

Dedicated to all of my family members,

My supervisor,

My all teachers and my all friends

CERTIFICATE

It is certified that the work contained in the thesis titled “**Study of aqueous blends of (2-(methylamino)ethanol + aminoethylethanolamine) and (2-(ethylamino)ethanol + aminoethylethanolamine) for post-combustion CO₂ capture**” by “**Diwakar Pandey**” has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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DECLARATION BY THE CANDIDATE

I, *Diwakar Pandey*, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of *Prof. M. K. Mondal* from July-2016 to July-2021, at the *Department of Chemical Engineering & Technology*, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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Table of contents

<u>Title</u>	<u>Page No.</u>
Thesis certificate	ii
Acknowledgements	v
Table of contents	viii
List of Figures	xiii
List of Tables	xviii
List of abbreviation and symbols	xx
Preface	xxii
Chapter 1 Introduction	1
1.1 CO ₂ EMISSION	1
1.2 CONSEQUENCES OF CO ₂ EMISSIONS ON THE ENVIRONMENT	3
1.3 CO ₂ CAPTURE TECHNOLOGIES	4
1.3.1 Post-combustion CO ₂ capture	4
1.3.2 Pre-combustion CO ₂ capture	4
1.3.3 Oxy-fuel combustion	5
1.4 CO ₂ SEPARATION TECHNIQUES	5
1.4.1 Absorption technique	5
1.4.2 Adsorption technique	6
1.4.3 Membrane separation technique	6
1.4.4 Cryogenic distillation technique	7
1.5 POST – COMBUSTION CO ₂ CAPTURE USING CHEMICAL ABSORPTION TECHNIQUE	7
1.6 CO ₂ ABSORPTION USING AMINE-BASED ABSORBENTS	9
1.6.1 Literature review related to CO ₂ absorption into 2-(methylamino)ethanol (MAE) and (2-(ethylamino)ethanol (EAE)	10
1.6.2 Literature review related to CO ₂ absorption into	13

aminoethylethanolamine (AEEA)	
1.6.3 CO ₂ solubility models	16
1.6.4 Physicochemical properties of absorbents	17
1.7 RESEARCH GAP	21
1.8 OBJECTIVES FOR PRESENT RESEARCH WORK	22
Chapter 2 Equilibrium CO₂ solubility in the aqueous mixture of MAE and AEEA: Experimental study and development of modified thermodynamic model	23
ABSTRACT	23
2.1 INTRODUCTION	24
2.2 EXPERIMENTAL SECTION	27
2.2.1 Materials	27
2.2.2 Solution preparation method	28
2.2.3 CO ₂ absorption experiment	28
2.3 MODIFIED KENT-EISENBERG MODEL FOR MAE+AEEA+H ₂ O+CO ₂ SYSTEM	30
2.3.1 Reaction mechanism	30
2.3.2 Equilibrium constants	32
2.3.3 Mass balance, charge balance and CO ₂ balance	35
2.4 RESULTS AND DISCUSSIONS	36
2.4.1 Experimental set up and procedure validation	36
2.4.2 CO ₂ loading	37
2.4.2.1 Effect of fraction of AEEA in the blend	37
2.4.2.2 Effect of total concentration of amine blend	39
2.4.2.3 Effect of partial pressure of CO ₂	41
2.4.2.4 Effect of temperature	42
2.4.3 Modified Kent-Eisenberg model with newly introduced correction factor (F_k) for MAE+AEEA+H ₂ O+CO ₂ system	43
2.4.4 Heat of absorption measurement	46
2.5 CONCLUSIONS	47
Chapter 3 Thermodynamic modeling and new experimental CO₂	48

solubility into aqueous EAE and AEEA blend, heat of absorption, cyclic absorption capacity and desorption study for post-combustion CO₂ capture	
ABSTRACT	48
3.1 INTRODUCTION	49
3.2 EXPERIMENTAL SECTION	52
3.2.1 Materials	52
3.2.2 CO ₂ absorption study	54
3.2.3 CO ₂ desorption study	55
3.2.4 Heat of absorption measurement	57
3.3 KENT-EISENBERG MODEL FOR EQUILIBRIUM CO ₂ SOLUBILITY INTO AQUEOUS AMINE BLEND	57
3.3.1 Reaction mechanism	57
3.3.2 Equilibrium constants	59
3.3.3 Mass balance, charge balance and CO ₂ balance	60
3.4 RESULTS AND DISCUSSIONS	61
3.4.1 Experimental set-up validation	61
3.4.2 Equilibrium CO ₂ solubility	61
3.4.3 Semi-empirical Kent-Eisenberg thermodynamic model	67
3.4.4 Empirical model for equilibrium CO ₂ solubility into aqueous EAE + AEEA blend	70
3.4.5 Heat of CO ₂ absorption (ΔH_{abs})	72
3.4.6 CO ₂ desorption study	74
3.4.7 Rate of change of initial CO ₂ solubility	75
3.5 CONCLUSIONS	77
Chapter 4 Viscosity, density, and derived thermodynamic properties of aqueous 2-(ethylamino)ethanol (EAE), aqueous aminoethylethanolamine (AEEA), and its mixture for post-combustion CO₂ capture	79
ABSTRACT	79
4.1 INTRODUCTION	80
4.2 EXPERIMENTAL SECTION	82

4.2.1 Chemicals	82
4.2.2 Solution preparation method	82
4.2.3 Viscosity measurement	83
4.2.4 Density measurement	84
4.3 RESULTS AND DISCUSSIONS	84
4.3.1 Validation of used apparatus and experimental procedure	84
4.3.2 Viscosity	86
4.3.2.1 Viscosity of aqueous EAE and aqueous AEEA	86
4.3.2.2 Viscosity of EAE + AEEA + H ₂ O blend	93
4.3.3 Density	97
4.3.3.1 Density of aqueous EAE and aqueous AEEA	97
4.3.3.2 Density of EAE + AEEA + H ₂ O blend	101
4.3.4 Isobaric thermal expansion coefficient	104
4.3.5 Derived thermodynamic properties for activation of viscous flow	106
4.4 CONCLUSIONS	108
Chapter 5 Experimental data and modeling for density and viscosity of carbon dioxide (CO₂)-loaded and -unloaded aqueous blend of 2-(ethylamino)ethanol (EAE) and aminoethylethanolamine (AEEA) for post-combustion CO₂ capture	110
ABSTRACT	110
5.1 INTRODUCTION	111
5.2 EXPERIMENTAL SECTION	113
5.2.1 Chemicals and -unloaded sample preparation	113
5.2.2 CO ₂ -loaded sample preparation	114
5.2.3 Density measurement	115
5.2.4 Viscosity measurement	115
5.3 RESULTS AND DISCUSSIONS	115
5.3.1 Density	115

5.3.1.1 Density of CO ₂ -unloaded aqueous EAE + AEEA	115
5.3.1.2 Density of CO ₂ -loaded aqueous EAE + AEEA	121
5.3.2 Viscosity	125
5.3.2.1 Viscosity of CO ₂ -unloaded aqueous EAE + AEEA	125
5.3.2.2 Viscosity of CO ₂ -loaded aqueous EAE + AEEA	128
5.3.3 Diffusivity of CO ₂ into aqueous EAE + AEEA blend	131
5.4 CONCLUSIONS	132
Chapter 6 Overall conclusions and recommendations	134
6.1 OVERALL CONCLUSIONS	134
6.2 RECOMMENDATIONS FOR FUTURE WORKS	137
References	138
Appendix - A	159
Appendix- B	171
Publications	172

List of Figures

<u>Figure No.</u>	<u>Caption</u>	<u>Page No.</u>
Figure 1.1	Contributions of different major source of energy in CO ₂ emission in 2018 (a) World, and (b) India (IEA, 2019)	2
Figure 2.1	Schematic diagram of experimental set up for absorption	29
Figure 2.2	Effect of weight fraction of AEEA in the aqueous (MAE+AEEA) blend mixture at T = 303.15 K, p _{CO₂} = 15.2 kPa, and C _T = 10 wt. %	37
Figure 2.3	Effect of total concentration of blend on (a) CO ₂ loading, and (b) CO ₂ absorption capacity, at T = 303.15 K, p _{CO₂} = 15.2 kPa, and w _{AEEA} = 0.30	40
Figure 2.4	Effect of partial pressure of CO ₂ on CO ₂ loading for T: ▲ 303.15 K; ■ 313.15 K, respectively, C _T = 30 wt.%, and w _{AEEA} = 0.30	41
Figure 2.5	Effect of temperature on CO ₂ loading for p _{CO₂} : ▲ 15.2 kPa; ■ 20.67kPa, respectively, and w _{AEEA} = 0.30 and (a) C _T = 10 wt. %, and (b) C _T = 30 wt. %	43
Figure 2.6	Experimental (denoted by symbols) and model predicted (denoted by lines) plot (p _{CO₂} vs α) for aqueous MAE + AEEA blend for, T: ▲ 303.15 K; ■ 313.15 K, respectively, C _T = 30 weight %, and w _{AEEA} = 0.30	45
Figure 2.7	Model predicted CO ₂ solubility vs. experimental CO ₂ solubility data	45
Figure 3.1	Experimental set-up for CO ₂ desorption study	56
Figure 3.2	Effect of AEEA weight fraction (w _{AEEA}) on the CO ₂ solubility at constant 298.15 K temperature and constant 20.27 kPa partial pressure of CO ₂ gas for aqueous EAE and AEEA blend: Experimental (Exp.) and model (Eq. 3.35) predicted data	64
Figure 3.3	Effect of total concentration (C _T) of the aqueous EAE and AEEA blend with 0.30 w _{AEEA} and at 15.20 kPa partial pressure of CO ₂ on the CO ₂ (a) solubility, and (b) absorption capacity:	65

	Experimental (Exp.) and model (Eq. 3.35) predicted data	
Figure 3.4	Effect of CO ₂ partial pressure on the CO ₂ solubility for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend: Experimental (Exp.) and model (Eq. 3.35) predicted data.	66
Figure 3.5	Effect of temperature on the CO ₂ solubility for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend of constant concentration: Experimental (Exp.) and model (Eq. 3.35) predicted data	67
Figure 3.6	Parity plot of experimental and calculated (by Eq. 3.40) CO ₂ solubility for the aqueous EAE and AEEA blend	72
Figure 3.7	Plot of $\ln(p_{CO_2})$ vs. $(1/T)$ for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend	73
Figure 3.8	Cyclic CO ₂ solubility and cyclic absorption capacity of 30 wt.% MEA solution and aqueous EAE and AEEA blend with 0.30 w_{AEEA}	75
Figure 3.9	CO ₂ solubility vs. time plot of 30 wt. % MEA and 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend during (a) CO ₂ absorption, and (b) CO ₂ desorption	76
Figure 4.1	Viscosity versus temperature of EAE + H ₂ O for different concentration of EAE in terms of weight fraction (w_1) of EAE, w_1 : \blacklozenge 0.05; \blacksquare 0.10; \blacktriangle 0.15; \blacktimes 0.20; $*$ 0.25; \bullet 0.30; — calculated values with Eq. 4.3	91
Figure 4.2	Viscosity versus temperature of AEEA + H ₂ O for different concentration of AEEA in terms of weight fraction (w_1) of AEEA, w_1 : \blacklozenge 0.05; \blacksquare 0.10; \blacktriangle 0.15; \blacktimes 0.20; $*$ 0.25; \bullet 0.30; — calculated values with Eq. 4.3	91
Figure 4.3	Viscosity versus temperature of EAE + AEEA + H ₂ O for concentration in weight fraction ($w_1 + w_2$) of EAE + AEEA, ($w_1 + w_2$): \blacklozenge 0.10; \blacksquare 0.20; \blacktriangle 0.30; — calculated values with Eq. 4.4 with different weight ratio of EAE/AEEA (w_1/w_2) for (a) (w_1/w_2) = 9/1, (b) (w_1/w_2) = 8/2, and (c) (w_1/w_2) = 7/3	96
Figure 4.4	Density versus temperature of EAE + H ₂ O for different concentration of EAE in terms of weight fraction (w_1) of EAE,	100

- w_1 : \blacklozenge 0.05; \blacksquare 0.10; \blacktriangle 0.15; \times 0.20; $*$ 0.25; \bullet 0.30; —
calculated values with Eq. 4.9
- Figure 4.5** Density versus temperature of AEEA + H₂O for different concentration of AEEA in terms of weight fraction (w_1) of AEEA, w_1 : \blacklozenge 0.05; \blacksquare 0.10; \blacktriangle 0.15; \times 0.20; $*$ 0.25; \bullet 0.30; — calculated values with Eq. 4.9 100
- Figure 4.6** Density versus temperature of EAE + AEEA + H₂O for concentration in weight fraction ($w_1 + w_2$) of EAE + AEEA, ($w_1 + w_2$): \blacklozenge 0.10; \blacksquare 0.20; \blacktriangle 0.30; — calculated values with Eq. 4.11 with different weight ratio of EAE/AEEA (w_1/w_2) for (a) (w_1/w_2) = 9/1, (b) (w_1/w_2) = 8/2, and (c) (w_1/w_2) = 7/3 102
- Figure 5.1** Density of aqueous EAE+AEEA blend versus temperature for different concentration (in weight fraction) of EAE+AEEA, w : for (\blacklozenge) 0.10; (\blacksquare) 0.20; (\blacktriangle) 0.30; and lines (—) for calculated values with Eq. 5.5 116
- Figure 5.2** Relative deviations of experimental and calculated density data of CO₂-unloaded aqueous EAE +AEEA blend from Eq. 5.6 as a function of (a) temperature and (b) concentration (EAE+AEEA weight fraction) 120
- Figure 5.3** Experimental and calculated density data of CO₂-loaded aqueous EAE +AEEA blend as a function of temperature for different (EAE+AEEA) concentration and CO₂ loading (α); (a) $w = 0.10$ and α : for (\blacklozenge) 0.27; (\blacksquare) 0.52; (\blacktriangle) 0.77; and (\times) 0.981; (b) $w = 0.20$ and α : for (\blacklozenge) 0.155; (\blacksquare) 0.502; (\blacktriangle) 0.657; and (\times) 0.754; (c) $w = 0.30$ and α : for (\blacklozenge) 0.129; (\blacksquare) 0.464; (\blacktriangle) 0.644; and (\times) 0.76; and lines (—) for calculated values with Eq. 5.7 124
- Figure 5.4** Viscosity of aqueous EAE+AEEA blend versus temperature for different concentration (in weight fraction) of EAE+AEEA, w : for (\blacklozenge) 0.10; (\blacksquare) 0.20; (\blacktriangle) 0.30; and lines (—) for calculated values with Eq. 5.8 125
- Figure 5.5** Relative deviations of experimental and calculated viscosity data of CO₂-unloaded aqueous EAE +AEEA blend from Eq. 127

	5.9 as a function of (a) temperature and (b) concentration (EAE+AEEA weight fraction)	
Figure 5.6	Experimental and calculated viscosity data of CO ₂ -loaded aqueous EAE +AEEA blend as a function of CO ₂ loading (α) at different temperature; T: for (\blacklozenge) 293.15 K; (\blacktriangle) 298.15 K; and ($*$) 303.15 K; ($+$) 308.15 K; ($-$) 313.15 K; (\blacksquare) 318.15 K; (\times) 323.15 K; and lines (—) for calculated values with Eq. 5.10. For different (EAE+AEEA) concentration in weight fraction with $(w_1/w_2) = 7/3$ (a) $w = 0.10$, (b) $w = 0.20$, and (c) $w = 0.30$	129
Figure 5.7	Comparison of relative deviations of experimental and calculated viscosity data of CO ₂ -loaded aqueous EAE +AEEA blend from Eq. 5.10 (\blacktriangle) and Eq. 5.11 (\blacklozenge) as a function of (a) temperature, (b) CO ₂ loading, and (c) concentration (EAE+AEEA weight fraction)	130
Figure 5.8	Diffusivity of CO ₂ into the aqueous EAE + AEEA blend versus temperature for different concentration (in weight fraction) of EAE+AEEA, w : for (\blacklozenge) 0.10; (\blacksquare) 0.20; and (\blacktriangle) 0.30	132
Figure A1	Comparison of experimental data and literature data of CO ₂ solubility (mol CO ₂ /mol amine) for 30 wt. % aqueous MEA at 313.15 K temperature and CO ₂ partial pressure of 12.16, 15.20, and 20.27 kPa	159
Figure A2	Effect of AEEA weight fraction (w_{AEEA}) on the CO ₂ solubility at 298.15 K temperature and 20.27 kPa partial pressure of CO ₂ gas for the EAE and AEEA blend, lines (—) are for polynomial trend line	160
Figure A3	Effect of total concentration (C_T) of the aqueous EAE and AEEA blend with 0.30 w_{AEEA} and at 15.20 kPa partial pressure of CO ₂ on the CO ₂ solubility, lines (—) are for polynomial trend line	161
Figure A4	Effect of CO ₂ partial pressure on the CO ₂ solubility for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend,	162

	lines (—) are for polynomial trend line	
Figure A5	Effect of temperature on the CO ₂ solubility for the 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend, lines (—) are for polynomial trend line	163
Figure A6	CO ₂ solubility vs. time plot of 30 wt. % MEA and 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend during CO ₂ absorption, lines (—) are for linear trend line	164
Figure A7	CO ₂ solubility vs. time plot of 30 wt. % MEA and 30 wt. % (21 wt. % + 9 wt. %) aqueous EAE and AEEA blend during CO ₂ desorption, lines (—) are for linear trend line	165
Figure A8	Viscosity of EAE + H ₂ O versus weight fraction of EAE (w_1) at different temperature (T), T: ■ 293.15 K; ▲ 303.15 K; dashed lines are for corresponding available literature data (Gao et al., 2017 a)	166
Figure A9	Density of AEEA + H ₂ O versus mole fraction of AEEA (x_1) at different temperature (T), T: ■ 298.15 K; ▲ 313.15 K; ● 328.15 K; dashed lines are for corresponding available literature data (Stec et al., 2014)	167
Figure A10	Density of aqueous EAE+AEEA blend versus temperature for different concentration (in weight fraction) of EAE+AEEA, w : for (◆) 0.10; (■) 0.20; (▲) 0.30; and lines (—) for calculated values with Eq. 5.6	168
Figure A11	Relative deviations of experimental and calculated density data of CO ₂ -loaded aqueous EAE +AEEA blend from Eq. 5.7 as a function of (a) temperature, (b) CO ₂ loading, and (c) concentration (EAE+AEEA weight fraction)	169
Figure A12	Viscosity of aqueous EAE+AEEA blend versus temperature for different concentration (in weight fraction) of EAE+AEEA, w : for (◆) 0.10; (■) 0.20; (▲) 0.30; and lines (—) for calculated values with Eq. 5.9	170

List of Tables

<u>Table No.</u>	<u>Captions</u>	<u>Page No.</u>
Table 1.1	CO ₂ emissions data (IEA, 2020)	2
Table 1.2	Literature related to CO ₂ solubility into aqueous MAE and aqueous EAE	11
Table 1.3	Literature related to CO ₂ solubility into aqueous AEEA and its blends	14
Table 1.4	Literature related to physicochemical properties of MAE, EAE, and AEEA	19
Table 2.1	Chemical sample information	27
Table 2.2	Values of coefficients for temperature dependency of Henry's law constant and equilibrium constants	34
Table 2.3	CO ₂ solubility data in aqueous blend of MAE+AEEA with standard uncertainties ^a	38
Table 2.4	Values of coefficients of correction factor F_k for Equation 2.31	44
Table 3.1	Information of used chemicals	53
Table 3.2	Equilibrium CO ₂ solubility data of aqueous EAE and AEEA blend at atmospheric pressure	62
Table 3.3	Values of coefficients for temperature dependent equilibrium constants	68
Table 3.4	Regressed coefficients of Eq. (3.38) for estimated reaction equilibrium constants	69
Table 3.5	Values of coefficients of model (Eq. 3.40) to calculate equilibrium CO ₂ solubility of the aqueous EAE and AEEA blend	71
Table 4.1	Details of used chemicals in this study	83
Table 4.2	Experimental data of density and viscosity of EAE and AEEA at T = (293.15-323.15) K and 101.325 kPa pressure and comparison with data available in the literature [*]	85
Table 4.3	Viscosity (μ), density (ρ), and excess molar volume (V^E), of aqueous EAE and aqueous AEEA at T = (293.15-	87

	333.15) K and 101.325 kPa pressure ^a	
Table 4.4	Fitting parameters of Eq. 4.2 in the range of T = (293.15-333.15) K and for different weight fraction of amine (w_1)	89
Table 4.5	Standard deviation ^a (s.d.) (mPa.s) for experimental data of viscosity of binary mixture and model predicted viscosity data in the range of T = (293.15-333.15) K and for different weight fraction of amine (w_1)	92
Table 4.6	Viscosity (μ), density (ρ), and excess molar volume (V^E), of EAE + AEEA + H ₂ O blend at T = (293.15-333.15) K and 101.325 kPa pressure ^a	94
Table 4.7	Coefficients of Redlich-Kister equation (Eq. 4.8) for calculation of density of aqueous EAE and aqueous AEEA	99
Table 4.8	Regressed coefficients of Eq. 4.11 to calculate density of EAE + AEEA + H ₂ O	103
Table 4.9	The values of isobaric thermal expansion coefficient for EAE+H ₂ O, AEEA+H ₂ O, and EAE + AEEA + H ₂ O at T = (293.15-333.15) K and 101.325 kPa pressure	105
Table 4.10	Activation molar enthalpy, entropy, and Gibbs free energy at 298.15 K for activation of viscous flow of EAE + H ₂ O, AEEA + H ₂ O, and EAE + AEEA + H ₂ O blend	107
Table 5.1	Details of used chemicals in this work	114
Table 5.2	Density, excess volume, viscosity, and diffusivity of aqueous EAE + AEEA blend at T = (293.15-323.15) K and 101.325 kPa pressure ^a	117
Table 5.3	Regressed parameters (c_0 , c_1 , and c_2) of Eq. 5.5 and Eq. 5.8 at different temperature	119
Table 5.4	Density and viscosity of CO ₂ -loaded aqueous EAE + AEEA blend at T = (293.15-323.15) K and 101.325 kPa pressure ^a	121
Table B1	Values of fitting parameters of Eq. 4.13	171

Nomenclature

Abbreviations/ Symbols/ Subscripts	Full form/Meaning
Abbreviations	
1MPZ	1-methylpiperazine
3DMA1P	3-dimethyl amino-1-propanol
ADD	Absolute average deviation
AEEA	Aminoethylethanolamine
AMP	2-amino-2-methyl-1-propanol
ARD	Absolute relative deviation
BAE	2-(butylamino)ethanol
BZA	Benzylamine
DEA	Diethanolamine
DEAE	Diethylaminoethanol
DETA	Diethylenetriamine
DIPA	Diisopropanolamine
DMAP	4-Dimethylaminopyridine
EAE	2-(ethylamino)ethanol
EDA	Dthylinediamine
HMDA	Hexamethylenediamine
IEA	International Energy Agency
IPAE	2-(isopropylamino)ethanol
IPCC	Intergovernmental panel on climate change
MAE	2-(methylamino)ethanol
MAPA	3-(methylamino)propanolamine
MDEA	N-methyl-diethanolamine
MEA	Monoethanolamine
MPDL	N-methyl-4-piperidinol
NMP	N-methyl-2-pyrrolidone
PSA	Pressure swing adsorption
PZ	Piperazine
TEA	Triethanolamine
TEPA	Triethylenepentamine
TETA	Triethylenetetramine

TSA	Thermal swing adsorption
Symbols	
α	CO ₂ Solubility (mol CO ₂ /mol amine)
α_p	Isobaric thermal expansion coefficient
C_T	total concentration
ΔG^*	Activation molar Gibbs free energy
ΔH^*	Activation molar enthalpy
ΔH_{abs}	Heat of absorption
h	Plank constant ($6.626 \cdot 10^{-23}$ J.s),
K_i	i^{th} Equilibrium constant
μ	Viscosity
N_A	Avogadro number
p_{CO_2}	Partial pressure of CO ₂ gas
ρ	Density
R	Universal gas constant
ΔS^*	activation molar entropy
T	Temperature (K)
t	Temperature (°C)
V^E	Excess volume
V_m	Molar volume
w	Concentration in weight fraction
wt. %	Weight %
Subscripts	
calc	Calculated data
eqlm	At the equilibrium
exp	Experimental data

Preface

Greenhouse gases are the main cause of global warming. Carbon dioxide (CO₂) contributes to a major fraction of greenhouse gases. CO₂ emitted into the atmosphere by the combustion of fossil fuels during industrial activities. CO₂ capture from the flue gases is important due to environmental concern. The post-combustion absorption technique is most matured and useful for CO₂ capture containing low partial pressure CO₂. The aqueous monoethanolamine (MEA) has been shown good CO₂ absorption capability with fast reaction kinetics and considered as an industrial benchmark solution for CO₂ absorption. But its high heat of CO₂ absorption is a major drawback because of the high energy requirement for regeneration of CO₂-loaded solution. In order to minimize demerits and utilize the advantages of individual single amines, amine blends are used. However, it is still a matter of research to find out a solvent that has high CO₂ solubility, a faster CO₂ absorption-desorption rate, and low heat of absorption as well.

2-(methylamino)ethanol (MAE) and 2-(ethylamino)ethanol (EAE) produce less stable carbamate, with fast reaction kinetics towards CO₂, have better favorable properties of CO₂ absorption, and reported as a better alternative to MEA in the literature. Aminoethylethanolamine (AEEA) is a di-amine containing one primary and one secondary amine. Its absorption capacity and absorption rate are high. AEEA was used as an activator for secondary and tertiary amines in the literature.

So, the research objectives were decided to study of aqueous MAE + AEEA and aqueous EAE + AEEA blend for post-combustion CO₂ capture. The complete research work of this thesis can be summarized in different chapters as follows:

Chapter 1 explains the CO₂ emission scenario and its consequences on the environment based on fossil-fuel combustion. Various technologies and techniques for

CO₂ capture are discussed. Post-combustion CO₂ capture using chemical absorption technique based on the amine solvents are described. Literature reviews related to CO₂ absorption into MAE, EAE, and AEEA are given in detail. Literature reviews about CO₂ solubility models and physicochemical properties of amine absorbents are also depicted briefly. The literature gaps have been identified and included in this chapter. The objectives of the present work also have been provided in this chapter.

Chapter 2 describes CO₂ solubility data of aqueous (MAE + AEEA) blend at different operating conditions. Modified Kent-Eisenberg (K-E) thermodynamic model has been given for CO₂ solubility in aqueous (MAE + AEEA) blend. Determination of heat of CO₂ absorption for aqueous (MAE + AEEA) blend using CO₂ solubility data has also been provided.

Chapter 3 explains experimental CO₂ solubility measurement and modified K-E model for aqueous (EAE + AEEA) blend. The development of an empirical model for CO₂ solubility prediction has been also shown. The heat of CO₂ absorption for the aqueous (EAE + AEEA) blend has been discussed based on Gibbs-Helmholtz equation. The initial rate of change of CO₂ solubility with respect to time during absorption as well as desorption has been discussed. Cyclic capacity of aqueous (EAE + AEEA) blend and its comparison with cyclic capacity of aqueous monoethanolamine (MEA) are discussed.

Chapter 4 describes the viscosity and density of EAE + H₂O, AEEA + H₂O, and EAE + AEEA + H₂O. Excess molar volume has been calculated for mixtures in the range of 293.15 K to 333.15 K and correlated to the Redlich-Kister model. Experimental viscosity and density data have been correlated to the newly developed empirical models. In order to extend the knowledge of molecular interaction, derived thermodynamic properties have been studied.

Chapter 5 illustrates the density and viscosity of the CO₂-loaded and -unloaded aqueous (EAE+AEEA) blend. Excess volume has been calculated in the temperature range of 293.15 to 323.15 K for -unloaded aqueous (EAE+AEEA) blend and fitted to the newly developed empirical model. Newly proposed empirical correlations have been given to predict the density and viscosity of the CO₂-loaded and -unloaded aqueous (EAE+AEEA) blend. CO₂ diffusivity into the aqueous EAE+AEEA blend has been discussed.

Chapter 6 contains the overall conclusions of this research work and recommendations for future work. On the basis of this research work, it has been concluded that the aqueous (EAE+AEEA) blend has a good potential for post-combustion CO₂ absorption.