities and viscosities of binary ([gua][OTf] - H₂O) and ternary ([gua][OTf] - MDEA - H₂O) systems were carried out at a wide temperature range from 293 to 363 K and at atmospheric pressure. The results show that the density and viscosity were strongly affected by the presence of water. Correlations for both viscosity and density for binary and ternary systems were ± 3.5 % in temperature ranges from 293 and 363 K except 2M2G and 1M3G have shown deviation up to 9.587 %. Also, binary systems of [gua][OTf] – H₂O *i.e.* 0M0.1G, 0M0.3G, 0M0.5G, 0M0.7G, 0M0.9, 0M1G and 0M4G showed higher deviation in viscosities which is up to 8.442 %.

As for solubility studies, this work was focused in determining the ability of aqueous binary ([gua][OTf] – H₂O) and ternary (MDEA – [gua][OTf] – H₂O) systems in capturing CO₂ at high pressures. The experiments were conducted at CO₂ partial pressures from 500 to 3000 kPa and temperatures at 303, 323 and 333 K. It has been found that the effect of partial pressures was most pronounced for 1 M aqueous [gua][OTf] (0M1G) which showed a competitive performance in capturing CO₂, up to 1.63 mol CO₂/ total mol system at 323.2 K and 3000 kPa, as compared to

other pure ionic liquids such as [emim][C₂N₃], [emim][MDEGSO₄] and [emim][OTf] with 0.8132, 0.9587 and 1.0753 mol CO₂/ total mol system, respectively, which were also recorded in the same environments. The solubility to pressure data also supported that 0M1G is involved mainly in physical absorption and the effect of partial pressure was more significant at lower alkanolamine concentration. Correlations of solubility as a function of pressure and temperature have been determined with difference of $\pm 0.957\%$.

The solubility was also measured at lower partial pressure of CO₂ at 10, 50 and 100 kPa and temperature 303.2 K. This experiment was predominantly on chemical absorption and it showed that the addition of 1 M [gua][OTf] induced 14 % of CO₂ solubility at 303.2 K and 100 kPa of the CO₂ partial pressure as compared to 1 M [bmim][BF₄], in 4 M MDEA. Also, the solubility of CO₂ in 4 M [gua][OTf] gave 27.5 % higher CO₂ loading compared to 1 M [gua][OTf]. Compared to 4 M MDEA, the CO₂ loading of blended system 4M1G was found to be slightly lower *i.e.* 0.6498 mol CO₂/ total mol system at 100 kPa. The presence of [gua][OTf] could not make up the loss of the CO₂ absorption capacity of MDEA due to the reducing amount of water with increasing amount of [gua][OTf] as physical absorption of CO₂ will only play a significant role at high operating pressure. The R² values from plot of P_{CO₂} versus ($\alpha_{\text{CO}_2}^2 / 1 - \alpha_{\text{CO}_2}$) range from 0.94232 to 0.96272 for partial pressure between 0 - 100 kPa. These R² values were finely fitted.

ABSTRAK

Kajian mengenai ciri-ciri fizikal seperti ketumpatan, kelikatan and kelarutan CO₂ bagi sistem *N*-methyldiethanolamine (MDEA) (1 – 4 M) dan guanidinium trifluorometanasulfonat [gua][OTf] (0.1 – 2 M) telah dilakukan. Suhu dan tekanan dipelbagaikan bergantung kepada kajian yang terlibat.

Kajian mengenai ketumpatan dan kelikatan sistem binari ([gua][OTf] - H₂O) dan ternari ([gua][OTf] - MDEA - H₂O) dijalankan pada tekanan atmosfera dan suhu bermula 293 ke 363 K. Keputusan eksperimen menunjukkan ketumpatan dan kelikatan dipengaruhi oleh kuantiti air dalam sistem. Peratus perbezaan antara kelikatan dan ketumpatan yang didapati dari eksperimen dan pengiraan bagi sistem binari dan ternari adalah $\pm 3.5 \%$ pada suhu antara 293 dan 363 K kecuali 2M2G dan 1M3G yang menunjukkan 9.587 %. Dalam pada itu, sistem binari [gua][OTf] – H₂O *i.e.* 0M0.1G, 0M0.3G, 0M0.5G, 0M0.7G, 0M0.9, 0M1G dan 0M4G menunjukkan perbezaan kelikatan yang lebih besar sehingga 8.442 %.

Manakala, bagi kelarutan CO₂, kajian ini memberi fokus kepada penentuan kebolehan sistem akuas binari ([gua][OTf] – H₂O) dan ternari (MDEA – [gua][OTf] – H₂O) dalam menjerap CO₂ pada tekanan tinggi. Eksperimen dijalankan pada tekanan separa CO₂ bermula dari 500 ke 3000 kPa dan suhu pada 303, 323 dan 333 K. Kajian mendapati kesan tekanan separa paling ketara pada 1 M akuas [gua][OTf] (0M1G) yang mana turut menunjukkan kelarutan CO₂ sebanyak 1.63 mol CO₂/jumlah mol sistem pada 323.2 K dan 3000 kPa, berbanding cecair ionik yang lain seperti [emim][C₂N₃], [emim][MDEGSO₄] dan [emim][OTf] dengan 0.8132, 0.9587

and 1.0753 mol CO₂/ jumlah mol sistem yang mana turut dicatat pada keadaan yang sama. Kesan ketara terhadap kelarutan CO₂ oleh 0M1G pada perubahan tekanan separa turut membuktikan sistem tersebut melibatkan penjerapan fizikal secara keseluruhan dan turut memberi kesan ketara kepada alkanolamina yang berkepekatan lebih rendah. Hubungkait antara kelarutan, tekanan dan suhu telah ditentukan dengan ketepatan $\pm 0.957 \%$.

Kelarutan juga diukur pada tekanan separa CO₂ yang lebih rendah iaitu 10, 50 dan 100 kPa dan suhu 303.2 K. Eksperimen ini melibatkan penjerapan kimia dan keputusan menunjukkan penambahan 1 M [gua][OTf] menaikkan kelarutan CO₂ sebanyak 14 % pada 303.2 K dan 100 kPa berbanding 1 M [bmim][BF₄] terhadap 4 M MDEA. Di samping itu, kelarutan CO₂ terhadap 4 M [gua][OTf] meningkat 27.5 % berbanding 1 M [gua][OTf]. Kelarutan 4M1G pula adalah lebih rendah berbanding 4M0G iaitu sebanyak 0.6498 mol CO₂/ jumlah mol sistem pada 100 kPa. Kehadiran [gua][OTf] mengurangkan kelarutan ternari sistem berikutan pengurangan kuantiti air dengan penambahan jumlah [gua][OTf] yang mana penjerapan fizikal hanya berkesan pada operasi bertekanan tinggi. Nilai R² dari plot P_{CO_2} versus $(\alpha_{CO_2}^2 / 1 - \alpha_{CO_2})$ adalah antara 0.94232 ke 0.96272 bagi tekanan separa 0 - 100 kPa. Nilai R² telah ditentukan dengan tepat.

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TABLE OF CONTENTS

Abstract	III
Abstrak	V
Acknowledgement	VII
Table of contents	VIII
List of figures	XII
List of tables	XVIII
Nomenclature	XX

CHAPTER ONE: INTRODUCTION

1.1 Background	1
1.2 Problem statement	4
1.3 Scope and research objectives	6
1.4 Outline of the thesis	7

CHAPTER TWO: LITERATURE REVIEW

2.1 Carbon capture technology	10
2.2 The solvent capture	19
2.2.1 Chemical solvents	21
2.2.2 Blended alkanolamines	24
2.2.3 Physical solvents	26
2.3 Process chemistry	27
2.4 Ionic liquids	28
2.4.1 Ionic liquids and CO ₂ absorption	32
2.4.2 Task-specific ionic liquids in CO ₂ absorption	37
2.5 The CO ₂ solubility study	42
2.6 Modelling for CO ₂ solubility	44
2.7 Physicochemical properties	48
2.7.1 Density	49
2.7.1.1 Density of alkanolamine	50
2.7.1.2 Density of ionic liquids	51
2.7.1.3 Density-derived thermodynamic properties	54
2.7.2 Viscosity	58

2.7.2.1 Viscosity of alkanolamine	59
2.7.2.2 Viscosity of ionic liquids	60
2.7.2.3 Viscosity-derived thermodynamic properties	63
2.8 Summary	65

CHAPTER THREE: METHODOLOGY

3.1 Introduction	66
3.2 Materials	66
3.3 Solutions preparations	67
3.3.1 Density	67
3.3.2 Viscosity	68
3.3.3 Solubility of CO ₂ at low pressure	69
3.3.4 Solubility of CO ₂ at high pressure	70
3.4 Validation of system preparations	70
3.5 Experimental procedures	72
3.5.1 Density measurement	72
3.5.2 Viscosity measurement	72
3.5.3 of CO ₂ at high pressure	74
3.5.3.1 CO ₂ absorption set-up	74
3.5.3.2 CO ₂ loading calculation techniques	76
3.5.4 Solubility of CO ₂ at low pressure	77
3.5.4.1 CO ₂ absorption set-up	77
3.5.4.2 Determination of amine concentration	80
3.5.4.3 Determination of CO ₂ loading	81
3.5.4.4 Calculation	83

CHAPTER FOUR: DENSITY

4.1 Introduction	85
4.2 Validation of the density measurement	85

4.3 Effect temperatures and concentrations	85
4.4 Comparison of studied binary and ternary systems with literature	88
4.5 Correlations of density in function of temperature, concentration of MDEA and [gua][OTf]	94
4.6 Thermal expansion	98
4.7 Conclusion	101

CHAPTER FIVE: VISCOSITY

5.1 Introduction	102
5.2 Validation of the viscosity measurement	102
5.3 Viscosity of binary [gua][OTf] - H ₂ O systems	103
5.4 Viscosity of ternary [gua][OTf] – MDEA - H ₂ O systems	105
5.5 Comparison of studied systems with the literature	107
5.6 Correlations of viscosity as function of temperature, concentration of MDEA and [gua][OTf]	112
5.7 Conclusion	117

CHAPTER SIX: CO₂ ABSORPTION AT HIGH PRESSURE

6.1 Introduction	118
6.2 Validation of experimental procedure and comparison with literature	119
6.3 Effect of temperature on the solubility of CO ₂	120
6.4 Effect pressure to solubility of CO ₂	127
6.5 Effect of addition ionic liquids	131
6.6 Comparison absorption between 1 M MDEA (1M0G) and 1 M [gua][OTf] (0M1G)	134
6.7 Comparison with other ionic liquids	136
6.8 Correlation of solubility as function of pressure and temperature	138
6.9 Conclusion	142

CHAPTER SEVEN: CO₂ ABSORPTION AT LOW PRESSURE

7.1 Introduction	144
7.2 Validation of experimental procedure and comparison with literature	144
7.2.1 Comparison on CO ₂ loading of 4 M MDEA	145

7.2.2 Validation of the titration method in determining the CO ₂ Loading	145
7.3 Amine concentration	146
7.4 pH profile of the systems	147
7.5 Effect of CO ₂ partial pressure on CO ₂ loading	151
7.6 Effect [gua][OTf] presence on CO ₂ loading	154
7.7 Correlation of solubility data at low pressure	157
7.8 Conclusion	164

CHAPTER EIGHT: GENERAL CONCLUSIONS AND FURTHER WORK

8.1 General conclusions	166
8.2 Suggestion for further work	170

REFERENCES	172
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APPENDIX	193
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LIST OF FIGURES

Figure 2.1	Process flow diagram (PFD) of an alkanolamine treating unit	14
Figure 2.2	Equilibrium curves of CO ₂ in various solvents. Physical absorption: a) H ₂ O (30 °C); b) <i>N</i> -methyl-2-pyrrolidone (110 °C); c) Methanol (-15 °C); d) Methanol (-30 °C); Chemical absorption: e) Hot potassium carbonate solution (110 °C); f) Sulfinol solution (50 °C); g) 2.5 M Diethanolamine solution (50 °C); h) 3 M Amisol DETA solution	17
Figure 2.3	General trends for loading capacity of chemical and physical solvents at a range of partial pressure of CO ₂ .	19
Figure 2.4	Several structural formulas for alkanolamines used in gas treating	22
Figure 2.5	Evolution of ionic liquid generations	29
Figure 2.6	Some examples of cations described in ionic liquids based on ammonium 1, sulfonium 2, phosphonium 3, lithium 4, imidazolium 5, pyridinium 6, pyrroldium 7, thiazolium 8, triazolium 9, oxazolium 10 and pyrazolium 11	30
Figure 2.7	Schematic of an ionic liquid interaction with carbon dioxide	32
Figure 2.8	Solubilities of CO ₂ , C ₂ H ₄ , C ₂ H ₆ , CH ₄ , Ar and O ₂ in [bmim][PF ₆] at 25 °C	34
Figure 2.9	Relationship between the solubility of CO ₂ and pressure in six kinds of conventional ionic liquids	37
Figure 2.10	Proposed reaction mechanism between [pabim][BF ₄] and CO ₂	39
Figure 2.11	An infinite hydrogen-bonded sheet in guanidinium Trifluoromethanesulfonate	41
Figure 3.1 (a)	Structure of guanidinium trifluoromethanesulfonate, ([gua][OTf]) with molecular weight 209.1 g mol ⁻¹	67
Figure 3.1 (b)	Structure of <i>N</i> -methylethanolamine, (MDEA) with molecular weight 119.16 g mol ⁻¹	67
Figure 3.2	Schematic diagram of this coaxial cylinder	73

Figure 3.3	A diagram of stirred cell reactor	75
Figure 3.4	A schematic process flow diagram of the high pressure system	75
Figure 3.5	Schematic diagram of the experimental set-up	78
Figure 3.6	Typical pH curve of the solution during the reaction of alkanolamine and CO ₂	80
Figure 3.7	Typical titration curve of alkanolamine solution using 1 M standard solution of HCl	82
Figure 3.8	Titration curve of carbonated solution using a solution of 1 M HCl	83
Figure 4.1	Comparison of densities for pure MDEA with literatures	85
Figure 4.2	Density of binary systems 4M0G, 1M0G, 0M4G, 0M1G various temperatures	86
Figure 4.3	Density of ternary systems 4M2G, 4M1G, 3M1G, 2M2G, 1M3G at various temperatures	87
Figure 4.4	Comparison in density between the binary system from this work <i>i.e.</i> 4M0G, 1M0G, 0M4G and 0M1G, and the dried ionic liquids <i>i.e.</i> [bmim][PF ₆], [bmim][BF ₄], [bmim][NTf ₂], [emim][NTf ₂], [emim][EtSO ₄] and [N ₄₁₁₁][NTf ₂]	89
Figure 4.5	Comparison in density between the ternary system from this work <i>i.e.</i> 4M2G, 4M1G, 3M1G, 2M2G and 1M3G, and the dried ionic liquids <i>i.e.</i> [bmim][PF ₆], [bmim][BF ₄], [bmim][NTf ₂], [emim][NTf ₂], [emim][EtSO ₄] and [N ₄₁₁₁][NTf ₂]	90
Figure 4.6	Comparison in density between the binary system from this work <i>i.e.</i> 4M0G, 1M0G, 0M4G and 0M1G, and the water-saturated ionic liquids <i>i.e.</i> [bmim][PF ₆], [bmim][BF ₄], [bmim][NTf ₂], [emim][NTf ₂], [emim][EtSO ₄] and [N ₄₁₁₁][NTf ₂]	91
Figure 4.7	Comparison in density between the ternary system from this work <i>i.e.</i> 4M2G, 4M1G, 3M1G, 2M2G and 1M3G, and the water-saturated ionic liquids <i>i.e.</i> [bmim][PF ₆], [bmim][BF ₄], [bmim][NTf ₂], [emim][NTf ₂], [emim][EtSO ₄] and [N ₄₁₁₁][NTf ₂]	92
Figure 4.8	Comparison in density between aqueous binary ([gua][OTf] - H ₂ O) <i>i.e.</i> 0M1G and 0M4G with aqueous [hmim][Br] [196] and aqueous [BuPy][BF ₄] [231]	93

Figure 4.9	The density comparison between the calculated and the measured density	98
Figure 5.1	Comparison of pure MDEA with literature review	103
Figure 5.2	Viscosity of various concentrations of aqueous [gua][OTf]	104
Figure 5.3	Enlargement graph (refer Figure 5.1) for viscosity of systems with concentration from 0.1 G to 1.0 G	105
Figure 5.4	Figure 5.4. Viscosity of 4M0.1G, 4M0.3G, 4M0.5G, 4M0.7G, 4M0.9G, 4M1G and 4M2G at 303.2, 313.2, 323.2 and 333.2 K.	106
Figure 5.5	Comparison of the viscosity between ternary system <i>i.e.</i> 4M0.1G, 4M0.3G, 4M0.5G, 4M0.7G, 4M0.9G, 4M1G, 4M2G and dried ionic liquids <i>i.e.</i> [bmim][PF ₆], [bmim][BF ₄], [bmim][NTf ₂], [emim][NTf ₂], [emim][EtSO ₄] and [N ₄₁₁₁][NTf ₂]	109
Figure 5.6	Comparison of the viscosity between ternary system <i>i.e.</i> 4M0.1G, 4M0.3G, 4M0.5G, 4M0.7G, 4M0.9G, 4M1G, 4M2G and saturated ionic liquids <i>i.e.</i> [bmim][PF ₆], [bmim][BF ₄], [bmim][NTf ₂], [emim][NTf ₂], [emim][EtSO ₄] and [N ₄₁₁₁][NTf ₂]	110
Figure 5.7	Comparison in viscosity between the aqueous binary [bmim][BF ₄] and aqueous binary [gua][OTf] at 298 K	111
Figure 5.8	Comparison between the calculated and experimental viscosity for all systems	116
Figure 6.1	Comparison of solubility data for CO ₂ at 333.2 K in 4 M MDEA between published data [272] and this work	119
Figure 6.2	The effect of temperature on the solubility of CO ₂ for 1M0G and 0M1G systems at 500 kPa	121
Figure 6.3	The effect of temperature on the solubility of CO ₂ for 1M0G and 0M1G systems at 1000 kPa	121
Figure 6.4	The effect of temperature on the solubility of CO ₂ for 1M0G and 0M1G systems at 1500 kPa	122
Figure 6.5	The effect of temperature on the solubility of CO ₂ for 1M0G and 0M1G systems at 2000 kPa	122
Figure 6.6	The effect of temperature on the solubility of CO ₂ for 1M0G and 0M1G systems at 2500 kPa	123

Figure 6.7	The effect of temperature on the solubility of CO ₂ for 1M0G and 0M1G systems at 3000 kPa	123
Figure 6.8	The effect of temperature on the solubility of CO ₂ for 4M0G and 4M1G systems at 500 kPa	124
Figure 6.9	The effect of temperature on the solubility of CO ₂ for 4M0G and 4M1G systems at 1000 kPa	124
Figure 6.10	The effect of temperature on the solubility of CO ₂ for 4M0G and 4M1G systems at 1500 kPa	125
Figure 6.11	The effect of temperature on the solubility of CO ₂ for 4M0G and 4M1G systems at 2000 kPa	125
Figure 6.12	The effect of temperature on the solubility of CO ₂ for 4M0G and 4M1G systems at 2500 kPa	126
Figure 6.13	The effect of temperature on the solubility of CO ₂ for 4M0G and 4M1G systems at 3000 kPa	126
Figure 6.14	The effect of pressure on the solubility of CO ₂ for 1M0G and 0M1G systems at T = 303.2 K	128
Figure 6.15	The effect of pressure on the solubility of CO ₂ for 1M0G and 0M1G systems at T = 323.2 K	128
Figure 6.16	The effect of pressure on the solubility of CO ₂ for 1M0G and 0M1G systems at T = 333.2 K	129
Figure 6.17	The effect of pressure on the solubility of CO ₂ for 4M0G and 4M1G systems at T = 303.2 K	129
Figure 6.18	The effect of pressure on the solubility of CO ₂ for 4M0G and 4M1G systems at T = 323.2 K	130
Figure 6.19	The effect of pressure on the solubility of CO ₂ for 4M0G and 4M1G systems at T = 333.2 K	130
Figure 6.20	Effect addition of 1 M [gua][OTf] to 4 M MDEA at temperature 303.2, 323.2 and 333.2 K and at pressure up to 3000 kPa	132
Figure 6.21	Comparison of absorption between 1 M MDEA (1M0G) and 1 M [gua][OTf] (0M1G) at temperatures 303.2, 323.2 and 333.2 K at pressure up to 3000 kPa	134
Figure 6.22	The deviation in CO ₂ solubility between 1M0G and 0M1G at temperatures 303.2, 323.2 and 333.2 K and at pressure up to 3000 kPa	136

Figure 6.23	Comparison in solubility of CO ₂ between 1 M [gua][OTf] (0M1G) and other conventional ionic liquids [274] at temperature 303.2 K and pressure up to 3000 kPa	137
Figure 6.24	Comparison between the calculated and experimental CO ₂ loading for 1M0G at various temperatures	140
Figure 6.25	Comparison between the calculated and experimental CO ₂ loading for 0M1G at various temperatures	140
Figure 6.26	Comparison between the calculated and experimental CO ₂ loading for 4M0G at various temperatures	141
Figure 6.27	Comparison between the calculated and experimental CO ₂ loading for 4M1G at various temperatures	141
Figure 7.1	Equilibrium curve for reaction of 4 M MDEA with pure CO ₂ at 303.2 K, 100 kPa	149
Figure 7.2	Equilibrium curve for reaction of 4 M MDEA + 1 M [gua][OTf] with pure CO ₂ at 303.2 K, 100 kPa	149
Figure 7.3	Equilibrium curve for reaction of 1 M [gua][OTf] with pure CO ₂ at 303.2 K, 100 kPa	150
Figure 7.4	CO ₂ loading for 4M0G and 4M1G at 303.2 K at different CO ₂ partial pressure	152
Figure 7.5	CO ₂ loading for 4M0G, 3M1G, 2M2G and 1M3G at 303.2 K at different CO ₂ partial pressure	153
Figure 7.6	CO ₂ loading for aqueous 1 M MDEA (1M0G) and 1 M [gua][OTf] (0M1G) at 303.2 K at different CO ₂ partial Pressure	153
Figure 7.7	CO ₂ loading for 0M4G and 0M1G at 303.2 K at different CO ₂ partial pressure	154
Figure 7.8	Comparison CO ₂ loading in 4M1G (4 M MDEA + 1 M [gua][OTf]) and 4M1B (4 M MDEA + 1 M [bmim][BF ₄])	156
Figure 7.9	Correlation results of CO ₂ absorption in a mixture of 4M0G at 303 K	160
Figure 7.10	Correlation results of CO ₂ absorption in a mixture of 4M1G at 303 K	160
Figure 7.11	Correlation results of CO ₂ absorption in a mixture of 3M1G at 303 K	161

Figure 7.12	Correlation results of CO ₂ absorption in a mixture of 2M2G at 303 K	161
Figure 7.13	Correlation results of CO ₂ absorption in a mixture of 1M3G at 303 K	162
Figure 7.14	Correlation results of CO ₂ absorption in a mixture of 1M0G at 303 K	162
Figure 7.15	Correlation results of CO ₂ absorption in a mixture of 0M4G at 303 K	163
Figure 7.16	Correlation results of CO ₂ absorption in a mixture of 0M1G at 303 K	163

LIST OF TABLES

Table 1.1	An annual rate of atmospheric CO ₂ increase from 1960 to 2009	2
Table 2.1	The advantages and disadvantages of post-combustion, pre-combustion and oxy-combustion	11
Table 2.2	Typical characteristics of absorption processes	18
Table 2.3	Comparison of chemical and physical solvents	20
Table 3.1	Compositions of the binary and ternary system densities Study	68
Table 3.2	Compositions of the binary and ternary system for viscosity study	69
Table 3.3	Compositions of the aqueous and blended MDEA – [gua][OTf] systems	69
Table 3.4	Compositions of the aqueous and blended MDEA – [gua][OTf] systems	71
Table 3.5	Specification of double jacket cell reactor	78
Table 3.6	Operating condition of the experiment	79
Table 4.1	The correlated parameter for densities at various concentrations	95
Table 4.2	Coefficients <i>a</i> , <i>b</i> and <i>c</i> at different concentrations of MDEA	95
Table 4.3	Coefficients <i>p</i> , <i>q</i> and <i>r</i> at different concentration of MDEA	96
Table 4.4	Coefficients of thermal expansion for blended binary and ternary systems of MDEA - [gua][OTf] using Equation 4.2	101
Table 5.1	The correlated parameter for densities at various Concentrations	113
Table 5.2	Coefficients <i>e</i> , <i>f</i> , <i>g</i> and <i>h</i> for aqueous [gua][OTf] and aqueous blended MDEA - [gua][OTf]	113
Table 5.3	Coefficients <i>i</i> , <i>j</i> , <i>k</i> and <i>m</i> for aqueous [gua][OTf] and aqueous blended MDEA - [gua][OTf]	114
Table 6.1	Various compositions of the systems used in this work	118

Table 6.2	The comparison of CO ₂ loading obtained between this study and the data extracted from the literature [272] at 333.2 K for 4 M MDEA	119
Table 6.3	Effect of addition 1 M [gua][OTf] to 4 M MDEA at temperature 303.2, 323.2 and 333.2 K at pressure up to 3000 kPa	133
Table 6.4	Comparison of absorption between 1 M MDEA (1M0G) and 1 M [gua][OTf] (0M1G) at temperatures 303.2, 323.2 and 333.2 K at pressure up to 3000 kPa	135
Table 6.5	The coefficients of Equation 6.1, the solubility as a function of pressure	139
Table 7.1	Comparison on CO ₂ loading of 4 M MDEA solution at atmospheric pressure with 100 % CO ₂ at 303 and 323 K	145
Table 7.2	CO ₂ loading of 4 M MDEA system containing a known amount of NaHCO ₃	146
Table 7.3	Amine concentrations before and after CO ₂ absorption test at 303.2 K	148
Table 7.4	CO ₂ loading for 4M0G and 4M1G at 303.2 K at different CO ₂ partial pressure	151
Table 7.5	CO ₂ loading in variety composition of MDEA [gua][OTf] at 303.2 K and 100 % CO ₂	155

NOMENCLATURE

AGR	Acid gas removal process
PFD	Process flow diagram
GHG	Greenhouse gas
ESRL	Earth systems research laboratory
NOAA	National oceanic and atmospheric administration
CCS	Carbon capture and storage
MDEA	<i>N</i> -methyldiethanolamine
MEA	Monoethanolamine
DEA	Diethanolamine
DETA	Diethylenetriamine
PZ	Piperazine
AMP	2-amino-2-methyl-1-propanol
DIPA	Diisopropanolamine
DGA	Diglycolamine
AEEA	Diamine 2-[(2-aminoethyl) amino]-ethanol
H ₂ O	Water
CO ₂	Carbon dioxide
SO ₂	Sulphur dioxide
O ₂	Oxygen
H ₂ S	Hydrogen sulphite
NaHCO ₃	Sodium bicarbonate
ILs	Ionic liquids
TSILs	Task-specific ionic liquids
RTILs	Room temperature ionic liquids
CO ₂ BOLs	CO ₂ -binding organic liquids
COS	Carbonyl sulfide
[gua][OTf]	Guanidinium trifluoromethanesulfonate
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[bmim][OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[bmim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[bmim][NTf ₂]	1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

[emim][C ₂ N ₃]	1-ethyl-3-methylimidazolium dicyanamide
[emim][NTf ₂]	1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide
[emim][EtSO ₄]	1-ethyl-3-methylimidazolium ethyl sulfate
[emim][OTf]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
[emim][MDEGSO ₄]	1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate
[N ₄₁₁₁][NTf ₂]	<i>N</i> -butyltrimethylammonium bis[(trifluoromethyl)sulfonyl]imide
AAD	Absolute average deviation
MET	Measurement Equivalence-point Titration
ρ	Density of the system (g cm ⁻³)
α_p	Coefficient of thermal expansion
η	Viscosity of the system (mPas)
η_∞	Viscosity at infinite temperature (mPas)
α_{CO_2}	CO ₂ loading (mol of CO ₂ / total mol system) <i>note:</i> total mol system = mol (MDEA + [gua][OTf] + H ₂ O)
T	Temperature (K)
T_θ	Standard temperature (298 K)
P_{CO_2}	Partial pressure of CO ₂ (kPa)
P_T	Total pressure (kPa)
P_V	Vapor pressure (kPa)
R	Gas constant, 8.314 (kJ/ mol K)
E_a	Activation energy (kJ/ mol)
V_{HCl}	Volume of HCl needed to neutralize the basic species (mL)
V_{sample}	Volume of sample taken for analysis (mL)
V_{gc}	Volume of gas container (L)
V_{cell}	Volume cell (L)
V_{sol}	Volume solution (L)
i	Initial condition
f	Final condition
M	Molarity (mol dm ⁻³)

$[\text{MDEA}]_t$	Total concentration of MDEA (mol dm^{-3})
n_{total}	Summation of moles of MDEA and/ or the other absorbents in the liquid phase
K_{ov}	Overall equilibrium constant
H_{CO_2}	Henry's constant
x_{il}	Mole fraction of ionic liquid
x_{CO_2}	Mole fraction of CO_2
ω	Angular velocity of spindle (rad/ sec)
R_c	Radius of container (cm)
R_b	Radius of spindle (cm)
L	Effective length of spindle (cm)
ml	Millilitre
K	Kelvin
kJ	Kilojoule
kg	Kilogram
m	Meter
cm	Centimeter
MPa	Megapascal
kPa	Kilopascal
M	Mol dm^{-3}
mPas	Millipascal
ppm	Parts per million
cP	Centipoise
h	Planck constant, $6.62606896 \times 10^{-34} \text{ J}^{-1}$
Y^E	Excess Gibbs energy of activation for viscosity flow
N_A	Avogadro's number, $6.022\ 141\ 99 \times 10^{23}$
γ	Thermal pressure coefficient
V^E	Excess molar volume