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 + aminoehtylethanolamine) for post-combustion CO_2 capture"** by "**Diwakar Pandey"** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. 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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CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

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Date:

Varanasi (**Diwakar Pandey**)

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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 *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 (^oC)
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 (CO_2) contributes to a major fraction of greenhouse gases. CO_2 emitted into the atmosphere by the combustion of fossil fuels during industrial activities. CO_2 capture from the flue gases is important due to environmental concern. The post-combustion absorption technique is most matured and useful for CO_2 capture containing low partial pressure CO_2. The aqueous monoethanolamine (MEA)) has been shown good CO_2 absorption capability with fast reaction kinetics and considered as an industrial benchmark solution for CO_2 absorption. But its high heat of CO_2 absorption is a major drawback because of the high energy requirement for regeneration of CO_2-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 CO_2 solubility, a faster CO_2 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 CO_2, have better favorable properties of CO_2 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 CO_2 capture. The complete research work of this thesis can be summarized in different chapters as follows:

Chapter 1 explains the CO_2 emission scenario and its consequences on the environment based on fossil-fuel combustion. Various technologies and techniques for

CO_2 capture are discussed. Post-combustion CO_2 capture using chemical absorption technique based on the amine solvents are described. Literature reviews related to CO_2 absorption into MAE, EAE, and AEEA are given in detail. Literature reviews about CO_2 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 CO_2 solubility data of aqueous (MAE + AEEA) blend at different operating conditions. Modified Kent-Eisenberg (K-E) thermodynamic model has been given for CO_2 solubility in aqueous (MAE + AEEA) blend. Determination of heat of CO_2 absorption for aqueous (MAE + AEEA) blend using CO_2 solubility data has also been provided.

Chapter 3 explains experimental CO_2 solubility measurement and modified K-E model for aqueous (EAE + AEEA) blend. The development of an empirical model for CO_2 solubility prediction has been also shown. The heat of CO_2 absorption for the aqueous (EAE + AEEA) blend has been discussed based on Gibbs-Helmholtz equation. The initial rate of change of CO_2 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 + H_2O, AEEA + H_2O, and EAE + AEEA + H_2O. 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 CO_2-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 CO_2-loaded and –unloaded aqueous (EAE+AEEA) blend. CO_2 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 CO_2 absorption.