CO₂ Capture Using Ionic Liquids

Master Thesis

By

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Preface

This thesis is submitted as a partial fulfillment of the requirements for the Master degree at the Technical University of Denmark. The work has been carried out at IVC-SEP (Center for Phase Equilibria and Separation Processes), one of the research centers in the Department of Chemical and Biochemical Engineering, from November 2008 to April 2009 under the supervision of Associate Professor Kaj Thomsen.

This report consists of seven chapters. Chapter 1 (Introduction) describes the background and description of the problem and objective of the thesis. Chapter 2 (Ionic liquids) covers the theoretical background of ionic liquids. History, types, typical synthesis methods and different properties of ionic liquids like melting point, density, viscosity, thermal stability and some environmental issues etc along with compilation of some of these properties data are presented in this chapter. Some industrial applications of ionic liquids are also presented at the end of the chapter. In chapter 3 (CO₂ Capture), a brief introduction of CO₂ emissions from stationary sources is presented. Different CO₂ capture systems (Pre-combustion, post-combustion and oxy-fuel combustion capture) along with current state-of-the-art amine based technology and some emerging technologies are discussed briefly. Finally, a review of CO₂ solubility in different ionic liquids and some related issues are presented in this chapter. Chapter 4 (Material and Methods) covers the experimental details of this work. A brief description of the materials (ionic liquids: [emim][Tf₂N] and [bmim][Tf₂N], and CO₂ gas) used in this work and related important data is presented. Different experimental methods for gas absorption available in literature are presented briefly and the method and experimental setup used in this work in detail. “Results and Discussion” is the 5th chapter of this report which covers the details of experimental results of CO₂ solubility in ionic liquids. This chapter also covers the discussion on some problems related to the experimental setup.
used in this study. “Process Evaluation” on the basis of energy consumption both for ionic liquids and amine-based solvent (MEA) is made and presented in chapter 6. A comparison is also made between ionic liquids and MEA on the basis of energy usage and parameters for a “Theoretical Ionic Liquid” competitive to MEA solvent are calculated and presented. Finally, in the last chapter 7, a short summary of some concluding remarks is presented together with some future directions for “CO₂ Capture Using Ionic Liquids”.

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Abstract

Current post combustion CO₂ capture systems in power plants typically employ amine based solvent, such as monoethanolamine (MEA), to capture CO₂ from flue gas followed by a desorption (or solvent regeneration) step, usually a stripping column, to recover the captured CO₂ and regenerate the solvent. The MEA solvent has high heat of reaction with CO₂ that leads to higher stripping energy consumption during CO₂ recovery, thus making amine scrubbing an energy expensive process. The solvents suggested for CO₂ capture in this work belong to a group of compounds called ionic liquids (ILs). Many ILs have shown a remarkably good CO₂ solubility. Ionic liquids have also shown good selective CO₂ absorption, thus making ILs a potential candidate for CO₂ capture from flue gas. Since CO₂ absorption in ILs involves physisorption (physical absorption) rather than chemisorption (chemical absorption) of CO₂ in amine based solvents, there is a potential to develop energy efficient ionic liquid based absorption-stripping process.

Two ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) and 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) are investigated in this work for their CO₂ solubility at 25 °C and low pressures (up to 10 bar) using High Pressure Microbalance (HP balance). Since, the HP balance is being used for the first time to measure the gas (CO₂) solubility in liquids (ionic liquids) at low pressures, it is important to check the reliability of the equipment for these kinds of solubility measurements. A process evaluation is also made on the basis of energy consumption for CO₂ absorption and recovery in ionic liquids using temperature-swing technique and compared with state-of-the-art MEA-based CO₂ capture technology. The CO₂ solubility results are not good enough and are also not in good agreement with the data published in literature. The disagreement in data is due to some technical problems in the experimental setup e.g. problem in geometry (alignment) of the pressure tube of HP balance, inadequate vacuum system, pressure drop in the system,
improper pressure control system and related problems. Some recommendations are presented to overcome these problems. Since, no good solubility results are obtained, the process evaluation is made using Henry’s constants reported in literature. The amount (kilogram) of ionic liquid required per kilogram of CO$_2$ capture and corresponding energy required to recover the captured CO$_2$ in the stripping column are calculated. Both ionic liquids require significantly greater energy to capture and recover CO$_2$ compared to MEA solvent due to low CO$_2$ carrying capacity of the ionic liquids which results in high solvent amount requirements per kilogram CO$_2$ capture. But the CO$_2$ carrying capacity of the ionic liquids can be increased by tailoring the choice of anions and cations of the ionic liquids, thus parameters (Henry’s constant at 25 °C and 100 °C) for a theoretical ionic liquid that would be competitive to MEA are presented.
Dedication

To my Family
Especially to my
Mother and Grandfather
And my
Late Father
Acknowledgements

First and foremost, I want to thank my supervisor, Associate Professor Kaj Thomsen, and express my deep gratitude for his continuous guidance, support and help throughout my master thesis work. I feel fortunate to have had the opportunity to work with such a wonderful mentor.

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# Table of Contents

PREFACE ........................................................................................................................................... III

ABSTRACT ........................................................................................................................................ V

ACKNOWLEDGEMENTS ................................................................................................................ VIII

1 INTRODUCTION .......................................................................................................................... 1
   1.1 PROBLEM BACKGROUND AND DESCRIPTION ............................................................ 1
   1.2 OBJECTIVE ......................................................................................................................... 2

2 THEORY: IONIC LIQUIDS ......................................................................................................... 4
   2.1 INTRODUCTION ................................................................................................................... 4
   2.2 TYPES OF IONIC LIQUIDS ................................................................................................. 6
   2.3 HISTORY AND NEW DEVELOPMENTS ............................................................................. 7
   2.4 IONIC LIQUIDS SYNTHESIS .............................................................................................. 8
   2.5 CHARACTERISTICS OF IONIC LIQUIDS .......................................................................... 11
      2.5.1 Melting Point ............................................................................................................. 11
      2.5.2 Density ...................................................................................................................... 12
      2.5.3 Viscosity .................................................................................................................. 15
      2.5.4 Vapour Pressure ....................................................................................................... 19
      2.5.5 Thermal Stability ...................................................................................................... 19
      2.5.6 Surface Tension ......................................................................................................... 21
      2.5.7 Miscibility with Water ............................................................................................... 22
      2.5.8 Toxicity and Occupational Health ........................................................................... 24
      2.5.9 Flammability and Corrosion ..................................................................................... 28
   2.6 POTENTIAL APPLICATIONS OF IONIC LIQUIDS ............................................................. 30
   2.7 CHALLENGES WITH IONIC LIQUIDS ............................................................................. 33
3  THEORY: CO₂ CAPTURE .......................................................................................... 34
  3.1  INTRODUCTION .............................................................................................. 34
  3.2  CO₂ CAPTURE SYSTEMS ............................................................................. 35
  3.3  POST-COMBUSTION CAPTURE .................................................................... 38
  3.4  CURRENT TECHNOLOGIES .......................................................................... 40
    3.4.1  State-of-the-art Amine based technology ............................................. 40
  3.5  EMERGING TECHNOLOGIES ..................................................................... 42
    3.5.1  Cryogenic Separation ........................................................................... 42
    3.5.2  Soluble Carbonate based systems ......................................................... 43
    3.5.3  Ammonia based systems ....................................................................... 43
    3.5.4  Membrane systems ............................................................................... 44
    3.5.5  Enzyme-based systems ......................................................................... 45
    3.5.6  Solid sorbent based systems (Adsorption) ............................................ 46
  3.6  REVIEW OF CO₂ SOLUBILITY IN IONIC LIQUIDS ...................................... 48
    3.6.1  Introduction ............................................................................................ 48
    3.6.2  Henry’s Law ........................................................................................... 48
    3.6.3  Classification of ionic liquids for CO₂ solubility ................................... 49
    3.6.4  CO₂ solubility in Conventional Ionic Liquids ........................................ 49
      3.6.4.1  Anion effect on CO₂ Solubility ......................................................... 52
      3.6.4.2  Fluorination Effect of Anion on CO₂ solubility ............................... 53
      3.6.4.3  Cation effect on CO₂ solubility ....................................................... 55
      3.6.4.4  Fluorination Effect of Cation on CO₂ solubility ............................... 56
      3.6.4.5  Effect of Fluoroalkylation of [PF₆] anion on CO₂ solubility .......... 58
      3.6.4.6  CO₂ solubility in non-fluorinated ionic liquids ............................... 59
    3.6.5  CO₂ solubility in Task Specific Ionic Liquids ....................................... 62
    3.6.6  Selective CO₂ absorption ....................................................................... 63
    3.6.7  Effect of water on CO₂ solubility ............................................................ 64
    3.6.8  Henry’s constant Data Compilation ....................................................... 66
    3.6.9  CO₂ capture systems for ionic liquids .................................................... 68
  4  MATERIALS AND METHODS ............................................................................. 69
  4.1  MATERIALS ..................................................................................................... 69
  4.2  METHODS FOR MEASURING GAS SOLUBILITY ....................................... 71
    4.2.1  Pressure drop and Volumetric methods .................................................. 72
    4.2.2  Gas chromatography ............................................................................. 72
    4.2.3  Gravimetric method ............................................................................. 73
    4.2.4  High Pressure Microbalance .................................................................. 74
  4.3  OPERATING PROCEDURE ............................................................................ 78
5 RESULTS AND DISCUSSION ................................................................. 82
  5.1 INTRODUCTION .............................................................................. 82
  5.2 SOLUBILITY MEASUREMENTS ...................................................... 82
      5.2.1 [emim][Tf2N] ........................................................................ 82
      5.2.2 [bmim][Tf2N] ........................................................................ 85
      5.2.3 Henry’s Constant ..................................................................... 88
  5.3 DISCUSSION ON EXPERIMENTAL SETUP ...................................... 89
      5.3.1 HP Balance ............................................................................. 89
      5.3.2 Vacuum System ....................................................................... 92
      5.3.3 Gas Pressure System .............................................................. 93
      5.3.4 Low Pressure Absorption ....................................................... 93
      5.3.5 System Pressure Drop ............................................................. 94
      5.3.6 Equilibrium Time .................................................................... 96
      5.3.7 Strange weight loss on Drying and Degassing ......................... 97
  6 PROCESS EVALUATION ................................................................. 99
  6.1 INTRODUCTION .............................................................................. 99
  6.2 IONIC LIQUIDS AS CO2 CAPTURE MEDIA ........................................ 99
  6.3 CONVENTIONAL MEA BASED ABSORPTION TECHNOLOGY ........... 101
  6.4 ENERGY CALCULATIONS AND COMPARISON ................................ 101
  6.5 DISCUSSION ON TEMPERATURE-SWING TECHNIQUE ..................... 105
  6.6 THEORETICAL IONIC LIQUID COMPETITIVE TO MEA ..................... 106
  7 CONCLUSIONS .................................................................................. 107
  7.1 CONCLUSIONS .............................................................................. 107
  7.2 FUTURE DIRECTIONS ..................................................................... 108

APPENDIX ............................................................................................ 110

A-1 [EMIM][TF2N] ............................................................................... 110
A-2 [BMIM][TF2N] ............................................................................... 112
A-3 HENRY’S CONSTANT CALCULATIONS .......................................... 113

REFERENCES ....................................................................................... 117
List of Figures

FIGURE 2.1: DIFFERENCE BETWEEN AN IONIC SOLUTION AND AN IONIC LIQUID ......................... 5

FIGURE 2.2: SOME COMMONLY USED IONIC LIQUID SYSTEMS. THE ABBREVIATION [C<sub>N</sub>MPYR]<sup>+</sup> REPRESENTS THE 1-ALKYL-1-METHYL PYRROLIDINIUM CATION, WHERE THE INDEX N REPRESENTS THE NUMBER OF CARBON ATOMS IN THE LINEAR ALKYL CHAIN. [P<sub>WXYZ</sub>]<sup>+</sup>, [N<sub>WXYZ</sub>]<sup>+</sup> AND [S<sub>WXYZ</sub>]<sup>+</sup> ARE NORMAL TO REPRESENT TETRAALKYLPHOSPHONIUM, TETRAALKYLAMMONIUM AND TRIALKYL SULFONIUM CATIONS, RESPECTIVELY, WHERE THE INDICES W, X, Y AND Z INDICATE THE LENGTH OF THE CORRESPONDING LINEAR ALKYL CHAINS ............................................................... 5

FIGURE 2.3: GROWTH RATE OF IONIC LIQUID PUBLICATIONS, 1986-2006 ......................... 8

FIGURE 2.4: ANNUAL GROWTH OF IONIC LIQUID PATENTS, 1996-2006 .............................. 8

FIGURE 2.5: COMMON ROUTES FOR THE PREPARATION OF IONIC LIQUIDS ......................... 9

FIGURE 2.6: KUGELROHR APPARATUS FOR THE PREPARATION OF A TYPICAL CARBENE .... 10

FIGURE 2.7: EXAMPLES OF DIFFERENT IONIC LIQUIDS PREPARED BY THE CARBENE METHOD ................................................................................................................................... 10

FIGURE 2.8: MELTING POINT PHASE DIAGRAM FOR (A) [RMIM][PF<sub>6</sub>] AND (B) [RMIM][BF<sub>4</sub>] IONIC LIQUIDS AS A FUNCTION OF ALKYL CHAIN LENGTH N SHOWING THE MELTING TRANSITIONS FROM CRYSTALLINE (CLOSED SQUARE) AND GLASSY (OPEN SQUARE) MATERIALS AND THE CLEARING TRANSITION (CLOSED CIRCLE) OF THE LIQUID CRYSTALLINE (LC) TERMS ................................................................. 12

FIGURE 2.9: DENSITY OF [C<sub>N</sub>MIM][BF<sub>4</sub>] (N = 2 TO N = 10) VS TEMPERATURE ............. 13

FIGURE 2.10: DENSITIES OF [PC<sub>6</sub>C<sub>6</sub>C<sub>14</sub>] RTILS WITH ANIONS: (A) NTF<sub>2</sub>, (B) [Co(NCSe)<sub>4</sub>], (C) BIS-DICARBOLYL COBALT(III) (COCB), (D) [Co(NCS)<sub>4</sub>], (E)
DITHIOMALEONITRILE (DTMN), (F) METHYLXANTHATE (XAN), AND (G) DICYANAMIDE \([N(CN)_2]\) .................................................................................................................. 14

**Figure 2.11:** Density of \([C_{4}MIM}][BF_4]\) at 30 °C vs molal concentration of chloride, mol/kg, added as \([C_{4}MIM}][Cl]\) .................................................................................................................. 14

**Figure 2.12:** Viscosities of \([C_{3}MIM}][BF_4]\) (n = 2 to n = 14) vs temperature. .......... 16

**Figure 2.13:** Viscosity at 20 °C of \([C_{4}MIM}][BF_4]\) vs molal concentration of chloride, mol/ kg, added as \([C_{4}MIM}][Cl]\) .................................................................................................................. 17

**Figure 2.14:** Viscosity (at 20 °C) of molecular solvent - \([C_{4}MIM}][BF_4]\) mixtures, where \(X_o\) is the mole fraction of added organic solvent. .......... 18

**Figure 2.15:** Surface tension as a function of temperature for different ionic liquids. ........................................................................................................................................... 22

**Figure 2.16:** Water content on saturation at ambient temperature (ca. 22 °C) for \([C_{4}MIM}][PF_6]\) (n = 4 to n = 8) (white) and for \([C_{4}MIM}][BF_4]\) (n = 6 to n = 10) (gray). ........................................................................................................................................... 23

**Figure 2.17:** Absorption of water from atmospheric air at ambient temperature and moisture, with constant stirring as a function of time of exposure. (Δ) corresponds to \([C_{8}MIM}][NO_3]\), (*) to \([C_{4}MIM}][Cl]\), (O) to \([C_{4}MIM}][BF_4]\) and ( ) to \([C_{4}MIM}][PF_6]\) ........................................................................................................................................... 24

**Figure 2.18:** LC50 values for 1-n-butyl-3-methylimidazolium cations with PF6 and BF4 anions and some commonly used industrial solvents. .......... 25

**Figure 2.19:** Ionic liquid ecotoxicity to Daphnia. (a = Ref. 56, b = Ref. 54) .......... 26

**Figure 2.20:** Ionic liquid ecotoxicity to freshwater snails. .......... 26

**Figure 2.21:** Ignition test of 1 g of protonated [1-Bu-3-H-im][NO3] .......... 28

**Figure 2.22:** (A) Image showing the breakdown of the copper specimens after 48 hr immersion test at 150 °C in \([C_{4}MIM}][TF_2N]\). The breakdown occurs mainly near to the contact between the support and the metal. The whole samples are shown (diameter 12.7 mm). (B) Localized corrosion phenomena at the nickel specimen surface after 48 hr immersion test at 275 °C in \([C_{4}MIM}][TF_2N]\). The whole samples are shown (diameter 12 mm). (C) Localized corrosion phenomena at the inconel specimen surface after 48 hr immersion test at 275 °C in \([C_{4}MIM}][TF_2N]\). The whole sample is shown (diameter 12.7 mm). ........................................................................................................................................... 29

**Figure 2.23:** Growth in the number of IL publications and representative areas of interest. Data obtained from SciFinder Scholar using the search terms
“IONIC LIQUID” OR “IONIC LIQUIDS” AND THEN REFINED BY PUBLICATION YEAR. THE DATA FOR TOTAL PUBLICATIONS INCLUDES THE NUMBER OF PATENTS, AND THE AREA OF THE PARTICULAR FIELD DOES NOT REPRESENT THE NUMBER OF PUBLICATIONS IN THE SUBFIELD. ................................................................. 30

FIGURE 2.24: (A) SYNTHESIS OF DIETHOXYPHENYLPHOSPHINE WITH ETHANOL AND TERTIARY AMINE, (B) SYNTHESIS OF DIETHOXYPHENYLPHOSPHINE WITH 1-METHYLIMIDAZOLE. ................................................................................................... 31

FIGURE 2.25: BASIL PROCESS IN A LITTLE JET REACTOR (COURTESY OF BASF AG) ...... 33

FIGURE 3.1: DIFFERENT CO₂ CAPTURE SYSTEMS IN SIMPLIFIED FORM ......................... 36

FIGURE 3.2: PRE-COMBUSTION CAPTURE SYSTEM (PHOTO COURTESY OF WWW.KJELL-DESIGN.COM / VATTENFALL) .................................................................................................................. 37

FIGURE 3.3: OXY-FUEL COMBUSTION CAPTURE SYSTEM (PHOTO COURTESY OF WWW.KJELL-DESIGN.COM / VATTENFALL) ........................................................................................................... 37

FIGURE 3.4: POST-COMBUSTION CAPTURE SYSTEM (PHOTO COURTESY OF WWW.KJELL-DESIGN.COM / VATTENFALL) ............................................................................................................. 39

FIGURE 3.5: AMINE-BASED CO₂ CAPTURE PROCESS .......................................................... 41

FIGURE 3.6: SCHEMATIC OF AMMONIA BASED CO₂ CAPTURE SYSTEM ......................... 44

FIGURE 3.7: SCHEMATIC OF THE CARBOZYME PERMEATION PROCESS ............................. 46

FIGURE 3.7: SOLUBILITY OF VARIOUS GASES IN [BMIM][PF₆] AT 25°C ....................... 50

FIGURE 3.9: SOLUBILITY OF CO₂ IN [BMIM][PF₆] AT DIFFERENT TEMPERATURES ....... 50

FIGURE 3.10: LIQUID PHASE COMPOSITIONS OF SIX IONIC LIQUID-CO₂ MIXTURES AT 40°C. ......................................................................................................................... 51

FIGURE 3.11: CO₂ SOLUBILITY IN [BMIM][PF₆], [BMIM][BF₄], AND [BMIM][TF₂N] AT 25°C. ..................................................................................................................... 52

FIGURE 3.12: SOLUBILITY (x) OF CO₂ IN [BMIM][TF₂N]: COMPARISON OF DATA FROM LEE ET AL.¹¹¹(*) AT 279.98 K; ◆ AT 299.98 K; ■ AT 319.98 K; ▲ AT 339.97 K) WITH DATA FROM ANTHONY ET AL.⁶⁹(○ AT 283.15 K; ◊ AT 298.15 K; □ AT 323.15 K) .................................................. 53

FIGURE 3.13: EFFECT OF THE ANION AND PRESSURE ON THE SOLUBILITY OF CO₂ IN [BMIM] CATION BASED ILS WITH SEVEN DIFFERENT ANIONS AT 25°C .................................................. 54
FIGURE 4.7: ABSORPTION RUN FOR CO2 IN [EMIM][Tf2N] AT 25 °C AND 2 BAR. THE DIFFERENCE BETWEEN THE INITIAL AND FINAL MASSES IS THE AMOUNT OF GAS ABSORBED. ................................................................................................................. 79

FIGURE 4.8: DESORPTION RUN FOR CO2 IN [EMIM][Tf2N] AT 25 °C AND UNDER VACUUM (0.16 BAR). THE DIFFERENCE BETWEEN THE INITIAL AND FINAL MASSES IS THE AMOUNT OF GAS DESORBED. ................................................................................................................. 79

FIGURE 4.9: TWO DIFFERENT TYPES OF GLASS CUPS USED; CONICAL SHAPED CUP (LEFT) AND FLAT BOTTOM CUP (RIGHT). ............................................................................... 80

FIGURE 4.10: ABSORPTION RUN FOR CO2 IN [EMIM][Tf2N] AT 25 °C AND 1 BAR USING FLAT BOTTOM CUP SHOWING SUDDEN DROPS IN MASS AT DIFFERENT INTERVALS OF TIME SHOWN BY RED CIRCLES. ................................................................................... 81

FIGURE 5.1: CO2 SOLUBILITY IN [EMIM][Tf2N] AT 25 °C AS A FUNCTION OF PRESSURE.... 83

FIGURE 5.2: SOLUBILITY OF CO2 IN [EMIM][Tf2N] AT 25 °C AS A FUNCTION OF PRESSURE FOR THIS WORK AND ANTHONY ET AL. ............................................................................... 84

FIGURE 5.3: ABSORPTION-DESORPTION ISOTHERMS FOR CO2 SOLUBILITY IN [EMIM][Tf2N] AT 25 °C. ................................................................................................................... 84

FIGURE 5.4: ABSORPTION AND DESORPTION ISOTHERMS FOR CO2 SOLUBILITY IN [EMIM][Tf2N] AT 25 °C. ............................................................................................................... 85

FIGURE 5.5: CO2 SOLUBILITY IN [BMIM][Tf2N] AT 25 °C AS A FUNCTION OF PRESSURE. .. 86

FIGURE 5.6: SOLUBILITY OF CO2 IN [BMIM][Tf2N] AT 25 °C AS A FUNCTION OF PRESSURE FOR THIS WORK AND ANTHONY ET AL. ............................................................................... 87

FIGURE 5.7: ABSORPTION AND DESORPTION ISOTHERMS FOR CO2 SOLUBILITY IN [BMIM][Tf2N] AT 25 °C. ............................................................................................................... 87

FIGURE 5.8: ABSORPTION AND DESORPTION ISOTHERMS FOR CO2 SOLUBILITY IN [BMIM][Tf2N] AT 25 °C AND 50 °C. .................................................................................................. 88

FIGURE 5.9: ABSORPTION ISOTHERMS FOR CO2 SOLUBILITY IN [EMIM][Tf2N] AND [BMIM][Tf2N] FROM 3-7 BAR AT 25 °C. ..................................................................... 89

FIGURE 5.10: HP BALANCE LEFT METALLIC PRESSURE TUBE (A) PRESSURE TUBE WITH COUNTER WEIGHT GLASS CUP (B) PROPER ALIGNMENT OF THE PRESSURE TUBE AND GLASS WIRE (C) IMPROPER ALIGNMENT OF PRESSURE TUBE AND GLASS WIRE DUE TO BENDING OF PRESSURE TUBE. ..................................................................................... 90

FIGURE 5.11: HP BALANCE LEFT PRESSURE TUBE IS ALIGNED TEMPORARILY USING THREAD (SEE RED BOX). ........................................................................................................... 91
FIGURE 5.12: MAGNIFIED VIEW OF RIGHT PRESSURE TUBE OF HP BALANCE SHOWING THE ASSEMBLY USED FOR PROPER ALIGNMENT OF PRESSURE TUBE AND GLASS WIRE........ 91

FIGURE 5.13: CO₂ ABSORPTION IN [EMIM][TF₂N] AT 25 °C AND 1 BAR................................. 94

FIGURE 5.14: CO₂ ABSORPTION IN [BMIM][TF₂N] AT 25 °C AND 2 BAR................................. 94

FIGURE 5.15: PRESSURE DROP DURING CO₂ ABSORPTION AT 25 °C IN [EMIM][TF₂N] AND [BMIM][TF₂N]........................................................................................................... 95

FIGURE 5.16: DESORPTION ISOTHERM FOR [BMIM][TF₂N] AT 25 °C I.E. FROM 5 BAR TO 0.15 BAR ........................................................................................................................................... 96

FIGURE 5.17: DESORPTION ISOTHERM FOR [BMIM][TF₂N] AT 25 °C I.E. FROM 7 BAR TO 0.15 BAR ........................................................................................................................................... 97

FIGURE 5.18: DRYING AND DEGASSING OF [EMIM][TF₂N] AT 70 °C AND 0.15 BAR. ....... 97

FIGURE 6.1: BREAKTHROUGH CURVES FOR THE REMOVAL OF CO₂ FROM N₂ USING [BMIM][PF₆] AS THE ABSORBENT. DIFFERENT SYMBOLS SHOW VARIOUS RUNS UNDER SLIGHTLY DIFFERENT OPERATING CONDITIONS. .................................................................................. 100

FIGURE 6.2: CO₂ ABSORPTION SYSTEM USING MEA AS SOLVENT. ............................ 101

FIGURE 6.3: COMPARISON OF TEMPERATURE-SWING ENERGY CALCULATION BETWEEN 30% MEA SOLUTION AND IONIC LIQUIDS, [EMIM][TF₂N] AND [BMIM][TF₂N] .............. 104

FIGURE 6.4: COMPARISON OF TEMPERATURE-SWING ENERGY CALCULATION BETWEEN 30% MEA SOLUTION AND VARIOUS IONIC LIQUIDS. ................................................................. 105

FIGURE F-1: SECOND ORDER POLYNOMIAL FITTING TO THE DATA FOR [EMIM][TF₂N] AND [BMIM][TF₂N] AT 25 °C. ................................................................. 113
## List of Tables

**Table 2.1:** Melting point data for various ionic liquids ........................................ 11

**Table 2.2:** Density data for various ionic liquids ..................................................... 15

**Table 2.3:** Viscosity data for various ionic liquids ..................................................... 16

**Table 2.4:** Comparison of the viscosity of chloride-contaminated ionic liquids. ................................................................. 17

**Table 2.5:** Thermal decomposition temperature data for various ionic liquids ........... 20

**Table 2.6:** Surface tension data for various ionic liquids .......................................... 22

**Table 2.7:** Density and water solubility data for \([\text{C}_{4,9}\text{MIM}][\text{PF}_6]\) .......................... 23

**Table 2.8:** Overview of industrial applications of ionic liquids (commercial/pilot plants). ........................................................................................................... 32

**Table 3.1:** Profile of worldwide large CO₂ stationary sources emitting more than 0.1 Mt CO₂ per year ................................................................. 35

**Table 3.2:** Advantages and disadvantages of different CO₂ capture pathways ............................... 38

**Table 3.3:** Henry’s law constant at different temperatures and enthalpy of absorption for various ionic liquids ................................................................. 67

**Table 4.1:** Ionic liquids with their chemical structures and some useful properties ................................................................. 71

**Table 6.1:** Energy calculation results for CO₂ absorption-desorption by temperature-swing (298 K to 373 K) using two ionic liquids ([EMIM][TF₂N])
TABLE 6.2: ENERGY CALCULATION RESULTS FOR CO₂ ABSORPTION-DESORPTION BY TEMPERATURE-SWING (298 K TO 373 K) USING TWO IONIC LIQUIDS ([EMIM][TF₂N] AND [BMIM][TF₂N]) AND 30 WT% MEA SOLUTION FOR CO₂ PARTIAL PRESSURE = 0.1 BAR ................................................................. 102

TABLE 6.3: ENERGY CALCULATION RESULTS FOR CO₂ ABSORPTION-DESORPTION BY TEMPERATURE-SWING (298 K TO 373 K) USING TWO IONIC LIQUIDS ([EMIM][TF₂N] AND [BMIM][TF₂N]) AND 30 WT% MEA SOLUTION FOR CO₂ PARTIAL PRESSURE = 1 BAR .......................................................................................................................... 103

TABLE 6.4: PARAMETERS FOR THEORETICAL IONIC LIQUID THAT WOULD BE COMPETITIVE TO MEA USING TEMPERATURE-SWING (298 K TO 373 K) ABSORPTION AND RECOVERY WITH SAME HEAT CAPACITY AND ENTHALPY OF ABSORPTION AS THAT OF [BMIM][TF₂N] (I.E. GIVE $Q = 6.9$ MMBTU/TON CO₂) ............................................. 106

TABLE T-1: IONIC LIQUIDS WITH HENRY’S LAW CONSTANTS AT 10, 25, 50 AND 70 °C FROM LITERATURE (SEE TABLE 3.3) AND EXTRAPOLATED HENRY’S LAW CONSTANTS AT 75 AND 100 °C ............................................................................................................. 114

TABLE T-2: ENERGY CALCULATIONS FOR CO₂ CAPTURE IN DIFFERENT IONIC LIQUIDS AT DIFFERENT CO₂ PARTIAL PRESSURES IN THE FEED FLUE GAS ........................................ 115
1 Introduction

1.1 Problem Background and Description

There is growing concern that anthropogenic carbon dioxide (CO₂) emissions are contributing to global climate change through global warming. Therefore, it is critical to develop technologies to mitigate this problem. One very promising approach to reduce CO₂ emissions is to capture CO₂ at a power plant, transport to an injection site, and sequestration for long-term storage in any of a variety of suitable geologic formations. The injection site could be a petroleum reservoir and CO₂ can be used in Enhanced oil recovery (EOR) process. Therefore, CO₂ capture is expected to become an important part of the future power production.

Current post combustion CO₂ capture systems in power plants typically employ solvent based absorption followed by a desorption step, usually a stripping column, to strip off CO₂ and regenerate the solvent. The typical solvents used for this purpose are the amine based absorption agents, such as monoethanolamine (MEA). The flue gas from power plants contains normally 12 vol % CO₂ besides nitrogen. CO₂ from flue gas is selectively absorbed in MEA solution through a chemical reaction in the absorption step. After the absorption, CO₂ is desorbed in a stripping column in its pure form, compressed, and transported in liquid form to the storage place. MEA has high CO₂ carrying capacity, low hydrocarbon solubility, reacts quickly with CO₂ and is relatively inexpensive, thus making it a popular choice in commercial processes. Besides these advantages, there are several disadvantages associated with MEA. It has high vapour pressure which leads to fugitive emissions during regeneration and its corrosive nature which limits its use to dilute aqueous solutions. It also forms degradation products due to side reactions between
some minor constituents of the flue gas. Finally, it has high reaction heat with CO\textsubscript{2} that leads to higher stripping energy consumption, thus making the process energy expensive.\textsuperscript{63} Thus there is a need to develop cost-efficient techniques that have low energy requirements and that do not cause environmental problems, such as the release of volatile organic compounds (VOCs) to the atmosphere.

The solvents suggested for CO\textsubscript{2} capture in this project belong to a group of compounds called ionic liquids (ILs). ILs are molten salts consisting of ions i.e. anions and cations. Unlike common salts, ionic liquids are liquid even at temperature below 100 °C. The terms room temperature ionic liquid (RTIL), nonaqueous ionic liquid, molten salt, liquid organic salt and fused salt have also been used to describe these salts in the liquid phase.\textsuperscript{64} They are frequently referred to as “Green Solvents” due to their immeasurably low vapour pressure. This lack of volatility essentially eliminates the possibility of solvent release to the atmosphere.\textsuperscript{65} An important feature associated with ILs is that their properties (e.g. density, conductivity, viscosity, Lewis acidity, hydrophobicity, gas solubility and hydrogen-bonding capability) can be tuned by varying the structure of the component ions to obtain desired solvent properties. Due to this reason ILs possesses a large range of industrial applications.\textsuperscript{1, 66}

A number of investigations have shown that CO\textsubscript{2} is remarkably soluble in many ionic liquids.\textsuperscript{67-78} This attractive feature makes ILs a potential candidate for gas separation. These ionic liquids show a greater tendency to dissolve CO\textsubscript{2} than other gases like methane, ethane, ethene, oxygen, nitrogen, argon and carbon monoxide, so selective absorption of CO\textsubscript{2} from flue gas is possible.\textsuperscript{71, 73} During absorption process CO\textsubscript{2} is only absorbed physically, therefore the energy required during desorption process could be smaller compared to the amine based technology.

### 1.2 Objective

The objective of this work is to measure the CO\textsubscript{2} solubility in two different imidazolium ionic liquids with same anion, bis(trifluoromethylsulfonylimide ([Tf\textsubscript{2}N]), using available facility of High Pressure Microbalance (HP balance). The ionic liquids are:

a) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide, ([emim][Tf\textsubscript{2}N])

b) 1-\textit{n}-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide, ([bmim][Tf\textsubscript{2}N])
The HP balance has previously been used to measure solubilities of gases (CO₂ and CH₄) in different polymers (solids) at high pressures (up to 46 bar for CO₂) and this set up is being used for the first time for solubility of CO₂ in any kind of liquid (ionic liquids in this work) at low pressures, so it is also one of the main objectives of this work to check the performance and reliability of this setup for measuring gas (CO₂) solubility in liquids (ionic liquids) at low pressures (up to 12 bar). The final objective of the thesis is to make a process evaluation in terms of energy consumption (simple basic calculations) for CO₂ capture and recovery in ionic liquids using temperature-swing technique and compare it with state-of-the-art MEA-based CO₂ capture technology.
2 Theory: Ionic Liquids

2.1 Introduction

Ionic liquids are defined as the liquids which solely consist of ions (cations and anions), as opposed to an ionic solution, which is a solution of a salt in a molecular solvent (Figure 2.1) and have a melting point of 100 °C or below. ILs which are liquid at room temperature are called Room temperature ionic liquid (RTIL). In the older (and some current) literature, ionic liquids are sometimes called liquid organic salts, fused salts, molten salts, ionic melts, NAILs (nonaqueous ionic liquids), room-temperature molten salts, OILs (organic ionic liquids) and ionic fluids. Heating normal salts, such as sodium chloride (NaCl, mp 801 °C), to high temperature produces also a liquid, that consists entirely of ions, but this is a molten salt and not defined as an ionic liquid. Usually ILs consist of a large bulky and asymmetric organic cations based on 1-alkyl-3-methylimidazolium (abbreviated [Cₙmim]+, where \( n \) = number of carbon atoms in a linear alkyl chain), \( N \)-alkylpyridinium (accordingly abbreviated [Cₙpy]+), tetraalkylammonium or tetraalkylphosphonium cations, and many others; and organic or inorganic anions such as hexafluorophosphate \([PF_6]^-\), tetrafluoroborate \([BF_4]^-\), alkylsulfates \([RSO_4]^-\), alkylsulfonates \([RSO_3]^-\), halides as chloride \([Cl^-]\), bromide \([Br^-]\) or iodide \([I^-]\), nitrate \([NO_3^-]\), sulfate \([SO_4]^-\), aluminum chloride \([AlCl_4]^-\), triflate \(([CF_3SO_3]^- = [TfO])\), bis(trifluoromethylsulfonyl)imide \((([CF_3SO_2]_2N]^- = [Tf_2N])\), etc. Some commonly used ionic liquid systems are presented in Figure 2.2.
CO₂ Capture Using Ionic Liquids

Theory: Ionic Liquids

Figure 2.1: Difference between an ionic solution and an ionic liquid.

![Diagram showing the difference between an ionic solution and an ionic liquid.]

**Most commonly used cations:**

- 1-alkyl-3-methylimidazolium
- 1-alkyl-pyridinium
- 1-alkyl-N-methylpiperidinium
- Tetraalkylammonium
- Tetraalkylphosphonium
- 1,2-dialkylpyrazolium
- 1,2-dialkylpyridazinium
- Trialkylthiazolium
- Trialkylsulfonium

R₁₂₃₄ = CH₃(CH₂)ₙ (n = 1, 3, 5, 7, 9); aryl; etc.

**Some possible anions:**

- Water-immiscible: [PF₆⁻], [N(Tf)₆⁻], [BF₄⁻]
- Water-miscible: [CH₃CO₂⁻], [C₂F₃CO₂⁻], [NO₃⁻], [Br⁻], [Cl⁻], [F⁻], [Al₂Cl₆⁻], [AlCl₃⁺] (decomp.)

Figure 2.2: Some commonly used ionic liquid systems. The abbreviation [Cₙmpyr]⁺ represents the 1-alkyl-1-methylpyrrolidinium cation, where the index n represents the number of carbon atoms in the linear alkyl chain. [P₃₉₅₁]⁺, [N₃₉₅₁]⁺ and [S₃₉₅₁]⁺ are normally used to represent tetraalkylphosphonium, tetraalkylammonium and trialkylsulfonium cations, respectively, where the indices w, x, y and z indicate the length of the corresponding linear alkyl chains.
Asymmetry of the cation is believed to be responsible for the low melting points of ionic liquids, while the nature of the anion is considered to be responsible for many of the physical properties of ionic liquids such as their miscibility with conventional solvents and hygroscopicity. A key feature of ionic liquids is that their physical properties such as melting point, viscosity, density, and hydrophobicity can be tailored to design different ionic liquids with a particular end use in mind by selection of different cation, anion, and substituents. Therefore ionic liquids are also described as “Designer Solvent”. Ionic liquids have a number of advantages as solvents over molecular solvents such as negligible vapor pressure, high thermal stability, non-flammability and wide temperature range, therefore, these fluids have been proposed as an attractive alternative to volatile organic compounds (VOCs) for “green processing”. Replacement of conventional solvents with ionic liquids would prevent the emission of VOCs, a major source of environmental pollution.

2.2 Types of Ionic Liquids

Ionic liquids that fall within this definition (stable molten salts with melting point of around or below 100 °C) can be divided into three categories: First-generation; Second-generation; and Third-generation ionic liquids.

First-generation ionic liquids consist of bulky cations such as 1, 3-dialkylimidazolium (or N, N'-dialkylimidazolium) or 1-alkylpyridinium (or N-alkylpyridinium), and anions based mostly on haloaluminate (III); these have been studied extensively. The merit of these ionic liquids is their tuneable Lewis acidity. The drawback of these systems is their great sensitivity towards water, which forms hydroxoaluminate(III) species with the aluminium(III) chloride and therefore decomposes the ionic liquid. The sensitivity towards water necessitates their handling in a dry-box.

The ionic liquids of the second category, the so-called second-generation ionic liquids, are usually air-stable and water-stable and can be used on the bench-top. However, it should be noted that water-stable does not imply that there is no interaction with water at all. Second-generation ionic liquids gradually absorb water from the atmosphere.

Recently, a third generation of “task-specific” ionic liquids have emerged. These novel ionic liquids feature chemical functionalities which have been designed for specific applications. Very little is known to date about their physical properties, preparative methods, etc, and the future will show if they can bring about an ecological or economic benefit; but that future does look bright.
2.3 History and New Developments

Ionic liquids have been known for a long time, but their extensive use as solvents in chemical processes for synthesis, separation processes and catalysis has recently become significant. The first low melting salt (ionic liquid), ethylammonium nitrate ([EtNH₃][NO₃]), with melting point of 12 °C was synthesized by Paul Walden in 1914. During 1940s, aluminum chloride-based molten salts were utilized for electroplating at temperatures of hundreds of degrees Celsius. In 1951, low melting salts with chloroaluminate ions for low-temperature electroplating of aluminum were developed.

During the 1970s and 1980s, these liquids were studied mainly for electrochemical applications in nuclear warheads batteries. In the early 1970s, Wilkes tried to develop better batteries for nuclear warheads and space probes which required molten salts to operate. These molten salts were hot enough to damage the nearby materials. Therefore, the chemists searched for salts which remain liquid at lower temperatures and eventually they identified one which is liquid at room temperature. Wilkes and his colleagues continued to improve their ILs for use as battery electrolytes and then a small community of researchers began to make ILs and test their properties. In the mid 1980s, low melting point ionic liquids were proposed as solvents for organic synthesis. In the late 1990s, ILs became one of the most promising chemicals as solvents. Initially, new ionic liquids such as organo-aluminate, have limited range of applications because they were unstable to air and water. Furthermore, these ILs were not inert towards various organic compounds. In 1992, after the first reports on the synthesis and applications of water and air stable ILs such as 1-ethyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-ethyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), the number of air and water stable ILs have started to increase rapidly.

Interest in ionic liquids has now been grown dramatically in the scientific community (both in academia and industry) with over 8000 papers having been published in the last decade. This growth can be observed in Figure 2.3 (number of publications per year) and Figure 2.4 (number of patents per year), where the number of publications and patents are increasing exponentially. There are about one million (10⁶) simple ionic liquids that can be easily prepared in the laboratory by combination of different cations and anions and this total is just for simple primary systems. If there are one million possible simple IL systems, then there are one billion (10¹²) possible binary combinations of these, and one trillion (10¹⁸) ternary possible IL systems that can be prepared from the combination of anions, cations, and substituents. At the moment only about 300 ionic liquids are commercialized, so one can imagine how many opportunities in this field are still undiscovered and why this field of chemistry is so tempting.
2.4 Ionic Liquids Synthesis

In the laboratory, the common first step of the synthesis of both first and second generation ionic liquids is identical. Thus, imidazolium-based ionic liquids are derived from a corresponding common precursor, the 1-alkyl-3-methylimidazolium halide (which is an ionic liquid itself, if the melting point is lower than 100 °C), in most cases the
chloride. This precursor is prepared by the alkylation of 1-methylimidazole as depicted in Figure 2.5. If the chloroalkane is gaseous at room temperature, eg, chloroethane, the alkylation is usually carried out in an autoclave, at autogenous pressures and 90 °C, without addition of solvent. The preparation of the 1-alkylpyridinium or 1-alkyl-2,3-dimethylimidazolium derivatives follows the same method, starting from pyridine or 1,2-dimethylimidazole, respectively.15,16

This intermediate salt is then either used in a metathetic reaction (ion exchange), where the 1-alkyl-3-methylimidazolium halide (in most cases the chloride) is exchanged with the anion of a Group 1 metal or silver(I) salt, MY or it is treated with an acid, HY, as can be seen in Figure 2.5. Both methods are carried out in water at room-temperature, although some organic solvents can also be used.17 Depending on the anion (and to a lesser extent on the cation) chosen, the resulting ionic liquid forms either a biphasic system with water, or a homogeneous solution. In the former case (e.g. if the anion is [PF6]− or [NTf2]), an aqueous extraction is followed to remove the excess of chloride (MX or HX, or any unreacted starting material). For water-miscible ionic liquids, the
work-up of the metathetic reaction involves the removal of water under reduced pressure, addition of trichloromethane, and repeated cooling to 5 °C to precipitate MX, followed by several filtration steps. The work-up of the water-miscible ionic liquids prepared by treatment with acid includes repetitive addition of water and removal of water/HX under reduced pressure and elevated temperature.18

Ionic liquids can also be prepared from their corresponding carbenes. To achieve this, the chloride precursor is heated in a Kugelrohr apparatus (see Figure 2.6) in the presence of a base, such as potassium t-butoxide, yielding potassium chloride, t-butanol and the carbene, which is isolated by distillation. This method of preparation is not applicable to ionic liquids other than 1,3-dialkylimidazolium-based salts.19 The addition of a carbene (e.g. 1-butyl-3-methylimidazol-2-ylidene) to acids yields clean, chloride free-ionic liquids19 as shown in Figure 2.7.

Figure 2.6: Kugelrohr apparatus for the preparation of a typical carbene

Figure 2.7: Examples of different ionic liquids prepared by the carbene method
Ionic liquids based on phosphonium cations are prepared in a similar fashion to the imidazolium (and other ammonium) ionic liquids. A trialkylphosphine is alkylated either using a chloroalkane, phenyl alkyl sulfonate, or similar esters. The trisubstituted precursor may be derived from the reaction of phosphine with a single alkene, or a mixture of two alkenes, resulting in a symmetrical \((PR_3)\) or unsymmetrical \((PRR'_2)\) trialkylphosphine, respectively.\(^{20}\)

### 2.5 Characteristics of Ionic Liquids

#### 2.5.1 Melting Point

Ionic liquids have been defined to have melting points 100 °C or below and most of them are liquid at room temperature. Both cations and anions contribute to the low melting points of ionic liquids. The increase in anion size leads to a decrease in melting point.\(^{21}\) For example, the melting points of 1-ethyl-3-methylimidazolium type ionic liquids with different anions, such as \([\text{BF}_4]^-\), \([\text{Tf}_2\text{N}]^-\) and \([\text{C}_2\text{H}_5\text{SO}_4]^-\) are 15 °C, -3 °C and -20 °C respectively.\(^{22}\) Melting points of some of the ionic liquids is tabulated in Table 2.1.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Melting Point (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_4\text{mim}][\text{Cl}])</td>
<td>41</td>
<td>37</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{I}])</td>
<td>-72</td>
<td>37</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{PF}_6])</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{TF}_2\text{N}])</td>
<td>-4</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{TF}_2\text{O}])</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_4\text{mim}][\text{NfO}])</td>
<td>20</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NO}_3])</td>
<td>38</td>
<td>25</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NO}_2])</td>
<td>55</td>
<td>25</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{CH}_3\text{CO}_2])</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{TF}_2\text{O}])</td>
<td>58-60</td>
<td>25</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{NfO}])</td>
<td>-9</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{TA}])</td>
<td>28</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{TF}_2\text{N}])</td>
<td>-3</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{TA}])</td>
<td>-14</td>
<td>17</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{BF}_4])</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{BF}_4])</td>
<td>-81</td>
<td>30</td>
</tr>
<tr>
<td>([\text{C}_2\text{mim}][\text{PF}_6])</td>
<td>-61</td>
<td>30</td>
</tr>
</tbody>
</table>
Cations size and symmetry make an important impact on the melting points of ionic liquids. Large cations and increased asymmetric substitution results in a melting point reduction. This can readily be seen by examining the melting point phase diagrams for the hexafluorophosphate and tetrafluoroborate anions based ionic liquids of 1-alkyl-3-methylimidazolium cation as shown in Figure 2. 8, where the melting point shows a pronounced dependence on the chain length.\textsuperscript{23, 24}

![Figure 2. 8: Melting point phase diagram for (a) [Rmim][PF\textsubscript{6}] and (b) [Rmim][BF\textsubscript{4}] ionic liquids as a function of alkyl chain length \(n\) showing the melting transitions from crystalline (closed square) and glassy (open square) materials and the clearing transition (closed circle) of the liquid crystalline (LC) terms](image)

### 2.5.2 Density

Ionic liquids in general are denser than water with values ranging from 1 to 1.6 g/cm\(^3\) and their densities decrease with increase in the length of the alkyl chain in the cation.\textsuperscript{26} For example, in ionic liquids composed of substituted imidazolium cations and [CF\(_3\)SO\(_3\)]\(^-\) anion the density decreases from 1.39 g/cm\(^3\) for [EMIm]\(^+\) to 1.33 g/cm\(^3\) for [EEIm]\(^+\), to 1.29 g/cm\(^3\) for [BMIm]\(^+\) and to 1.27 g/cm\(^3\) for [BEIm]\(^+\).\textsuperscript{27} The densities of ionic liquids are also affected by the identity of anions. For example, the densities of 1-butyl-3-methylimidazolium type ionic liquids with different anions, such as BF\(_4\), PF\(_6\), TFA and Tf\(_2\)N are 1.12 g/cm\(^3\), 1.21 g/cm\(^3\), 1.36 g/cm\(^3\) and 1.43 g/cm\(^3\) respectively.\textsuperscript{22}

The density of \([C_{n\text{mim}}]^-\) and \([C_{n\text{py}}]^-\) based ionic liquids containing inorganic anions such as [BF\(_4\)]\(^-\) or [PF\(_6\)]\(^-\), is higher than that of water, i.e., if one of these ionic liquids is immiscible with water, it will form the heavier, lower phase. Within a homologous series,
CO₂ Capture Using Ionic Liquids

Theory: Ionic Liquids

e.g. [C₄-C₁₀mim][BF₄], the ionic liquids with shorter alkyl chain possess higher densities than the ones with longer chains as presented in Figure 2.9. It can also be seen in Table 2.7 for [C₄-mim][PF₆].

Figure 2.9: Density of [Cₙmim][BF₄] (n = 2 to n = 10) vs Temperature

This can be explained by the ability of the shorter alkyl chain analogues to close-pack and therefore achieve a higher density, whereas the bulkiness of the longer chain derivatives leads to less efficient close-packing. Although no such data are available at present, Figure 2.9 shows that theoretically, imidazolium-based ionic liquids with densities less than 1 g/cm³ are conceivable, if the alkyl chain length and temperature are increased. Recently, it has been observed that phosphonium-based ionic liquids possess very low densities: at 30 °C, the density of trihexyltetradecylphosphonium chloride ([P₆₆₆₁₄][Cl]) is 0.88 g/cm³, while that of the corresponding [BF₄]⁺ was found to be 0.93 g/cm³. A plot of densities of [P₆₆₆₁₄]⁺ cation with various anions as a function of temperature is shown in Figure 2.10. This also shows the effect of different anions on density. Thus, a large range of densities is covered by ionic liquids, and this could be easily extended by design. Ionic liquids should be free of impurities or moisture, because contamination of the ILs with chloride led to a decrease of the density as depicted in Figure 2.11. Density of some of the ionic liquids is tabulated in Table 2.2.
Figure 2.10: Densities of [PC$_6$C$_6$C$_{14}$] RTILs with anions: (a) NTf$_2$, (b) [Co(NCSe)$_4$], (c) bis-dicarbollylcobalt(III) (CoCB), (d) [Co(NCS)$_4$], (e) dithiomaleonitrile (dtmn), (f) methylxanthate (xan), and (g) dicyanamide [N(CN)$_2$].

Figure 2.11: Density of [C$_4$mim][BF$_4$] at 30 °C vs molal concentration of chloride, mol/kg, added as [C$_4$mim][Cl].
Table 2.2: Density data for various Ionic Liquids

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Density (g/cm³)</th>
<th>Temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][PF₆]</td>
<td>1.37⁵⁹, 1.37⁷⁰, 1.36¹⁷</td>
<td>20, 25, 25</td>
<td>39, 30, 37</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>1.08</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>1.12⁵⁷, 1.17⁷⁰</td>
<td>30, 25</td>
<td>37, 30</td>
</tr>
<tr>
<td>[C₆mim][I]</td>
<td>1.44</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>1.43³⁷, 1.429¹⁷</td>
<td>25, 25</td>
<td>37,17</td>
</tr>
<tr>
<td>[C₂mim][OTf]</td>
<td>1.39</td>
<td>22</td>
<td>17</td>
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<tr>
<td>[C₆mim][PF₆]</td>
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<tr>
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<td>[C₆mim][BF₄]</td>
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<tr>
<td>[C₆mim]Cl</td>
<td>1.00</td>
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<tr>
<td>[C₈mim][BF₄]</td>
<td>1.08</td>
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</tr>
<tr>
<td>[C₄mim][PF₆]</td>
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<td>[P₆₆₆₄][Cl]</td>
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<tr>
<td>[P₆₆₆₄][BF₄]</td>
<td>0.93</td>
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</table>

### 2.5.3 Viscosity

Generally, ionic liquids are more viscous than common molecular solvents and their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature. The viscosity of ionic liquids is determined by van der Waals forces and hydrogen bonding. For imidazolium-based cations, the viscosity of ionic liquids is dependent on the alkyl chain length of the cation, as well as the nature of the anion. The viscosity of the [BF₄]⁻ series with increasing temperature is shown in Figure 2. ¹² It is obvious that the viscosity increases with increasing alkyl chain length, due to the increased possibility of van der Waals-type interactions between the cations. Ionic liquids with short chains (n < 12) exhibit Newtonian behavior (i.e. the viscosity is independent of the shear rate), whereas those derivatives that exhibit liquid crystalline phases (see Section 2.5.1 for Melting point) show non-Newtonian behavior. ²⁸ Besides the length of the alkyl chain, the symmetry of the anion, its molar mass and the ability to form hydrogen bonds all influence the viscosity. The fluorinated anions such as [BF₄]⁻ and [PF₆]⁻ form viscous ionic liquids due to the formation of complexes with hydrogen bonding donors. ³⁰
Table 2.3: Viscosity data for various Ionic Liquids

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Viscosity (cP)</th>
<th>Temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C2mim][BF4]</td>
<td>66.5&lt;sup&gt;18&lt;/sup&gt;, 43&lt;sup&gt;42&lt;/sup&gt;</td>
<td>20, 25</td>
<td>18, 42</td>
</tr>
<tr>
<td>[C2mim][PF6]</td>
<td>23.4</td>
<td>70</td>
<td>18</td>
</tr>
<tr>
<td>[C2mim][OTf]</td>
<td>50</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>[C2mim][Tf2N]</td>
<td>28&lt;sup&gt;42&lt;/sup&gt;, 32.6&lt;sup&gt;129&lt;/sup&gt;</td>
<td>25</td>
<td>42, 129</td>
</tr>
<tr>
<td>[C2mim][Cl]</td>
<td>1534</td>
<td>50</td>
<td>18</td>
</tr>
<tr>
<td>[C2mim][I]</td>
<td>1110</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C4mim][BF4]</td>
<td>154&lt;sup&gt;18&lt;/sup&gt;, 219&lt;sup&gt;17&lt;/sup&gt;</td>
<td>20, 25</td>
<td>18, 37</td>
</tr>
<tr>
<td>[C4mim][PF6]</td>
<td>371&lt;sup&gt;18&lt;/sup&gt;, 450&lt;sup&gt;37&lt;/sup&gt;, 312&lt;sup&gt;30&lt;/sup&gt;</td>
<td>20, 25, 25</td>
<td>18, 37, 30</td>
</tr>
<tr>
<td>[C4mim][Tf2N]</td>
<td>69&lt;sup&gt;37&lt;/sup&gt;, 52&lt;sup&gt;17&lt;/sup&gt;</td>
<td>25</td>
<td>37, 17</td>
</tr>
<tr>
<td>[C4mim][Cl]</td>
<td>1124&lt;sup&gt;18&lt;/sup&gt;, 716&lt;sup&gt;37&lt;/sup&gt;</td>
<td>50, 25</td>
<td>18, 37</td>
</tr>
<tr>
<td>[C4mim][BF4]</td>
<td>314</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>[C6mim][BF4]</td>
<td>690&lt;sup&gt;18&lt;/sup&gt;, 585&lt;sup&gt;37&lt;/sup&gt;</td>
<td>20, 25</td>
<td>18, 37</td>
</tr>
<tr>
<td>[C8mim][Cl]</td>
<td>1930&lt;sup&gt;18&lt;/sup&gt;, 337&lt;sup&gt;17&lt;/sup&gt;</td>
<td>50, 25</td>
<td>18, 37</td>
</tr>
<tr>
<td>[C8mim][PF6]</td>
<td>682</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C8mim][CF3COO]</td>
<td>73</td>
<td>25</td>
<td>17</td>
</tr>
<tr>
<td>[C8mim][CF3SO3]</td>
<td>90</td>
<td>25</td>
<td>18</td>
</tr>
<tr>
<td>[C8mim][BF4]</td>
<td>439</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>[P66614][Cl]</td>
<td>~1500</td>
<td>25</td>
<td>29</td>
</tr>
</tbody>
</table>

Ionic liquids should be free of impurities or moisture, because contamination of the ILs with chloride led to an increase of the viscosity of the ILs. It can be observed in Table 2.4<sup>18</sup> that the presence of even low concentrations of chloride in the ionic liquids substantially increases the viscosity. In order to assess the magnitude of the increase in viscosity with chloride content, known quantities of [C₉mim][Cl] were deliberately added...
CO₂ Capture Using Ionic Liquids

Theory: Ionic Liquids

to [C₄mim][BF₄] and to [C₄mim][PF₆]. In all cases, the viscosity increased dramatically with the concentration of chloride.²⁸,¹⁸ This is shown for [C₄mim][BF₄] with added [C₄mim][Cl] in Figure 2.¹³,¹⁸ It can be seen that the addition of [C₄mim][Cl] to [C₄mim][BF₄] produced a nonlinear increase in viscosity of the ionic liquid. Discrepancy in viscosity data can be seen in Table 2.³ and chloride contamination may be one of the reasons of this disagreement in data reported by different researchers.

Table 2. 4: Comparison of the viscosity of chloride-contaminated ionic liquids.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>[Cl]⁻ (mol/ kg)</th>
<th>η (mPa s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₂mim][BF₄]</td>
<td>0.01</td>
<td>66.5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>92.4</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>0.01</td>
<td>154</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>201</td>
<td></td>
</tr>
<tr>
<td>[C₄mim][NO₃]</td>
<td>0.02</td>
<td>67</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>222.7</td>
<td></td>
</tr>
<tr>
<td>[C₈mim][NO₃]</td>
<td>0.01</td>
<td>1238</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>8465</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. 13: Viscosity at 20 °C of [C₄mim][BF₄] vs molal concentration of chloride, mol/ kg, added as [C₄mim][Cl].

The viscosity of second-generation ionic liquids ranges from 20 to 2000 cP, which appears to be quite high from an engineering point of view. However, upon addition of organic solvents with varying properties, the viscosity of any ionic liquid decreases dramatically, even if present in quantities <10 mol%.¹⁸ This phenomenon is illustrated in
Figure 2.14 by the example of [C₄mim][BF₄]. For the practical application of a very viscous ionic liquid as a solvent this is advantageous, as the viscosity may be lowered by the addition of reactants, thus facilitating some engineering aspects.

The decrease in viscosity can be easily predicted using Eq. 2.1.

\[
\eta = \eta_s \exp \left( -\frac{X_{cs}}{\alpha} \right)
\]  

(2.1)

where \( \eta_s \) is the viscosity of the pure ionic liquid, \( X_{cs} \) is the mole fraction of the molecular solvent, and \( \alpha \) is a constant value specific to each ionic liquid (i.e. \( \alpha = 0.23 \) for [C₄mim][BF₄] and \( \alpha = 0.19 \) for [C₄mim][PF₆]). Nevertheless, one of the future challenges of ionic liquid research is to reduce the viscosity of ionic liquids by at least one order of magnitude.

Figure 2.14: Viscosity (at 20 °C) of molecular solvent - [C₄mim][BF₄] mixtures, where \( X_{cs} \) is the mole fraction of added organic solvent.
2.5.4 Vapour Pressure

Due to their ionic nature and the fact that their chemical and thermal stability can be designed to be high, ionic liquids can possess a negligibly small vapor pressure, even at high temperatures. Owing to this property, ionic liquids cannot evaporate from the reaction vessels and separation equipments (e.g. distillation and absorption columns) and are retained quantitatively, unlike other industrially used volatile organic solvents, such as dichloromethane or dimethyl sulfoxide. Therefore, the impact on the environment and the process operation personnel is minimal. It means that volatile products, and even products with conventionally low vapor pressures, can be isolated from ionic liquids by distillation.

However, a negligibly small vapor pressure is not the same as zero vapor pressure, and Earle et al.\textsuperscript{31} reported that many ionic liquids which had been believed to be involatile (such as $[C_m\text{mim}][\text{NTf}_2]$) can be distilled without decomposition at high temperatures and low pressures (e.g. 300 °C and 0.1 mbar). Thus, ionic liquids can be designed to be volatile, if that offers a processing advantage.

2.5.5 Thermal Stability

Except for the physical properties, the thermal stability of an ionic liquid will determine its applicability in different separation processes and reactions. At present, little is known about the instability of ionic liquids, although from an industrial application point of view, this aspect might be one of the most important factors.

Ionic liquids can be thermally stable up to 450 °C. The thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds, respectively.\textsuperscript{21} Wilkes et al.\textsuperscript{32} reported that the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and 1,2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide are stable up to temperatures of 445, 423 and 457 °C, respectively. However, such high temperatures can only be tolerated by most ionic liquids for a short time. Long time exposure to such high temperatures inevitably leads to decomposition. Most of the ionic liquids have extremely low vapour pressures, which allow to remove water by simple heating under vacuum. Water contents below 1 ppm are quite easy to achieve with most of the liquids due to their good thermal stability.\textsuperscript{22} Thermal decomposition temperature of various ionic liquids is presented in Table 2.5.
Many researchers have observed that ionic liquids often alter in their color, depending on the method of preparation. For instance, when heated above 80 °C at reduced pressure to remove traces of water, ionic liquids frequently turn dark brown, whereas they stay almost colorless when heated gently. Gale and Osteryoung attributed this observation to the formation of impurities by degradative side-reactions.34 The nature of these colored impurities is yet unknown and they are not detectable by nuclear magnetic resonance (NMR) or other spectroscopic methods.33 However, recent investigations under high thermal stress (sonication at 135 °C) reported that the thermal decomposition products of 1-butyl-3-methylimidazolium chloride include chlorobutane, chloromethane, and imidazole decomposition products such as buta-1,3-diene, butadi-1,3-yne, ethanenitrile/isocyanomethane, 2-methylpropane, 2-propenenitrile and pent-3-en-1-yne.33

Early, and unfortunately current, investigations overestimate the thermal stability (placing them at 400 °C and higher) of many 1,3-dialkylimidazolium based ionic liquids by thermogravimetric analysis.4 Since the heat transfer in ionic liquids is slow, the sample temperature lags behind the measured temperature by between 75 and 150 °C, at the high heating rates (between 10 and 20 °C/min) that were used. Under these

---

Table 2.5: Thermal decomposition temperature data for various Ionic Liquids

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Decomposition Temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][Cl]</td>
<td>254</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][I]</td>
<td>265</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>403</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][PF₆]</td>
<td>349</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>439</td>
<td>37</td>
</tr>
<tr>
<td>[C₆mim][Cl]</td>
<td>253</td>
<td>37</td>
</tr>
<tr>
<td>[C₆mim][PF₆]</td>
<td>417</td>
<td>37</td>
</tr>
<tr>
<td>[C₈mim][Cl]</td>
<td>243</td>
<td>37</td>
</tr>
<tr>
<td>[C₈mim][PF₆]</td>
<td>417</td>
<td>37</td>
</tr>
<tr>
<td>[C₂mim][Cl]</td>
<td>285</td>
<td>41</td>
</tr>
<tr>
<td>[C₂mim][I]</td>
<td>303</td>
<td>41</td>
</tr>
<tr>
<td>[C₂mim][PF₆]</td>
<td>375</td>
<td>41</td>
</tr>
<tr>
<td>[C₂mim][BF₄]</td>
<td>412</td>
<td>41</td>
</tr>
<tr>
<td>[C₂mim][Tf₂N]</td>
<td>455</td>
<td>41</td>
</tr>
<tr>
<td>[C₃mim][Cl]</td>
<td>~ 440</td>
<td>17</td>
</tr>
<tr>
<td>[C₃mim][CF₃COO]</td>
<td>~ 150</td>
<td>17</td>
</tr>
<tr>
<td>[C₃mim][CF₃SO₃]</td>
<td>~ 440</td>
<td>17</td>
</tr>
<tr>
<td>[C₁₈mim][Cl]</td>
<td>282</td>
<td>41</td>
</tr>
<tr>
<td>[C₁₈mim][PF₆]</td>
<td>335</td>
<td>41</td>
</tr>
<tr>
<td>[C₁₈mim][Tf₂N]</td>
<td>452</td>
<td>41</td>
</tr>
<tr>
<td>[C₁₈mim][BF₄]</td>
<td>360</td>
<td>24</td>
</tr>
</tbody>
</table>
conditions, the decomposition reaction does not reach equilibrium before the end of the experiment. The most accurate data require isothermal studies. Under isothermal conditions, however, \([\text{C}_4\text{mim}][\text{OTf}]\) shows long-term stability at 200 °C,\(^{35}\) and for \([\text{C}_2\text{mim}][\text{NTf}_2]\) a weight-loss of 1% was found over 10 hour at 250 °C.\(^{36}\)

### 2.5.6 Surface Tension

There have been few measurements on the surface tension of ionic liquids. Values range from 33.8 N/m for \([\text{C}_8\text{mim}][\text{Cl}]\) to 54.7N/m for \([\text{bmim}][\text{I}]\) while \([\text{bmim}][\text{PF}_6]\) has a value of 49.8N/m. Surface tension values were not significantly effected by the presence of water.\(^{37}\) The surface tensions of RTILs are lower than that for water (72.7N/m at 20 °C) but higher than the values for \(n\)-alkane (16.0N/m for pentane to 25.6N/m for dodecane, all at 20 °C). As the alkyl chain length on the RTIL increases the surface tension value decreases towards the values for the alkanes. Surface tension decreases linearly with an increase in temperature as shown in Figure 2. 15.\(^{38}\) Surface tension of some of the ILs is shown in Table 2. 6.
Figure 2.15: Surface tension as a function of temperature for different ionic liquids.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Surface Tension (dyn/cm)</th>
<th>Temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][I]</td>
<td>54.7</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][BF₄]</td>
<td>46.6</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₆mim][PF₆]</td>
<td>48.8</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₄mim][Tf₂N]</td>
<td>37.5</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₆mim][Cl]</td>
<td>42.5</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₆mim][PF₆]</td>
<td>43.4</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₈mim][Cl]</td>
<td>33.8</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>[C₈mim][PF₆]</td>
<td>36.5</td>
<td>25</td>
<td>37</td>
</tr>
</tbody>
</table>

2.5.7 Miscibility with Water

The solubility of water in ionic liquids is strongly influenced by their composition and in particular by the nature of the anion. As indicated in Figure 2.2, the choice of anion is one of the factors determining the solubility of the ionic liquid with water. At room temperature, all [C₅mim][PF₆] and [C₇mim][(CF₃SO₂)₂N] ionic liquids are insoluble in water, and all halide, ethanoate, nitrate, and trifluoroacetate based ionic liquids are fully water-soluble. However, ionic liquids based on [BF₄]⁻ and [CF₃SO₃]⁻ are positioned somewhere in between. Depending on the alkyl chain length on the cation, they are either fully miscible with water (e.g., [C₂mim][BF₄] and [C₄mim][BF₄]) or form biphasic systems ([C₅mim][BF₄], n > 4). Thus, the anion has a primary effect on water miscibility and the cation a secondary effect.

1-Alkyl-3-methylimidazolium hexafluorophosphate ionic liquids form biphasic systems with water, and are therefore commonly referred to as “hydrophobic” in the literature. This is in fact misleading, which is depicted in Figure 2.16. This shows the water-saturation of so-called hydrophobic ionic liquids [C₄-8mim][PF₆] and [C₆-10mim][BF₄], which is a function of the alkyl chain length and the anion. As a rule, the [PF₆]⁻ based ionic liquids dissolve less water than the [BF₄]⁻ based ionic liquids, and the solubility of water decreases with increasing alkyl chain length (see Table 2.7 for 1-Alkyl-3-methylimidazolium Hexafluorophosphates, [Cₙmim][PF₆], with n = 4 to n = 9).
CO₂ Capture Using Ionic Liquids  

Theory: Ionic Liquids

Figure 2.16: Water content on saturation at ambient temperature (ca. 22 °C) for [Cₙmim][PF₆] (n = 4 to n = 8) (white) and for [Cₙmim][BF₄] (n = 6 to n = 10) (gray).

Table 2.7: Density and water solubility data for [C₄-₉mim][PF₆].

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Density (g/ml)</th>
<th>Water Solubility (g/100ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][PF₆]</td>
<td>1.363</td>
<td>1.88</td>
</tr>
<tr>
<td>[C₅mim][PF₆]</td>
<td>1.333</td>
<td>1.23</td>
</tr>
<tr>
<td>[C₆mim][PF₆]</td>
<td>1.307</td>
<td>0.75</td>
</tr>
<tr>
<td>[C₇mim][PF₆]</td>
<td>1.274</td>
<td>0.37</td>
</tr>
<tr>
<td>[C₈mim][PF₆]</td>
<td>1.237</td>
<td>0.20</td>
</tr>
<tr>
<td>[C₉mim][PF₆]</td>
<td>1.202</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Additionally, the so-called hydrophobic ionic liquids are in fact hygroscopic. Figure 2.17 shows the extent of the hygroscopicity of [C₅mim][Cl], [C₅mim][NO₃], [C₄mim][BF₄], and [C₄mim][PF₆], which was revealed in an experiment in which the absorption of water from atmospheric air at ambient temperature was measured as a function of time. Although the fully water-soluble chloride and nitrate ionic liquids absorb much more water than the corresponding hexafluorophosphate, an uptake of 1% w/w (0.16 mole fraction of water) over 3 hour is significant. This should be kept in mind, especially when the ionic liquid is used as solvent in reactions with moisture-sensitive compounds, and efficient drying and anhydrous handling has to be ensured (i.e., under reduced pressure at 70 °C for 8 hr). It should also be stressed that the presence of water in [PF₆]⁺ ionic liquids has been reported to lead to decomposition reactions producing HF.
Figure 2. 17: Absorption of water from atmospheric air at ambient temperature and moisture, with constant stirring as a function of time of exposure. (Δ) corresponds to $[\text{C}_8\text{mim}]\text{[NO}_3\text{]}$, (*) to $[\text{C}_8\text{mim}]\text{[Cl]}$, (O) to $[\text{C}_4\text{mim}]\text{[BF}_4\text{]}$ and ( ) to $[\text{C}_4\text{mim}]\text{[PF}_6\text{]}$.

2.5.8 Toxicity and Occupational Health

Although ionic liquids are also known as “green solvents”, they are not always green. They can be corrosive, flammable, or toxic. Due to their nonvolatile nature, ionic liquids are generally considered as having a low impact on the environment and human health, and thus recognized as solvents for green chemistry. The risk of air pollution by ionic liquids is minimal due to their nonvolatile characteristics. However, if large-scale industrial applications of ionic liquids commence, their entry to the aquatic environment through accidental spills or as effluents is the most probable pathway for their contributing to environmental hazards. Consequently, aquatic toxicology investigations were the earliest topic of interest concerning ionic liquid environmental safety.$^{51}$

Maginn$^{52}$ provides the LC$_{50}$ levels for two imidazolium-based ionic liquids with Daphnia magna. Daphnia are common fresh water crustaceans (a large group of Phylum Arthropoda). They are filter feeders, and are at the base of the aquatic foodchain. Their response to ionic liquids is, therefore, crucial for assessing how these new solvents will impact an environmental ecosystem. The LC$_{50}$ values obtained for 1-n-butyl-3-
methylimidazolium cations with PF$_6$ and BF$_4$ anions are shown in Figure 2. It can be seen, these two ionic liquids are about as toxic to Daphnia as benzene, and are far more toxic than acetone.

![Figure 2.18: LC50 values for 1-n-butyl-3-methylimidazolium cations with PF$_6$ and BF$_4$ anions and some commonly used industrial solvents.](image)

In another study Wells and co-workers examined some common ionic liquids based on imidazolium, pyridinium, phosphonium, and ammonium cations in a freshwater toxicity investigation using EC$_{50}$ (medium effective concentration) value and subjected to *Daphnia magna* (see Figure 2.19) and green algae. It was found that the four groups of ionic liquids could not be described as having low toxicity, with all of them having EC$_{50}$ values below 100 mg/L. In this study, a clear trend is seen that shorter alkyl substituted chains (C$_1$–C$_4$) demonstrate lower toxicity to algae and invertebrates, whereas the toxicity of C$_8$–C$_{18}$ substituted salts worsens severely, irrespective of the type of cation present. It can also be concluded that both the type of cation and anion can fundamentally affect the toxicity of ionic liquids to *Daphnia*, i.e., the imidazolium cation shows the highest toxicity in general, whereas the ammonium cation demonstrates the lowest toxicity. The influence of the anion type is more complicated and further clarification through more detailed investigation is required.
Bernot and co-workers investigated freshwater snails (*Physa acuta*) to probe the toxicity of ionic liquids based on imidazolium and pyridinium cations. The acute toxicity of these ionic liquids was tested by the LC$_{50}$ method. Once again, the substituted alkyl chain length on the cation played a significant role by influencing the toxicity, i.e. ionic liquids with C$_8$ were found to be more toxic than those with C$_6$ and C$_4$, regardless of the cation type (whether imidazolium or pyridinium, see Figure 2.20).

<table>
<thead>
<tr>
<th>Cation Type</th>
<th>R1</th>
<th>R2</th>
<th>Anion</th>
<th>LC50 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_2$N$^+$R$_1$</td>
<td>C$_4$H$_9$</td>
<td>CH$_3$</td>
<td>PF$_6^-$</td>
<td>123.3</td>
</tr>
<tr>
<td></td>
<td>C$_6$H$_9$</td>
<td>CH$_3$</td>
<td>Br$^-$</td>
<td>229.0</td>
</tr>
<tr>
<td></td>
<td>C$<em>8$H$</em>{13}$</td>
<td>CH$_3$</td>
<td>Br$^-$</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>C$<em>{17}$H$</em>{17}$</td>
<td>CH$_3$</td>
<td>Br$^-$</td>
<td>8.2</td>
</tr>
<tr>
<td>R$_2$N$^+$R$_1$</td>
<td>C$_4$H$_9$</td>
<td>CH$_3$</td>
<td>Br$^-$</td>
<td>325.2</td>
</tr>
<tr>
<td></td>
<td>C$_6$H$_9$</td>
<td>CH$_3$</td>
<td>Br$^-$</td>
<td>226.7</td>
</tr>
<tr>
<td></td>
<td>C$<em>8$H$</em>{17}$</td>
<td>CH$_3$</td>
<td>Br$^-$</td>
<td>1.0</td>
</tr>
<tr>
<td>R$_2$N$^+$R$_1$</td>
<td>C$_4$H$_9$</td>
<td>C$_4$H$_9$</td>
<td>Br$^-$</td>
<td>208.0</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_9$</td>
<td>C$_4$H$_9$</td>
<td>Br$^-$</td>
<td>580.2</td>
</tr>
</tbody>
</table>

*Figure 2.20: Ionic liquid ecotoxicity to freshwater snails.*
CO₂ Capture Using Ionic Liquids

The soil roundworm *caenorhabditis elegans* was used to test the toxicity of various 1-alkyl-3-methylimidazolium chlorides. The lethality increased with the length of the alkyl substituent.⁴⁹ Alkoxy-substituted ionic liquids display anti-microbial activity against different bacteria (coccis, rods) and fungi. The alkyl chain length greatly affected these activities. Shorter substituents render the ionic liquid less active, while substituents with 10-14 carbon atoms in the alkoxy-group gave rise to very high anti-microbial activities. On the other hand, relatively little influence of the anion was found.⁵⁰

Pernak and co-workers⁴⁸ assessed the acute oral toxicity of the ionic liquid 3-hexyloxymethyl-1-methylimidazolium tetrafluoroborate by the Gadumm method, and found that the LD₅₀ = 1400 mg/kg for female and the LD₅₀ = 1370 mg/kg for male Wistar rats. Landry and co-workers used Fischer 344 rats to test the acute toxicity of [C₄mim][Cl].⁵⁵ It was found that 175 mg/kg of [C₄mim][Cl] oral gavage to the rats had no influence on their body weight, activity and health during a two-week period. However, when the concentration was increased to 550 mg/kg, death of the rats occurred. Moreover, when a 2000 mg/kg concentration was used, all the rats tested died within one day, with adverse clinical signs including hypoactivity and abnormal posture. It is noteworthy that the ionic liquid mixed with dichloromethane results in higher acute toxicity than in its pure form or in water solution, which should be considered when handling dissolved ionic liquids.

Several ionic liquids were assessed for mutagenicity using the Ames test.⁵⁹ The ionic liquids tested were imidazolium based ILs ([bmim][Br], [hmim][Br] and [omim][Br]), pyridinium based ILs ([mebupy][Br], [mehepy][Br] and [meocpy][Br]), and quaternary ammonium based ILs ([4m-amm][Br], [4eamm][Br], [4b-amm][Br] and [4h-amm][Br]). The Ames test for mutagenicity indicated that none of the ILs tested caused frameshift or missense mutations. Only some ILs, [bmim][Br] and [omim][Br], indicated trends toward potential mutagenicity at high doses, but did not meet the USEPA criteria for classification as a mutagen.

Because of the relative stability features of ionic liquids, their accumulation in the environment becomes feasible, if they are applied in operational use. Thus, the fundamentals of ionic liquid biodegradability turn out to be an important issue for the reduction of ignition and landfill-waste risks. Wells and co-worker used measurements of Biochemical Oxygen Demand in five days (BOD₅) to evaluate the biodegradation of ionic liquids.⁵⁴ They found that none of the selected ionic liquids, which are based on imidazolium, pyridinium, phosphonium, and ammonium, showed any sign of biodegradation by the BOD₅ method. Gathergood and co-workers also tested the biodegradation of [bmim][PF₆] using a Closed Bottle Test (OECD 301D), in which no
biodegradation was observed.\textsuperscript{57} All these facts demonstrate that the commonly used ionic liquids are not readily biodegradable. However, the properties of ionic liquids can be tuned through structural adjustment to produce biodegradable and bio-renewable ionic liquids.

2.5.9 Flammability and Corrosion

The nonflammability of ionic liquids is often highlighted as a safety advantage of ILs over volatile organic compounds (VOCs), but the fact that many ILs are not flammable themselves does not mean that they are safe to use near fire and/or heat sources. A large group of ILs (including commercially available ILs) are combustible due to the nature of their positive heats of formation, oxygen content, and decomposition products.\textsuperscript{45} Smiglak \textit{et al.}\textsuperscript{45} tested 20 ILs based on protonated imidazolium nitrates and picrates, protonated C-nitro-substituted imidazolium nitrates and picrates, 1-butyl-3-methylimidazolium azolates, 2-hydroxyethylhydrazinium nitrate ([2-HEH][NO\textsubscript{3}]) and the commercially produced trihexyltetradecylyphosphonium chloride ([PC\textsubscript{6}C\textsubscript{6}C\textsubscript{6}C\textsubscript{14}][Cl]). To determine combustibility, \(\sim\) 40 mg of each sample was loaded into a small aluminium pan with a diameter of 2.6 mm and heated with a small flame torch for no longer than 5-7 seconds. All of the 20 tested ILs will ignite under these conditions. As an example, ignition test of protonated 1-butyl-3-hexylimidazolium nitrate is shown in Figure 2.21.\textsuperscript{45} The apparent rate of combustion appears to depend on the nitrogen and oxygen content. While some of the ILs burned for a short period of time and went out, others, after first ignition, burned quickly to complete or nearly complete combustion.

![Figure 2.21: Ignition test of 1 g of protonated [1-Bu-3-H-im][NO\textsubscript{3}].](image)

The corrosivity for a given metal is determined by the chemical structure of the IL cation and the nature of the anion. Negative effects were observed with tosylate and
dimethylphosphate anions. Dilution with water could lead to hydrolysis of many anions used in ILs which then produce acids (e.g. HF, HCl, sulfuric or phosphoric acid) and, hence, cause acid corrosion. Additionally, residual halide impurities, from the preparation of the ionic liquid, may corrode metal vessels, so that high-grade stainless steel, Teflon, or glass equipment should be used. The corrosion behavior of several metals and metal alloys (copper, nickel, brass, Inconel 600) exposed to a typical ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, ([bmim][Tf$_2$N]), has been investigated by electrochemical and weight-loss methods. At room temperature, there is hardly any corrosion, but at temperatures > 70 °C, the corrosion increases dramatically showing a strong dependence on temperature. A few examples of corrosion in copper, nickel and Inconel at high temperatures are shown in Figure 2.22,24

Figure 2.22: (a) Image showing the breakdown of the copper specimens after 48 hr immersion test at 150 °C in [C$_4$mim][Tf$_2$N]. The breakdown occurs mainly near to the contact between the support and the metal. The whole samples are shown (diameter 12.7 mm). (b) Localized corrosion phenomena at the nickel specimen surface after 48 hr immersion test at 275 °C in [C$_4$mim][Tf$_2$N]. The whole samples are shown (diameter 12 mm). (c) Localized corrosion phenomena at the Inconel specimen surface after 48 hr immersion test at 275 °C in [C$_4$mim][Tf$_2$N]. The whole sample is shown (diameter 12.7 mm).
2.6 Potential Applications of Ionic Liquids

In recent years, ionic liquids have been used for a wide variety of applications at lab scale, such as the recovery of biofuels, desulfurization of diesel oil and supercritical fluid extractions etc. Ionic liquids also have potential as lubricants, in solar cells, for heat storage, in nuclear fuel processing, in membrane technology, as sol-gel templates and in the dissolution of cellulose. Ionic liquids have also been used successfully as solvent or catalyst in many reactions such as hydrogenations, hydroformylations, isomerizations, dimerizations, alkylations, Diels-Alder reactions and Heck and Suzuki coupling reactions. Until 1998, the number of entries with the terms “ionic liquid” or “ionic liquids” in the Chemical Abstracts was below or around twenty per year, but this number is increasing from 45 per year in 1999 to 1255 per year in 2005 and 1717 in 2006 with their different use in various field. The total number of entries is over 8000 (in 2007) which show huge potential of ionic liquids applications in different areas as shown in Figure 2.23.

Figure 2.23: Growth in the number of IL publications and representative areas of interest. Data obtained from SciFinder Scholar using the search terms “ionic liquid” OR “ionic liquids” and then refined by publication year. The data for total publications includes the number of patents, and the area of the particular field does not represent the number of publications in the subfield.
Since the interest in ionic liquids has only increased after 1999, the development of ionic liquids is still mostly in the research phase. Therefore, only few processes have reached commercialization to date.\textsuperscript{147} However, there is a large field of potentially interesting applications. Currently, BASF is operating the most successful first commercial multi-ton process using ionic liquid technology since 2002, called the BASIL \textsuperscript{TM} (Biphasic Acid Scavenging utilizing Ionic Liquids) process.\textsuperscript{1,4,147} The BASIL process is a general solution for all kinds of acid scavenging problems. The BASIL process is utilized in a plant producing diethoxyphenylphosphine, a photoinitiator intermediate prepared by the reaction of dichlorophenylphosphene with ethanol. The reaction generates HCl as a byproduct, which must be removed to avoid an unwanted side reaction (see Figure 2.24 reaction-A). The acid is normally removed by adding a tertiary amine, but this generates ammonium salt slurry that is difficult to filter from the reaction mixture. BASF adds now 1-methylimidazole, which forms ionic liquid 1-methyimidazolium chloride ($mp$ 75 °C) (see Figure 2.24 reaction-B).

![Figure 2.24: (A) Synthesis of diethoxyphenylphosphine with ethanol and tertiary amine, (B) Synthesis of diethoxyphenylphosphine with 1-methylimidazole.](image)

After the reaction, two phases are formed, which can easily be separated: an upper phase of pure product and a lower phase of pure IL. The IL formed is deprotonated, regenerating the 1-methylimidazole for reuse. This new process uses a much smaller reactor (see Figure 2.25) than the initial process and the space–time yield for the formation of an alkoxyphenylphosphine was thus increased from 8 kg.m\textsuperscript{-3}.h\textsuperscript{-1} to 690,000 kg.m\textsuperscript{-3}.h\textsuperscript{-1} and the yield increased from 50% to 98%. An overview of different pilot plant and industrial scale applications of ionic liquids is shown in Table 2.8. The details of these processes can be found elsewhere.\textsuperscript{1,4,147}
<table>
<thead>
<tr>
<th>Company</th>
<th>Process</th>
<th>IL is acting as</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>BASIL™ (Biphasic Acid Scavenging utilizing Ionic Liquids)</td>
<td>Auxiliary</td>
<td>Commercial</td>
</tr>
<tr>
<td>Eastman Chemical</td>
<td>Production of 2,5-dihydrofuran</td>
<td>Catalyst ([P88818]I)</td>
<td>Commercial until 2004</td>
</tr>
<tr>
<td>BASF</td>
<td>Chlorination</td>
<td>Solvent</td>
<td>Commercial</td>
</tr>
<tr>
<td>Eli Lilly</td>
<td>Cleavage of ethers</td>
<td>Catalyst/ reagent (Pyridinium hydrochloride, [pyH]Cl)</td>
<td>Pilot</td>
</tr>
<tr>
<td>Degussa</td>
<td>Hydrosilylation</td>
<td>Solvent</td>
<td>Pilot</td>
</tr>
<tr>
<td>Arkema</td>
<td>Fluorination</td>
<td>Solvent</td>
<td>Pilot</td>
</tr>
<tr>
<td>IFP (Axens)</td>
<td>Olefin dimerization (Dimersol process)</td>
<td>Solvent (Chloroaluminate(III) ILs)</td>
<td>Pilot</td>
</tr>
<tr>
<td>Chevron Phillips</td>
<td>Olefin oligomerization</td>
<td>Catalyst</td>
<td>Pilot</td>
</tr>
<tr>
<td>BASF</td>
<td>Extractive distillation (Breaking water-ethanol and water-tetrahydrofuran azeotropes)</td>
<td>Extractant</td>
<td>Pilot</td>
</tr>
<tr>
<td>University of Twente</td>
<td>Extraction</td>
<td>Extractant</td>
<td>Pilot</td>
</tr>
<tr>
<td>Scionix</td>
<td>Electroplating (Cr)</td>
<td>Electrolyte (Choline-chromium(III) derived ILs)</td>
<td>Pilot</td>
</tr>
<tr>
<td>Degussa</td>
<td>Compatibilizer</td>
<td>Performance additive</td>
<td>Commercial</td>
</tr>
<tr>
<td>Iolitec/Wandres</td>
<td>Cleaning fluid</td>
<td>Performance additive</td>
<td>Commercial</td>
</tr>
<tr>
<td>Air Products</td>
<td>Storage of gases (Phosphine (PH3), arsine (AsH3) and boron trifluoride (BF3))</td>
<td>Liquid support ([bmim][Cu2Cl3] for PH3 and [bmim][BF4] for BF3)</td>
<td>Pilot</td>
</tr>
<tr>
<td>Linde</td>
<td>Gas compression</td>
<td>Liquid piston</td>
<td>Pilot</td>
</tr>
<tr>
<td>Central Glass Company</td>
<td>Sonogashira coupling reaction (to produce pharmaceutical intermediates)</td>
<td>Catalyst ([P44416]Br / tetraalkylphosphonium cation based ILs)</td>
<td>Commercial</td>
</tr>
<tr>
<td>SASOL</td>
<td>Metathesis and Olefin trimerisation</td>
<td>Solvent ([C,dmim][NTf2])</td>
<td>Pilot</td>
</tr>
<tr>
<td>PetroChina</td>
<td>Alkylation</td>
<td>Catalyst (Aluminium(III) chloride based ILs)</td>
<td>Pilot</td>
</tr>
<tr>
<td>BP</td>
<td>Aromatic alkylation</td>
<td>Catalyst (Chloroaluminate ILs)</td>
<td>Confidential</td>
</tr>
<tr>
<td>BP</td>
<td>Ethylbenzene production</td>
<td>Catalyst ([C,n,mim]Cl-AlCl3 (n = 2, 4 or 8))</td>
<td>Confidential</td>
</tr>
</tbody>
</table>
2.7 Challenges with Ionic Liquids

Although ionic liquids have received enormous attention in the literature and hold a great potential to improve industrial processes both environmentally and economically, there are some main issues which have to be addressed soon to make it quicker for their implementation in the industry. Firstly, there is still a lack of reliable physical data, due to the fact that the purity of ionic liquids has only recently been recognized to be of utmost importance for any measurements e.g. contamination of ionic liquids with chloride increase the viscosity and decreases the density of ionic liquids (as discussed earlier in sections 2.5.2 for Density and 2.5.3 for Viscosity). The viscosity of second-generation ionic liquids ranges from 20 to 2000 cP, which appears to be quite high from an engineering point of view. Attempts should be made to lower down the viscosity of ionic liquids for their practical use in the industry. Another issue related to ionic liquids is the current deficiency of toxicological and eco-toxicological data, and only one preliminary study has dealt with the life-cycle assessment of ionic liquids to date. Also, the question of how ionic liquids are to be disposed off has not been fully addressed. Finally, although many ionic liquids became commercially available from companies such as Merck, Cytec, SACHEM, DuPont, BASF, Fluka, Solchemar, Scionix, Solvent Innovation, Acros, Chemada, Degussa etc, but still a lot of ionic liquids are made primarily in laboratory scale quantities and sell for around $1–$10/g. To be competitive with conventional solvents, this will have to be reduced by a factor of 100 or more.
3 Theory: CO$_2$ Capture

3.1 Introduction

Today, fossil fuels produce over 60% of the world’s electricity. Coal is the most abundant fossil fuel, playing an essential role as fuel for power plant operation and contributing to about 38% of the total electricity generation.\textsuperscript{79} Due to security, sustainability of supply, strategic and energetic dependence reasons, it is well accepted the necessity to continue using coal as main fuel for producing electricity from power plants. Therefore, for the coming decades it is expected to continue as a prominent fuel for electricity production.\textsuperscript{80} However, CO$_2$ emissions have great negative impact on the atmosphere due to greenhouse effect causing approximately 55% of the global warming.\textsuperscript{81} Therefore it is the need of the time to reduce the CO$_2$ emissions. In order to reduce CO$_2$ concentrations in the atmosphere, it is essential to develop carbon capture and storage technologies that lead to zero emissions fossil fuels power plants.

Capturing CO$_2$ directly from small and mobile sources in the transportation, residential & commercial building sectors or the possibility of CO$_2$ capture from ambient air\textsuperscript{82} where CO$_2$ concentration in ambient air is around 380 ppm, a factor of 100 or more lower than in flue gas, is expected to be more difficult and expensive than from large point sources such as fossil fuel power plants, fuel processing plants and other industrial plants, particularly for the manufacture of iron, steel, cement and bulk chemicals etc. A rough figure of number of these large stationary CO$_2$ emission sources along with their corresponding CO$_2$ emissions is reported in the literature\textsuperscript{81,83} and presented in Table 3.1. Based on the numbers presented in Table 3.1, power generation contributes 78% of the total CO$_2$ emissions from large stationary sources. Furthermore, 41% power plants are
coal based and produce 76% of the total CO₂ emissions from power generation sector. The remaining 59% power plants are natural gas, fuel oil, hydrogen and other fuels based (landfill gas, digester gas and other oils) and produce remaining 24% CO₂ emissions of power generation sector.

Table 3.1: Profile of worldwide large CO₂ stationary sources emitting more than 0.1 Mt CO₂ per year.

<table>
<thead>
<tr>
<th>Process</th>
<th>Number of sources</th>
<th>Emissions (Mt CO₂ / yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fossil Fuels</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power (Coal)</td>
<td>4,942 (2,025)</td>
<td>10,539 (7,984)</td>
</tr>
<tr>
<td>Cement Production</td>
<td>1,175</td>
<td>932</td>
</tr>
<tr>
<td>Refineries</td>
<td>638</td>
<td>798</td>
</tr>
<tr>
<td>Iron and Steel Industry</td>
<td>269</td>
<td>646</td>
</tr>
<tr>
<td>Petrochemical Industry</td>
<td>470</td>
<td>379</td>
</tr>
<tr>
<td>Oil and Gas Processing</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Other Sources</td>
<td>90</td>
<td>33</td>
</tr>
<tr>
<td><strong>Biomass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol and Bioenergy</td>
<td>303</td>
<td>91</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>7,887</td>
<td>13,466</td>
</tr>
</tbody>
</table>

3.2 CO₂ Capture Systems

There are three basic systems for capturing CO₂ from use of fossil fuels and/or biomass.⁶¹,⁸⁹

- a) Post-combustion capture
- b) Pre-combustion capture
- c) Oxy-fuel combustion capture

These systems are shown in simplified form in Figure 3.1. A brief description of these systems is given as follows:

- **a) Post-combustion capture:**
  Capture of CO₂ from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO₂. The CO₂ is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. In this work we will focus only on post-combustion capture of CO₂ from power generation later in this chapter.
b) Pre-combustion capture:
Pre-combustion capture involves reacting a fuel with oxygen or air and/or steam to give mainly a “synthesis gas (syngas)” or “fuel gas” composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to give CO₂ and more hydrogen. CO₂ is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells. Figure 3.2 shows pre-combustion capture with some additional equipments to remove particulates and sulfur before CO₂ capture. Pure hydrogen is used in gas turbine and then burnt to produce electricity.

c) Oxy-fuel combustion capture:
In oxy-fuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that is mainly CO₂ and H₂O. If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO₂ and/or H₂O-rich flue gas can be recycled to the combustor to moderate this. This is necessary because currently available materials of construction cannot withstand the high temperatures resulting from coal combustion in pure oxygen. Oxygen is usually produced by low temperature (cryogenic) air separation to supply oxygen to the fuel. For a new unit, it should be possible to use smaller boiler equipment due to increased efficiency. The main attraction of this process is that it produces a flue gas which is predominantly CO₂ and water. The water is easily removed by condensation, and the remaining CO₂ can be purified relatively inexpensively. Figure 3.3 shows oxy-fuel combustion capture with some additional equipments to remove particulates and sulfur before CO₂ capture.
Pre-combustion capture

Figure 3.2: Pre-combustion capture system (Photo Courtesy of www.kjell-design.com / Vattenfall)

Oxyfuel combustion capture

Figure 3.3: Oxy-fuel combustion capture system (Photo Courtesy of www.kjell-design.com / Vattenfall)
A summary of advantages and disadvantages of each of the above mentioned three CO₂ capture pathways are presented in Table 3.2. Post-combustion capture applies primarily to coal fueled power generators that are air fired. Pre-combustion capture applies to gasification plants. Oxy-fuel combustion can be applied to new plants or retrofitted to existing plants.

### Table 3.2: Advantages and Disadvantages of Different CO₂ capture pathways

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Post-combustion</strong></td>
<td>• Applicable to the majority of existing coal fired power plants&lt;br&gt;• Retrofit technology option</td>
<td>Flue gas is:&lt;br&gt;• Dilute in CO₂&lt;br&gt;• At ambient pressure&lt;br&gt;Resulting in:&lt;br&gt;• Low CO₂ partial pressure&lt;br&gt;○ Significantly higher performance or circulation volume required for high capture levels&lt;br&gt;○ CO₂ produced at low pressure compared to sequestration requirements</td>
</tr>
<tr>
<td><strong>Pre-combustion</strong></td>
<td>Synthesis gas is:&lt;br&gt;• Concentrated in CO₂&lt;br&gt;• High pressure&lt;br&gt;Resulting in:&lt;br&gt;• High CO₂ partial pressure&lt;br&gt;○ Increased driving force for separation&lt;br&gt;○ More technologies available for separation&lt;br&gt;• Potential for reduction in compression costs/loads</td>
<td>• Applicable mainly to new plants, as few gasification plants are currently in operation&lt;br&gt;• Barriers to commercial application of gasification are common to pre-combustion capture&lt;br&gt;○ Availability&lt;br&gt;○ Cost of equipment&lt;br&gt;○ Extensive supporting systems requirements</td>
</tr>
<tr>
<td><strong>Oxy-fuel combustion</strong></td>
<td>• Very high CO₂ concentration in flue gas&lt;br&gt;• Retrofit and repowering technology option</td>
<td>• Large cryogenic O₂ production requirement may be cost prohibitive&lt;br&gt;• Cooled CO₂ recycle required to maintain temperatures within limits of combustor materials&lt;br&gt;○ Decreased process efficiency&lt;br&gt;○ Added auxiliary load</td>
</tr>
</tbody>
</table>

### 3.3 Post-Combustion Capture

Post-combustion capture involves the removal of CO₂ from the flue gas produced by combustion of fossil fuel. Figure 3.4 shows a general post-combustion capture process in which additional unit operations are deployed to remove the air pollutants prior to CO₂ capture. Existing power plants use air, which is almost four-fifth nitrogen, for combustion and generate a flue gas that is at atmospheric pressure and typically has a CO₂ concentration of less than 15%. Thus, the thermodynamic driving force for CO₂ capture is significantly lower.
capture from flue gas is low ($\text{CO}_2$ partial pressure is typically less than 0.15 atm), creating a technical challenge for the development of cost effective advanced capture processes. In spite of this difficulty, post-combustion carbon capture has the greatest near-term potential for reducing greenhouse gas (GHG) emissions, because it can be retrofitted to existing units that generate two-thirds of the $\text{CO}_2$ emissions in the power sector.81

![Postcombustion capture](image.png)

**Figure 3. 4: Post-combustion capture system (Photo Courtesy of www.kjell-design.com / Vattenfall)**

$\text{CO}_2$ contents of flue gases vary depending on the type of fuel used (between 3% for a natural gas combined cycle to less than 15% by volume for a coal-fired combustion plant). This low concentration of $\text{CO}_2$ in flue gas means that a large volume of gas has to be handled, resulting in large and expensive equipment. A further disadvantage of the low $\text{CO}_2$ concentration is that powerful solvents have to be used to capture $\text{CO}_2$ and regeneration of these solvents, to release the $\text{CO}_2$, requires a large amount of energy. The $\text{CO}_2$ concentration can be increased greatly by using concentrated oxygen instead of air for combustion, either in a boiler or gas turbine. If fuel is burnt in pure oxygen, the flame temperature is excessively high, so some $\text{CO}_2$-rich flue gas would be recycled to the combustor to make the flame temperature similar to that in a normal combustor. The advantage of oxygen-blown combustion is that the flue gas has a $\text{CO}_2$ concentration of typically $>90\%$, so only simple $\text{CO}_2$ purification is required. The disadvantage is that
production of oxygen is expensive, both in terms of capital cost and energy consumption.\textsuperscript{88}

In principle post-combustion capture systems can be applied to flue gases produced from the combustion of any type of fuel. However, the impurities in the fuel are very important for the design and costing of the complete plant.\textsuperscript{84} Flue gases coming from coal combustion will contain not only CO\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2} and H\textsubscript{2}O, but also air pollutants such as SO\textsubscript{x}, NO\textsubscript{x}, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants. Different technologies are available for post-combustion CO\textsubscript{2} capture. Some of them have been commercialized, while others are under development. These different currently available and emerging technologies are discussed briefly here.

### 3.4 Current Technologies

There are several commercially available process technologies which can in principle be used for CO\textsubscript{2} capture from flue gases. However, comparative assessment studies have shown that absorption processes based on chemical solvents (e.g. amine solutions) are currently the preferred option for post-combustion CO\textsubscript{2} capture.\textsuperscript{85, 86, 87} At this point in time, they offer high capture efficiency and selectivity, and the lowest energy use and costs when compared with other existing post-combustion capture processes. A short description of amine-based CO\textsubscript{2} capture technology is given below.

#### 3.4.1 State-of-the-art Amine based technology

Amine scrubbing technology was established over 60 years ago in the oil and chemical industries, for removal of hydrogen sulphide and CO\textsubscript{2} from gas streams. Commercially, it is the most well established of the techniques available for CO\textsubscript{2} capture. There are several facilities in which amines are used to capture CO\textsubscript{2} from flue gas streams today.\textsuperscript{88}

The solvent most frequently encountered for CO\textsubscript{2} capture is monoethanolamine (MEA), an amine solvent. A typical amine-based CO\textsubscript{2} capture process with an absorber and stripper is shown in Figure 3.5. In the amine scrubbing process, the cooled flue gas is brought into contact with the solvent (MEA) in the absorber at temperatures typically between 40 and 60\degree C, CO\textsubscript{2} is bound by the amine solvent in the absorber. The flue gas is then water washed to balance water in the system and to remove any solvent droplets or solvent vapour carried over, and then it leaves the absorber. It is possible to reduce CO\textsubscript{2}
concentration in the exit gas down to very low values, as a result of the chemical reaction in the solvent, but lower exit concentrations of CO₂ tend to increase the height of the absorption column. The “rich solvent”, which contains the chemically bound CO₂ is then pumped to the top of a stripper, via a heat exchanger. The regeneration of the solvent is carried out in the stripper at elevated temperatures (100-140°C) and around atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO₂ and for steam production which acts as a stripping gas. The desorbed CO₂ leaves at the top of the stripper. The “lean solvent”, containing far less CO₂ is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.81

Figure 3.5: Amine-based CO₂ capture process

MEA has several advantages as a solvent such as its high reactivity, low cost, high absorbing capacity on a mass basis and reasonable thermal stability. However it also has some disadvantages such as high vapour pressure which leads to fugitive emissions during regeneration and its corrosive nature. It also forms degradation products due to side reactions between some minor constituents of the flue gas.63 Besides these disadvantages, the major drawback of solvent scrubbing is the cost due to the high energy requirements of the process. The energy required using MEA as a solvent can cause a 20% reduction of power generation for a pulverised coal power plant. A reference example comes from the Ratcliffe power station in the UK. At present the thermal efficiency of this station is 38.9% (LHV). If the plant is retrofitted with Advanced
Supercritical Boiler/ Turbine (ASC BT) technology the efficiency would rise to 44.9%. Further addition of an amine scrubbing CO₂ capture plant would then reduce the efficiency by 20.9 % to 35.5%.104

Much research has been devoted to finding or developing solvents that are superior to MEA. A better solvent would not degrade, it would work under normal flue gas outlet conditions, and it would require less energy for regeneration. Some of the ways in which alternative solvents might perform better than MEA include:

- Higher capacity for CO₂ capture
- Lower energy for regeneration
- Higher absorption/desorption rates and regeneration at lower temperatures
- Lower volatility and better thermal stability
- Less degradation and lower corrosivity
- Low cost

3.5 Emerging Technologies

Emerging technologies involve a combination of products and processes that have demonstrated, either in the laboratory or in the field, significant improvements in efficiency and cost over state-of-the-art technologies. Emerging technologies range from major improvements to existing processes to highly novel approaches, as discussed below.

3.5.1 Cryogenic Separation

CO₂ can be separated from other gases by cooling and condensation. Cryogenic separation is widely used commercially for streams that already have high CO₂ concentrations (typically >90%) but it is not used for more dilute CO₂ streams.88 A major disadvantage of cryogenic separation of CO₂ is the amount of energy required to provide the refrigeration necessary for the process, particularly for dilute gas streams. Another disadvantage is that some components, such as water, have to be removed before the gas stream is cooled, to avoid blockages. Cryogenic separation has the advantage that it enables direct production of liquid CO₂, which is needed for certain transport options, such as transport by ship. Cryogenics would normally only be applied to high concentration, high pressure gases, such as in pre-combustion capture processes or oxygen fired combustion.61
3.5.2 Soluble Carbonate based systems

Carbonate systems are based on the ability of a soluble carbonate to react with CO₂ to form bicarbonate, which when heated releases CO₂ and reverts to a carbonate. A major advantage of carbonates over amine-based systems is the significantly lower energy required for regeneration. K₂CO₃ based system in which the solvent is promoted with catalytic amounts of piperazine (PZ) are under development.⁹⁰ The K₂CO₃/ PZ system (5 molar K₂CO₃; 2.5 molar PZ) has an absorption rate 10-30% faster than a 30% solution of MEA and favorable equilibrium characteristics. A benefit is that oxygen is less soluble in K₂CO₃/ PZ solvents; however, piperazine is more expensive than MEA, so the economic impact will be about the same. Analysis has indicated that the energy requirement is approximately 5% lower with a higher loading capacity of 40% versus about 30% for MEA. System integration studies indicate that improvements in structured packing can provide an additional 5% energy savings, and multi-pressure stripping can reduce energy use 5-15%.⁹⁰

3.5.3 Ammonia based systems

Ammonia-based wet scrubbing is similar in operation to amine systems. Ammonia and its derivatives react with CO₂ via various mechanisms, one of which is the reaction of ammonium carbonate (AC), CO₂, and water to form ammoniumbicarbonate (ABC). This reaction has a significantly lower heat of reaction than amine-based systems, resulting in energy savings, provided the absorption/ desorption cycle can be limited to this mechanism. Ammonia-based absorption has a number of other advantages over amine-based systems, such as the potential for high CO₂ capacity, lack of degradation during absorption/ regeneration, tolerance to oxygen in the flue gas, low cost, and potential to regenerate at around 20 bar to generate high pressure CO₂ streams. However, a few concerns exist related to ammonia’s higher volatility compared to that of MEA. One is that the flue gas must be cooled to the 15-25 °C range to enhance the CO₂ absorptivity of the ammonia compounds and to minimize ammonia vapor emissions during the absorption step. Additionally, there is concern over ammonia losses during regeneration, which occurs at elevated temperatures.⁹¹, ⁹², ⁹³ A Schematic of Ammonia-based (NH₃-CO₂-H₂O process) CO₂ Capture System is shown in Figure 3. ⁹⁶
Another ammonia-based system, under development by Alstom, is the chilled ammonia process (CAP). This process uses the same AC/ABC absorption chemistry as the aqueous system described above, but differs in a way that no fertilizer is produced and a slurry of aqueous AC and ABC and solid ABC is circulated to capture CO₂. The process operates at near freezing temperatures (0-10°C), and the flue gas is cooled prior to absorption using chilled water and a series of direct contact coolers. Technical hurdles associated with the technology include cooling the flue gas and absorber to maintain operating temperatures below 10°C (required to reduce ammonia slip, achieve high CO₂ capacities, and for AC/ABC cycling), mitigating the ammonia slip during absorption and regeneration, achieving 90% removal efficiencies in a single stage, and avoiding fouling of heat transfer and other equipment by ABC deposition as a result of absorber operation with a saturated solution. Both the aqueous and chilled ammonia processes have the potential for improved energy efficiency over amine-based systems, if the hurdles can be overcome.

3.5.4 Membrane systems

There are a variety of options for using membranes to recover CO₂ from flue gas. Solvent assisted membranes are being developed to combine the best features of membranes and solvent scrubbing. In this concept, flue gas would be passed through a bundle of
membrane tubes, while an amine solution flowed through the shell side of the bundle. CO₂ would pass through the membrane and be absorbed in the amine, while impurities would be blocked from the amine, thus decreasing the loss of amine as a result of stable salt formation. Also, it should be possible to achieve a higher loading differential between rich amine and lean amine. After leaving the membrane bundle, the amine would be regenerated before being recycled. Gas separation membranes allow one component in a gas stream to pass through faster than the others. There are many different types of gas separation membrane, including porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. Membranes cannot usually achieve high degrees of separation, so multiple stages and/or recycle of one of the streams is necessary. This leads to increased complexity, energy consumption and costs. Several membranes with different characteristics may be required to separate high-purity CO₂. Therefore, much development is required before membranes could be used on a large scale for capture in power stations.

### 3.5.5 Enzyme-based systems

Biologically based capture systems are another potential avenue for improvement in CO₂ capture technology. These systems are based upon naturally occurring reactions of CO₂ in living organisms. One of these possibilities is the use of enzymes. An enzyme-based system, which achieves CO₂ capture and release by mimicking the mechanism of the mammalian respiratory system, is under development by Carbozyme (see Figure 3.7). The process, utilizing carbonic anhydrase (CA) in a hollow fiber contained liquid membrane, has demonstrated at laboratory-scale the potential for 90% CO₂ capture followed by regeneration at ambient conditions. This is a significant technical improvement over the MEA temperature swing absorption process. The CA process has been shown to have a very low heat of absorption that reduces the energy penalty typically associated with absorption processes.
The rate of CO\(_2\) dissolution in water is limited by the rate of aqueous CO\(_2\) hydration, and the CO\(_2\)-carrying capacity is limited by buffering capacity. Adding the enzyme CA to the solution speeds up the rate of carbonic acid formation; CA has the ability to catalyze the hydration of 600,000 molecules of carbon dioxide per molecule of CA per second compared to a theoretical maximum rate of 1,400,000.\(^9\) This fast turnover rate minimizes the amount of enzyme required. Coupled with a low make-up rate, due to a potential CA life of 6 months based on laboratory testing, this biomimetic membrane approach has the potential for a step change improvement in performance and cost for large scale CO\(_2\) capture in the power sector. Although the reported laboratory and economic results may be optimistic, “Carbozyme biomimetic process can afford a 17-fold increase in membrane area or a 17 times lower permeance value and still be competitive in cost with MEA technology”\(^1\). The idea behind this process is to use immobilized enzyme at the gas/liquid interface to increase the mass transfer and separation of CO\(_2\) from flue gas. Technical challenges exist before this technology can be pilot tested in the field. These challenges include membrane boundary layers, pore wetting, surface fouling, loss of enzyme activity, long-term operation and scale-up.\(^9\)

### 3.5.6 Solid sorbent based systems (Adsorption)

A number of solid adsorbents, such as zeolites and activated carbon, can be used to react with CO\(_2\) to form stable compounds at one set of operating conditions and then, at another set of conditions, be regenerated to liberate the absorbed CO\(_2\) and reform the original compound. In pressure swing adsorption (PSA), the gas mixture flows through a
packed bed of adsorbent at elevated pressure until the concentration of the desired gas approaches equilibrium. The bed is regenerated by reducing the pressure. In temperature swing adsorption (TSA), the adsorbent is regenerated by raising its temperature. Since, solids are inherently more difficult to work with than liquids and the capacity and CO₂ selectivity of available adsorbents is low, no solid sorbent system for large scale recovery of CO₂ from flue gas has yet been commercialized. Thus, research has been going on in this field to develop new solid sorbents with high CO₂ capacity and selectivity along with good chemical and mechanical stability for long periods of operation in repeated cycles.

Metal organic frameworks (MOFs) are a new class of hybrid material built from metal ions with well-defined coordination geometry and organic bridging ligands. They have extended structures with carefully sized cavities that can adsorb CO₂. High storage capacity is possible, and the heat required for recovery of the adsorbed CO₂ is low. Over 600 chemically and structurally diverse MOFs have been developed over the past several years. MOF-177 has shown one of the highest surface areas and adsorption capacity for CO₂ at elevated pressure. Additional work is needed to determine stability over thousands of cycles and the effect of impurities at typical flue gas temperature and pressure.

Research Triangle Institute (RTI) is investigating a dry, inexpensive, regenerable, supported sorbent, sodium carbonate (Na₂CO₃), which reacts with CO₂ and water to form sodium bicarbonate (NaHCO₃). A temperature swing is then used to regenerate the sorbent and produce a pure CO₂/ water stream. After condensing the water, the CO₂ is ready for commercial use or sequestration. Laboratory and pilot plant tests have consistently achieved over 90% CO₂ removal from simulated flue gas. The process economic evaluation shows lower capital costs and energy requirements than conventional MEA technology based on a preliminary economic analysis.
3.6 Review of CO₂ solubility in Ionic Liquids

3.6.1 Introduction

Ionic liquids have recently gained great attention in a variety of chemical processes due to their unique properties such as non-volatility, non-flammability, high thermal stability and nature of tailoring physical properties by selection of different cations and anions, and so on. A potential application of ionic liquids is for gas separation processes e.g. post combustion CO₂ capture from power plants and CO₂ removal from natural gas etc. The nonvolatile nature of ionic liquids would not cause any contamination to a gas stream, and thus this feature gives ionic liquids a big advantage over conventional solvents used for absorbing gases. To select an efficient ionic liquid for use as a gas separation medium, it is necessary to know the solubility of the gas in the ionic liquid phase. Reliable information on the solubility of gases in ILs is needed for the design and operation of any possible processes involving IL.

3.6.2 Henry’s Law

The solubility of a gas in a liquid is frequently described in terms of Henry’s law, which is defined as

\[ H_i(T,P) = \lim_{x_i \to 0} \frac{f_i^L}{x_i} \tag{3.1} \]

where \( H_i(T,P) \) is the Henry’s constant, \( x_i \) is the mole fraction of gas dissolved in the liquid phase and \( f_i^L \) is the fugacity of the gas dissolved in the liquid phase. Knowing the fugacity of the gas in the liquid phase must be equal to the fugacity of the gas in the gas phase and approximating the gas phase fugacity as the gas phase pressure, the following form of Henry’s law can be obtained

\[ P_i = H_i(T).x_i \tag{3.2} \]

where \( P_i \) is the partial pressure of the gas and \( H_i(T) \) will have units of pressure and is inversely proportional to the mole fraction of gas in the liquid. For gases that behave nearly ideally (e.g. C₂H₄, C₂H₆, CH₄, O₂, and Ar), the solubility is linearly related to the pressure. Therefore, the Henry’s constant can be found by calculating the linear slope of
the data. On the other hand gases like CO\textsubscript{2} exhibits a nonlinear trend as the CO\textsubscript{2} pressure is increased (the curves begin to flatten out, indicating that the IL is beginning to approach its maximum, pressure-independent capacity for CO\textsubscript{2}) so the Henry’s constant can be found by fitting a second-order polynomial to the data and calculating the limiting slope as the solubility (or pressure) approaches zero.\textsuperscript{67}

### 3.6.3 Classification of ionic liquids for CO\textsubscript{2} solubility

Various experimental studies on gas separation processes using ionic liquids have been conducted by researchers and available in literature. A number of investigations have shown that CO\textsubscript{2} is remarkably soluble in ILs. According to the structural features and absorption mechanisms, the ILs can be classified into two categories; conventional ILs (generally second generation ILs) and task-specific ILs (third generation ILs).\textsuperscript{14} The conventional ILs can only absorb less amount of CO\textsubscript{2} because of the physical nature of the interactions between CO\textsubscript{2} and ILs whereas the task-specific ILs with alkaline groups could sequester larger amount of CO\textsubscript{2} than that of conventional ILs because of the chemical interactions or reactivities between CO\textsubscript{2} and alkaline groups of ILs. Now we will discuss the solubility of CO\textsubscript{2} in conventional ILs and task specific ILs in details.

### 3.6.4 CO\textsubscript{2} solubility in Conventional Ionic Liquids

Anthony et al.\textsuperscript{67} investigated solubility of nine different gases: carbon dioxide, ethylene, ethane, methane, argon, oxygen, carbon monoxide, hydrogen, and nitrogen up to 13 bar in a conventional ionic liquid [bmim][PF\textsubscript{6}]. These gases were chosen for several reasons: CO\textsubscript{2} solubility is important due to the possibility of using supercritical CO\textsubscript{2} to extract solutes from ILs and post combustion CO\textsubscript{2} capture from power plants; ethylene, hydrogen, carbon monoxide, and oxygen are reactants in several types of reactions studied in IL such as hydrogenations, hydroformylations and oxidations. Due to the nonvolatile nature of IL, the gas solubilities in IL were measured using a gravimetric technique, usually with a microbalance. The study showed that CO\textsubscript{2} has the highest solubility and strongest interactions with [bmim][PF\textsubscript{6}], followed by ethylene and ethane. Argon and oxygen had very low solubilities and immeasurably weak interactions. While all the remaining gases i.e. H\textsubscript{2}, CO and N\textsubscript{2} had solubilities below the detection limit of the apparatus. Solubility of various gases (CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4}, Ar, O\textsubscript{2}) in [bmim][PF\textsubscript{6}] at 25 °C and at different pressures is presented in Figure 3. 8. The relatively high solubility of CO\textsubscript{2} was explained as a result of its large quadrupole moment.\textsuperscript{67} The solubility of CO\textsubscript{2} in [bmim][PF\textsubscript{6}] at different temperatures is also demonstrated in Figure 3. 9 which shows
that the solubility decreases with increase in temperature. Using ATR-IR spectroscopy, Kazarian and coworkers found that there is evidence of chemical interactions between the anion [PF₆⁻] and CO₂ but those interactions are not large enough to be the sole factor leading to the high CO₂ solubility. They conclude that they observed Lewis acid-base interactions where the anion acts as the Lewis base. Anthony and coworkers also compare the CO₂ solubility in [bmim][PF₆] and common polar and nonpolar solvents. The Henry’s constants show higher solubilities of CO₂ in the ILs compared to conventional organic solvents. For example, the Henry’s constant at 25 °C is 53.4 bar in [bmim][PF₆], while it is 84.3 bar in heptane, 133.3 bar in cyclohexane, 104.1 bar in benzene and 159.2 bar in ethanol.

![Figure 3.8: Solubility of various gases in [bmim][PF₆] at 25°C](image)

![Figure 3.9: Solubility of CO₂ in [bmim][PF₆] at different temperatures](image)
Blanchard et al.\textsuperscript{40} determined the high pressure solubility of CO\textsubscript{2} in a series of imidazolium-type ILs including 1-\textit{n}-butyl-3-methylimidazolium hexafluorophosphate ([\textit{bmim}][PF\textsubscript{6}]), 1-\textit{n}-octyl-3-methylimidazolium hexafluorophosphate ([\textit{omim}][PF\textsubscript{6}]), 1-\textit{n}-octyl-3-methylimidazolium tetrafluoroborate ([\textit{omim}][BF\textsubscript{4}]), 1-\textit{n}-butyl-3-methyl imidazolium nitrate ([\textit{bmim}][NO\textsubscript{3}]), 1-ethyl-3-methylimidazolium ethyl-sulfate ([\textit{emim}][EtSO\textsubscript{4}]) and \textit{n}-butylpyridinium tetrafluoroborate ([\textit{N-bupy}][BF\textsubscript{4}]). The solubility data at 40°C is presented in Figure 3. 10.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Liquid phase compositions of six ionic liquid-CO\textsubscript{2} mixtures at 40 \textdegree C.}
\end{figure}

It can be seen that the solubility of CO\textsubscript{2} is the greatest in the ILs with the [PF\textsubscript{6}] anion, with [\textit{C8mim}][PF\textsubscript{6}] and [bmim][PF\textsubscript{6}] giving nearly identical results. The solubility of CO\textsubscript{2} in [\textit{C8mim}][BF\textsubscript{4}] is approximately 10\% less than in [bmim][PF\textsubscript{6}] and [\textit{C8mim}][PF\textsubscript{6}] but 20\% greater than in [\textit{N-bupy}][BF\textsubscript{4}]. The isotherms for [\textit{N-bupy}][BF\textsubscript{4}] are shaped somewhat differently than those of the imidazolium-based salts. Thus, the isotherms for [\textit{N-bupy}][BF\textsubscript{4}] and [\textit{bmim}][NO\textsubscript{3}] cross at 55 bar, with CO\textsubscript{2} solubility slightly higher in [bmim][NO\textsubscript{3}] at lower pressures and higher in [\textit{N-bupy}][BF\textsubscript{4}] at high pressures. [bmim][NO\textsubscript{3}] dissolved less CO\textsubscript{2} than the other two [bmim] salts. The IL that exhibited the lowest solubility of CO\textsubscript{2} in the liquid phase is [\textit{emim}][EtSO\textsubscript{4}]. For all of the ionic liquids tested, large quantities of CO\textsubscript{2} dissolved in the ionic liquid phase, but no appreciable amount of ionic liquid solubilized in the CO\textsubscript{2} phase. In addition, the liquid phase volume expansion with the introduction of even large amounts of CO\textsubscript{2} is
negligible, in dramatic contrast to the large volume expansion observed for organic liquids. For example, the liquid phase composition of 0.69 mole fraction CO$_2$ in [bmim][PF$_6$] produces a mere 18% volume increase over the pure IL, whereas a liquid phase composition of 0.740 mole fraction CO$_2$ in toluene gives a 134% volume increase over the pure solvent.\textsuperscript{40}

3.6.4.1 Anion effect on CO$_2$ Solubility

Solubility measurements,\textsuperscript{67, 68} spectroscopic studies,\textsuperscript{108} and molecular simulations\textsuperscript{68} indicate that CO$_2$ solubility in ILs depends primarily on the strength of interaction of CO$_2$ with the anion. Cadena et al.\textsuperscript{68} studied the mechanism of CO$_2$ dissolution in imidazolium-type ILs by experimental and molecular modeling and found that the anions have larger impact on the solubility of CO$_2$. Anthony and coworkers made a comparison between different ionic liquids with same cation and different anions to see their affinity to absorb CO$_2$. They used three ionic liquids with same cation i.e. 1-butyl-3- methylimidazolium ([bmim]) and three different anions i.e. tetrafluoroborate ([BF$_4$]), hexafluorophosphate ([PF$_6$]), bis(trifluoromethylsulfonyl)imide ([Tf$_2$N]) to check the effect of anion on CO$_2$ solubility. The results showed that the CO$_2$ solubility is dependent on the choice of the anion.\textsuperscript{109} Isotherms for the three ionic liquids at 25 °C are shown in Figure 3.11.

![Figure 3.11: CO$_2$ solubility in [bmim][PF$_6$], [bmim][BF$_4$], and [bmim][Tf$_2$N] at 25 °C.](image)

The ionic liquid with the [Tf$_2$N] anion has a considerably higher affinity for CO$_2$ than either of the other two ionic liquids. The [bmim][ BF$_4$] and [bmim][ PF$_6$] have basically the same solubility, although the [bmim][ PF$_6$] appears more soluble at higher pressures.
The solubility of CO$_2$ in [bmim][Tf$_2$N] at different temperatures is also measured which shows that the solubility decreases with increase in temperature and increases with increase in pressure. $^{69}$ Lee et al. $^{111}$ measure the CO$_2$ solubility in [bmim][Tf$_2$N] at different temperatures and pressures. Figure 3. 12 shows the solubilities of carbon dioxide in [bmim][Tf$_2$N] at temperatures ranging from 280 to 340 K and at pressures up to about 4.8 MPa. The solubility data measured is compared with the data reported by Anthony et al.$^{69}$ The two sets of data are measured at slightly different temperatures. The figure shows that the two sets of solubility data are in good agreement qualitatively. At low pressures, the gas solubilities appear linear as a function of the pressure but exhibited a nonlinear trend as the pressure increased, at all four different temperatures.$^{111}$

![Figure 3. 12: Solubility ($x_1$) of CO$_2$ in [bmim][Tf$_2$N]: comparison of data from Lee et al.$^{111}$ (● at 279.98 K; ● at 299.98 K; ■ at 319.98 K; ▲ at 339.97 K) with data from Anthony et al.$^{69}$ (○ at 283.15 K; ◊ at 298.15 K; □ at 323.15 K).](image)

### 3.6.4.2 Fluorination Effect of Anion on CO$_2$ solubility

Aki et al.$^{110}$ further investigate the influence of fluorination of anion on CO$_2$ solubility. They investigate seven ILs which have 1-butyl-3-methylimidazolium ([bmim]) as the cation. The seven different anions are dicyanamide ([DCA]), nitrate ([NO$_3$]), tetrafluoroborate ([BF$_4$]), hexafluorophosphate ([PF$_6$]), bis(trifluoromethylsulfonyl)imide ([Tf$_2$N]), trifluoromethanesulfonate ([TfO]) and tris(trifluoromethylsulfonyl)methide ([methide]). The effect of the anion on the solubility of CO$_2$ in [bmim] ionic liquids at 25 $^o$C is shown in Figure 3. 13.
Figure 3.13: Effect of the anion and pressure on the solubility of CO$_2$ in [bmim] cation based ILs with seven different anions at 25 °C.

Results show that the solubility of carbon dioxide is strongly dependent on the choice of anion. The solubility of CO$_2$ increases with increasing pressure for all seven ILs, as expected. CO$_2$ is least soluble in the two ILs with nonfluorinated anions, [NO$_3$] and [DCA]. It has the highest solubility in ILs with anions containing fluoroalkyl groups, [TfO], [Tf$_2$N], and [methide]. The solubility in the two ILs with inorganic fluorinated anions, [BF$_4$] and [PF$_6$], lie in between these two groups (see Figure 3.14). The relatively high solubility of CO$_2$ in [TfO], [Tf$_2$N], and [methide] may be due to favorable interactions between CO$_2$ and the fluoroalkyl substituents on the anion. In fact, CO$_2$ solubility increases with increasing number of CF$_3$ groups in the anion. For instance, at approximately 20 bar, the solubility of CO$_2$ in [bmim][methide] is 40% greater than in [bmim][TfO] at the same pressure.
3.6.4.3 Cation effect on CO₂ solubility

Aki et al.\textsuperscript{110} also investigate the effect of cation on CO₂ solubility. For this purpose they chose three ionic liquids with same anion ([Tf₂N]) and three different imidazolium based cations with varying number and length of alkyl chains on the cation, including 1-hexyl-3-methylimidazolium ([hmim]), 1-octyl-3-methylimidazolium ([omim]) and 2, 3-dimethyl-1-hexylimidazolium ([hmmim]). The solubility of CO₂ in these three ionic liquids [bmim][Tf₂N], [hmim][Tf₂N] and [omim][Tf₂N] is measured at 25, 40, and 60 °C. The results at 40 °C are shown in Figure 3. 15. In general, the CO₂ solubility slightly increases with an increase in the alkyl chain length at low pressures and this increase becomes more apparent at higher pressures. For instance, at a pressure of 83.7 bar, the solubility increased from 0.72 ± 0.009 mole fraction for [hmim][Tf₂N] to 0.763 ± 0.007 mole fraction for [omim][Tf₂N].\textsuperscript{110} Similar trends were observed at 25 and 60 °C. Blanchard et al. reported that CO₂ solubility increased when the alkyl chain length was increased from butyl to octyl for ILs with both [PF₆] and [BF₄] anions.\textsuperscript{40}
3.6.4.4 Fluorination Effect of Cation on CO₂ solubility

Muldoon et al.\textsuperscript{78} investigate the effect of fluorination of cation on CO₂ solubility in ionic liquids. They examined ionic liquids with partially fluorinated alkyl chains on the cation. They compare [hmim][Tf₂N] directly to [C₆H₄F₉mim][Tf₂N], as can be seen in Figure 3.16, and concluded that fluorinating the last four carbons of the alkyl chain (see Figure 3.17) does increase the CO₂ solubility. The Henry’s law constant at 25 °C for [C₆H₄F₉mim][Tf₂N] is 28.4 ± 0.1 bar compared to 31.6 ± 0.2 bar for [hmim][Tf₂N]. However, this increase in the solubility of CO₂ was less than expected, based on the results of a previous report by Baltus. Earlier, Baltus et al. reported a Henry’s law constant in an analogous ionic liquid, [C₈H₄F₁₃mim][Tf₂N], to be 4.5 ± 1 bar\textsuperscript{112} at 25 °C and later revised this value to 6 ± 1 bar.\textsuperscript{113} Despite this IL have two more fluorinated carbons on the chain (see Figure 3.17), Henry’s law constant can not expected to be so dramatically different from Muldoon’s data. Muldoon and coworkers received the same sample of [C₈H₄F₁₃mim][Tf₂N] from Baltus’s group and reported Henry’s law constant for [C₈H₄F₁₃mim][Tf₂N] to be 27.3 ± 0.2 bar at 25 °C. As expected, the CO₂ solubility was higher in [C₈H₄F₁₃mim][Tf₂N] than in [C₆H₄F₉mim][Tf₂N] (see Figure 3.16) but not as high as previously reported.\textsuperscript{78} The low pressure CO₂ solubility in imidazolium (1-Hexyl-3-methylimidazolium, [hmim]) and pyridinium (1-Hexyl-3-methylpyridinium,
[hmim] based cation with same [Tf$_2$N] anion is also compared and shown in Figure 3.16. The solubility of CO$_2$ in [hmim][Tf$_2$N] and that in [hmpy][Tf$_2$N] are very similar, with Henry’s law constants of 31.6 ± 0.2 bar and 32.8 ± 0.2 bar at 25 °C, respectively. Therefore, it can be concluded that at low pressures there is very little difference between imidazolium and pyridinium cations.

![Figure 3.16: Low pressure CO$_2$ solubility at 25 °C for different ionic liquids.](image)

![Figure 3.17: [hmim] cation with its analogous fluorinated alkyl chain cations.](image)
3.6.4.5 Effect of Fluoroalkylation of [PF₆] anion on CO₂ solubility

As mentioned above, fluorination is a proven method of increasing the CO₂-philicity of compounds. Some results for the ILs with fluorinated anions: [bmim][BF₄], [bmim][PF₆], [bmim][TfO], [bmim][Tf₂N] and [bmim][methide] have already been presented above (Figure 3.13 and Figure 3.14). Muldoon et al. further investigate the fluorination effect of anions on CO₂ solubility. They tested three fluoroalkylyphosphonates: [hmim][eFAP], [hmim][pFAP], and [p₅mim][bFAP]. Since the effect of cation on CO₂ solubility is secondary in nature compared to anion effect (i.e. the effect of cation alkyl chain length on CO₂ solubility is minor), therefore, the third ionic liquid cation (1-pentyl-3-methylimidazolium, [p₅mim]) which differ from the first two ILs, can not overcome or change the anion effect. The FAP-type anion is analogous to the [PF₆] anion, where replacement of three of the fluorine atoms of [PF₆] anion with fluoroalkyl groups of varying carbon chain length (see Figure 3.18) increases the CO₂ solubility significantly (see Figure 3.16). The solubility of CO₂ in [hmim][Tf₂N], the IUPAC standard IL, is also shown in the plot. It can be seen that the solubility increases as the fluorinated alkyl chain length increases. Ionic liquid with longest fluoroalkyl chain exhibit highest CO₂ solubility. The Henry’s law constants for [hmim][eFAP] and [hmim][pFAP] are 25.2 ± 0.1 and 21.6 ± 0.1 respectively, and highest value of 20.2 ± 0.1 for [p₅mim][bFAP] at 25 °C. Since, increase in the alkyl chain length on the cation slightly increases the CO₂ solubility, therefore, the CO₂ solubility can expected to be slightly greater in [hmim][bFAP] than in [p₅mim][bFAP].

![Figure 3.18: [PF₆] anion with its analogous, fluoroalkyl groups of varying carbon chain length, FAP-type anions.](image-url)
3.6.4.6 CO₂ solubility in non-fluorinated ionic liquids

Although the fluorination of anion and cation of ionic liquid has improved the CO₂ solubility but the disadvantages associated with these fluorinated ionic liquids are that they are very costly and environmentally less benign. The high stability and low reactivity of the fluorinated compounds gives them many excellent properties, but these also lead them to being poorly biodegradable and persistent in the environment. Therefore attempts have been made to develop ionic liquids with enhanced CO₂ solubility without additional fluorination of cation or anion. Carbonyl, esters, and ether groups are known to enhance a molecule’s CO₂-philicity and Muldoon et al. examined a number of ILs that include these functional groups and tested them for CO₂ solubility. The results are shown in Figure 3. 19. [b2-Nic][Tf₂N] is a pyridinium-based IL with a butyl ester group (see Figure 3. 20). This functional group did not improve the solubility of CO₂ in the IL compared to [hmim][Tf₂N] and has almost the same solubility. The [Tf₂N] anion appears to be the dominant factor in both ionic liquids. At higher pressures, [b2-Nic][Tf₂N] does have slightly higher CO₂ solubility compared to [hmim][Tf₂N], which may be due to secondary interactions between CO₂ and the cation.

![Figure 3. 19: Comparison of CO₂ solubility of nonfluorinated and fluorinated ILs at 60 °C.](image)
The addition of ether groups is believed to improve CO$_2$-philicity by increasing the flexibility of alkyl chains, leading to increased free volume.$^{115,116}$ The ether oxygen has also been shown to interact with the carbon of CO$_2$.$^{117}$ Thus two commercially available ILs possessing ether groups, Ecoeng 500 and Ecoeng 41M, have been investigated. The solubility of CO$_2$ in Ecoeng 500 is similar to that in [hmim][Tf$_2$N] at all pressures (see Figure 3. 19). It is worth noting that the higher viscosity of Ecoeng 500 (viscosity = 300 cP at 60 °C)$^{118}$ may result in large measurement uncertainties at low pressures, due to inadequate mixing. On the other hand, as the CO$_2$ dissolves in the liquid, it lowers the viscosity of the sample, providing better mixing, faster equilibration times, and less uncertainty at higher pressures. In comparison, the solubility of CO$_2$ in Ecoeng 41 M, an IL possessing an ether functionalized alkyl sulfate anion paired with the [bmim] cation, is not as good. The good performance of Ecoeng 500 is most likely due to large free volume of the IL due to the long alkyl chains (see Figure 3. 20). Ether functionality is also beneficial for ILs as the resultant flexibility allows preparation of ILs that are liquid at room temperature, where in some cases their alkyl analogues would be solids. A further benefit of using an IL such as Ecoeng 500 is that it possesses some ions of known toxicity, and that are not likely to be as environmentally persistent as fluorinated ILs, while maintaining good capacity for CO$_2$. 

![Figure 3. 20: Some non fluorinated or less fluorinated ionic liquids with ether [(a) and (b)] and ester [(c) and (d)] functionality.](image-url)
The solubility of CO$_2$ in another nonfluorous IL, [N$_{4444}$][doc], is also measured. Once again due to the IL’s high viscosity (12,100 cP at 25 °C)$^{118}$, the measurements at low pressures have significant uncertainty, even at 60 °C. [N$_{4444}$][doc] also contains an anion of known low toxicity$^{119}$ and has a good affinity for CO$_2$. As seen in Figure 3.19, at the highest pressures measured the solubility of CO$_2$ was nearly identical to that in [hmim][eFAP], one of the best performing fluorinated ILs. Although this nonfluorinated IL has a very large viscosity (12,100 cP at 25 °C), the docusate anion has several features that lead to good solubility of CO$_2$: carbonyl functionality and long, branched, alkyl chains (see Figure 3.20). Thus, it is possible to design nonfluorinated ILs with good capacity for CO$_2$, although not significantly higher than [hmim][Tf$_2$N] except for [N$_{4444}$][doc] at the high pressures.$^{78}$ The main drawback of all the investigated ILs is their relatively high viscosity.

Much effort has been made for increasing CO$_2$ solubility in imidazolium-type and fluorinated ionic liquids. Recently there are some reported works on the solubility of CO$_2$ in sulfonate ILs. Zhang et al.$^{121}$ determined the solubility of CO$_2$ in two sulfonate ionic liquids i.e. trihexyl (tetradeacyl) phosphonium dodecylbenzenesulfonates ([P$_{6,6,6,14}$][C$_{12}$H$_{25}$PhSO$_3$]) and trihexyl (tetradeacyl) phosphonium methylsulfonate ([P$_{6,6,6,14}$][MeSO$_3$]), at different temperatures ((322.15, 317.45, 312.45, and 307.55) K and pressures ranging from 4 to 9 MPa. The solubility of CO$_2$ in [P$_{6,6,6,14}$][MeSO$_3$] is higher than that in [P$_{6,6,6,14}$][C$_{12}$H$_{25}$PhSO$_3$]. The solubility of CO$_2$ in both ionic liquids increases with increasing pressure at all temperatures but decreases by increasing temperature. However, the solubility of CO$_2$ in sulfonate ILs is generally lower than that in imidazolium-type ionic liquids.

Ferguson et al.$^{122}$ measured the solubility of CO$_2$ in five different phosphonium-based ionic liquids, Trihexyl (tetradeacyl) phosphonium chloride [P$_{14}$][Cl], trihexyl (tetradeacyl) phosphonium dicyanamide [P$_{14}$][DCA], trihexyl (tetradeacyl) phosphonium bis(trifluoromethylsulfonyl)imide [P$_{14}$][Tf$_2$N], tributyl (ethyl) phosphonium diethylphosphate [P$_{244}$][DEP] and tributyl (tetradeacyl) phosphonium dodecylbenzenesulfonate [P$_{14}$][DBS], at 30 °C. The gas solubilities of the phosphonium-based ionic liquids are of the same magnitude as the gas solubilities for the more familiar imidazolium-based liquids. The Henry’s constants for different ionic liquids are, [P$_{14}$][Cl] = 35 ± 3.6 atm, [P$_{14}$][DCA] = 29.3 ± 1.6 atm, [P$_{14}$][Tf$_2$N] = 33 ± 3.3 atm, [P$_{244}$][DEP] = 69 ± 8.1 atm and [P$_{14}$][DBS] = 30 ± 4.5 atm.
3.6.5 CO₂ solubility in Task Specific Ionic Liquids

The absorption of CO₂ in the conventional ionic liquids, as discussed above, such as imidazolium, phosphonium and sulfonate based ILs along with other tailored fluorinated ILs, is very limited because of its physical nature of interactions, although it is relatively higher than the solubility of CO₂ in some conventional organic solvents such as heptane, ethanol, benzene, cyclohexane etc. The equilibrium solubility of CO₂ in these conventional ILs is about 0.10-0.15 wt% at room temperature and atmospheric pressure, which is obviously too low for industrial application for CO₂ capture.¹²³

Thus, considering the very limited capability of the conventional ILs in the absorption of CO₂ due to its physical nature of interaction, it is essentially necessary to explore novel ILs with the specific function for absorption of CO₂. To do so, a way of increasing the solubility of CO₂ in ILs is to append functional groups to the IL with which the CO₂ can react. This idea was set forth by Davis and coworkers¹⁴ (Bates et al.), who showed that appending a free amine (-NH₂) and exposure to CO₂ can result in the formation of a carbamate, with subsequent high uptake of CO₂. Their designed task specific ionic liquid (TSIL) is 1-n-propylamine-3-butylimidazolium tetrafluoroborate ([pabim][BF₄]). The proposed reaction mechanism is shown in Figure 3. ²¹, which is basically the same as for the amines currently used as CO₂ absorbents. CO₂ molecule attacks the free electron-pair of N atom of [pabim]⁺ cation and forms a new COO⁻ group, simultaneously the -NH₂ group of another [pabim]⁺ cation accepts one H⁺ and becomes -NH₃⁺ group, which accounts for the saturation molar ratio of 1:2 between CO₂ and [pabim][BF₄].

Bates et al.¹⁴ reported that when 1.2896 g of pure TSIL is exposed to a stream of bone dry CO₂ for 3 h at 1 atm and room temperature (~295 K), a total mass gain of 0.0948 g (7.4%) is observed, compared to 0.0881 wt % CO₂ uptake for [hmim][PF₆] at room
The molar uptake of CO\(_2\) per mole of TSIL during the 3 h exposure period approaches 0.5, the theoretical maximum for CO\(_2\) sequestration as an ammonium carbamate salt (see Figure 3.22). This per mole uptake of CO\(_2\) by the amine-appended TSIL is comparable to those of standard sequestering amines such as monoethanolamine (MEA), diisopropanolamine (DIPA) and \(\beta,\beta'\)-hydroxyaminoethyl ether (DGA). The process of CO\(_2\) uptake is reversible, CO\(_2\) being extruded from the IL upon heating (80-100 °C) for several hours under vacuum. The recovered ionic liquid has been repeatedly recycled for CO\(_2\) uptake (five cycles) with no observed loss of efficiency.

Although the TSIL has shown greater CO\(_2\) solubility than conventional ionic liquids, there are a variety of issues that must be considered in selecting a physically absorbing versus a chemically complexing IL for CO\(_2\) capture. For instance, there may be significant changes in physical properties (e.g., viscosity) with chemical complexation. In addition, one may expect higher heats of absorption and desorption when the CO\(_2\) reacts with the IL.

### 3.6.6 Selective CO\(_2\) absorption

The flue gas from coal fired power plants constitutes up to 15% vol. CO\(_2\). The other gas is mainly nitrogen along with oxygen and water vapours. Therefore, in post combustion CO\(_2\) capture using ionic liquids the important factors, besides CO\(_2\) solubility in ionic
liquids, which have to take in account, are: (a) solubility of N\textsubscript{2} and O\textsubscript{2} in ionic liquid (b) effect of water on CO\textsubscript{2} solubility. Ionic liquid used for CO\textsubscript{2} capture should selectively absorb CO\textsubscript{2} i.e. ionic liquid should have very low solubility of nitrogen and oxygen. Anthony et al.\textsuperscript{67} reported solubility of O\textsubscript{2} in [bmim][PF\textsubscript{6}] ionic liquid to be extremely low (Henry’s constant = 8000 ± 5400 bar at 25 °C) and N\textsubscript{2} solubility was beyond the detection limit of the apparatus (Henry’s constant >20,000 bar at 25 °C). Carbon monoxide solubility was also immeasurably low (Henry’s constant >20,000 bar at 25 °C).

In another investigation CO\textsubscript{2}, N\textsubscript{2} and O\textsubscript{2} solubilities are measured in an IL with pyridinium-based cation and [Tf\textsubscript{2}N] anion i.e. 1-Hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [hmpy][Tf\textsubscript{2}N].\textsuperscript{69} The results are shown in Figure 3.23, where the solubilities of these gases are measured up to 13 bar at 25 °C. The results show negligibly small solubilities for nitrogen and oxygen compared to CO\textsubscript{2} which shows the ionic liquid’s potential for selective CO\textsubscript{2} sorption from flue gas.

![Figure 3.23: Low pressure solubilities of three main gases (CO\textsubscript{2}, N\textsubscript{2} and O\textsubscript{2}) of flue gas in [hmpy][Tf\textsubscript{2}N] at 25 °C](image)

3.6.7 Effect of water on CO\textsubscript{2} solubility

Even though most ionic liquids are water stable, they are highly hygroscopic in nature. Therefore, the knowledge of CO\textsubscript{2} solubility in water saturated ILs will be important for practical application of CO\textsubscript{2} capture. Aki et al.\textsuperscript{110} investigate the effect of water on the solubility of CO\textsubscript{2} in [bmim][Tf\textsubscript{2}N] at 25 °C. They compared a dried [bmim][Tf\textsubscript{2}N]
CO₂ Capture Using Ionic Liquids

Theory: CO₂ Capture

Sample ([H₂O] = 450 ppm) with one containing 1.35 wt % (13,500 ppm) water, as determined by Karl Fischer titration and the solubility results are shown in Figure 3. 24. It can be seen that the presence of water had essentially no effect on the solubility of CO₂ in [bmim][Tf₂N]. One possible explanation is that any hydrogen bonding of the water with the [Tf₂N] anion does not eliminate [Tf₂N] anion/CO₂ interactions.⁶⁸

![Figure 3. 24: Effect of water content on the solubility of CO₂ in [bmim][Tf₂N] at 25 °C. The IL was saturated with water ([H₂O] = 1.35 wt %).](image)

Fu et al.¹²⁰ investigate the effect of water on CO₂ solubility in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) for water mass fraction of [bmim][PF₆] ranging from 0.0067 % to 1.6 % and over temperature and pressure ranges of (40 to 60) °C and (1 to 25) MPa respectively. The deviation in solubility, at the same temperature and pressure, with different water mass fractions was not more than 15 %, and the average deviation is 6.7 %. Solubility of CO₂ in [bmim][PF₆] with different water wt % (0.0067 %, 0.15 %, 0.89 % and 1.6 %) at 50 °C is shown in Figure 3. 25.
3.6.8 Henry’s constant Data Compilation

Although various research groups have measured the solubility of CO₂ in different ionic liquids at different conditions of temperatures and pressure, but still the CO₂ solubility data is very scarce. The data available in the literature is reported in the form of Henry’s constant. This Henry’s constant data for various ionic liquids at different temperatures along with the enthalpy of CO₂ absorption in different ionic liquids has been compiled and presented in tabular form in Table 3. 3.
### Table 3.3: Henry’s law constant at different temperatures and enthalpy of absorption for various ionic liquids.

<table>
<thead>
<tr>
<th>No</th>
<th>Ionic Liquid Name</th>
<th>Abbreviation</th>
<th>Henry’s Law constant, $H$, (bar)</th>
<th>$\Delta H$, (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 °C</td>
<td>25 °C</td>
</tr>
<tr>
<td>1</td>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate</td>
<td>[bmim][PF6]</td>
<td>38.8±0.2</td>
<td>53.4±0.3</td>
</tr>
<tr>
<td>2</td>
<td>1-Butyl-3-methylimidazolium tetrafluoroborate</td>
<td>[bmim][BF4]</td>
<td>41.8±2.3</td>
<td>59±2.6</td>
</tr>
<tr>
<td>3</td>
<td>1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[bmim][TF2N]</td>
<td>25.3±0.3</td>
<td>33±0.3</td>
</tr>
<tr>
<td>4</td>
<td>1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[hmim][TF2N]</td>
<td>24.2±0.1</td>
<td>31.6±0.2</td>
</tr>
<tr>
<td>5</td>
<td>1-Hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>[bmpy][TF2N]</td>
<td>25.4±0.1</td>
<td>32.8±0.2</td>
</tr>
<tr>
<td>6</td>
<td>1-Butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>[bmpy][TF2N]</td>
<td>26±1</td>
<td>33±1</td>
</tr>
<tr>
<td>7</td>
<td>1,2-Dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[pmmim][TF2N]</td>
<td>29.6±0.6</td>
<td>38.5±0.9</td>
</tr>
<tr>
<td>8</td>
<td>1-Methyl-3-(3,4,4,5,6,6,6,7,8,8,8-tridecafluorooctyl)imidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C12H23F23nim][TF2N]</td>
<td>174.1±2</td>
<td>263.4±3</td>
</tr>
<tr>
<td>9</td>
<td>1-Methyl-3-(3,4,4,5,5,6,7,8,8,8-tridecafluorooctyl)imidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[C12H23F23nim][TF2N]</td>
<td>174.1±2</td>
<td>263.4±3</td>
</tr>
<tr>
<td>10</td>
<td>1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate</td>
<td>[hmim][eFAP]</td>
<td>16±0.3</td>
<td>36±0.3</td>
</tr>
<tr>
<td>11</td>
<td>1-Hexyl-3-methylimidazolium tris(heptafluoropropyl)trifluorophosphate</td>
<td>[hmim][pFAP]</td>
<td>21.6±0.1</td>
<td>36±0.3</td>
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<tr>
<td>12</td>
<td>1-Pentyl-3-methylimidazolium tris(nonafluorobutyl)trifluorophosphate</td>
<td>[p5mim][BFAP]</td>
<td>20.2±0.1</td>
<td>32.9±0.2</td>
</tr>
<tr>
<td>13</td>
<td>(1-Methylimidazol-1-yl)(triethylamin)boronium bis(trifluoromethylsulfonyl)imide</td>
<td>[Et3NBH2mim][TF2N]</td>
<td>22.3±0.1</td>
<td>33.1±1.2</td>
</tr>
<tr>
<td>14</td>
<td>1-Hexyl-3-methylimidazolium acesulfamate</td>
<td>[hmim][ACE]</td>
<td>113.1±16.9</td>
<td>113.1±16.9</td>
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<tr>
<td>15</td>
<td>1-Hexyl-3-methylimidazolium saccharinate</td>
<td>[hmim][SAC]</td>
<td>132±19.7</td>
<td>132±19.7</td>
</tr>
<tr>
<td>16</td>
<td>1-Butyl-2,3-dimethylimidazolium hexafluorophosphate</td>
<td>[bmim][PF6]</td>
<td>47.3±7.5</td>
<td>61.8±2.1</td>
</tr>
<tr>
<td>17</td>
<td>1-Butyl-2,3-dimethylimidazolium tetrafluoroborate</td>
<td>[bmim][BF4]</td>
<td>45.7±3.4</td>
<td>61±1.6</td>
</tr>
<tr>
<td>18</td>
<td>1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[emim][TF2N]</td>
<td>25.3±1.3</td>
<td>35.6±1.4</td>
</tr>
<tr>
<td>19</td>
<td>1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[emim][TF2N]</td>
<td>28.6±1.2</td>
<td>39.6±1.4</td>
</tr>
<tr>
<td>20</td>
<td>1-Ethyl-3-methylimidazolium tetrafluoroborate</td>
<td>[emim][BF4]</td>
<td>81.06±4</td>
<td>131.7±3</td>
</tr>
<tr>
<td>21</td>
<td>1,3-Dimethylimidazolium methylsulfate</td>
<td>[mmim][MeSO4]</td>
<td>131.7±2</td>
<td>223±2</td>
</tr>
<tr>
<td>22</td>
<td>Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide</td>
<td>[P14666][TF2N]</td>
<td>33.4±3.3</td>
<td>33.4±3.3</td>
</tr>
<tr>
<td>23</td>
<td>Trihexyltetradecylphosphonium chloride</td>
<td>[P14666][Cl]</td>
<td>35.46±3.6</td>
<td>35.46±3.6</td>
</tr>
<tr>
<td>24</td>
<td>Trihexyltetradecylphosphonium dicyanamide</td>
<td>[P14666][DCA]</td>
<td>29.69±1.6</td>
<td>29.69±1.6</td>
</tr>
<tr>
<td>25</td>
<td>Tributylethylphosphonium diethylphosphate</td>
<td>[P244][DEP]</td>
<td>69.91±8.1</td>
<td>69.91±8.1</td>
</tr>
<tr>
<td>26</td>
<td>Tributylethylphosphonium dodecylbenzenesulfonate</td>
<td>[P15444][DBS]</td>
<td>30.4±4.5</td>
<td>30.4±4.5</td>
</tr>
</tbody>
</table>

$a = 55^\circ C$, $b = 70^\circ C$ and $c = 30^\circ C$
3.6.9 CO\textsubscript{2} capture systems for ionic liquids

There are two systems which can be used for CO\textsubscript{2} capture using ionic liquids. Absorption system (absorber and stripper) is one of the most common techniques for gas purification in which the flue gas is bubbled through the solvent (e.g. ionic liquid), the solvent will absorb the gas of interest (e.g. CO\textsubscript{2}) from flue gas and the solvent is then regenerated in the stripper to use it again in the system.\textsuperscript{125} Supported liquid membrane (SLM) is the second technique that can be use for CO\textsubscript{2} capture medium using ionic liquids. In SLM system, the pores of a membrane are filled with the solvent (e.g. ionic liquid). The more soluble gas is able to permeate across the membrane, while the less soluble gas remains on the feed side. The major advantage of a supported liquid membrane system is that a large surface area is achieved with a small amount of solvent. Another advantage is the membranes do not require a regeneration step; the gas is continually desorbing out of the solvent due to a pressure and/or concentration gradient. However, one of the limiting factors inhibiting the use of SLM is membrane instability. The flux of the gas across the membrane is affected by the thickness of the membrane. A thinner membrane yields a higher flux, but the thinner the layer of solvent, the quicker the solvent evaporates. But, due to non volatile nature of ionic liquids this problem can be eliminated in case of ionic liquids SLM systems.\textsuperscript{126} However, the choice of either of the two systems can be made on the basis of capital cost and energy requirements of the system.
4 Materials and Methods

4.1 Materials

Two different kinds of ionic liquids with same bis(trifluoromethylsulfonyl)imide cation are used in this study to measure the solubility of CO$_2$. A small description of these ionic liquids is as follows:

$[\text{emim}][\text{Tf}_2\text{N}]$:  
The sample of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide used in the CO$_2$ solubility measurements was obtained from Prof. Rasmus Fehrmann’s laboratory at Department of Chemistry, Technical University of Denmark. The sample has been used before in gas absorption but was purified before handing over. It is a clear, colourless liquid (see Figure 4.1) and used as received.

$[\text{bmim}][\text{Tf}_2\text{N}]$:  
The sample of 1-$n$-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide was also obtained from Prof. Rasmus Fehrmann’s laboratory. It is a clear liquid with pale yellow colour (see Figure 4.1) and used for CO$_2$ solubility as received. Different research groups used this ionic liquid for CO$_2$ solubility and reported this ionic liquid as a colourless liquid. According to Prof. Fehrmann, they tested the IL for any kind of impurity but could not find any. So, it was assumed to be free of impurities.
Gas:

Carbon dioxide (CO₂) gas is purchased from Linde (Germany) with a purity of 99.99%.

Ionic liquids with their formula, chemical structures and CAS number along with some important properties are tabulated in Table 4.1. It can be seen that there is much discrepancy in reported viscosity data, the reason may be due to different chloride contents in the tested samples which we have discussed earlier. (see section 2.5.3 for Viscosity). Heat capacity data for ionic liquids is very scarce. Only a few data points at different temperatures are reported in the literature and there is a small dependence of heat capacity on temperature. For example, heat capacity values for [emim][Tf₂N] is 1.3399 and 1.36 kJ/kg K at temperatures 25 and 50 °C, and for [bmim][Tf₂N] these values are 1.2788 and 1.2969 kJ/kg K at temperatures 25 and 50 °C respectively. So, the heat capacity is considered to be constant (i.e. independent of temperature) and their average values are reported here.
Table 4.1: Ionic liquids with their chemical structures and some useful properties.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</th>
<th>1-(n)-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>[emim][Tf₂N]</td>
<td>[bmim][Tf₂N]</td>
</tr>
<tr>
<td>Formula</td>
<td>(\text{C}<em>8\text{H}</em>{11}\text{F}_6\text{N}_3\text{O}_4\text{S}_2) or ([\text{C}<em>6\text{H}</em>{11}\text{N}_2][\text{CF}_3\text{SO}_2\text{N}])</td>
<td>(\text{C}<em>{10}\text{H}</em>{15}\text{F}_6\text{N}_3\text{O}_4\text{S}_2) or ([\text{C}<em>8\text{H}</em>{15}\text{N}_2][\text{CF}_3\text{SO}_2\text{N}])</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="image1" alt="Structure of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide" /></td>
<td><img src="image2" alt="Structure of 1-(n)-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide" /></td>
</tr>
<tr>
<td>CAS number</td>
<td>174899-82-2</td>
<td>174899-83-3</td>
</tr>
<tr>
<td>M. Wt. (g/mol)</td>
<td>391.32</td>
<td>419.37</td>
</tr>
<tr>
<td>Melting pt. (°C)</td>
<td>-18 (^{129}), -17 (^{131})</td>
<td>-3 (^{129}), -2 (^{131})</td>
</tr>
<tr>
<td>Decomposition Temperature (°C)</td>
<td>280 (^{132})</td>
<td>275 (^{132})</td>
</tr>
<tr>
<td>Density, 25 °C (g/cm(^3))</td>
<td>1.5187 (^{127}), 1.5219 (^{130})</td>
<td>1.4366 (^{127}), 1.4397 (^{130}), 1.43 (^{37})</td>
</tr>
<tr>
<td>Viscosity, 25 °C (cP)</td>
<td>28 (^{42}), 32.6 (^{129})</td>
<td>69 (^{37}), 52 (^{17}), 49.9 (^{129})</td>
</tr>
<tr>
<td>Heat Capacity (kJ/kg K)</td>
<td>1.35 (^{131})</td>
<td>1.288 (^{131})</td>
</tr>
<tr>
<td>Enthalpy of absorption (kJ/mol CO(_2))</td>
<td>-14.2±1.6 (^{68}) (-322.66 kJ/kg)</td>
<td>-12.5±0.4 (^{69}) (-284.03 kJ/kg)</td>
</tr>
</tbody>
</table>

4.2 Methods for Measuring Gas Solubility

There are many factors that can influence accuracy of the results when measuring gas solubilities in liquids.\(^{139}\) The purity of the gas and the liquid under investigation is important because any impurities (such as water vapours and dissolved gas in the solvent etc) could affect the results. Fully degassing the solvent prior to the experiment is necessary to ensure that the gas absorbed as measured during the course of the
experiment is the true gas solubility. Accurate measurement of the relevant parameters such as temperature, pressure, volume, and/or mass, as well as precise control of any adjusted parameters (e.g. temperature and pressure control) is extremely important. One of the very important parameter for accurate gas solubility measurements is to attain the true equilibrium value of absorbed gas. Finally, an accurate method to ascertain the true amount of dissolved gas must be developed for the particular system used. The following sections will address various experimental methods for measuring gas solubilities in short and the method used in this study (gravimetric method) in detail and how these factors are addressed.

### 4.2.1 Pressure drop and Volumetric methods

These are the most typical methods used for measuring the solubility of gases in liquids, both occurring at constant temperature. In the first technique, often referred to as the pressure-drop method, the volume is held constant and the pressure drop is monitored as the gas absorbs into the liquid. In the second case, frequently called the volumetric technique, the pressure is kept constant and the volume change needed to maintain the pressure as the gas is absorbed by the liquid is measured. In either case, the pressure, temperature and volume before and after absorption are known. Therefore, the amount of gas absorbed by the liquid can be calculated frequently by using an equation of state to convert pressure, volume and temperature to moles. In general, the majority of the gas solubility measurements in liquids (volatile liquids) reported in the literature have been measured using the fundamental concepts involved in either the volumetric (isobaric and isothermal) or the pressure drop (isochoric and isothermal) techniques. Several groups have reported gas solubility measurements in ionic liquids using variations on these techniques. Many modifications on the apparatus used for these techniques have been made to improve the different aspects of the measurements, such as improving equilibration time by changing the stirring method or gas/liquid interface area, improving the degassing method of the solvent and improving the temperature, volume, or pressure measurement and control.

### 4.2.2 Gas chromatography

Gas chromatography (GC) is another method that can be used to measure gas solubilities in liquids in two different ways. In the first technique called the extractive technique, the solvent is saturated with the gas of interest and then coated on a column. A non-absorbing carrier gas is passed though the column to extract the gas of interest. The
carrier gas phase is analyzed in the GC to determine the amount of solute gas removed. In this technique, it is important to saturate the carrier gas with the solvent prior to flowing it through the column to avoid removing the solvent in the carrier gas phase. However, this carrier gas pre-saturation step can be eliminated in case of ionic liquids due to their non volatile nature. In the second gas chromatographic technique, gas solubilities are measured in the solvent at infinite dilution by first coating the pure (degassed) solvent on a column and then flowing a non-absorbing carrier gas containing the solute of interest. The amount of gas absorbed by the solvent can be calculated from the retention time of the solute in the column. To our knowledge there has been no reported study of measuring gas solubilities in ionic liquids using gas chromatography.

4.2.3 Gravimetric method

In the gravimetric method, the gas solubility is determined by measuring the change in weight of the sample upon absorption. This technique is commonly used for adsorption of gases onto solids but rarely used for absorption of gases in liquids because any loss of the liquid due to evaporation affects the final weight of the sample. However, due to the non-volatile nature of the ionic liquids, the gravimetric technique works well for these systems and is used for the gas solubility measurements in this work.

There are several advantages of using a gravimetric microbalance to measure gas solubilities. As mentioned earlier, ensuring that equilibrium has been reached is an important issue when measuring gas solubilities. The gravimetric balance allows the user to monitor the mass change as time progresses; as equilibrium is reached, the mass change will approach zero. Once the mass no longer changes, the sample is at equilibrium. Ensuring the initial liquid has been fully degassed prior to the measurement is also an important factor in order to determine how much gas is dissolved in the sample during absorption. Again, the ability to monitor the mass change as time progresses allows the user to ensure that the mass has stopped decreasing during the degassing step (equilibrium is reached) before proceeding to the solubility measurement. These advantages and several others related to the high pressure microbalance, the apparatus used in this work for solubility measurements, will be elaborated further in the following section.
4.2.4 High Pressure Microbalance

The gas solubility measurements in this work were performed in high-pressure microbalance (HP balance) provided by Sartorius AG (Göttingen, Germany). HP balance is a gravimetric microbalance capable of measuring absorption isotherms. This apparatus has previously been used to measure solubilities of gases (CO$_2$ and CH$_4$) in different polymers.$^{134, 135, 136}$ The operating limits of the balance are, temperature ranging from 0-150 °C and pressure up to 150 bar. The maximum weighing limit is 100 mg. Experimental setup and a schematic diagram of the apparatus used to perform the solubility measurements are shown in Figure 4.2 and Figure 4.3 respectively.

![Figure 4.2: Experimental setup for measuring CO$_2$ solubility in Ionic Liquids.](image-url)
The most important part of the HP balance is a weighing beam located in the weighing cell enclosed by a pair of metallic slabs that are held together with several bolts (see Figure 4. 4). The pressure integrity is maintained by a rubber ‘O’ ring placed between the two metallic slabs. The top end of the two thin glass wires are hooked onto either side of the weighing beam, whereas the two glass weighing cups are hooked onto the lower ends of the glass wires. These thin glass wires and the glass weighing cups are enclosed in metallic tubes and metallic cups respectively (see Figure 4. 5). The metallic tubes are connected to the weighing cell from the top end and with metallic cups from the bottom end. The metallic cups are separated into two parts which can be screwed together with rubber ‘O’ rings placed in between them to maintain the pressure in the system.
Figure 4.4: Different views of weighing beam.

Figure 4.5: Pictorial view of working with HP balance.
The measured mass reading from the balance is displayed on an electronic display and is accurate to ± 0.001 mg. The data (mass in mg against time in second) is collected in a computer. The pressure in the system is measured by Entran pressure transducer (from Entran Sensors & Electronics). The pressure is not directly displayed but is logged in terms of mV instead of bar. The mV signal can be converted into bar using the Equation 4.1 obtained from the calibration of Entran transducer (see Figure 4.6). The pressure transducer can measure the pressure in the pressure tubes and weighing chambers (metallic cups) to ± 0.1 bar. The temperature can be maintained in the system by submersion of the weighing chamber (metallic cups) in glycerin in a jacketed and insulated tank, with water (or glycerin) circulating through the jacket. The temperature is kept constant with an automatic controller.

\[ y = 19.5383x - 3.3179 \]  \hspace{1cm} (4.1)

where, \( x = \text{mV Signal} \) and \( y = \text{Pressure in bar} \)

![Calibration of Entran transducer for HP-Balance](image)

Figure 4.6: Entran pressure transducer calibration used to convert mV signals into bar (pressure).
4.3 Operating Procedure

Before working with the setup the valves are opened to evacuate any kind of pressure or vacuum in the apparatus. When the pressure becomes atmospheric the setup is opened and the weighing cups (one with sample ionic liquid and the other with counterweight glass beads) are removed carefully. A sample weight of around 200 mg of ionic liquid is used for CO$_2$ solubility measurements and same weight of glass beads is used in counterweight glass cup. Before loading the glass cups on the glass wires make sure that these glass wires are hanging freely (this is one of the serious problems in the setup). After loading glass cups on glass wires the metallic cups are closed tightly and immersed in the glycerin tank and the whole setup is closed. Before starting CO$_2$ solubility measurement the ionic liquid sample is first dried and degassed by putting the sample under vacuum using Alcatel vacuum pump (Drytel 30) and at 70 °C temperature. The lowest possible achievable pressure with this vacuum pump is 0.13 bar. The lower temperature is used during this process in order to decrease the risk of sample decomposition. During this process the sample mass slowly decreased as residual water and gases were driven off. Once the mass has stabilized, the sample is considered fully degassed, and the absorption measurements are initiated.

After degassing the temperature is lowered down to required temperature (e.g. 25 °C) and CO$_2$ gas is introduced into the weighing chamber through a valve until a predetermined pressure is reached. The sample mass increased as the gas absorbed into the sample. Data is collected as mass against time. The weight change is monitored until the mass did not change significantly, after which the sample is deemed to have reached equilibrium, thus yielding a single point on the absorption isotherm. After completing absorption run, desorption run is started immediately by evacuating the gas from the chamber using vacuum pump. Decrease in mass is observed due to desorption of gas and logged as mass against time until there is no change in mass i.e. equilibrium is reached. An absorption and desorption run for [emim][Tf$_2$N] is shown in Figure 4. 7 and Figure 4. 8 respectively. Similarly, above procedure is used for different sets of operating conditions of temperature and pressure. Note that the gas absorbed in IL must be equal to the gas desorbed from IL. After the completion of an all absorption/ desorption loops, the sample is dried and degassed and the mass is compared with the initial mass to confirm that the ionic liquid did not volatilize or decompose during the runs. Even after performing multiple absorption/ desorption experiments over several months, none of the samples exhibited a detectable loss in mass.
Figure 4. 7: Absorption run for CO\textsubscript{2} in [emim][Tf\textsubscript{2}N] at 25 °C and 2 bar. The difference between the initial and final masses is the amount of gas absorbed.

Figure 4. 8: Desorption run for CO\textsubscript{2} in [emim][Tf\textsubscript{2}N] at 25 °C and under vacuum (0.16 bar). The difference between the initial and final masses is the amount of gas desorbed.

Once the absorption-desorption experiment is finished the solubility of CO\textsubscript{2} in IL can be determined using following relation.
CO₂ Capture Using Ionic Liquids

Materials and Methods

\[
S = \frac{\text{mass of gas absorbed or desorbed (mg or g)}}{\text{mass of IL sample (mg or g)}}
\]

\[
S' = \frac{\text{moles of gas absorbed or desorbed (mol)}}{\text{moles of IL sample (mol)}}
\]

(4.2)

where, \( S \) is the solubility in term of mass ratio i.e. mg/mg or g/g and \( S' \) is molar solubility.

As mentioned earlier this HP balance has previously been used for solubility of gases like CO₂ and CH₄ in different polymers. The cups (or pans) used for polymer samples and glass beads are flat base pans with dimensions of 14mm inner diameter and 7 mm height (about 1 cc volume) as shown in Figure 4.9 (right). Polymer disc samples of about 10 mm diameter and 0.5 mm thick are used for gas solubility measurements. Initially, the same pans are used for ionic liquid samples but during the experiment it is observed that the mass of absorbed gas showed sudden drops in mass at different intervals of time as shown in Figure 4.10 as red circles. When the setup is opened it is observed that the pan is tilted to one side and some ionic liquid has escaped from the pan and stuck to the inner side of the metallic cup. Thus, we can say these sudden drops in mass are due to escape of tiny droplets of ionic liquid from pan at different intervals of time. It is also observed that this pan has the tendency to tilt on one side (Figure 4.9, right), thus moving all the liquid to that side i.e. greater chance to escape. Remember this escape of ionic liquid is not due to evaporation, it may be due to some kind of unavoidable disturbances in the system e.g. flowing in or out of the gas during pressurizing and evacuation etc. To overcome this problem conical shaped glass cups of 1 cc volume each are used. These cups are used in all experiments.

Figure 4.9: Two different types of glass cups used; Conical shaped cup (left) and Flat bottom cup (right).
Figure 4.10: Absorption run for CO₂ in [emim][Tf₂N] at 25 °C and 1 bar using flat bottom cup showing sudden drops in mass at different intervals of time shown by red circles.
5 Results and Discussion

5.1 Introduction

Two different ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([emim][Tf$_2$N]) and 1-$n$-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([bmim][Tf$_2$N]), have been investigated for their CO$_2$ solubility using High Pressure Microbalance (HP balance). The purpose of this study is to measure the CO$_2$ solubility in these ionic liquids and to check the performance and reliability of the setup for these kinds of measurements. The following section presents various results obtained in this work.

5.2 Solubility Measurements

In this sub-section the solubility measurements of the investigated ionic liquids are presented. The results obtained in this work are also compared with the published work in literature. The details of solubility measurements are presented below.

5.2.1 [emim][Tf$_2$N]

Before starting experiment the ionic liquid is degassed at 70 °C and 0.15 bar to remove any kind of absorbed gas or moisture in the ionic liquid. The lower temperature is used during this process in order to decrease the risk of sample decomposition. The measurements are made using conical shaped glass cups at 25 °C with varying pressure
and 30-40 hr to get the equilibrium for each point of the isotherm. The absorption isotherm for CO₂ in [emim][Tf₂N] at 25 °C is shown in Figure 5.1.

![CO₂ Solubility (25 °C)](image)

Figure 5.1: CO₂ solubility in [emim][Tf₂N] at 25 °C as a function of pressure.

The results in Figure 5.1 show a different trend of decrease in solubility by increasing pressure initially up to 7 bar and then the solubility starts increasing with pressure compare to general trend of increase in solubility by increasing pressure at constant temperature. The data obtained in this work is also compared with Anthony et al. data for the same system at 25 °C and presented in Figure 5.2. It can be seen that this work is not in good agreement with Anthony et al. The measured solubility is way above the published results especially at 2, 3 and 10 bar.

The degree of hysteresis between the two isotherm branches (absorption and desorption) gives an indication of the accuracy of each value. Lesser is the degree of hysteresis greater will be the accuracy and vice versa. An absorption-desorption isotherm for CO₂ solubility in [emim][Tf₂N] at 25 °C reported in literature is presented in Figure 5.3 which shows a very small hysteresis between the absorption and desorption isotherm branches, thus indicating a good accuracy of data points. Another absorption-desorption isotherms diagram for same system (CO₂ in [emim][Tf₂N] at 25 °C) of this work is shown in Figure 5.4 which shows a large hysteresis between the the two isotherm branches at the middle resultantly high inaccuracy in the measured data.
CO₂ Capture Using Ionic Liquids

Results and Discussion

Figure 5.2: Solubility of CO₂ in [emim][Tf₂N] at 25 °C as a function of pressure for this work and Anthony et al.

Figure 5.3: Absorption-desorption isotherms for CO₂ solubility in [emim][Tf₂N] at 25 °C.

It can also be seen that the initial (2 and 4 bar) and the final data points (10 bar) show high accuracy but the measured solubility at all these pressures is almost the same which
is a clear indication of inaccuracy in data because solubility should increase with pressure (see Figure 5.2 for the same system reported in literature). Furthermore, absorption isotherm shows less solubility at 5 bar compared to solubility at 3 bar and similarly solubility at 7 bar is less than solubility at 5 bar. The desorption isotherm shows 2.2 times more solubility at 5 bar and 3.6 times more solubility at 7 bar compared to respective solubilities at respective pressures on absorption isotherm.

![Absorption-Desorption Isotherms](image)

**Figure 5.4: Absorption and desorption isotherms for CO₂ solubility in [emim][Tf₂N] at 25 °C.**

The reasons, for data inaccuracy in this work and disagreement in results between this work and published work, are related to some problems in experimental setup (HP balance, pressure control and vacuum pump etc) which were observed during experimentation. Before discussing these problems, the results of second investigated ionic liquid ([bmim][Tf₂N]) are presented shortly.

### 5.2.2 [bmim][Tf₂N]

Again, before starting CO₂ solubility experiments in [bmim][Tf₂N], the ionic liquid is degassed at 70 °C and 0.15 bar to make sure that there is no absorbed gas or moisture left in the ionic liquid. The measurements are made using the same conical shaped glass cups at 25 °C with varying pressure. In these experiments it took 36-48 hr to get the equilibrium for each point of the isotherm. The absorption isotherm for CO₂ in [bmim][Tf₂N] at 25 °C is shown in Figure 5.5.
Figure 5.5: CO$_2$ solubility in [bmim][Tf$_2$N] at 25 °C as a function of pressure.

Figure 5.5 shows decrease in solubility by increasing pressure which looks contrary to the typical solubility trend, of gases in liquids, to increase with increase in pressure. The data obtained in this work is also compared with Anthony et al.$^{69}$ data for the same system ([bmim][Tf$_2$N] at 25 °C) and presented in Figure 5.6. It can be seen that this work is again not in good agreement with Anthony et al.

To see the degree of hysteresis between the two isotherm branches, an absorption-desorption isotherm for CO$_2$ solubility in [bmim][Tf$_2$N] at 25 °C of this work and reported in literature$^{109}$ is presented in Figure 5.7 and Figure 5.8 respectively. Figure 5.8 shows a very small hysteresis between the absorption and desorption isotherm branches, thus indicating a good accuracy of data points whereas Figure 5.7 (this work) shows large hysteresis i.e. inaccuracy in data. It can also be seen that hysteresis is comparatively low at low pressure and increases with increase in pressure (crocodile mouth opening).
CO₂ Capture Using Ionic Liquids

Results and Discussion

CO₂ Solubility (25 °C)

![CO₂ Solubility Graph]

Figure 5. 6: Solubility of CO₂ in [bmim][Tf₂N] at 25 °C as a function of pressure for this work and Anthony et al.

Absorption-Desorption Isotherms

![Absorption-Desorption Isotherms Graph]

Figure 5. 7: Absorption and desorption isotherms for CO₂ solubility in [bmim][Tf₂N] at 25 °C.
5.2.3 Henry’s Constant

It is not possible to calculate a realistic Henry’s constant from the above results for both ionic liquids. But as an attempt, if the two absorption isotherms for [emim][Tf₂N] and [bmim][Tf₂N] are observed carefully, it can be seen that both of these isotherms show similar trends from 3 bar to 7 bar as shown in Figure 5.9 (both trends show negative slope opposite to those reported in literature). Based on these isotherms, Henry’s constants are calculated to be -9.97 bar and -10 bar for [emim][Tf₂N] and [bmim][Tf₂N] respectively. These values seem unrealistic compared to the values reported by Anthony et al.69 which are 35.6 bar and 33 bar for [emim][Tf₂N] and [bmim][Tf₂N] respectively.
CO2 Capture Using Ionic Liquids  Results and Discussion

89

Absorption Isotherms at 25 °C

Figure 5. 9: Absorption isotherms for CO2 solubility in \([\text{emim}][\text{Tf}_2\text{N}]\) and \([\text{bmim}][\text{Tf}_2\text{N}]\) from 3-7 bar at 25 °C.

5.3 Discussion on Experimental Setup

Performance and reliability of the experimental setup for CO2 solubility in ionic liquids is also one of the main objective of this work. Solubility measurements in ionic liquids presented above suggest that neither the results are accurate nor they are in good agreement with the published results. The main reasons for this inaccuracy in the results are some problems related to the experimental setup which were observed during the course of experimentation. These problems include improper alignment of counter weight side pressure tube of HP balance, inadequate vacuum system, inadequate gas pressure control system and pressure drop problem in the system etc, and some other related problems. In the following section, we will discuss these problems in details.

5.3.1 HP Balance

One of the major problems associated with HP balance is improper alignment of counter weight side pressure tube i.e. the thin glass weighing wire which hooked to the weighing beam at the top end and to the weighing cup at the bottom end is not hanging right at the center (axis) of the tube because the metallic pressure tube is slightly bent to one side resultanty touching the glass wire and causing disturbance in weighing (see Figure 5. 10).
Due to shortage of time, it was tried to temporarily align the pressure tube and glass wire properly using thread as can be seen in Figure 5.11. Permanent alignment can be done similar to that of right pressure tube (see Figure 5.11) by fixing it with a metallic ring around the tube with three metallic bolts each at an angle of 120 degree to each other through the ring to adjust the alignment of the tube (see Figure 5.12). This metallic ring is fixed to one side of a 90 degree angled plate whose other side is fixed to the two legs of the HP balance. Although the left pressure tube is aligned with the help of thread, some wrong weight measurements were observed during the experiments. In addition, this temporary alignment can be changed with any external or internal disturbance. Thus the fixed proper alignment of left pressure tube is recommended prior to future absorption experimentation.
Figure 5. 11: HP balance left pressure tube is aligned temporarily using thread (see red box).

Figure 5. 12: Magnified view of right pressure tube of HP balance showing the assembly used for proper alignment of pressure tube and glass wire.
5.3.2 Vacuum System

Available Alcatel vacuum pump (Drytel 30) is used in the present set up for desorbing the absorbed gas in desorption steps of the experiments. This vacuum pump can only evacuate the system up to 0.13 bar which is inadequate for these systems i.e. CO₂ absorption in ionic liquids at low pressure. High vacuum is needed for these systems and this is explained below in detail.

Brennecke and coworkers 67, 68, 69, 73, 78 measured low pressure (up to 13 bar) CO₂ solubilities in ionic liquids using gravimetric microbalance i.e. gravimetric method (same used in this study). During drying and degassing of the ionic liquid sample they first pull a coarse vacuum on the sample with a diaphragm pump (MZ 2d, Vacuubrand) and then fully evacuating the chamber to approximately 10⁻⁹ bar with a turbomolecular pump (TMU 064, Pfeiffer). Under this condition the chamber was assumed to be free of air (although an extremely small amount of air is still present in the chamber but it can be ignored) and then at least two absorption measurements are taken below 1 bar by pressurizing the system with CO₂ (see Figure 5. 2 and Figure 5. 6) and then further measurements are taken. Whereas in this work the system could only be evacuated up to 0.13 bar and a lot of air is still present in the system. When the system is pressurized to 1 bar with CO₂ for measuring the absorption, it is not only CO₂ in the system but a mixture of air and CO₂. To overcome this problem after drying and degassing the ionic liquid, the system is flushed with CO₂ to remove air from the system before starting absorption. But by doing so we are disturbing the system e.g. there may a small absorption during this flushing process and the final results may also be affected. In addition, we are unable to measure the solubility below 1 bar. Moreover, at 0.13 bar during drying and degassing it can not be assured that the ionic liquid is fully dried and degassed.

On the other hand in previous studies of CO₂ absorption in polymers (solid) using this set up, 134, 135, 136 no degassing or drying is needed and also at high pressures like 30 or 40 bar (used in these studies) that small amount of air in the set up at atmospheric condition can be flushed easily and if there is still some air left in the system that can be ignored for such high pressures. Thus, it is suggested to replace the current vacuum system with more efficient one prior to further ionic liquid based low pressure CO₂ solubility measurements on this set up.
5.3.3 Gas Pressure System

Gas pressure in the system is measured by an Entran pressure transducer. The measured pressure in the system is not directly displayed but is logged in terms of mV instead of bar. The mV signal can be converted into bar (pressure) using the equation \( y = 19.5383x - 3.3179 \) obtained from the calibration of Entran transducer (as discussed earlier in chapter 4).\(^{141}\) The pressure transducer can measure the pressure in the pressure tubes and weighing chambers (metallic cups) accurate only to ± 0.1 bar. Since the experiments for CO\(_2\) absorption in polymers were running on the setup just before starting CO\(_2\) absorption measurements in ionic liquids (present work), it was assumed that he set up is in good working condition and the same pressure calibration was used.

For CO\(_2\) solubility measurement, Brennecke and coworkers\(^{67, 68, 69}\) used Intelligent Gravimetric Analyser (IGA-003) from Hiden Isochema with a very precise PID pressure control system ranging from ultra-high vacuum to 20 bar.\(^{142}\) They used a capacitance manometer (Baratron 626, MKS) for measuring gas pressure from 0-100 mbar and a strain gauge (PDCR 910, Druck) for pressures above 100 mbar. This pressure setup gave very good and accurate results. Whereas, the present setup contains only manually controlled pressure system with pressure accuracy of ± 0.1 bar i.e. inadequate for low pressure measurements, thus unable to produce good results at low pressure. Thus a total replacement of this pressure system is needed with precise pressure control equipment suitable for very low pressure measurements prior to further experimentation.

5.3.4 Low Pressure Absorption

The setup is unable to measure CO\(_2\) solubility at low pressure like 1 and 2 bar. During absorption process, when the system in pressurized with CO\(_2\), ionic liquid start absorbing the gas until the equilibrium is reached. But a strange trend of decrease in mass (instead of increasing) during absorption is observed in some cases. For example, when absorption experiments are run for [emim][Tf\(_2\)N] at 1 bar (& 25 °C) and for [bmim][Tf\(_2\)N] at 2 bar (& 25 °C), they showed a 10 mg and 18 mg loss in weight respectively (see Figure 5. 13 and Figure 5. 14). The possible reason of these strange results could be the problems related to the gas pressure system as discussed earlier.
5.3.5 System Pressure Drop

Another problem which is observed during the course of experimentation is pressure drop in the system. A significant pressure drop is observed for the first time during CO₂ absorption run in [emim][Tf₂N] at 5 bar i.e. a little less than 6% (see Figure 5.15). The experiment is repeated for the same conditions of temperature and pressure and again showed 5.5% pressure drop in the system. Similarly, higher pressure drop is observed at
high pressures particularly at 10 bar, a pressure drop of around 54% is observed. Pressure drop is also observed for second investigated ionic liquid ([bmim][Tf2N]). It showed two times more pressure drop at 3 bar, around 3 times more at 5 bar and a little higher at 7 bar compared to pressure drop observed in [emim][Tf2N] at respective pressures. All main joints in the set up are checked from time to time for any kind of leakage but no apparent leakage is detected. Since the time to reach equilibrium in these ionic liquid varies between 30-50 hr, therefore a leak in the system can not explain this pressure drop because if there could be even a very small leak in the system then the system must have lost all pressure during this long time. In addition, this pressure drop can not be even explained in a way that the pressure drop equivalent CO2 has been absorbed in the ionic liquid. For example, [emim][Tf2N] shows almost same CO2 solubility at 2 bar and 10 bar (see Figure 5.1) whereas the pressure drop at these pressures is less than 1% and around 54% respectively. Since, there is no such thing as absolutely airtight equipment so the only possible reasons for this pressure drop could be the micro scale leakage in the system.

Figure 5. 15: Pressure drop during CO2 absorption at 25 °C in [emim][Tf2N] and [bmim][Tf2N].
5.3.6 Equilibrium Time

The diffusion of gas in the ionic liquid depends on its viscosity i.e. greater is the viscosity of IL, greater will be the diffusion time and resultantly greater will be the time required to reach equilibrium and vice versa. The ionic liquids used in this study are somewhat viscous, so the diffusion of gas into the liquid can be quite slow. In the present set up, it took 30-40 hr for [emim][Tf$_2$N] and 36-48 hr for [bmim][Tf$_2$N] to reach equilibrium in absorption and desorption isotherms. Anthony et al.\textsuperscript{67} reported equilibrium time ranged from 90 to 180 min (1.5 to 3 hr) per point for these ionic liquids. Zhang et al.\textsuperscript{144} also reported minimum equilibrium time of 1 hr to maximum 3 hr for different ionic liquids used in the study. The equilibrium time in this work seems very much greater than both Anthony et al. and Zhang et al. which put a question mark on the reliability of the present set up. It is also noted that in some cases the proper equilibrium is not achieved even after two days. This phenomenon is more often in desorption isotherms. Figure 5.16 and Figure 5.17 are the illustration of this phenomenon.

![Desorption 25 °C](5bar to Vaccume (0.15bar))

Figure 5.16: Desorption isotherm for [bmim][Tf$_2$N] at 25 °C i.e. from 5 bar to 0.15 bar.
5.3.7 Strange weight loss on Drying and Degassing

A very strange and unexplainable behavior is observed during the drying and degassing of ionic liquid prior to gas absorption measurements. When [emim][Tf₂N] is dried and degassed under conditions of temperature and pressure of 75 °C and 0.15 bar respectively, the ionic liquid showed 60 mg loss in weight i.e. 29% ionic liquid is lost during drying and degassing process compared to initial mass of ionic liquid sample (see Figure 5. 18).
But on opening the set up and weighing the ionic liquid again, it is observed that there is no loss in weight. Similarly, [bmim][Tf$_2$N] ionic liquid showed 3.5% weight loss during drying and degassing but on weighing it after opening the setup it showed only 0.33% weight loss (which seems OK). This “strange” observation of loss in weight may be due to inadequate vacuum system or some other problems related to HP balance as discussed earlier.
6 Process Evaluation

6.1 Introduction

In the final part of the report, a process evaluation is made on the basis of energy requirements both for investigated ionic liquids ([emim][Tf₂N] and [bmim][Tf₂N]) and current amine based solvent (monoethanolamine, MEA). A comparison is also made between ionic liquids and MEA, and between the ionic liquids themselves. Since, the experimental results from this work are not good enough, energy calculations are made on the basis of Henry’s constant (and other required data for these calculation e.g. heat capacity, enthalpy of absorption etc) reported in literature for [emim][Tf₂N] and [bmim][Tf₂N]. Besides these ILs, energy requirement results for some other ILs reported in literature (see Table 3.3) are also presented and compared with MEA.

6.2 Ionic Liquids as CO₂ Capture media

Before doing process evaluation on energy basis and comparing ionic liquids system with MEA-based technology, it is important to establish that the ionic liquids can selectively absorb CO₂ from flue gas and then can be recovered in desorption step. Anthony et al.⁶⁵ reported that ionic liquids can selectively capture CO₂ from a gas mixture of 10% CO₂ in N₂. In a standard absorber setup, the gas and liquid flow through the system in a counter-current configuration. The liquid absorbs the compound of interest out of the feed gas stream, resulting in a “purified” gas stream and a “saturated” liquid stream leaving the absorber. However, Anthony and coworkers used a static setup in their work i.e. only the gas phase (mixture of CO₂ and N₂) is flowing. The ionic liquid phase is coated on glass beads in the absorber, rather than flowing through the absorber. They used between 12 g
to 18 g of ionic liquid ([bmim][PF$_6$]) and the column height ranged between 8 to 23 cm. The pressure drop across the column varied from 0.28 bar to 0.69 bar and the effluent flow rate ranged from 0.5 mL/min to 4 mL/min. All absorber experiments were conducted at room temperature (22 °C). Very little difference in absorber performance was observed within these ranges. The absorber breakthrough curves (the ratio of the concentration of the compound of interest, CO$_2$, detected in the effluent stream to its concentration in the feed stream as a function of time) obtained in these experiments are shown in Figure 6.1.

![Figure 6.1: Breakthrough curves for the removal of CO$_2$ from N$_2$ using [bmim][PF$_6$] as the absorbent. Different symbols show various runs under slightly different operating conditions.](image)

The different curves shown in Figure 6.1 are the runs conducted with slightly different operating conditions (amount of IL, flow rates, inlet pressure), as described above. Initially, no CO$_2$ is detected in the effluent mixture (the ratio is zero), indicating that the IL is successfully removing all the CO$_2$ present in the feed. The CO$_2$ detected in the effluent increases over time until reaching the breakthrough point where the effluent composition is essentially the same as the feed composition i.e. the ratio is one, indicating the system has become saturated (IL is saturated with CO$_2$) and is no longer working as a separation system. Subsequent runs were conducted after removing the absorbed gas by vacuum so the IL could be reused; no significant difference was observed as seen by the similarity of the various breakthrough curves shown in Figure 6.1. These experiments illustrate that it is possible to use [bmim][PF$_6$] to capture CO$_2$ from a gas mixture and it can also safely be assumed that the ionic liquids can capture CO$_2$ from gas mixture in general.
6.3 Conventional MEA based Absorption Technology

Most of the current commercial plants, that have CO$_2$ capture facilities, employ chemical absorption technique using monoethanolamine (MEA) as solvent. A typical CO$_2$ capture and recovery system using absorber and stripper is shown in Figure 6. 2. As can be seen, the CO$_2$-rich feed gas come in contact with the solvent in the absorber to produce a CO$_2$-lean gas at the top of the absorber. The CO$_2$-rich solvent leaving at the bottom of the absorber is heated in a stripping column to recover pure CO$_2$ and regenerated solvent is pumped back to the absorber.

![Figure 6. 2: CO$_2$ absorption system using MEA as solvent.](image)

6.4 Energy Calculations and Comparison

Reference to Barniki (Eastman), Anthony et al. reported a detailed calculation for the energy required to capture and recover CO$_2$ using a 25 wt% MEA solution as the solvent in the process shown in Figure 6. 2. The total energy required (rigorous energy calculation) to be 3.4 MMBTU/ton CO$_2$ including the energy required to slightly compress the feed gas to 1.2 bar (0.15 MMBTU/ton CO$_2$), to desorb the CO$_2$ in the stripping column (2.9 MMBTU/ton CO$_2$), and to compress the CO$_2$ off-gas to 100 bar (2 stages, 0.18 MMBTU/ton CO$_2$ each).
Now, we will present here a simple energy calculation to compare the use of energy between CO₂ capture by the ionic liquids ([emim][Tf₂N] and [bmim][Tf₂N]) and by a 30% MEA solution. A simple temperature-swing method is used to mimic the absorber-stripper process in a typical system. Therefore, the energy required for the separation can be calculated by the following equation:

\[ Q = -\Delta H_{\text{abs/rea}} + mC_p\Delta T \]  

(6.1)

where \( Q \) is the energy needed, \( \Delta H_{\text{abs/rea}} \) is the enthalpy of absorption for ionic liquids ([emim][Tf₂N] and [bmim][Tf₂N]) or the enthalpy of reaction for MEA, \( m \) is the mass of solvent, \( C_p \) is the heat capacity of the solvent, and \( \Delta T \) is the temperature difference between the absorption and desorption step. The absorption step is assumed to occur at 25 °C and the desorption step at 100 °C (approximately the boiling temperature of MEA solutions). The feed gas (flue gas) is chosen to be at 1 bar and contain 10% CO₂. The partial pressure of CO₂ is kept the same for both absorption and desorption stages (\( P_{\text{CO}_2} = 0.1 \) bar); therefore, the desorption step occurred under vacuum conditions. The heat of reaction for CO₂ in a 30 wt% MEA solution is -85.4 kJ/mol. The heat of absorption of CO₂ in [emim][Tf₂N] and [bmim][Tf₂N] are -14.2 and -12.5 kJ/mol respectively (See Table 4.1). The heat capacity for 30 wt% MEA in water solution is taken to be that of water (4.18 kJ/kg K). The average heat capacity for [emim][Tf₂N] and [bmim][Tf₂N] are 1.35 and 1.288 kJ/kg K respectively (See Table 4.1). Note that there is very small effect of temperature on heat capacities of ionic liquids which can be ignored and average values are used here. The results of these calculations are shown in Table 6.1. Note that the detailed calculations are enclosed in Table T-1 and Table T-2 of Appendix along with sample calculations for calculating mass (kg) of ionic liquids required per kilogram CO₂ capture.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>[emim][Tf₂N]</th>
<th>[bmim][Tf₂N]</th>
<th>MEA (30 wt%)</th>
</tr>
</thead>
</table>
| Mass (kg solvent/kg CO₂) | 5506 | 5325 | 17  
| \( \Delta H_{\text{abs}} \) or \( \Delta H_{\text{rea}} \) (kJ/kg CO₂) | -322.66 | -284.03 | -1940 |
| \( C_p \) (kJ/kg K) | 1.35 | 1.288 | 4.18 |
| \( Q \) (kJ/kg CO₂) | 5.6×10⁵ | 5.15×10⁵ | 7.3×10³ |
| \( Q \) (kJ/mol CO₂) | 2.5×10⁴ | 2.3×10⁴ | 320 |
| \( Q \) (MMBTU/ton CO₂) | 529 | 488 | 6.9 |
Table 6.1 shows that the energy calculated using MEA solution as the absorbent is 6.9 MMBTU/ton CO₂, which is about two times larger than the energy found by Barnicki’s rigorous energy calculation. This difference is most likely due to the simple one-stage desorption step used in this study compared to the multi-stage stripping column used by Barnicki. But we can say, this number is consistent enough and can be used to compare with the results of ionic liquids ([emim][Tf₂N] and [bmim][Tf₂N]) energy requirements. The energy required for ionic liquids to capture and recover CO₂ at 0.1 bar CO₂ partial pressure is significantly larger than that of MEA solution i.e. about 76 and 71 times more energy (MMBTU) is needed per ton of CO₂ for [emim][Tf₂N] and [bmim][Tf₂N] respectively compared to MEA solution. This huge difference is due to small CO₂ carrying capacity of ionic liquids compare to MEA solution which results in about 323 and 313 times more ionic liquids being used per kilogram of CO₂ for [emim][Tf₂N] and [bmim][Tf₂N] respectively compared to MEA solution. To see the effect of CO₂ partial pressure on solvent mass requirement and subsequently on energy requirement, the calculations are repeated for both ionic liquids and MEA solution at 1 bar and 2 bar CO₂ partial pressures and the results are presented in Table 6.2 and Table 6.3 respectively. Results show that, increasing the CO₂ partial pressure from 0.1 to 1 bar, decrease both solvent mass and energy requirements for both ionic liquids by an order of magnitude, whereas it has no effect on MEA energy requirements (Table 6.2). Increasing the pressure further up to 2 bar, decreases the energy requirements even further for both ionic liquids and again there is no significant effect on MEA solution results. These results show that the CO₂ solubility in ionic liquids has strong dependence on CO₂ partial pressure.

Table 6.2: Energy calculation results for CO₂ Absorption-Desorption by Temperature-Swing (298 K to 373 K) using two Ionic Liquids ([emim][Tf₂N] and [bmim][Tf₂N]) and 30 wt% MEA solution for CO₂ partial pressure = 1 bar.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>[emim][Tf₂N]</th>
<th>[bmim][Tf₂N]</th>
<th>MEA (30 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (kg solvent/kg CO₂)</td>
<td>531</td>
<td>512</td>
<td>19.65</td>
</tr>
<tr>
<td>ΔHabs or ΔHrxn (kJ/kg CO₂)</td>
<td>-322.66</td>
<td>-284.03</td>
<td>-1940</td>
</tr>
<tr>
<td>Cp (kJ/kg K)</td>
<td>1.35</td>
<td>1.288</td>
<td>4.18</td>
</tr>
<tr>
<td>Q (kJ/kg CO₂)</td>
<td>5.4×10⁴</td>
<td>4.97×10⁴</td>
<td>7.9×10³</td>
</tr>
<tr>
<td>Q (kJ/mol CO₂)</td>
<td>2.4×10³</td>
<td>2.2×10³</td>
<td>347</td>
</tr>
<tr>
<td>Q (MMBTU/ton CO₂)</td>
<td>51</td>
<td>47</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Table 6.3: Energy calculation results for CO₂ Absorption-Desorption by Temperature-Swing (298 K to 373 K) using two Ionic Liquids ([emim][Tf₂N] and [bmim][Tf₂N]) and 30 wt% MEA solution for CO₂ partial pressure = 2 bar.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>[emim][Tf₂N]</th>
<th>[bmim][Tf₂N]</th>
<th>MEA (30 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (kg solvent/kg CO₂)</td>
<td>255</td>
<td>245</td>
<td>20.65</td>
</tr>
<tr>
<td>ΔHₐₙs or ΔHₓₑₙ (kJ/kg CO₂)</td>
<td>-322.66</td>
<td>-284.03</td>
<td>-1940</td>
</tr>
<tr>
<td>Cₚ (kJ/kg K)</td>
<td>1.35</td>
<td>1.288</td>
<td>4.18</td>
</tr>
<tr>
<td>Q (kJ/kg CO₂)</td>
<td>2.6×10⁴</td>
<td>2.4×10⁴</td>
<td>8.2×10³</td>
</tr>
<tr>
<td>Q (kJ/mol CO₂)</td>
<td>1.14×10³</td>
<td>1.05×10³</td>
<td>361</td>
</tr>
<tr>
<td>Q (MMBTU/ton CO₂)</td>
<td>25</td>
<td>23</td>
<td>7.8</td>
</tr>
</tbody>
</table>

All these above results of energy calculations for 30% MEA solution and ionic liquids, [emim][Tf₂N] and [bmim][Tf₂N], are presented graphically in Figure 6.3 along with some other results of energy calculation made on the same pattern for different ionic liquids (as shown in Table 3.3) which are presented in Figure 6.4. The results in Figure 6.4 illustrate that all ionic liquids show a similar behavior as that of [emim][Tf₂N] and [bmim][Tf₂N].

Figure 6.3: Comparison of temperature-swing energy calculation between 30% MEA solution and ionic liquids, [emim][Tf₂N] and [bmim][Tf₂N].
6.5 Discussion on Temperature-Swing Technique

Pressurizing the flue gas from 1 bar to 10 bar (i.e. 1 bar CO₂ partial pressure) or 20 bar (i.e. 2 bar CO₂ partial pressure) will, of course, required compressing energy. But it is noticeable that the energy required for compressing the pure CO₂, in two stage compressors from 1 bar to 100 bar, is 0.36 MMBTU/ton CO₂ according to Barnicki’s energy calculations as discussed above, which is much smaller than the energy required for the desorption step in the stripping column (\( mC_p \Delta T \)). In fact, physical absorption processes often employ a pressure-swing system rather than a temperature-swing system. Since there is no heat of reaction to overcome with a physical absorbent using ionic liquids ([emim][Tf2N] and [bmim][Tf2N]) as compared to MEA solution (chemisorption), it would be good idea to use pressure-swing approach rather than temperature-swing, which can decrease the energy requirements significantly. In case of using pressure-swing method, this point has to be take in to account that compressing of pure CO₂ in Barnicki’s calculation is associated with much smaller flow rate of gas i.e. only 10% of the feed flue gas, compared to high feed flue gas flow rates. An optimal design can also be achieved by combining both pressure-swing and temperature-swing operations. Obviously, any design would also have capital costs associated with it, which also has to take in to account while making an optimal design.
6.6 Theoretical Ionic Liquid competitive to MEA

The energy calculations results presented above illustrate that the investigated ionic liquids ([emim][Tf2N] and [bmim][Tf2N]) are not realistic replacement for MEA using a conventional temperature-swing recovery system due to very high consumption of solvent mass and consequently very high energy requirement for CO2 capture and recovery. However, MEA has been studied from decades and optimized as a CO2 capture media, whereas [emim][Tf2N] and [bmim][Tf2N] were chosen for this study simply because they are common ionic liquids and not specifically designed as CO2 capture solvents. To make ionic liquids a competitor to MEA-based CO2 capture technology, the CO2 carrying capacity of the ionic liquids need to be improved.

Table 6.4: Parameters for theoretical Ionic Liquid that would be competitive to MEA using Temperature-Swing (298 K to 373 K) absorption and recovery with same heat capacity and enthalpy of absorption as that of [bmim][Tf2N] (i.e. Give $Q = 6.9$ MMBTU/ton CO2)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CO2 Partial Pressure in Flue Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{CO_2} = 0.1$ bar</td>
</tr>
<tr>
<td>Mass kg solvent / kg CO2</td>
<td>72</td>
</tr>
<tr>
<td>$H$(bar) at 25 °C</td>
<td>0.7</td>
</tr>
<tr>
<td>$H$(bar) at 100 °C</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 6.4 presents Henry’s constant for a “theoretical ionic liquid” with the same heat capacity and heat of absorption as that of [bmim][Tf2N] that would result in comparable energy requirements to that of 30% MEA solution ($Q = 6.9$ MMBTU/ton CO2) using the same temperature-swing process. This can be done either by reverse calculations or using Solver in Excel. Results show that a theoretical ionic liquid having Henry’s constants less than 1 bar at 25 °C (or up to about 16 bar if exposed to a higher CO2 partial pressure) would provide reasonable carrying capacities for CO2 capture, and thus could be a competitor to current amine solvents.
7 Conclusions

7.1 Conclusions

The solubility of CO\textsubscript{2} in two different ionic liquids [emim][Tf\textsubscript{2}N] and [bmim][Tf\textsubscript{2}N] at 25 °C and pressure up to 10 bar has been measured and reported. The measured CO\textsubscript{2} solubilities (i.e. Henry’s constants) are not good enough and are also not in good agreement with the values published in the literature. The disagreement in data is due to some technical problems in the experimental setup used in this work. These problems make the experimental setup unreliable for low pressure CO\textsubscript{2} solubility. The main problems in the experimental setup, the results of those problems and suggested improvements are given as follows:

1. Improper alignment of one of the pressure tube of HP balance (left hand side counterweight pressure tube) which cause disturbance in weighing and sometimes give inaccurate mass readings. Proper alignment and fixation of pressure tube is needed to be done before future experimentation.

2. Inadequate vacuum system which results in improper evacuation of air from weighing chamber and consequently poor results for degassing and drying of ionic liquid samples and also poor results for CO\textsubscript{2} absorption and desorption isotherms. A powerful vacuum system which can evacuate the chamber to ultra-high vacuum is needed.

3. The (manual) pressure control system in the setup is not suitable for measuring low pressure in the weighing chamber. A highly precise automatic pressure control system is needed which can measure low pressure even up to ultra-high
vacuum during evacuation of weighing chamber and very small CO$_2$ pressure when injected in the fully evacuated weighing chamber for CO$_2$ solubility measurements.

4. Good gas absorption results can not be obtained if the experimental setup exhibits pressure drop. Pressure drop in the system can be overcome by thorough inspection of the all the tubes and joins in the setup and proper repairing of leaked tube and/or joint if present.

Process evaluation for CO$_2$ absorption and recovery in ionic liquids and MEA on the basis of energy consumption (simple calculations) is presented. None of the ionic liquid is a realistic replacement for MEA solvent using a conventional temperature-swing recovery system due to smaller CO$_2$ carrying capacity of ionic liquids (used in this work) which leads to very high consumption of solvent (ionic liquid) mass and consequently very high energy requirement for CO$_2$ capture and recovery. But these results are not surprising because these ionic liquids are not designed with the intention of using it for CO$_2$ capture. Developing an ionic liquid with a CO$_2$ carrying capacity that will make ionic liquids competitive to MEA for CO$_2$ capture should be a realistic possibility. Their lack of volatility and physical nature of CO$_2$ absorption gives ionic liquids the unique feature that they can perform clean and energy efficient CO$_2$ capture without any loss of solvent. Thus, parameters (Henry’s constant at 25 °C and 100 °C) for a theoretical ionic liquid that would be competitive to MEA solvent using temperature-swing (298 K to 373 K) absorption and recovery method are calculated and presented. If one would able to design an ionic liquid with these parameters, it would be possible to replace the current energy expensive MEA based CO$_2$ capture technology.

7.2 Future Directions

CO$_2$ solubility in ionic liquid is strongly dependent on the choice of anion used in the ionic liquid and cation has very small or no effect on CO$_2$ solubility. Therefore, attempts should be made to develop ionic liquids that have increased CO$_2$ carrying capacity. Although the fluorination of anion and cation of ionic liquid has improved the CO$_2$ solubility but the disadvantages associated with these fluorinated ionic liquids are that they are very costly and environmentally less benign. Therefore, gas solubilities in non-fluorinated anions also need to be studied. Ionic liquids with anions such as bis(methylsulfonyl) imide [(CH$_3$SO$_2$)$_2$N], acetate [CH$_3$CO$_2$], or nitrate [NO$_3$] could have reduced consequences if released into the environment, therefore making them a
more attractive choice, as long as they also have the desired physical and mixture properties.

Before ionic liquids could realistically be used for CO₂ capture, there are several issues that would need to be addressed, specifically relatively high viscosity of ionic liquids which is a major hurdle in using ionic liquids as CO₂ capture media and measuring the diffusion of gases into the ionic liquids. Attempts should be made to exploit the opportunity to “tailor” the properties of the ILs by changing cations and anions to design an ionic liquid with high CO₂ carrying capacity which results in minimizing the amount of solvent needed for CO₂ capture, low heat of absorption and heat capacity to minimize the energy needed to recover the captured CO₂, and a low viscosity to increase mass transfer/diffusivity and to minimize any associated pumping costs. Since, adding an increased fluorinated alkyl chain or an amine group to an imidazolium cation significantly increases the CO₂ carrying capacity but also increases the viscosity. There is likely an optimal structure that can increase the carrying capacity without significantly increasing the viscosity.

Since, the viscosity of ionic liquids can be reduced dramatically with an addition of organic solvent (facilitator), addition of facilitating agents to the ionic liquids which can enhance the CO₂ solubility and reduced the viscosity of ionic liquid should also be investigated. For example, it might be possible to add facilitators, such as MEA or other amine based solvents, to the ionic liquid to get reduced viscosity of ionic liquids and increased CO₂ solubility while still taking advantage of the non-volatile and wide liquid range of the ionic liquid.

In addition to develop an ionic liquid with an improved CO₂ carrying capacity and reduced viscosity, a more in-depth process simulation is need be done to truly evaluate the use of ionic liquids as potential CO₂ capturing agents compared to MEA. Since, the ionic liquids absorb CO₂ physically (physisorption), a pressure-swing technique alone or a combination of pressure and temperature swing technique and any capital costs associated with the use of ILs could produce an optimal design for CO₂ capture. Such simulation techniques could also be used to determine the “optimal” properties of an ideal ionic liquid i.e. what viscosity, CO₂ carrying capacity and heat capacity would yield an ideal ionic liquid competitive to MEA.
Appendix

A-1  [emim][Tf$_2$N]

Data for ionic liquid, [emim][Tf$_2$N], and related calculations i.e. Solubility, Pressure and Pressure drop.

Equation used to convert mV signal into pressure (bar):

\[ y = 19.5383x - 3.3179 \]  

(Equation A)

where, \( y \) = Pressure and \( x \) = mV Signal

Data:

<table>
<thead>
<tr>
<th>Sample Side</th>
<th>Initial</th>
<th>Counter wt. Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan wt (g)</td>
<td>0.6865</td>
<td>Pan wt (g) 0.6796</td>
</tr>
<tr>
<td>Pan + IL (g)</td>
<td>0.8939</td>
<td>Pan + Glass (g) 0.9038</td>
</tr>
<tr>
<td>IL (g)</td>
<td>0.2074</td>
<td>Glass beads (g) 0.2242</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After Degassing</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan + IL (g)</td>
<td>0.8939</td>
</tr>
<tr>
<td>IL (g)</td>
<td>0.2074</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>After running several weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan + IL (g)</td>
</tr>
<tr>
<td>IL (g)</td>
</tr>
</tbody>
</table>

IL Sample (mg) = 207.4
IL Mol wt. (g/mol) = 391.31
CO$_2$ Mol wt. (g/mol) = 44.01
### Solubility Calculations

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Absorption (mg)</th>
<th>Desorption (mg)</th>
<th>Solubility (g/g)</th>
<th>Molar Solubility (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Absorption</td>
<td>Desorption</td>
</tr>
<tr>
<td>2</td>
<td>11.45</td>
<td>11.82</td>
<td>0.05521</td>
<td>0.05699</td>
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<tr>
<td>3</td>
<td>11.11</td>
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<td>0.05357</td>
<td>0.05473</td>
</tr>
<tr>
<td>5 (1)</td>
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<td>19.6</td>
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<tr>
<td>5 (2)</td>
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<td>0.04219</td>
<td>0.09450</td>
</tr>
<tr>
<td>7</td>
<td>7.7</td>
<td>27.67</td>
<td>0.03713</td>
<td>0.13341</td>
</tr>
<tr>
<td>10</td>
<td>11.68</td>
<td>11.96</td>
<td>0.05632</td>
<td>0.05767</td>
</tr>
</tbody>
</table>

### Pressure and Pressure drop Calculations

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Pressurization Signal (mV)</th>
<th>Calculated Pressure, bar (Equation A)</th>
<th>Pressure Drop (bar)</th>
<th>% Pressure Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>2</td>
<td>0.272</td>
<td>0.271</td>
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<td>1.977</td>
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<tr>
<td>3</td>
<td>0.324</td>
<td>0.32</td>
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<td>5 (2)</td>
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<td>0.415</td>
<td>5.064</td>
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<td>7</td>
<td>0.531</td>
<td>0.496</td>
<td>7.057</td>
<td>6.373</td>
</tr>
<tr>
<td>10</td>
<td>0.682</td>
<td>0.407</td>
<td>10.007</td>
<td>4.634</td>
</tr>
</tbody>
</table>
### A-2  [bmim][Tf$_2$N]

Data for ionic liquid, [bmim][Tf$_2$N], and related calculations i.e. Solubility, Pressure and Pressure drop.

**Data:**

<table>
<thead>
<tr>
<th>Sample Side</th>
<th>Initial</th>
<th>Counter wt. Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan wt (g)</td>
<td>0.6865</td>
<td>Pan wt (g)</td>
</tr>
<tr>
<td>Pan + IL (g)</td>
<td>0.8965</td>
<td>Pan + Glass (g)</td>
</tr>
<tr>
<td>IL (g)</td>
<td>0.21</td>
<td>Glass beads (g)</td>
</tr>
</tbody>
</table>

After Degassing

<table>
<thead>
<tr>
<th>Sample Side</th>
<th>Initial</th>
<th>Counter wt. Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan + IL (g)</td>
<td>0.8958</td>
<td>Pan + Glass (g)</td>
</tr>
<tr>
<td>IL (g)</td>
<td>0.2093</td>
<td>Glass beads (g)</td>
</tr>
</tbody>
</table>

After running several weeks

<table>
<thead>
<tr>
<th>Sample Side</th>
<th>Initial</th>
<th>Counter wt. Side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan + IL (g)</td>
<td>0.8966</td>
<td>Pan + Glass (g)</td>
</tr>
<tr>
<td>IL (g)</td>
<td>0.2101</td>
<td>Glass beads (g)</td>
</tr>
</tbody>
</table>

**IL Sample (mg) = 209.3**

**IL Mol wt. (g/mol) = 419.37**

**CO$_2$ Mol wt. (g/mol) = 44.01**

#### Solubility Calculations

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Absorption (mg)</th>
<th>Desorption (mg)</th>
<th>Solubility (g/g)</th>
<th>Molar Solubility (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorption</td>
<td>Desorption</td>
<td></td>
<td>Absorption</td>
</tr>
<tr>
<td>3</td>
<td>4.29</td>
<td>8.4</td>
<td>0.02050</td>
<td>0.04013</td>
</tr>
<tr>
<td>5</td>
<td>2.74</td>
<td>10.14</td>
<td>0.01309</td>
<td>0.04845</td>
</tr>
<tr>
<td>7</td>
<td>2.612</td>
<td>16.55</td>
<td>0.01248</td>
<td>0.07907</td>
</tr>
</tbody>
</table>

#### Pressure and Pressure drop Calculations

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Pressurization Signal (mV)</th>
<th>Calculated Pressure, bar (Equation A)</th>
<th>Pressure Drop (bar)</th>
<th>% Pressure Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>3</td>
<td>0.325</td>
<td>0.317</td>
<td>3.032</td>
<td>2.876</td>
</tr>
<tr>
<td>5</td>
<td>0.43</td>
<td>0.39</td>
<td>5.084</td>
<td>4.302</td>
</tr>
<tr>
<td>7</td>
<td>0.53</td>
<td>0.492</td>
<td>7.037</td>
<td>6.295</td>
</tr>
</tbody>
</table>
A-3  Henry’s Constant Calculations

**Absorption Isotherms at 25 °C**

![Absorption Isotherms at 25 °C](image)

Figure F- 1: Second order polynomial fitting to the data for [emim][Tf$_2$N] and [bmim][Tf$_2$N] at 25 °C.

From Figure F-1, second order polynomial for [emim][Tf$_2$N] is

\[ y = 0.0064x^2 - 0.1003x + 0.7199 \]

\[ R^2 = 1 \]

Slope \( \frac{dy}{dx} = 0.0128x - 0.1003 \)

For \( x \to 0 \)

Slope \( = -0.1003 \)

Since Henry’s Law \( P = Hx \Rightarrow x = \frac{1}{H} P \)

\( \Rightarrow Slope = \frac{1}{H} \)

Therefore, by combining above two slope equations

Henry’s constant for [emim][Tf$_2$N] is found to be \( H = -9.97 \text{ bar} \)

Similarly Henry’s constant for [bmim][Tf$_2$N] from equation \( y = 0.0081x^2 - 0.1x + 0.4226 \) in Figure F- 1 is found to be \( H = -10 \text{ bar} \)
Table T-1: Ionic liquids with Henry’s law constants at 10, 25, 50 and 70 °C from literature (see Table 3.3) and Extrapolated Henry’s law constants at 75 and 100 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ionic Liquids</th>
<th>Abbreviation</th>
<th>Henry’s Law constant, $H$(bar), from Literature</th>
<th>Extrapolated Values of $H$(bar) $^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10 °C</td>
<td>25 °C</td>
</tr>
<tr>
<td>1</td>
<td>1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[emim][Tf$_2$N]</td>
<td>25.3</td>
<td>35.6</td>
</tr>
<tr>
<td>2</td>
<td>1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[bmim][Tf$_2$N]</td>
<td>25.3</td>
<td>33.3</td>
</tr>
<tr>
<td>3</td>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate</td>
<td>[bmim][PF$_6$]</td>
<td>38.8</td>
<td>53.4</td>
</tr>
<tr>
<td>4</td>
<td>1-Butyl-3-methylimidazolium tetrafluoroborate</td>
<td>[bmim][BF$_4$]</td>
<td>41.8</td>
<td>59.5</td>
</tr>
<tr>
<td>5</td>
<td>1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[hmim][Tf$_2$N]</td>
<td>24.2</td>
<td>31.6</td>
</tr>
<tr>
<td>6</td>
<td>1-Hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide</td>
<td>[hmpy][Tf$_2$N]</td>
<td>25.4</td>
<td>32.8</td>
</tr>
<tr>
<td>7</td>
<td>1-Butyl-2,3-dimethylimidazolium hexafluorophosphate</td>
<td>[bmmim][PF$_6$]</td>
<td>47.3</td>
<td>61.8</td>
</tr>
<tr>
<td>8</td>
<td>1-Butyl-2,3-dimethylimidazolium tetrafluoroborate</td>
<td>[bmmim][BF$_4$]</td>
<td>45.7</td>
<td>61.5</td>
</tr>
<tr>
<td>9</td>
<td>1-Ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>[emmim][Tf$_2$N]</td>
<td>28.6</td>
<td>39.6</td>
</tr>
<tr>
<td>10</td>
<td>1-Ethyl-3-methylimidazolium tetrafluoroborate</td>
<td>[emim][BF$_4$]</td>
<td>29.6</td>
<td>38.5</td>
</tr>
</tbody>
</table>

$^1$ For extrapolation: $y(x) = y_{k-1} + \frac{x - x_{k-1}}{x_k - x_{k-1}}(y_k - y_{k-1})$
Table T-2: Energy calculations for CO₂ capture in different ionic liquids at different CO₂ partial pressures in the feed flue gas.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ionic Liquids</th>
<th>Mol. wt. (g/mol)</th>
<th>( C_p ) (kJ/kg K)</th>
<th>( \Delta H ) (kJ/kg)</th>
<th>( H )(bar) (From Table T-1)</th>
<th>kg IL required / kg CO₂ capture for</th>
<th>Energy Required, ( Q ), (^2) (MMBTU/ton CO₂) for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( P_{CO_2} = 0.1 ) bar</td>
<td>( P_{CO_2} = 1 ) bar</td>
</tr>
<tr>
<td>1</td>
<td>[emim][Tf₂N]</td>
<td>391.31</td>
<td>1.35</td>
<td>-322.66</td>
<td>35.6</td>
<td>83.3</td>
<td>5506 (^2)</td>
</tr>
<tr>
<td>2</td>
<td>[bmim][Tf₂N]</td>
<td>419.37</td>
<td>1.288</td>
<td>-284.03</td>
<td>33</td>
<td>80.1</td>
<td>5325</td>
</tr>
<tr>
<td>3</td>
<td>[bmim][PF₆]</td>
<td>284.18</td>
<td>1.412</td>
<td>-324.93</td>
<td>53.4</td>
<td>137.1</td>
<td>5633</td>
</tr>
<tr>
<td>4</td>
<td>[bmim][BF₄]</td>
<td>226.02</td>
<td>1.570</td>
<td>-315.84</td>
<td>59</td>
<td>147.8</td>
<td>5031</td>
</tr>
<tr>
<td>5</td>
<td>[hmim][Tf₂N]</td>
<td>447.42</td>
<td>1.326</td>
<td>-268.12</td>
<td>31.6</td>
<td>73.6</td>
<td>5604</td>
</tr>
<tr>
<td>6</td>
<td>[hmpy][Tf₂N]</td>
<td>458.45</td>
<td>1.383</td>
<td>-261.30</td>
<td>32.8</td>
<td>73</td>
<td>6177</td>
</tr>
<tr>
<td>7</td>
<td>[bmmim][PF₆]</td>
<td>298.21</td>
<td>1.480</td>
<td>-295.39</td>
<td>61.8</td>
<td>141.9</td>
<td>7401</td>
</tr>
<tr>
<td>8</td>
<td>[bmmim][BF₄]</td>
<td>240.05</td>
<td>1.628</td>
<td>-329.47</td>
<td>61</td>
<td>154.6</td>
<td>5483</td>
</tr>
<tr>
<td>9</td>
<td>[emmim][Tf₂N]</td>
<td>405.36</td>
<td>1.223</td>
<td>-334.01</td>
<td>39.6</td>
<td>102.3</td>
<td>5930</td>
</tr>
<tr>
<td>10</td>
<td>[emmim][BF₄]</td>
<td>197.97</td>
<td>1.598</td>
<td>-295.39</td>
<td>81.06</td>
<td>222.96</td>
<td>5720</td>
</tr>
<tr>
<td>11</td>
<td>[pmmim][Tf₂N]</td>
<td>419.37</td>
<td>1.327</td>
<td>-249.94</td>
<td>38.5</td>
<td>82</td>
<td>6889</td>
</tr>
</tbody>
</table>

\(^*\) Sample Calculations (kg IL required / kg CO₂ capture)

Sample calculations of ionic liquid [emim][Tf₂N] amount (mass) required for CO₂ capture are presented. In the temperature-swing calculations for the recovery of carbon dioxide, the carbon dioxide is absorbed into the ionic liquid solvent at 298 K and then is desorbed from the solvent at 373 K.

\(^2\) For Energy Calculation: \( Q = -\Delta H_{abs} + m.C_p \Delta T \)
**Data:**
Henry’s constant (H) for [emim][Tf2N] at 25 °C = 35.6 bar (from literature)
Henry’s constant (H) for [emim][Tf2N] at 100 °C = 83.3 bar (extrapolated value)
Mol. wt. of [emim][Tf2N] = M\text{IL} = 391.31 g/mol
Mol. wt. of CO\text{2} = M\text{CO2} = 44.01 g/mol

**Henry’s law:** \( P = Hx \)

**Absorption Stage** (298K and partial pressure of CO\text{2} = 0.1 bar)

CO\text{2} Mole faction: \( \frac{x_{\text{CO2}}}{P_{\text{CO2}}} = \frac{0.1}{35.6} = 0.002808989 = 28 \times 10^{-4} \)

Therefore, the mass fraction is:
\[
\frac{M_{\text{CO2}}}{M_{\text{IL}}} = \frac{28 \times 10^{-4}}{1 - 28 \times 10^{-4}} \times \frac{44.01}{391.31} = 3.17 \times 10^{-4} \frac{\text{kg CO2}}{\text{kg IL}}
\]
\[
\text{or} \quad \frac{M_{\text{IL}}}{M_{\text{CO2}}} = 3156.5 \frac{\text{kg IL}}{\text{kg CO2}}
\]

**Desorption Stage** (373 K and bar partial pressure of CO\text{2} = 0.1)

CO\text{2} Mole fraction: \( \frac{x_{\text{CO2}}}{P_{\text{CO2}}} = \frac{0.1}{83.3} = 0.00120048 = 12 \times 10^{-4} \)

Therefore, the mass fraction is:
\[
\frac{M_{\text{CO2}}}{M_{\text{IL}}} = \frac{12 \times 10^{-4}}{1 - 12 \times 10^{-4}} \times \frac{44.01}{391.31} = 1.35 \times 10^{-4} \frac{\text{kg CO2}}{\text{kg IL}}
\]
\[
\text{or} \quad \frac{M_{\text{IL}}}{M_{\text{CO2}}} = 7397.7 \frac{\text{kg IL}}{\text{kg CO2}}
\]

Since this is a temperature swing calculation (not pressure swing), some of the physically absorbed CO\text{2} will still remain in the ionic liquid at 373 K. The amount of CO\text{2} that can be recovered is the difference between the CO\text{2} amount in the IL at 298 K and the CO\text{2} amount in the IL at 373 K.

\[
\Delta \frac{M_{\text{CO2}}}{M_{\text{IL}}} = 3.17 \times 10^{-4} - 1.35 \times 10^{-4} = 1.82 \times 10^{-4} \frac{\text{kg CO2}}{\text{kg IL}}
\]
\[
\text{or} \quad \frac{M_{\text{IL}}}{M_{\text{CO2}}} = 5506 \frac{\text{kg IL}}{\text{kg CO2}}
\]
References


<table>
<thead>
<tr>
<th>Reference</th>
<th>Details</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>73. Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. (2007). Solubility of CO\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, O\textsubscript{2} and N\textsubscript{2} in 1-Hexyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids. <em>Accounts of Chemical Research</em>, vol. 40, no. 11, 1208-1216.</td>
</tr>
</tbody>
</table>
References


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| References |
|-----------------|-----------------|
| 100. | Yang, W.C., Ciferno, J., 2006. Assessment of Carbozyme Enzyme-Based Membrane Technology for CO₂ Capture from Flue Gas. DOE/NELTL 401/072606. |


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