

UNIVERSITI TEKNOLOGI MARA

**SOLUBILITY OF CARBON DIOXIDE
IN AQUEOUS DIETHANOLAMINE
BLENDED WITH 1-BUTYL-1-
METHYLPYRROLIDINIUM
DICYANAMIDE AND 1-BUTYL-1-
METHYLPYRROLIDINIUM
TRIFLUOROMETHANESULFONATE
AT HIGH PRESSURE**

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ABSTRACT

Removing of CO₂ gases is very important process in many chemical industries today. Alkanolamines are mature in technology for efficiently capturing CO₂. However, even if the reaction between CO₂ and these amines is significantly fast, their potential application in CO₂ capture encounters several drawbacks. Alternatively, ionic liquids (ILs) seem very attractive with a great advantage. However, gas dissolution into ILs is a physical phenomenon with no chemical reaction and the absorption rate is quite slow. To achieve better performance, some special groups were introduced to the anion. In recent years, the mixed solutions consisted of amine and ILs have received particular interest. Generally, CO₂ capture with amine-ILs mixture have been reported having low capability of CO₂ loading. However, by tuning the ILs may increase the capacity of CO₂ absorption. Hence, the studies on the potential of different types of ionic liquid toward CO₂ absorption performance is necessary. Most of CO₂ capture with amine-ILs mixture also focused on absorption ability at ambient pressures, while seldom research was concerned at high pressure. This not only limits the CO₂ absorption application at high pressure, but also the determination of the operation condition. This work mainly reported CO₂ solubilities in aqueous Diethanolamine (DEA) mixed with pyrrolidinium based ILs; 1-Butyl-1-Methylpyrrolidinium Dicyanamide [BmPyrr][DCA] and 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate [BmPyrr][OTf] at various operating temperatures (303.15K-333.15K), pressures (500psi – 700 psi) with 0-10wt% concentration of ILs and 30-40wt% of DEA concentration. 1-Butyl-1-Methylpyrrolidinium Dicyanamide [BmPyrr][DCA] and 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate [BmPyrr][OTf] were selected as physical absorbents for capturing CO₂. The absorption performance was investigated by conducting the experiment using high pressure reactor. The absorption capacities were calculated based on pressure change until the equilibrium phase were achieved by the system. The results of CO₂ solubility in liquid are expressed as α_{CO_2} (mol CO₂/mol amine) for all the experimental. From the results of this research, it was found that the CO₂ solubility performance reduced when [BmPyrr][DCA] is added to the aqueous DEA solution at all temperatures measured and with addition of [BmPyrr][OTf] at temperatures of 303.15K and 313.15K. However, the absorption capacities for aqueous DEA-[BmPyrr][OTf] mixture exhibits good absorption performance at temperature condition of 323.15K-333.15K. Similar reducing trend of CO₂ absorption was observed for aqueous DEA for all measured temperatures. This shows that DEA-[BmPyrr][OTf] system has better performance compared to DEA-[BmPyrr][DCA], indicating that OTf anion has great potential for capturing CO₂ in future application. In term of pressure, the CO₂ absorption increases as pressure increases for both DEA-[BmPyrr][DCA] and DEA-[BmPyrr][OTf] systems. A solubility model was developed to predict the CO₂ solubility data as a function operating variables in the studied range in aqueous blends of DEA and ILs. There is an acceptable degree of agreement between experimental data and prediction by Jou and Mather model with an average absolute deviation of 5.165%. Therefore, it can be concluded that this work has achieved the objectives of this research.

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TABLE OF CONTENT

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF SYMBOLS	xii
LIST OF ABBREVIATIONS	xiii
CHAPTER ONE: INTRODUCTION	1
1.1 Research Background	1
1.2 Problem Statement	4
1.3 Research Objectives	5
1.4 Research Scope	6
1.5 Significant of Research	6
1.6 Thesis Structure	7
CHAPTER TWO: LITERATURE REVIEW	9
2.1 Introduction	9
2.2 Carbon Capture and Storage (CCS)	9
2.2.1 Pre- Combustion Capture	10
2.2.2 Post-Combustion Capture	11
2.2.3 Oxy-Fuel Combustion Capture	13
2.3 Carbon Dioxide Removal Method	14
2.3.1 Absorption	15
2.3.1.1 <i>Physical Absorption</i>	15
2.3.1.2 <i>Chemical Absorption</i>	15
2.4 Post-Combustion CO ₂ Capture with Chemical Absorption	16

CHAPTER ONE

INTRODUCTION

1.1 Research Background

The emissions of carbon dioxide (CO₂) in the atmosphere has been increasing significantly over the years since the revolution of commercialized industry expansion in the world. The uses of natural gas, petroleum-derived fuels, coal, cement production industry, electricity heat production are considered as major contributors of CO₂ emissions. Other than that, the human activities also clearly influences the emission of greenhouse gas (GHG) as stated in The Fifth Assessment Report of Intergovernmental Panel on Climate Change (2014) [1]. Figure 1.1 shows the percentages of estimated shares of global anthropogenic greenhouse gas (GHG) from fuel combustion and non-fuel combustion predicted by International Energy Agency (IEA) [2]. It can be clearly seen that the use of energy represents the largest shares of emission sources with 69% of greenhouse gas, while 14% corresponds to others including large scale biomass burning and post burn decay process, indirect N₂O emissions from non-agricultural emissions of NO_x and NH₃, waste, and solvent use. Smaller shares correspond to agriculture with 11% that mainly producing CH₄ and N₂O, followed by industrial process not related to energy 6% producing mainly fluorinated gases and N₂O. Within the energy sector, CO₂ dominates the total GHG emissions with 90% resulting from the oxidation of carbon in fuels during combustion. Besides that, the energy sector also includes emissions from “fugitive emissions”, which are intentional or unintentional releases of gases resulting from production, processes, transmission, storage and use of fuels.