Małgorzata Ewa Zakrzewska

Mestre em Biotecnologia

Mestre em Tecnologia de Protecção do Ambiente

Towards carbon dioxide utilisation: dense phase carbon dioxide and its mixtures with ionic liquids

Dissertação para obtenção do Grau de Doutor em

Química Sustentável

Orientador: Professor Manuel Nunes da Ponte

Professor Catedrático da FCT-UNL

Co-orientadora: Doutora Vesna Najdanovic-Visak

Universidade de Lancaster, Reino Unido

FACULDADE DE
CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Abril 2016

Towards carbon dioxide utilisation: dense phase carbon dioxide and its mixtures with ionic liquids

Małgorzata Ewa Zakrzewska
Faculdade de Ciências e Tecnologia
Universidade Nova de Lisboa

To my parents,

for their unconditional love and support and for always being there for me.

Acknowledgements

First, and most of all, I would like to express my enormous gratitude to Professor Manuel Nunes da Ponte who has been my supervisor for a quite some time already and has always been incredibly helpful and supportive, since the very first day. Professor, I sincerely appreciate your guidance and kind advice that you have provided through all these years, and especially during the weeks prior to handling in this thesis. Thank you for encouraging me to develop my idea in this thesis and for helping me in shaping it. For given trust, I guess, and freedom to work within my own schedule, which was invaluable in learning independence and self-organisation. I am really grateful for the opportunities to attend conferences and course on supercritical fluids. I think no words will ever be enough to express how indebted I am for helping me in the difficult time, for standing up for me and giving me the very much needed support. I consider myself extremely lucky to have a chance to work with such a friendly supervisor, with a great sense of humour and endless patience, and understanding, for my talkativeness.

Particular thanks must also be recorded to my co-supervisor, Doctor Vesna Najdanovic-Visak, for her constant support, availability, and dedication. Vesna, we got to work with each other quite unexpectedly, and in the same way our paths diverged. Even so, I must admit it was a pure pleasure to work with you and I miss it a lot! You started as my “boss”, but then became a friend really smoothly. Always positive, open-minded and (amazingly!) calm, you made the work in the laboratory so enjoyable. Together with Ana Nunes (I should write Doctor Ana Nunes, but it just simply sounds strange Ana), you both became my true friends, who I could always share my doubts with, whether work-related or not. I want to sincerely thank you for listening (and who met me will understand the effort) and words of encouragements or advice. You are two incredible mothers, to which I am really grateful for all the help and support, especially in the times of hormonal roller coaster and pregnancy mood shifts. For putting up with me and all the work we did together, I am honestly grateful!

I cannot forget Doctor Ricardo Couto and Doctor Google - Pedro Lisboa! Guys, I owe you lots of gratitude for being an invaluable support in the lab. For helping me out with building the apparatus, or simply for your advice and pairs of strong hands whenever needed. I have learnt a great deal from you, for which I give to you the most sincere Thank You!

I would also like to thank Doctor Rafał Bogel-Łukasik for introducing me to the world of ionic liquids and supercritical fluids, and teaching me the necessary basics. I am thankful to Doctor Pedro M.P. Gois for the collaboration on the project of lactams formation and to

Professor Carlos A.M. Afonso, and co-workers, for providing, over all these years, necessary ionic liquids.

This thesis would not have been possible without the Doctoral Program on Sustainable Chemistry and the financial support of the “Fundação para a Ciência e a Tecnologia” through the PhD fellowship SFRH/BD/74929/2010.

While almost everybody, at some point in their lives, goes through a period of adjustment (going off to college, beginning or changing a job etc.), moving to a foreign country is a bit more challenging I believe. When you start your “new life” from a scratch, main part of it revolves around your work. It is there where you meet new people and, most probably, make new friendships. I find myself very fortunate for that I have been surrounded with many good people since the very beginning of my life in Portugal.

Here, I would like to address my special Thank You! to Professor Isabel Moura and Doctor Marta S.P. Carepo, with whom my adventure in a new country began. I am truly grateful for a warm welcome in Portugal and for giving me the courage to follow my intuition.

There are no suitable words that could fully describe how thankful I am to Aleksandar Ilić and Jelena Milošević for making me company in this new chapter of my life. Aca, you have been there for me since the beginning, when my usual “emotional support system” – family and closest friends - stayed far away, in Poland. I want to thank you both for these years of living together, having fun and travelling, but also for sharing all the ups and downs of our researches. I am truly grateful for your support, understanding, advice and care.

I am also more than thankful to all people at work who made this PhD journey so enjoyable and unforgettable. There are too many names to mention individually, however I really need to give some special thanks to some of the people; to Joana Lopes and Catarina Melo (for all the work we did together “meninas”), Joana Afonso, Sofia Messi(as), Margarida Sousa, and Ana Inês Paninho (for all the positive energy, and gossip, in the lab. 512), Vanessa Correia, Patrícia Morgado, Carmen Alicia Moreno Montoya, Vanessa Almeida, Sara Correia, Anita Lourenço, Márcia Tavares (for being such a great company in the office and for all the fun, laughs, and…wait for it…snowballs!), Teresa Casimiro, Vasco Bonifacio and Zoran Visak (for all the “chit-chats” and making the working environment so friendly!), and to Iwona Bernacka-Wójcik and Paweł Wójcik (for all lunch breaks and for going through the most important plan of our lives together and talking about it in polish!). It’s really the little things that make all the difference and thank you all for really great memories!

My deepest gratitude though, goes to my family, especially to my parents, Dorota and Andrzej, without whom this thesis would not have been possible at all!

> Dziękuję za cały trud wychowania, za miłość, za nieocenioną pomoc i wsparcie, ale przede wszystkim dziękuję Wam za waszą wiarę w to, że mi się uda. Już jako rodzic, rozumiem jak ciężką decyzję mieliście do podjęcia zgadzając sie na moje życie tak daleko od domu i jestem wam za to bardzo wdzięczna!

I am also very grateful to my new "Portuguese" family, my husband João and parents-in-law, Julieta and Pedro, who helped me a lot during these last few months by taking care of our adorable and wonderful, yet very active and quite noisy, daughters. Writing the thesis wouldn't be the same without their help and for that I want to say Thank You!

Finally, I am really grateful for Portuguese expresso, coffee-flavoured candies called Kopiko and I would like to apologise to my bathroom scale for calling it a liar, repeatedly, during these last few weeks of writing this thesis.

Abstract

Compressed carbon dioxide, either by itself or in combination with an ionic liquid, can serve as a promising reaction/separation medium for many potential applications. This work addresses the subject of solubility of carbon dioxide in relatively new, or less explored, families of ionic liquids, and its influence on particular properties, i.e. volume expansion or melting point depression. For the purpose of measuring carbon dioxide solubility at high pressures, a new, especially designed apparatus, was custom-built and its detailed description is provided here. The application of carbon dioxide as a solvent for a process and subsequent separation of product is discussed, giving a perfect example of the currently developing field of carbon dioxide utilisation.

Ionic liquids based on tris(pentafluoroethyl)trifluorophosphate and tetracyanoborate anions coupled to 1-alkyl-3-methylimidazoilum cations presented one of the greatest capacities for carbon dioxide capture by physisorption mechanism among ionic liquids investigated in the literature. Exceptional volume expansions of the liquid phase upon carbon dioxide dissolution, reaching values of approximately 55 and 60 % for ionic liquids bearing fluoroalkylphosphate or tetracyanoborate anion, respectively, have been found. Results seem to confirm that the high carbon dioxide solubility is a consequence of the weak coordination between anion and cation, which allows for easy creation of cavities and more CO_2 molecule accommodation. Although still much smaller than commonly observed for mixtures of carbon dioxide and organic solvents, this notably high volume expansion of IL-CO_2 systems validates the free volume effect and the interspace filling mechanism of dissolution.

The solubility of carbon dioxide in ammonium-based ionic liquids, which display abnormally high carbon dioxide-induced melting point depressions was carried out. These solubilities do not show any positive correlation with previously measured melting temperature depressions.

Finally, a successful example of an application of carbon dioxide as both reaction and extraction medium in the process of C-H insertion of diazoacetamides is given. The process produces the expected lactam in yields over 97 %. Recycling experiments proves that carbon dioxide is capable of selectively extracting the product, leaving the catalyst behind for its reutilisation.

Key words: ionic liquid, supercritical carbon dioxide, high-pressure solubility, volume expansion, melting point depression, supercritical extraction

Resumo

O dioxide de carbon comprimido, quer por si próprio, quer em combinação com um líquido iónico, constitui um meio de reação/separação prometedor para muitas aplicações. Este trabalho foca o assunto da solubilidade de dióxido de carbono em famílias de líquidos iónicos desenvolvidas recentemente, ou menos exploradas, e da sua influência em propriedades específicas da mistura, a expansão volumétrica e o ponto de fusão. Para efeito da medida da solubilidade de dióxido de carbono a altas pressões, foi propositadamente projetada e construída uma nova instalação experimental, cuja descrição detalhada é feita nesta tese. Discute-se também uma aplicação de dióxido de carbono como solvente num processo químico com subsequente separação do produto, proporcionando um exemplo perfeito da árae em desenvolvimento da "utilização de dióxido de carbono".

Os líquidos iónicos baseados em aniões tris(pentafluoroetil)trifluorofosfato ou tetracianoborato e com catião 1-alquil-3-metilimidazólio apresentam das maiores capacidades de captura por fisissorção de dióxido de carbono de entre os referidos na litaeratura. Neste trabalho foram obtidas expansões volumétricas por dissolução de dióxido de carbono de 55% e 60% para os líquidos iónicos com aniões trifluorofosfato ou tetracianoborato, respetivamente. Estes resultados parecem confirmar que a alta solubilidade nestes líquidos iónicos é coinsequência duma fraca coordenação anião-catião, que permite uima criação mais fácil de cavidades e uma melhor acomodação de moléculas de CO_2. Embora esta ordem de grandeza das expansões volumétricas seja muito inferior às registadas para solventes orgânicos, elas são notavelmente altas para sistemas IL-CO_2 e constituem uma validação dum mecanismo de dissolução através dum efeito de volume livre e de preenchimento de espaço interiónico.

Foi também estudada a solubilidade de dióxido de carbono na fase líquida de sais de amónio que apresentam depressões anormalmente altas da temperatura de fusão em contacto com CO_2 sob pressão. Não foi encontrada nenhuma correlação positiva entre a solubilidade e a depressão crioscópica destes sais/líquidos iónicos.

Finalmente, apresenta-se um exemplo da aplicação com sucesso de dióxido de carbono simultaneamente como meio reacional e de extração no processo de inserção C-H em diazoacetamidas. O processo produz a lactama esperada com rendimentos superiores a 97%. O CO2 extrai seletivamente o produto, deixando o catalisador no meio reacional para futura reutilização.

Palavras chave: líquidos iónicos, dióxido de carbono supercrítico, solubilidade a alta pressão, expansão de volume, depressão do ponto de fusão, extração supercrítica

Table of contents

Figure captions

Table captions

List of abbreviations

Cations:

$[(C_{12}H_{25})_2(CH_3)_2N]$	didodecyldimethyl**ammonium**
$[(C_2H_5)NH_3]$	ethyl**ammonium**
$[(C_4H_9)_4N]$	tetrabutyl**ammonium**
$[(C_5H_{11})_4N]$	tetrapentyl**ammonium**
$[(C_6H_{13})_4N]$	tetrahexyl**ammonium**
$[(C_8H_{17})_3(CH_3)N]$	trioctylmethyl**ammonium**
$[(iC_4H_9)3(CH_3)N]$	methyl-tris(2-methyl-propyl)**ammonium**
[bmim]	1-butyl-3-methyl**imidazolium**
[C$_{16}$mim]	1-hexadecyl-3-methyl**imidazolium**
[emim]	1-ethyl-3-methyl**imidazolium**
[HCC-C$_1$mim]	1-propargyl-3-methyl**imidazolium**
[hmim]	1-hexyl-3-methyl**imidazolium**
[NC-C$_1$mim]	1-ethanenitrile-3-methyl**imidazolium**
[NH$_2$-bmim]	1-n-propylamine-3-methyl**imidazolium**
[p$_5$mim]	1-pentyl-3-methyl**imidazolium**
$[(N_{11})_2CH]$	N-((dimethyl-amino)methylene)-N-methyl**methanaminium**
[C$_4$Py]	1-butyl**pyridinium**

Anions:

[Ac]	acetate
$[B(CN)_4]$	tetracyanoborate
$[BF_4]$	tetrafluoroborate
[bFAP]	tris(pentafluorobutyl)trifluorophosphate
[Br]	bromide
$[C(CN)_3]$	tricyanomethane
$[CF_3SO_3]$	trifluoromethanesulfonate
[eFAP]	tris(pentafluoroethyl)trifluorophosphate
[FAP]	tris(pentafluoroalkyl)trifluorophosphate
[methide]	tris(trifluoromethylsulfonyl)methide
$[N(CN)_2]$	dicyanamide
$[NO_3]$	nitrate
[NTf$_2$]	bis(trifluoromethanesulfonyl)amide
$[PF_6]$	hexafluorophosphate anion

[sac]	saccharine
[tos]	tosylate

Compounds:

$CDCl_3$	deuterated chloroform
CH_2Cl_2	dichloromethane
CH_4	methane
CO_2	carbon dioxide
N_2O	nitrous oxide
$Rh_2(OAc)_4$	tetra-acetate dirhodium(II) complex
$Rh_2(Ooct)_4$	tetratkis octanoate dirhodium(II) complex
$Rh_2(pfb)_4$	tetratkis perfluorobutanoate dirhodium(II) complex
$Rh_2(S\text{-}PTPA)_4$	chiral dirhodium(II) complex (see Appendix C)
$Rh_2(S\text{-}PTTL)_4$	chiral dirhodium(II) complex (see Appendix C)

Other:

ATR-IR	attenuated total reflection infrared spectroscopy
CCS	carbon capture and storage
CCU	carbon capture and utilisation
COP	The Conference of the Parties
GHG	greenhouse gases
GXL	gas expanded liquid
IL	ionic liquid
IPCC	The Intergovernmental Panel on Climate Change
MPD	melting point depression
NMR	nuclear magnetic resonance
P_0	atmospheric pressure
P_c	critical pressure
$scCO_2$	supercritical carbon dioxide
scF	supercritical fluid
SLV	solid-liquid-vapour
T_c	critical temperature
TLC	thin layer chromatography
TSIL	task specific ionic liquid
UNFCCC	The United Nations Framework Convention on Climate Change
WCED	The World Commision on Environment and Development

1. Introduction

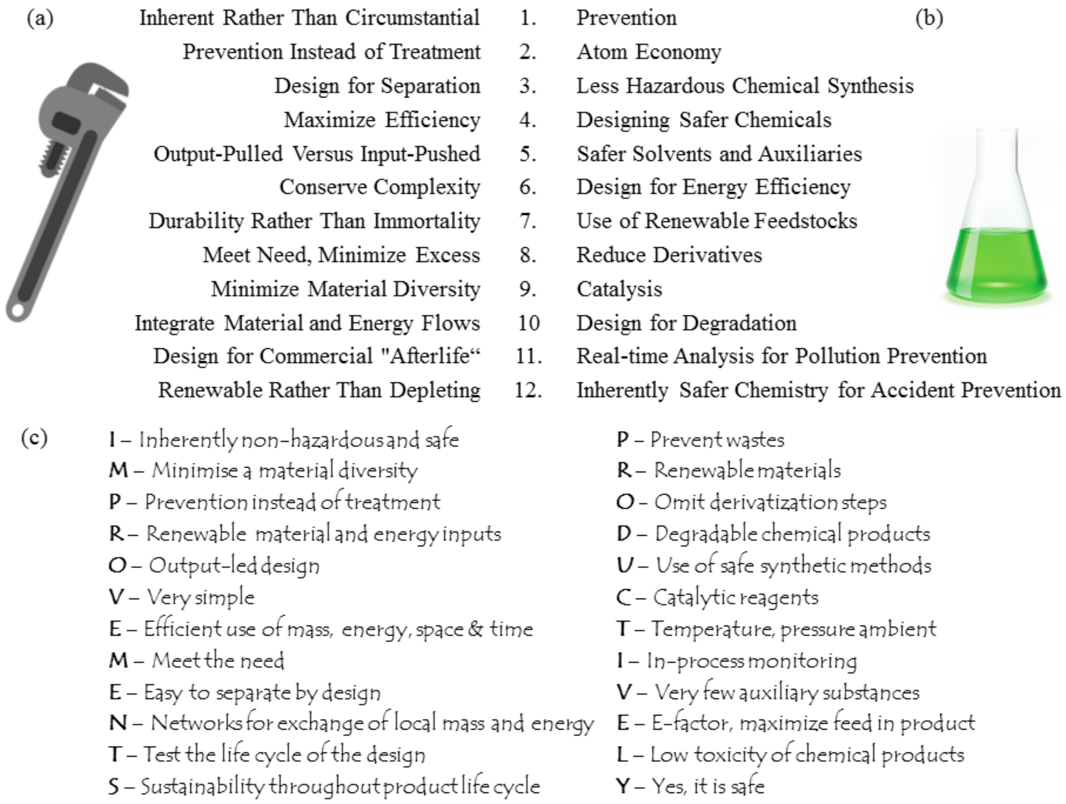
1.1. Problem definition

Within the worldwide efforts to combat global warming and to reduce the amount of carbon dioxide released to the environment, new strategies for carbon dioxide capture are being developed. As a result, it can be predicted that captured and compressed carbon dioxide will become a readily available and cheap feedstock, leading to a demand for new, environmentally friendly pathways for its utilisation.

1.2. Problem description

The World Commission on Environment and Development (WCED) by The United Nations Framework Convention on Climate Change (UNFCCC) defines sustainable development as “meeting the needs of the present generation without compromising the ability of future generations to meet their own needs” [1]. Sustainable development refers to the concept that the present generation should seek for resources and methods that do not compromise the welfare of future generations. This is closely linked to the definition of Green Chemistry given by the US Environmental Protection Agency “as the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances; green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal” [2]. That is: “If Sustainability is the goal, Green Chemistry will show the way!” [3].

The underlying idea of Green Chemistry is “benign by design” of both products and processes [4]. The strategy is concisely included within “12 Principles of Green Chemistry” proposed by Anastas and Warner nearly 20 years ago (Figure 1.1b) [5]. These principles, together with 12 Principles of Green Engineering, presented by Anastas and Zimmerman [6] shortly afterwards [Figure 1.1a], serve as a key to the evolution of sustainable technologies. More recently, Poliakoff and co-workers summarised Green Chemistry and Green Engineering principles in the readily communicative form of mnemonics (Figure 1.1c) [7,8].



(a)

Inherent Rather Than Circumstantial
Prevention Instead of Treatment
Design for Separation
Maximize Efficiency
Output-Pulled Versus Input-Pushed
Conserve Complexity
Durability Rather Than Immortality
Meet Need, Minimize Excess
Minimize Material Diversity
Integrate Material and Energy Flows
Design for Commercial "Afterlife“
Renewable Rather Than Depleting

(b)

1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Synthesis
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10 Design for Degradation
11. Real-time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

(c)

I – Inherently non-hazardous and safe
M – Minimise a material diversity
P – Prevention instead of treatment
R – Renewable material and energy inputs
O – Output-led design
V – Very simple
E – Efficient use of mass, energy, space & time
M – Meet the need
E – Easy to separate by design
N – Networks for exchange of local mass and energy
T – Test the life cycle of the design
S – Sustainability throughout product life cycle

P – Prevent wastes
R – Renewable materials
O - Omit derivatization steps
D – Degradable chemical products
U – Use of safe synthetic methods
C – Catalytic reagents
T – Temperature, pressure ambient
I – In-process monitoring
V – Very few auxiliary substances
E – E-factor, maximize feed in product
L – Low toxicity of chemical products
Y – Yes, it is safe

Figure 1.1. a) 12 Principles of Green Engineering [6]; b) 12 Principles of Green Chemistry [5]; c) Mnemonic version of the 24 principles of Green Chemistry and Green Engineering [7,8].

Design, development and implementation of any industrial process should follow “green principles” in order to minimise the environmental footprint. There are numerous ways to improve “green-ness” of a process (Figure 1.2) [9,10]; for example, by utilisation of renewable raw materials, reduction/elimination of waste, energy conservation, avoidance or replacement of toxic and/or hazardous substances with safer and/or more environmentally friendly ones.

Hydrogen economy					IMPROVEMENTS		PRODUCTIVELY	Core ideas									Heterogeneous catalysis
Low toxicity	Better efficiency											Benign	Clean	Neoteric solvents	Omit derivatisation	Functionalisation	Networks for exchange
Naturally derived	More green											Alternatives	Single pot reaction	Photochemistry	Safe	Cleaner processes	Clean Air
Kinetics	Creative analysis	Supercritical fluids	Think innovatively	Very simple	Catalytic reagents	Meet the need	Fail-safe mechanisms	Continuous flow	No impurities	Cellulose	OZone layer	Global partnership	Green energy	Asymmetric synthesis	Separation	Batch reactions	Knowledge driven
Renewables	Solvent reduction	Yes, it's safe	Zero emissions	No by-products	Microwave heating	Test life cycle	Reuse	Recover heat	Problem free disposal	Agricultural materials	Commercial design	In process monitoring	Solvent free	Sustainability	Micro reactor Tech	Ionic liquids	Recycle eXcess energy
Carbon capture & storage	Bulk chemicals	Life-cycle assessment	Hazard free	Temperature ambient	Water	Renewable energy	Output led design	Inherently safe	Prevent instead of treat	Auxiliary substances	Homogeneous catalysis	Twelve principles	Positive benefits	Biocatalysis	Polymers	Atom economy	Recycling
Flow reactors	Real time analysis	Ambient conditions	Risk free	Degradable	Safeguard our future	No Bio hazards	Highly selective	Metathesis	Avoid Derivatives	Really green	Commercial production		Fluorous biphasic		Long-term value		
		Conserve energy	Prevent waste	New designs	Process monitoring	Smart materials	Efficient use	Good durability	Think big	Design simplicity	Holistic view	E-Factor	Space Time efficient	Your backyard	Less uncertainty		
		High Throughput	Pressure ambient	Use safe methods	Nanoparticles	Pollution prevention	Appropriate materials	Conserve mass	Biological feed stocks	Carbon footprint	Easy separation	Free of metals	Minimise material diversity	Non-toxic	Less resources		

Figure 1.2. A periodic table of Green Chemistry [9].

Energy and the environment are two of the most important issues this century. Anthropogenic emissions of greenhouse gases (GHG) have increased since the pre-industrial era, driven largely by economic and population growth, reaching a value of 49 ± 4.5 gigatonne of CO_2-equivalent per year ($GtCO_2$-eq/yr) in 2010, the highest value in History [11]. Concentrations of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases (hydrofluorocarbons, perfluorocarbons, and sulphur hexafluoride) have all shown large increases since 1750 (Figure 1.3). The energy-related emissions account for roughly two-thirds of all anthropogenic GHG emissions today [12,13]. Emissions of carbon dioxide from fossil fuel combustion and industrial processes contributed to about 78% of the total GHG emissions increase from 1970 to 2010.

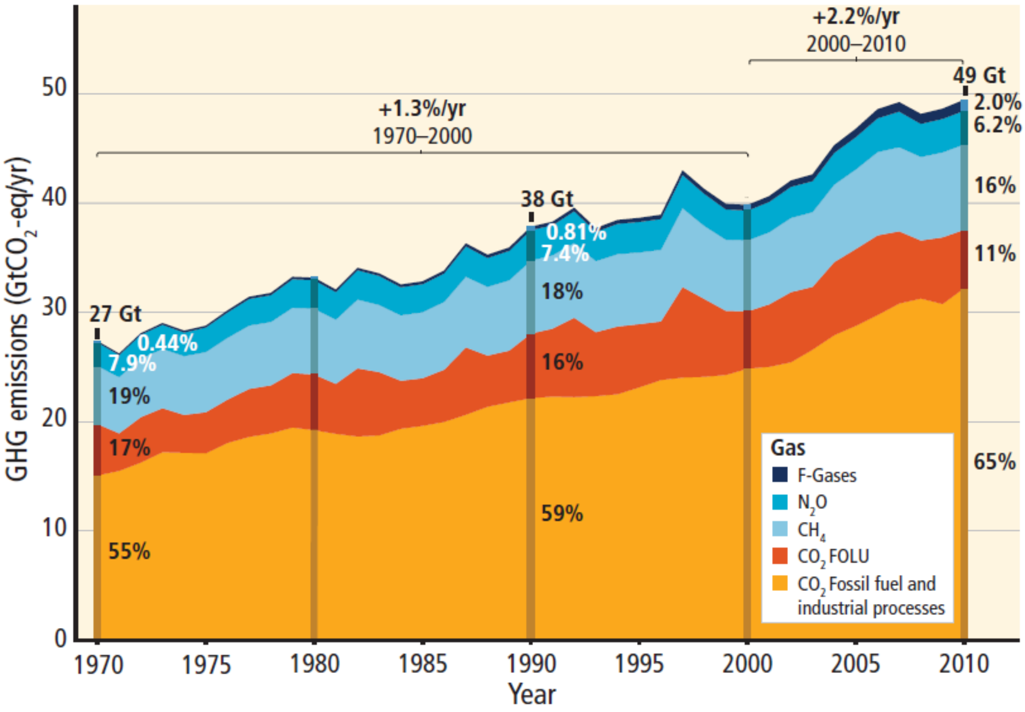


Figure 1.3. Total annual anthropogenic GHG emissions for the period 1970 to 2010. FOLU stands for Forestry and Other Land Use [11].

The international political response to climate change had its beginning at the Rio Earth Summit in 1992, where UNFCCC was adopted. The objective of the convention is to “stabilise atmospheric concentrations of greenhouse gases at a level that will prevent dangerous interference with the climate system” [14]. The annual Conferences of the Parties (COP) are intended to review the Convention’s implementations. Very recently, during the last session in Paris, COP21, a universal agreement on climate emergency has been achieved [15]. All of the 196 parties to the UNFCCC agreed to reduce their GHG emissions in order to limit global temperature rise to less than 2°C, with an aspirational target of a 1.5°C boundary, by 2100.

According to the research of the Intergovernmental Panel on Climate Change (IPCC), a temperature increase of over 2°C would lead to serious consequences, such as greater frequency of extreme climate events [11].

Stabilising temperature increase to below 2°C will require substantial and sustained reductions in global emissions by 40 to 70% till 2050, compared to 2010, and near zero emissions in 2100. Taking into consideration the scale of energy-related emissions, the power sector transformation is central to limit global warming. In recent years, progress has been made in developing cleaner and more efficient energy technologies. It was observed that while the global economy had grown by around 3% in 2014, the energy-related carbon dioxide emissions had stayed flat, mainly due to usage of low-carbon energy sources. This is the first time in at least 40 years that such an outcome has not been tied to an economic crisis. However, increased efforts are still needed in order to attain the ambitious goal of remaining under the 2°C. The recent COP21 (21st Session of the Conference of the Parties), held in Paris in December 2015, ended in a comprehensive agreement on a scale that had never been approached before. Each country attending the COP21 will need to estimate its individual contribution to the globally adopted plan, according to national circumstances, capabilities and priorities, for the benefit of future generations.

Adaptation, understood as adjustment to actual or expected climate and its effects, and mitigation, as intervention to reduce the sources or enhance removal of GHGs, are complementary approaches for reducing risks of climate change within the framework of sustainable development [11]. A potential mitigation scheme includes capture of carbon dioxide, from carbon dioxide point-sources [16,17,18], or directly from the atmosphere [19,20,21,22], to obtain concentrated carbon dioxide and subsequent sequestration (Carbon Capture and Storage, CCS) or alternative functional utilisation (Carbon Capture and Utilisation, CCU). In the first solution, compressed carbon dioxide is simply transported to a storage location, i.e. terrestrial or marine reservoir, for long term isolation from the atmosphere [23,24,25]. The second option concerns utilisation of carbon dioxide as a product, i.e. as a versatile processing fluid [26,27], or its conversion into other useful products [28,29,30,31,32]. Global emissions and increased interest in large-scale carbon dioxide capture technologies will result in an abundance of easily available and cheap carbon dioxide as a non-depleting, thus a renewable, feedstock. Therefore, new environmentally friendly methods for carbon dioxide utilisation, either as reaction/separation medium or as a reagent, or even as both simultaneously, will be of great value.

1.3. Scope, objectives and structure of the thesis

1.3.1. Scope

Compressed, supercritical carbon dioxide ($scCO_2$) and ionic liquids (ILs), or, in particular, biphasic systems composed of them ($scCO_2$/ILs system), are examples of systems that may lead to improvements in reaction and processing technologies, beyond just simply replacing hazardous conventional solvents. The search for alternative, more environmentally friendly solvents is perhaps the most active area of the Green Chemistry field, in both industry and academia [33,34,35,36]. Solvents are one of the major contributors to industrial waste streams. Many conventional solvents are toxic, flammable, and/or corrosive. Their recovery and recycle, if possible, is usually associated with energy-intensive distillation and can cause cross-contamination. A "green" solvent can be defined as "a solvent that addresses environmental issues, contributes to the optimisation of the overall process, and is cost-effective" [34]. In industry, the choice of solvent depends on a specific process or application. It is less important how "green" the solvent is itself, if it can make the overall process more sustainable [33].

In recent years, the strong interest in these two alternative solvents is primarily driven by two reasons, i.e., their potential application in advanced devices and processes, and scientific curiosity to understand underlying structure-property correlation. The latest research has been so far mostly centred on the usage of ionic liquids as solvents for reactions involving permanent gases, gas separation or storage applications, for instance CCS, and the use of gases (mainly carbon dioxide) to separate solutes from ionic liquids solutions.

The scope of this work is to investigate the properties of carbon dioxide + ionic liquids mixtures, as well as the evaluation of the possibility of using compressed carbon dioxide as reaction/separation medium.

1.3.2. Objectives

The main objective of this thesis is to determine the solubility of carbon dioxide in relatively new, or less explored, families of ionic liquids, and its influence on particular properties, i.e. volume expansion or melting point depression. Additionally, it aims at verifying the feasibility of carbon dioxide as both reaction and extraction media in the process of C-H insertion of diazoacetamides leading to formation of lactams, biologically active heterocycles.

Thus far, the most investigated ionic liquids are those based on imidazolium cations coupled with hexafluorophosphate, tetrafluoroborate or bis(trifluoromethanesulfonyl)amide anions. Although ammonium-centred ionic liquids provide a cheaper and easier to synthesise alternative, not much carbon dioxide solubility data can be found in the literature. Regarding anions, relatively new classes of fluoroalkylphosphate- and tetracyanoborate-based ionic liquids are gaining more attention due to their advantageous characteristics. It has been found already several years ago that ionic liquids with fluoroalkylphosphate anions show improved capability to capture carbon dioxide, compared with other ionic liquids reported in literature [37,38]. Not only till a few years ago though, the research became interested in these ionic liquids for their potential application in carbon dioxide capture/separation from exhaust gas streams of power plants or natural gas resources [39,40,41,42,43,44]. Ionic liquids with tetracyanoborate anion, besides exhibiting high carbon dioxide solubility, are characterised by low viscosity, which is very important in a perspective of potential gas processing applications [45,46].

β-lactam compounds demonstrate biological activity as inhibitors of a wide range of enzymes. Unfortunately, they are typically prepared in organic solvents, e.g. dichloromethane [47]. New catalytic processes for their synthesis, employing more benign reaction media, are therefore required. Dense-phase carbon dioxide may serve as a reaction solvent and extraction medium for products in supercritical extraction process.

1.3.3. Structure of the thesis

The present chapter describes the problem of worldwide climate change and explains the urgency for the reduction of greenhouse gases emission. It introduces the concept of sustainable development and Green Chemistry as possible pathways to combat global warming. The scope and objectives of the thesis were defined here.

The other chapters are organised as follows:

Chapter 2 – **Background**

A brief overview of alternatives to traditional organic solvents is given. Characteristic properties, challenges and applications of ionic liquids, dense-phase carbon dioxide, and a biphasic system composed of thereof are described in a view of sustainable development.

Chapter 3 – **Case study 1**

The solubility of high-pressure carbon dioxide in ammonium-based ionic liquids, exhibiting carbon dioxide-induce melting point depression, is reported. The study aims at determining whether there exists any correlation between the magnitude of solubility and the decrease in melting temperature upon carbon dioxide dissolution.

The described work was published in *Fluid Phase Equilibria* [48], and presented at 11th International Conference on Carbon Dioxide Utilisation in Dijon, France, in a form of a poster (*M.E. Zakrzewska, V. Najdanovic-Visak, M. Nunes da Ponte, "Solubility of* CO_2 *in quaternary ammonium ionic liquids"*).

Personal contribution:

Małgorzata E. Zakrzewska was responsible for the experimental work performed under high-pressure carbon dioxide. All syntheses and analyses of ionic liquids were performed by Professors Carlos A.M. Afonso and co-workers, at the Faculty of Pharmacy of the University of Lisbon.

Chapter 4 - **Case study 2**

Volumetric and phase behaviour of mixtures of ionic liquids based on tetracyanoborate and tris(pentafluoroethyl)trifluorophosphate anions with high pressure carbon dioxide are presented. The high solubility of carbon dioxide in the studied ionic liquids, as well as the considerably larger volume expansion of the liquid phase, brings on speculations about the origins of such behaviour.

The described work was published in *Journal of Supercritical Fluids* [49,50]. Previously, some results were presented at the 41st Conference on Phase Equilibria in Coimbra, Portugal, in a form of a poster (*M.E. Zakrzewska, M. Nunes da Ponte, "Solubility of* CO_2 *in fluoroalkylphosphate ionic liquids"*), and at the 2nd EuCheMS Congress on Green and Sustainable Chemistry in Lisbon, Portugal, in a form of an oral presentation (*M.E.Zakrzewska, M. Nunes da Ponte, "Ionic liquids that expand upon carbon dioxide dissolution"*).

Chapter 5 – **Case study 3**

The potential application of carbon dioxide as both reaction medium (for the intramolecular C-H insertion of diazoacetamide catalysed by dirhodium(II) complexes), and separation solvent in supercritical extraction, is discussed. The results were published in *Green Chemistry Letters and Reviews* journal [51].

Personal contribution:

Małgorzata E. Zakrzewska was responsible for experimental work performed under high-pressure carbon dioxide. All syntheses and analyses were performed by Professor Carlos A.M. Afonso and Pedro Gois, and co-workers, at the Faculty of Pharmacy of the University of Lisbon.

The last section provides conclusions and future perspectives for these research topics.

2. Background

2.1. Ionic liquids – custom-made media

Ionic liquids are composed entirely of ions, a bulky organic cation weakly coordinated to either an organic or an inorganic anion. The weak coordination and asymmetry of ions result in a reduction in the lattice energy and crystalline structure of the ionic liquid, and thus, lowers its melting point. The melting temperatures of ionic liquids are below 373.15 K. They also display a wide (200 – 300 K) liquid range [52]. Examples of some ions constituent of common ionic liquids can be found in Figure 2.1.

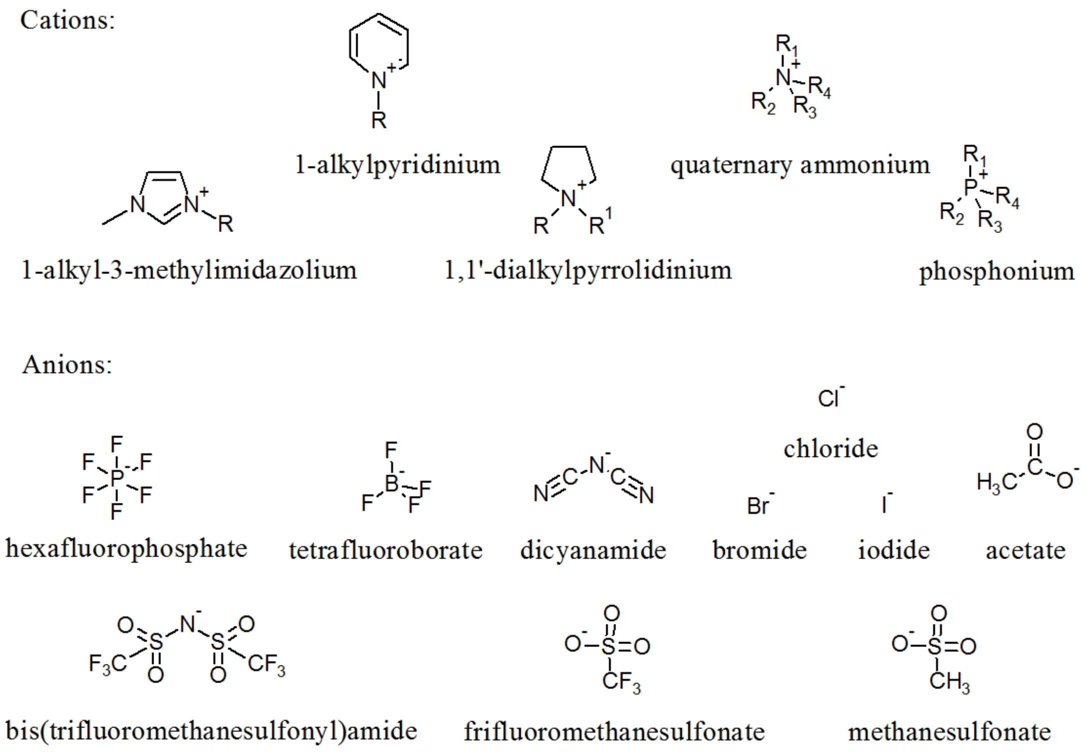


Figure 2.1. Ions in common ionic liquids.

Although the first low melting salt, ethylammonium nitrate ($[(C_2H_5)NH_3][NO_3]$), with melting point of 285.15 K, was synthesised by Paul Walden in 1914 [53], the golden age of ionic liquids began only in the late 1990s [54,55,56]. Early investigations used mainly haloaluminate-based ionic liquids (so called first generation ionic liquids), which unfortunately are very reactive towards certain materials and unstable in the presence of water [57,58,59,60]. The first water- and air-stable ionic liquids, developed in 1992 by Wilkes and Zaworotko [61], included 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) and 1-ethyl-3-methylimidazolium acetate ([emim][Ac]). Since then, there has been a dramatic growth in the development of new, water-stable (referred as second generation) ionic liquids [62,63]. It is estimated that there are approximately 10^{18} possible combinations of ionic liquids [64]. Recently, a third generation of “task specific” ionic liquids (TSILs) have emerged [65,66,67]. These novel ionic liquids possess chemical functionalities designed for particular applications.

Being composed entirely of ions, ionic liquids possess an abundance of charge carriers and, as such, appear a perfect choice for many electrochemical applications. It has been shown that ionic liquids have wide electrochemical window (even up to 7 V), broad range of ionic conductivity (0.1-20 mS/cm) and negligible vapour pressure, indicating that they are non-flammable and thus can be used safely [68,69,70]. In fact, ionic liquids first utilisations were as solvents in studies of solution electrochemistry, electrodeposition, and as electrolytes in electrochemical devices, i.e. semiconductors or batteries [71,72,73]. Ionic liquids have high chemical stability and excellent dissolving power for a wide range of compounds. However, among many useful properties, there are three particularly important intrinsic properties that distinguish ionic liquids from conventional organic solvents and water, i.e., nonvolatility, thermal stability and tunability [52,74]. Negligible vapour pressure eliminates loss of the solvent to the air, and thus, the negative impact on the environment, and reduces working exposure hazards. Additionally, in case of separation of reaction product by vapour phase, ionic liquids do not cause any contamination and can be easily recycled and reused. High thermal stability (decomposition temperature normally above 573.15 K [52]) makes ionic liquids suitable for higher temperature applications. However, it is the unique tuneable/designer nature of ionic liquids that may prove to be their most useful feature. Structure and properties of ionic liquids can be easily tailored, by changing cation/anion combinations and/or by attaching functional groups. Properties such as, for example, melting point, viscosity, conductivity or hydrophobicity, can be optimised according to the requirements of the intended use.

Ionic liquids are intrinsically heterogeneous liquids, with regions of high polarity, where the electrical charges of cations and anions group together, and other regions of low polarity, where the hydrocarbon tails of the cations superimpose on each other [75]. Such a self-organisation of ionic liquids creates spatially heterogeneous nonpolar domains embedded into the charged network. As a consequence, ionic liquids are able to dissolve both inorganic and organic compounds.

Ionic liquids have a large number of potential applications in many fields, such as electrochemistry, synthesis and catalysis, process technology, biorefinery, pharmaceuticals or functional fluids (lubricants, surfactants, anticorrosive agents), to mention just a few [70,76,77,78,79,80,81,82,83]. Recently, there is a considerable interest in ionic liquids as gas processing media. It has been observed that ionic liquids exhibit large solubility differences among various gases [84]. Carbon dioxide usually shows a higher solubility in ionic liquids than other gases, such as carbon monoxide, oxygen, nitrogen, hydrogen, methane, ethane or ethylene. This high solubility, combined with the desirable selectivity, makes ionic liquids an interesting alternative for carbon dioxide removal from exhaust gas streams of power plants or natural gas sources [40,85,86,87,88,89].

However, there are some challenges related to any application of ionic liquids on an industrial scale, which need to be addressed before any process commercialisation. From all theoretically possible cation/anion combinations, only a limited number of ionic liquids are, at the same time, actual liquids near room temperature and possess selected characteristics for a particular application. Moreover, ionic liquids are very expensive when compared to conventional solvents. They are also more viscous, which can lead to problems with mass transfer (lower reaction rates, extraction efficiencies, etc.) [90]. The smaller solubility of various gases, which was mentioned previously as an advantage for carbon dioxide separation, will be a disadvantage in case of reactions in ionic liquids that involve gaseous reagents [91]. Environmental impact, toxicity and biodegradability have yet to be fully examined [92,93,94].

Separation and recovery of ionic liquid seems to be one of the major challenges in future industry applications [95]. Due to their negligible vapour pressure, extraction of non-volatile products with organic solvent and distillation of volatile solutes/impurities from ionic liquids are still the most common separation methods used. These approaches are energy demanding and costly. Additionally, liquid-liquid extraction suffers from cross-contamination between phases and further organic waste production. Extraction with supercritical carbon dioxide is an alternative strategy that can separate both volatile and relatively non-volatile compounds from ionic liquid, without any contamination of the ionic liquids phase.

2.2. Supercritical fluids – an attractive process tool

A supercritical fluid (scF) is a fluid heated to above its critical temperature and compressed to above its critical pressure (Figure 2.2). At these conditions, the distinction between the gas phase and the liquid phase does not exist. As the temperature is raised, the density of a liquid decreases due to expansion, whereas the density of a gas increases due to increase in pressure. Under supercritical conditions densities become identical and vary rapidly with temperature and pressure. As a result, the thermophysical properties of supercritical fluids are also very sensitive to small changes in operating conditions, and hence, can be easily adjusted by small modifications of temperature and/or pressure. Supercritical fluids have the ability to diffuse through materials like a gas (lower viscosities or enhanced diffusion coefficients compared to traditional solvents), and to dissolve organic compounds like a non-polar solvent. The special combination of these properties makes them excellent solvents for various applications.

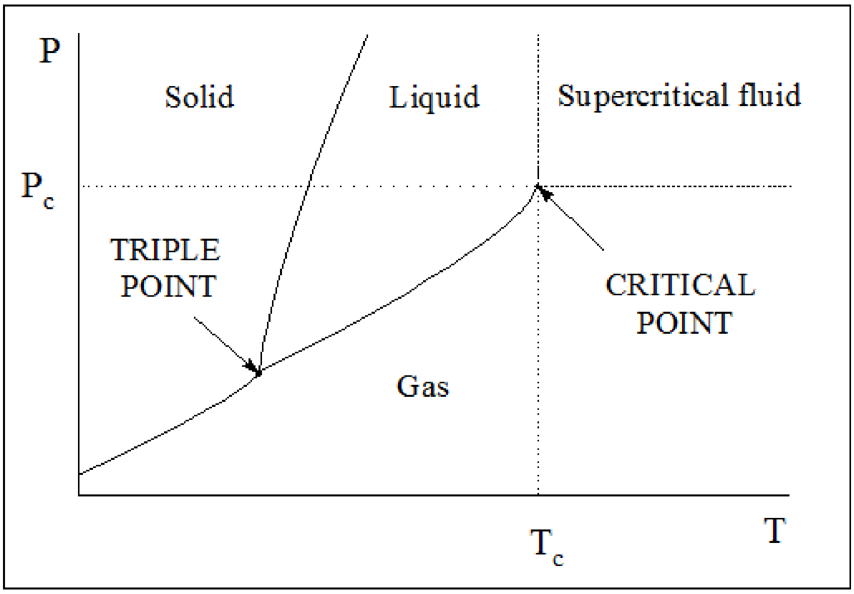


Figure 2.2. Pressure-temperature phase diagram.

Supercritical fluids are a tool that brings benefits, not only in the form of a replacement for volatile organic solvents, but also by improving products and processes [96]. There exist already several processes with supercritical fluids developed to commercial scale in pharmaceutical, food, and textile industries, and a large number and diversity of new potential applications are continuously being reported [26,97,98,99,100,101]. The early applications of supercritical fluids were extraction and separation, with the first major industrial application being decaffeination of roasted coffee beans using supercritical carbon dioxide [102]. Nowadays, supercritical fluids serve as solvents for reactions and extraction of solids and liquids, as heat carriers, refrigerant, or in materials processing, just to name a few.

Theoretically, any compound can be used in its supercritical state. However, what decides about its suitability for a particular application is mainly its technical viability (critical parameters, P_c and T_c), solvation power, toxicity and cost. Carbon dioxide (T_c = 304.25 K, P_c = 7.38 MPa) is the most common choice, because of its critical temperature just above room temperature, and its non-flammability, non-toxicity, and affordability (it is inexpensive and abundant as a major industrial waste) [103].

Carbon dioxide is only slightly polar, as it has a permanent quadrupole. Its solvent power is therefore generally low, and highest towards non-polar or slightly polar solutes, and it decreases with increasing molecular weight of the solute. It may cause some limitations due to the lack of solubility of polar organic compounds and currently used catalysts. However, as mentioned before, the density of carbon dioxide dramatically increases with pressure (Figure 2.3) [105], and so does solvent power. In order to ensure complete solubilisation of reactants, commercial reactions are typically carried out at pressure higher than 10 MPa, and in a very narrow temperature window (below 343.15 K).

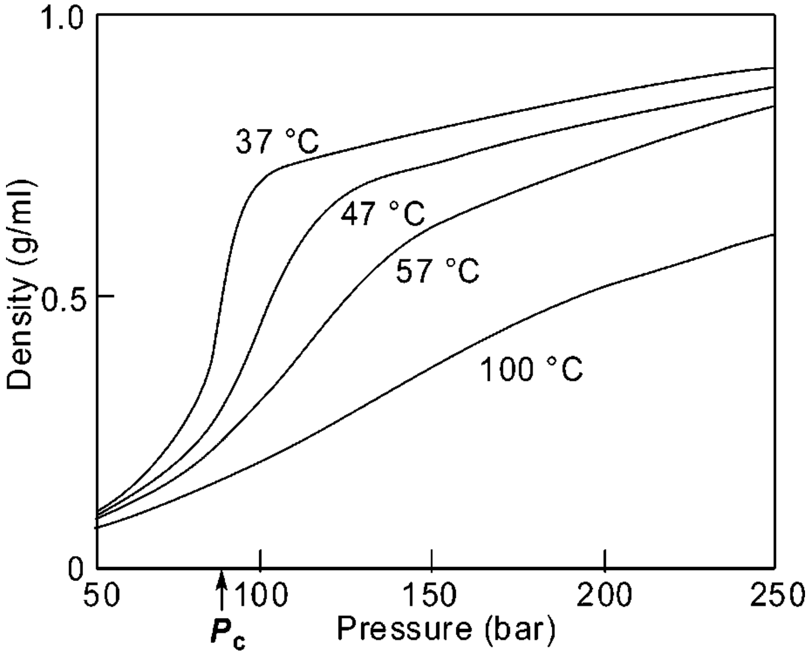


Figure 2.3. Variation of CO_2 density with temperature and pressure. [105].

A requirement of high process pressures makes industrial implementation less straightforward, since it is connected with higher investment and operating cost. There exist strategies to reduce energy consumption though. Examples include running sequential reactions without depressurisation between them, generating supercritical fluid from liquid precursors or simply using carbon dioxide compressed previously elsewhere, as a part of a different process, e.g. in a CCS facility, or compressed to a lower pressures, merely to expand liquid reactants or solvents (so called gas-expanded liquids, GXLs) [27].

A major advantage of using dense phase carbon dioxide is the possibility of running unique continuous processes using small, high-throughput reactors, where substrates are converted into products, while carbon dioxide is recycled [27,106]. Many of the more studied supercritical fluids, and in particular supercritical carbon dioxide, can be readily separated from the reaction mixture by mere depressurisation. Hence, it can be easily recovered, recycled and reused.

A great attention is focused on catalytic reactions in supercritical carbon dioxide [27,97,104,105,106,107]. In chemical reactions, carbon dioxide is relatively, but not completely, inert towards reactive compounds. Therefore, by-products owing to side reactions with carbon dioxide are rare. Since carbon dioxide is completely oxidised, it is particularly beneficial and safe to use in oxidation processes. More, because carbon dioxide is generally immune to free radical chemistry [108], it is an ideal solvent for use in polymerisation processes, despite the fact that it is typically a poor solvent for high molecular weight polymers. The interesting property of supercritical carbon dioxide, though, is its complete miscibility with gases (especially, reaction gases such as hydrogen, oxygen, carbon monoxide, etc.). For these reasons, supercritical carbon dioxide is reasonably established for hydrogenations, hydroformylations, or oxidations, and controlled polymerisation reactions [97,109,110,111,112].

2.3. Facing challenges – biphasic systems

When an organic liquid (substrate, solvent) is pressurised by carbon dioxide, and if carbon dioxide dissolves in this phase, causing its expansion (below the critical pressure of the mixture), it is called a gas-expanded liquid (GXL) [113]. By applying such a lower pressure of carbon dioxide, merely to expand liquid reactants or solvents, the solubility of polar and non-polar solutes of a mixture is enhanced, compared to pure supercritical carbon dioxide. Gas-expanded liquids offer the possibility to tune the solvent power and physiochemical properties of a mixture, in a range from the properties of a neat conventional solvent to those of pure supercritical fluid, by adjusting the gas pressure. There are many processes that were shown to display improved reaction performance with respect to rates, selectivity and separations [114,115,116]. Unfortunately, despite of the substantial share of a compressed gas in a mixture, the system still relies on the usage of environmentally unfriendly organic solvents.

An interesting answer to such a concern is the combination of supercritical carbon dioxide with ionic liquids. This unique case of gas-expanded liquid provides a versatile biphasic reaction and separation environment [117,118]. The main reason of the attention given to $scCO_2$/ILs system is its unusual phase behaviour noticed for the first time by Brennecke and co-workers [119], and presented here in Figure 2.4.

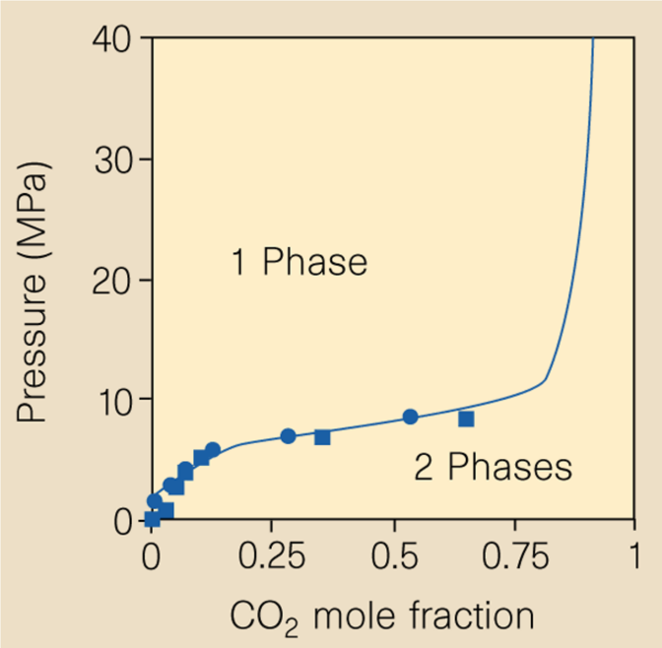


Figure 2.4. Phase diagram for CO_2-[bmim][PF_6] system [119].

While the ionic liquid is immeasurably insoluble in the pure carbon dioxide phase, up to high pressures, the solubility of carbon dioxide in the ionic liquid-rich phase is remarkably high. It increases rapidly with pressure, up to about 10 MPa, and may reach values of the order of 0.5 to 0.7 CO_2 mole fraction [84]. Further increase in pressure causes the carbon dioxide phase to become more dense, but the two phases will never become identical, i.e., a mixture critical point will never be reached [119], unlike carbon dioxide with most organic solvents, which become miscible (supercritical) at moderate, 8-20 MPa, pressures [113].

Brennecke and co-workers were the first to prove that supercritical carbon dioxide can be used to extract relatively non-volatile compound from ionic liquids, without any cross-contamination, allowing for easy recycling of both, ionic liquid and carbon dioxide [119,120].

Shortly after, they demonstrated a new method to separate ionic liquid from organic solvent [121] or water [122], using carbon dioxide as a separation switch. When carbon dioxide pressure is applied to a mixture of ionic liquid and organic solvent (Figure 2.5a), an additional, ionic liquid-rich phase is formed (Figure 2.5b). Consequently, the bottom liquid phase is rich in ionic liquid, the middle liquid phase is rich in organic solvent, and the upper vapour phase is rich in carbon dioxide and contains no ionic liquid. As pressure is increased, the relative volume of the organic-rich phase increases until it merges with the carbon dioxide phase. The system becomes biphasic, with an upper organic liquid + carbon dioxide phase, and a lower ionic-liquid-rich one.

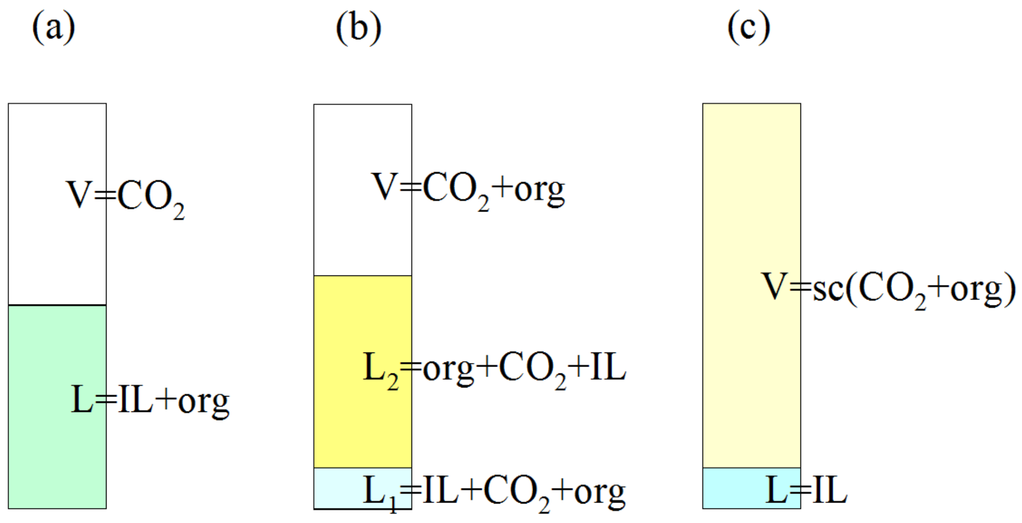


Figure 2.5. Schematic phase behaviour of IL/organic component mixture with increasing CO_2 pressure.

Since publications of these reports, many examples of such carbon dioxide-induced phase-transitions, for ternary [123,124,125] as well as quaternary [126,127,128] ionic liquid systems, have been published. More, many diverse applications have been developed for supercritical carbon dioxide/ionic liquid systems [129,130,131]. It was demonstrated that carbon dioxide can extract the product from the ionic liquid, leaving behind, not only ionic liquid, but also catalyst to reuse. In addition, the method can be adapted to continuous flow, where carbon dioxide delivers the substrates to the ionic liquid/catalyst phase and extracts the products out of it. Regarding the phenomenon of miscibility switch, it was shown that carbon dioxide can act also as anti-solvent in precipitations [132,133].

As pointed out previously in the text, extraction with dense carbon dioxide is an alternative strategy to distillation or extraction with traditional organic solvents to separate both volatile and relatively non-volatile compounds from ionic liquids, without any contamination of the ionic liquid phase. Coupling ionic liquids with carbon dioxide may overcome also other of ionic liquids limitations. It was shown that supercritical carbon dioxide can significantly decrease the viscosity of ionic liquids, and thus, increase the diffusivity of compounds [134,135,136]. The additional benefit is that carbon dioxide can enhance the solubility of reaction gases into the ionic liquid phase [137,138]. Moreover, the presence of carbon dioxide may lead to very large, up to 120 K, melting point depressions [139,140,141], allowing many more of estimated 10^{18} possible combinations of ionic liquids to be actually liquids near room temperature [64]. Considering the economic aspect of implementation of ionic liquids into industry, it is expected that the cost of ionic liquids will steadily decrease, along with their increasing demand. Plus, application of ionic liquid/carbon dioxide biphasic mixtures allows for the efficient recycling and reusing of the ionic liquid, minimising the relevance of their initial cost. The last challenge concerns ionic liquid toxicity and environmental impact. The limited data available in the literature on this topic is the main barrier to fully consider (or not) ionic liquids as “green” solvents [142,143,144]. Undoubtedly, the subject should be addressed with more detailed studies before employing ionic liquids in large scale industrial applications.

2.3 Solubility of carbon dioxide in ionic liquids

Dense carbon dioxide has become a partner of ionic liquids. These two environmentally friendly solvents could be utilised together in various applications, but for that, a complete understanding of the molecular-level interactions between them is necessary. Recently, the study of interactions of carbon dioxide and ionic liquids has become a focus of attention, due to the potential of ionic liquids as agents for CO_2 capture [42,85]. Most of these studies have been carried out at atmospheric or relatively low pressure. But, although mixtures of high pressure, supercritical carbon dioxide with ionic liquids play only a minor role in the undergoing research in this area, many applications in separations and chemical and biochemical reactions have been proposed [117,118,145]. The knowledge of the high pressure phase behaviour of these specific partners will be crucial for future development.

Since the pioneer report of Brennecke and co-workers on the phase behaviour of an IL-CO_2 system [119], various studies speculated on the different factors governing the gas solubility in ionic liquids. Over the years, the effects of pressure, temperature, ionic liquid structure (the choice of anions and cations), as well as the influence of water and other impurities, have been discussed.

There is no doubt that the solubility of carbon dioxide in ionic liquids increases with increasing pressure and decreases with increasing temperature. The choice of the anion has a strong effect on the carbon dioxide solubility, greater than the choice of the cation, and it was even proposed that the interaction of CO_2 with the anion plays a dominant role in the mechanism of gas dissolution in ionic liquids [146,147,148,153]. Cadena et al. [146], by means of molecular dynamics simulations on ionic liquids containing hexafluorophosphate ([PF_6]) anion, demonstrated a strong association between the carbon on the CO_2 molecule and the [PF_6] anion. Kazarian et al. [147] showed, using attenuated total reflection infrared spectroscopy (ATR-IR), that CO_2 molecules dissolved in 1‑butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) or 1‑butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) are perpendicularly oriented to the P-F or B-F bonds, respectively. Kanakubo et al. using X-ray scattering experiments for [bmim][PF_6]-CO_2 system deduced that molecules of carbon dioxide even slightly penetrate into hollows of the fluorinated anion [148]. However, even Kazarian et al. mentioned in their study that the strength of the anion-CO_2 interactions cannot be solely responsible for the carbon dioxide solubility in the investigated ionic liquids. The contribution of free volume in the ionic liquid structure was soon to be found as an important contributor, as discussed, among others, by Hu et al. [149] and Shannon et al. [150].

According to “free volume mechanism”, cations and anions are arranged to form a somewhat rigid network, with the carbon dioxide filling the interstices in the fluid. Berne et al. [151], using classical molecular dynamics simulations for the system [bmim][PF_6]–CO_2, showed that the size of the originally available cavities in ionic liquid is not big enough to accommodate a CO_2 molecule. They speculated that upon the addition of carbon dioxide, the anions undergo small angular rearrangements to form larger voids. All of that happens without causing any significant perturbation in the underlying structure of the ionic liquid, thereby without causing any volumetric expansion. This mechanism offers an explanation for the small increases in the liquid phase volume of ionic liquid-CO_2 mixtures, even when high quantities of carbon dioxide are dissolved, a fact noticed by Brennecke and co-workers [152,153]. It also explains why, having a finite free volume originally present within the structure of the ionic liquid, only a certain amount of carbon dioxide can be accommodated, even under very high pressure. Further addition of CO_2 molecules into ionic liquid framework would require a disruption of the strong cohesive structure of ionic liquid.

It was reported that the amount of free volume is a good indicator for ion cohesion in ionic liquids [154]. The strength of ion cohesion is primarily determined by the ion density, which in turn is given by the size of the constituting ions. Large and asymmetric ions lead to larger average distances between cations and anions, and thus weaker mutual attraction. Weak electrostatic cation-anion interaction densities, i.e., weak ion cohesion, allows for easy enlargement of cavities of the ionic liquids structure, which in turn results in higher carbon dioxide solubility as more CO_2 molecules can accommodate within the voids.

However, even ionic liquids with small and highly symmetric anions can exhibit weak cation-anion interactions, as shown by Babarao et al. [155]. The authors, using molecular dynamics simulation and quantum mechanical calculations, investigated the correlation between the interaction energy and carbon dioxide solubility. They showed that the cation-anion binding energy and carbon dioxide solubility (at atmospheric pressure and room temperature) for four ionic liquids with the same [emim] cation and different anions ([BF_4], [PF_6], bis(trifluoromethanesulfonyl)amide ([NTf_2]) and tetracyanoborate ([$B(CN)_4$])) show good correlation, contrarily to CO_2-anion interactions and solubility (Figure 2.6). It is speculated that the free volume lies in the interionic space between cation and anion, indicating that the weaker interaction between cation and anion is favourable for increasing carbon dioxide solubility.

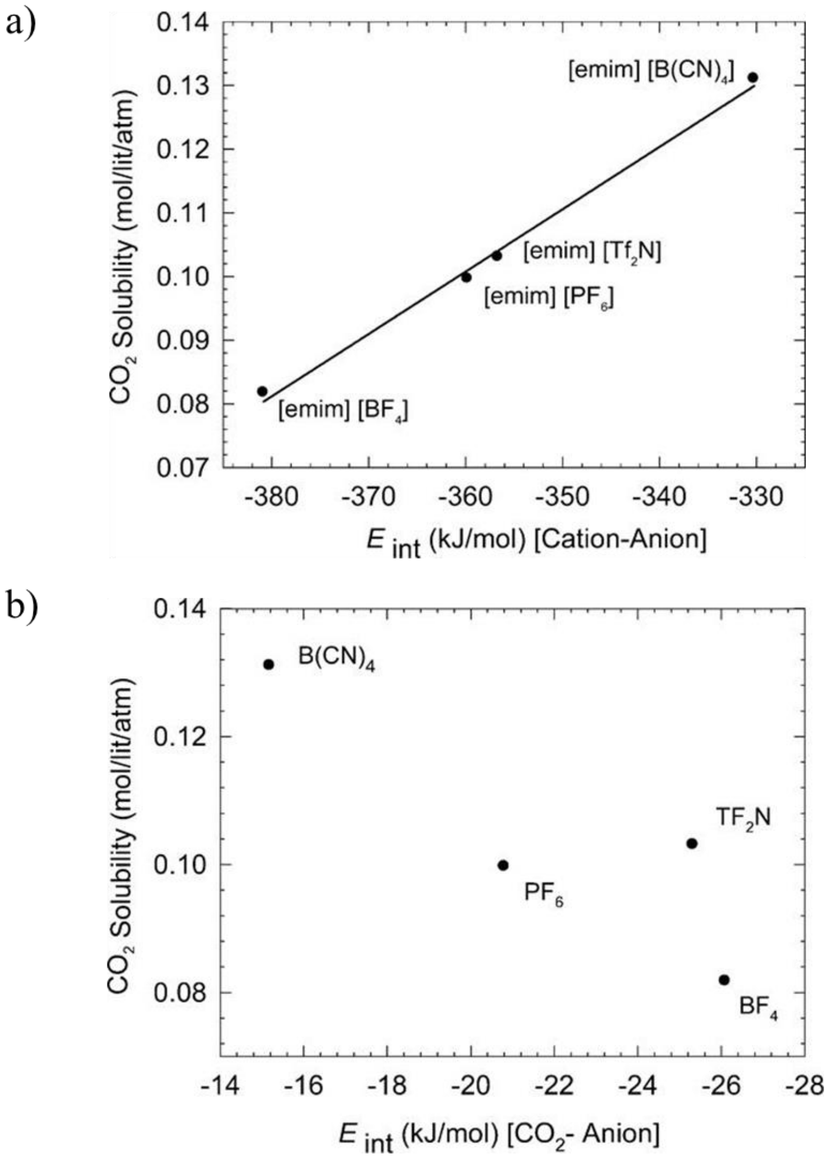


Figure 2.6 Correlation between gas-phase a) cation-anion and b) CO_2-anion interaction energy and the experimental CO_2 solubility at 1 bar and 298 K for four ionic liquids with the same [emim] cation but different anions [155].

There are a large number of experimental and theoretical studies on the solubility of carbon dioxide in ionic liquids [84], with a focus on describing the physical mechanism of dissolution. Although lots of improvements have already been made in order to increase the solubility, the carbon dioxide capacity of ionic liquids with physical dissolution is still rather low when compared to amine-based methods currently used in industry. Another strategy, initiated by Bates et al. [65], is based on the chemical reaction of carbon dioxide with, so called, task-specific ionic liquids (TSILs). The physical mechanism is considered for ionic liquids that do not bear any functional moieties and is dominated by van der Waals forces. It implies an easier desorption process (lower energy of regeneration), because only a decrease in pressure or an increase in temperature is required. The concept of chemical mechanism combines the advantages of ionic liquids with the incorporation of functional (task-specific) groups to allow, in this particular case, enhanced (chemical) bonding of carbon dioxide to the absorbent. Bates et al. showed that appending a free amine (-NH_2) to the cation of the imidazolium ring of an ionic liquid results in the formation of a carbamate, when exposed to carbon dioxide [65]. Such a designed 1-n-propylamine-3-methylimidazolium ([NH_2-bmim]) tetrafluoroborate was capable of chemically bonding carbon dioxide in a ratio of 1:2 for CO_2:[NH_2-bmim][BF_4]. Since that discovery, the research in this area has received an increased attention [156,157,158]. Very recently, a new possibility of utilisation of mixtures of ionic liquids has been proposed [159,160,161,162].

3. Carbon dioxide-induced melting point depression of ionic liquids

3.1. Introduction

The melting temperature is one of the most important properties of an ionic liquid. The possibility of decreasing the melting temperature of various organic substances by dissolution of compressed gases has long been known. Usually these melting point depressions are in the range of 10 K to 30 K. De Loos explained the thermodynamics of solid-liquid-gas equilibria in binary mixtures of a solid substance and a supercritical gas [163]. He concluded that negative slopes of the pressure-temperature equilibrium curve, that is, melting point depressions (MPDs), occur when the solubilities of the gas in the liquid (molten solid) are high. The first example of a high CO_2-induced melting point depression of an ionic liquid-like compound, tetrahexylammonium hexafluorophospate, $[(C_6H_{13})_4N][PF_6]$, was given by Niehaus et al. [164], who reported that pressurisation with moist carbon dioxide reduces the melting point of the salt up to 64 K. Later, Kazarian et al. studied the melting temperature of 1-hexadecyl-3-methylimidazolium hexafluorophosphate, $[C_{16}mim][PF_6]$, under pressure of dry carbon dioxide, using ATR-IR spectroscopy [165]. They reported a decrease from 348 K to 323 K at a pressure of 7 MPa. Their estimated solubility of carbon dioxide in the melt was 0.55 mole fraction at this pressure and 323 K.

Recently, it has been shown that, while carbon dioxide pressure induces “normal” melting point depressions for many ionic liquid-like salts, in the 10 to 30 K range, a few quaternary ammonium salts display very large MPDs, up to 120 K [139,140,141]. Examples of strikingly high values include: 120 K for tetrabutylammonium tetrafluoroborate ($[(C_4H_9)_4N][BF_4]$); 81 K for methyl-tris(2-methyl-propyl)ammonium trifluoromethanesulfonate ($[(iC_4H_9)_3(CH_3)N][CF_3SO_3]$); 71 K for tetrahexylammonium bromide ($[(C_6H_{13})_4N][Br]$). Equally striking is the enormous effect of small changes in the cation structure or alteration of the anion, which drastically reduce the effect of carbon dioxide pressure. Examples are $[(C_4H_9)_4N]^+$, where changing the anion from tetrafluoroborate to tosylate ([tos]) reduces MPD from 120 K to 33 K, or tetrapentylammonium bromide ($[(C_5H_{11})_4N][Br]$), with a melting point depression of 19 K, which is 52 K smaller than for the above mentioned $[(C_6H_{13})_4N][Br]$.

A better understanding of the causes of this peculiar behaviour is needed to predict which ionic liquid-like salts may show high melting point depressions, as the resulting carbon dioxide-induced ionic liquids/salts may have interesting applications. Cimpeanu et al. have recently demonstrated their potential, using CO_2-induced molten $[(C_4H_9)_4N][BF_4]$ (MPD = 120K), around 100 K below its normal melting point, to produce catalytically active matrix-embedded rhodium nanoparticles [166].

Scurto et al. [140] investigated the melting point depression of a large number of ionic liquids, and for few of them with the highest melting point depressions, presented the pressure–temperature projection of the solid-liquid-vapour (SLV) line. The change in the SLV temperature of these ionic liquids with pressure is extremely large and negative in the lower (< 15 MPa) pressure range, whereas at higher pressures, the increase in the melting point depressions with added carbon dioxide is marginal. This kind of behaviour is not noted if the pressure is induced mechanically, which normally increases the melting temperature. This shape of the SLV line indicates that the effect of the hydrostatic pressure is overcome by the solubility of the gas in the liquid phase. Valderrama and Arce were able to successfully correlate the data obtained by Scurto et al. [140] using the Peng–Robinson equation of state, with the Wong–Sandler mixing rule, and the van Laar model for activity coefficients and excess Gibbs free energy [167,168]. Cocero and co-workers measured the melting point depression of imidazolium chloride ionic liquids and observed analogous behaviour [169]. They correlated the results using the Group Contribution Equation of State (GC-EoS) of Skjold-Jørgensen adopting the solubility data already available in the literature. There are however no studies on whether the solubility of carbon dioxide in different ionic liquids is anyhow related to the above-mentioned striking differences between the values of their melting point depressions, as published solubility data for ammonium-based ionic liquids are very scarce.

We have therefore started to measure carbon dioxide solubility in different ammonium-based ionic liquids for which melting point depression results exist. The solubility of carbon dioxide in five different molten salts/ionic liquids was measured. Three of these salts have high melting temperatures (from 368 K to 429 K) and high (60 K) to extremely high (120 K) melting point depressions.

3.2. Materials and methods

3.2.1. Materials

The ionic liquids used in this work were tetrahexylammonium bromide, $[(C_6H_{13})_4N][Br]$, tetrabutylammonium tetrafluoroborate, $[(C_4H_9)_4N][BF_4]$, trioctylmethylammonium tosylate $[(C_8H_{17})_3(CH_3)N][tos]$, trioctylmethylammonium trifluoromethanesulfonate $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$ and didodecyldimethylammonium saccharine, $[(C_{12}H_{25})_2(CH_3)_2N][sac]$.

Tetrahexylammonium bromide was purchased from Sigma. The other salts were synthesised by Professor Carlos A.M. Afonso and co-workers at the Faculty of Pharmacy of the University of Lisbon. The procedure for their preparation was adapted from the literature [170] with several modifications as described:

Preparation of trioctylmethylammonium trifluoromethanesulfonate $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$: trioctylmethylammonium chloride (Aliquat®336), 3.71 g (8.58 mmol), was dissolved in 10 cm^3 of ethanol, and mixed with an aqueous solution of KCF_3SO_3 (1.2 equiv, 1.94 g in 10 cm^3 of water). The mixture was stirred overnight, at room temperature. After that the mixture of solvents was removed by evaporation (till dryness), and 50 cm^3 of dichlorometane was added to the residue forming a precipitate. The mixture was filtered and the solvent evaporated in a rotaevaporator and then kept under vacuum for 48 h at $(1\text{-}4)x10^{-2}$ mbar (rotatory pump) and 4 h at up to $6x10^{-5}$ mbar. $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$ was obtained in 89.9% (4.21g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (dd, *J* = 10.2, 6.7 Hz, 6H), 3.04 (s, 3H), 1.64 (s, 6H), 1.50 – 1.14 (m, 30H), 0.86 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 61.62, 31.80, 31.58, 29.37, 29.31, 29.21, 29.03, 28.96, 26.15, 22.61, 22.53, 22.22, 14.04, 13.99. Anal. Calc.: C, 60.31; H, 10.51; N, 2.71; S, 6.19 Found: C, 60.38; H, 10.50; N, 2.54; S, 6.17.

Preparation of trioctylmethylammonium tosylate $[(C_8H_{17})_3(CH_3)N][tos]$: A solution of trioctylmethylammonium chloride (Aliquat®336), 10 g (23.1 mmol), in methanol (75 cm^3) was passed through a column with Amberlite IRA-400 (OH) resin. A solution of *p*-toluenesulfonic acid (1 equiv., 4.4 g) in methanol was slowly added to the methanolic solution of $[(C_8H_{17})_3(CH_3)N][OH]$ obtained from the column and the mixture was stirred at room temperature for 30 minutes. The solvent was removed under vacuum, and then kept under vacuum for 48 h at $(1\text{-}4)x10^{-2}$ mbar (rotatory pump) and 4 h at up to $6x10^{-5}$ mbar. $[(C_8H_{17})_3(CH_3)N][tos]$ was obtained as a white solid in 98.7% (12,96 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.30 – 3.15 (m, 6H), 3.09 (s, 3H), 2.31 (s, 3H), 1.55 (s, 6H), 1.23 (m, 30H), 0.86 (td, *J* = 6.8, 1.9 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.50, 139.19, 128.50, 126.03, 61.33, 31.83, 31.65, 29.43, 29.40, 29.26, 29.15, 29.09, 29.04, 26.24, 22.63, 22.57, 22.28, 21.24, 14.06, 14.03. Anal. Calc.: C, 71.19; H, 11.39; N, 2.59; S, 5.94; Found: C, 71.27; H, 11.57; N, 2.44; S, 6.00.

Preparation of tetrabutylammonium tetrafluoroborate $[(C_4H_9)_4N][BF_4]$: A solution of tetrabutylammonium chloride, 2.5 g (9.1 mmol) in ethanol (50 cm^3) was mixed with a aqueous solution of sodium tetrafluoroborate (1.5 g in 10 cm^3 of water). The mixture was stirred at room temperature for four days. The solvent was removed under vacuum, and ice was added to the solution, so the desired product precipitated. The precipitate was filtered off and washed with water. The tetrabutylammonium tetrafluoroborate was kept under vacuum for 48 h at (1-4)x10^{-2} mbar (rotatory pump) and 4 h at up to 6x10^{-5} mbar. [$(C_4H_9)_4N$][BF_4] was obtained as a white solid in 65 % (4.6 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (dd, *J* = 10.0, 7.1 Hz, 8H), 1.65 – 1.52 (m, 8H), 1.45 – 1.33 (m, 8H), 0.96 (t, *J* = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 58.37, 23.69, 19.53, 13.52.

Preparation of didodecyldimethylammonium saccharine [$(C_{12}H_{25})_2(CH_3)_2N$][sac]: A solution of didodecyldimethylammonium bromide, 4.09 g (8.8 mmol), in methanol (75 cm^3) was passed through a column with Amberlite IRA-400 (OH) resin. A solution of saccharine (1 equiv., 1.6 g) in methanol was slowly added to the metanolic solution of [$(C_{12}H_{25})_2(CH_3)_2N$][OH] obtained from the column and the mixture was stirred at room temperature for 30 minutes. The solvent was removed under vacuum, and then kept under vacuum for 48 h at (1-4)x10^{-2} mbar (rotatory pump) and 4 h at up to 6x10^{-5} mbar. [$(C_{12}H_{25})_2(CH_3)_2N$][sac] was obtained as a white solid in 98% (4.89 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.73 – 7.68 (m, 1H), 7.56 – 7.48 (m, 2H), 3.41 – 3.31 (m, 4H), 3.28 (s, 6H), 1.63 (s, 4H), 1.34 – 1.09 (m, 36H), 0.86 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.88, 144.84, 134.96, 131.76, 131.13, 123.13, 119.52, 77.43, 77.11, 76.79, 63.81, 51.10, 31.88, 29.57, 29.44, 29.35, 29.30, 29.09, 26.16, 22.65, 14.09. Anal. Calc.: C, 70.16; H, 10.71; N, 4.96; S, 5.68; Found: C, 70.07; H, 10.78; N, 4.91; S, 5.61.

Additionally, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, [bmim][NTf_2], was purchased from Iolitec (Germany).

In order to reduce water and volatile organic content, vacuum at 343.15 K was always applied to the salts for at least 72 hours prior to their use. The water contents after vacuum procedure, determined by Karl Fischer coulometric titration (Metrohm 831 KF coulometer), were no higher than 150 ppm in all studied cases. Carbon dioxide (99.98 % purity) was supplied by Air Liquide and was used without further purification. Dichloromethane of ≥ 99.9 mass% purity was used as a solvent, in order to wash the lines and dissolve the salts precipitated after carbon dioxide expansion from the sample loop, as described below. Chemical names, abbreviations, purities and sources for all chemicals used in this work are presented in Table 3.1.

Table 3.1. Chemicals used in this study.

Name	Abbreviation	Purity/mass% (method*)	Source
Tetrahexylammonium bromide	$[(C_6H_{13})_4N][Br]$	> 99 (S)	Sigma-Aldrich
Tetrabutylammonium tetrafluoroborate	$[(C_4H_9)_4N][BF_4]$	> 97 (EA)	this work
Trioctylmethylammonium tosylate	$[(C_8H_{17})_3(CH_3)N][tos]$	> 97 (EA)	this work
Didodecyldimethylammonium saccharine	$[(C_{12}H_{25})_2(CH_3)_2N][sac]$	> 97 (EA)	this work
Trioctylmethylammonium trifluoromethanesulfonate	$[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$	> 98 (EA)	this work
1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide	$[bmim][NTf_2]$	> 99 (S)	Iolitec
Carbon dioxide	CO_2	99.98 (S)	AirLiquide
Dichloromethane	CH_2Cl_2	99.8 (S)	Sigma-Aldrich

* S stands for stated, EA stands for elemental analysis

3.2.2. Apparatus and experimental procedure for solubility measurements

The measurements of solubility were performed using an isochoric saturation, analytical method in an especially designed apparatus, which was custom-built in our laboratory to carry out the measurements presented here. A scheme of the apparatus is shown in Figure 3.1.

The design objectives were: (1) to measure the solubility of a gas in a molten solid that becomes liquid only under the gas pressure; (2) to avoid dead volumes and precipitation of solids in the sampling process. The core of the apparatus is a 3.5 cm^3, fixed volume, movable-position high-pressure cell, with a sapphire window allowing visualisation of the internal volume. Relatively wide bore tubing (1/8 inch inside diameter) connects the cell to the sampling valve. The cell was placed inside an air bath equipped with a transparent polycarbonate window. The temperature was measured by a RTD probe from Hart Scientific (model2622) coupled to a controller from the same supplier. The pressure was measured by a Setra pressure transducer (model Model204/C204). The transducer was calibrated against a Bourdon tube pressure gauge (Heise model CMM). The calibration of the temperature and pressure sensors was initially checked by measuring values of the vapour pressure of pure carbon dioxide. The estimated precision of the pressure determination is ±0.07 bar, while the estimated temperature uncertainty is ±0.1 K.

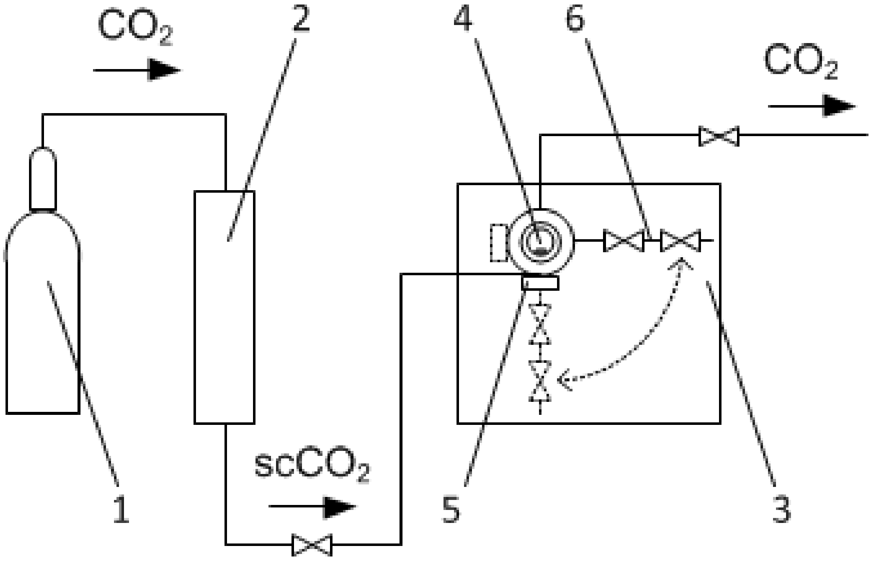


Figure 3.1. Scheme of the apparatus for solubility measurements: 1 - CO_2 supply; 2 - screw injector pump; 3 - air bath; 4 - movable-position high-pressure view cell; 5 - magnetic stirrer; 6 - sampling loop.

During the measurement process, the cell may be moved from a “horizontal” position to a “vertical” one, using appropriate handles that permit moving the cell from outside the bath (Figure 3.2). In the horizontal position, the sampling tube is on the gas side, and the molten salt phase is all inside the cell body and magnetically stirred to reach equilibrium with the gas phase. When the cell is rotated to the vertical position, after equilibration, the tube leading to the sampling valve is moved to a location below the liquid, which falls into the tube, displacing the gas to the cell body. Such a mechanism enabled the equilibration of phase composition and subsequent sampling, avoiding a non-equilibrated liquid phase in the dead volume near the sampling valve. Sampling of the liquid phase into a loop of 0.4 cm^3 volume is carried out through an on–off ball valve that maybe quickly opened and closed from outside the air bath.

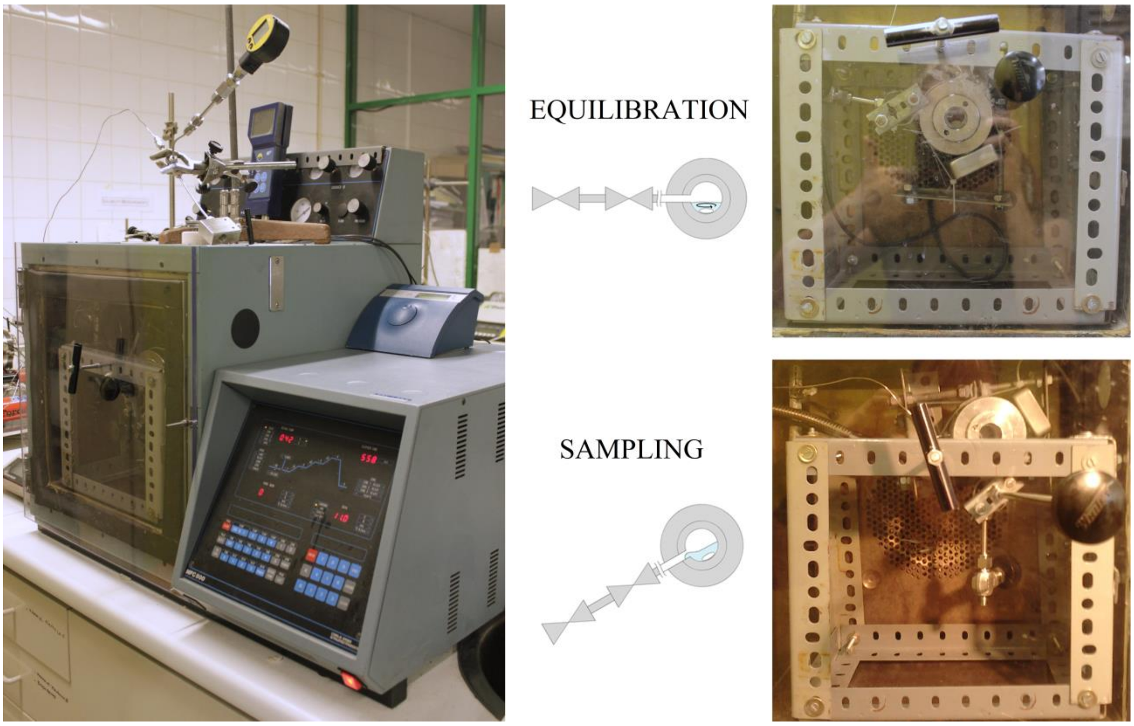


Figure 3.2. Operation of the cell from an outside (left); equilibration in a “horizontal” position (right, top corner), sampling in a “vertical” position (right, bottom corner).

After depressurisation of the cell, the sampling loop, containing carbon dioxide and ionic liquid under high pressure, is disconnected from the apparatus and connected to an expansion assembly (Figure 3.3). This assembly consists essentially of previously calibrated volumes. The expansion of the carbon dioxide content of the loop into those volumes, at monitored temperature, results in sub-atmospheric pressure. The quantity of carbon dioxide dissolved in the ionic liquid in the loop may then be calculated through the equation of state of Span and Wagner [14,171], using the measured pressure, and the calibrated volume of expansion. The mass of salt (ionic liquid) is then determined by weighing, after washing the loop with dichloromethane and subsequently evaporating the solvent.

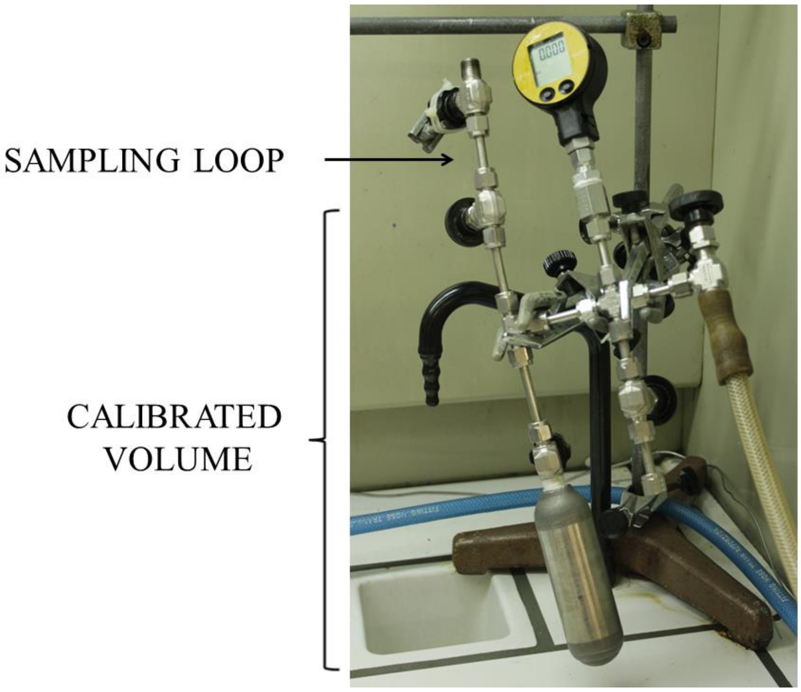


Figure 3.3. Expansion assembly.

Some experiments were repeated several times at the same conditions to ascertain the reproducibility of the measurements. The overall experimental uncertainty is less than ±0.02 mole fraction of carbon dioxide.

3.3. **Results and discussion**

Table 3.2 presents values of the solubility of carbon dioxide in five molten salts/ionic liquids – trioctylmethylammonium trifluoromethanesulfonate, trioctylmethylammonium tosylate, didodecyldimethylammonium saccharine, tetrahexylammonium bromide, and tetrabutylammonium tetrafluoroborate. Measurements were performed at 369.2 K and 15 MPa for all five substances. For the first two salts, solubilities of carbon dioxide were also measured at 329.2 K and 347.2 K. Table 3.2 also presents the values of the melting point depression measured at the given pressures [139,140,141].

Table 3.2. Experimental solubility of CO_2 in ammonium-based ionic liquids. x_{CO2} stands for mole fraction of carbon dioxide. Values of melting point depressions (MPDs) taken from literature [141].

T [K]	***p*** [MPa]	x_{CO2}	***MPD* / K**
	$[(C_8H_{17})_3(CH_3)N][tos]$		
347.2	5.5	0.66	42
	10	0.69	
	12	0.72	
	15	0.75	
329.2	10	0.75	
369.2	15	0.75	
	$[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$		
329.2	3.7	0.57	25
	10	0.74	
	12	0.79	
	15	0.80	
347.2	10	0.69	
369.2	15	0.70	
	$[(C_{12}H_{25})_2(CH_3)_2N][sac]$		
369.2	15	0.79	60
	$[(C_6H_{13})_4N][Br]$		
369.2	15	0.76	71
	$[(C_4H_9)_4N][BF_4]$		
369.2	15	0.57	120

The solubility of carbon dioxide in the ionic liquid $[bmim][NTf_2]$ was first measured, in order to compare the obtained results with literature values. At 313.2 K and at 6.0 MPa, the obtained solubility was 0.608 (mole fraction), which agrees within experimental error with the value reported by Aki et al. [153] These authors studied the same binary system, at an identical temperature, within a pressure range from 1.6 MPa to 7.8 MPa. A solubility of 0.627 was calculated, at 313.2 K and at 6.0 MPa, from a second degree polynomial fit to their data. Shin et al. [172] reported a solubility of 0.6642 at 6 MPa and at slightly higher temperature314.1 K. A value of 0.5852 was reported by Raeissi and Peters [173], at 313.7 K and 5.5 MPa.

Figure 3.4 displays the results obtained at 347.2 K and 329.2 K for the two ionic liquids with trioctylmethylammonium cations. Although there are no published results of carbon dioxide solubility for these specific ionic liquids from other authors, two recent papers of Manic et al. [174] and Nam and Lee [175] report data on trioctylmethylammonium bis(trifluoromethanesulfonyl)amide. These sets of data are in good agreement with one another.

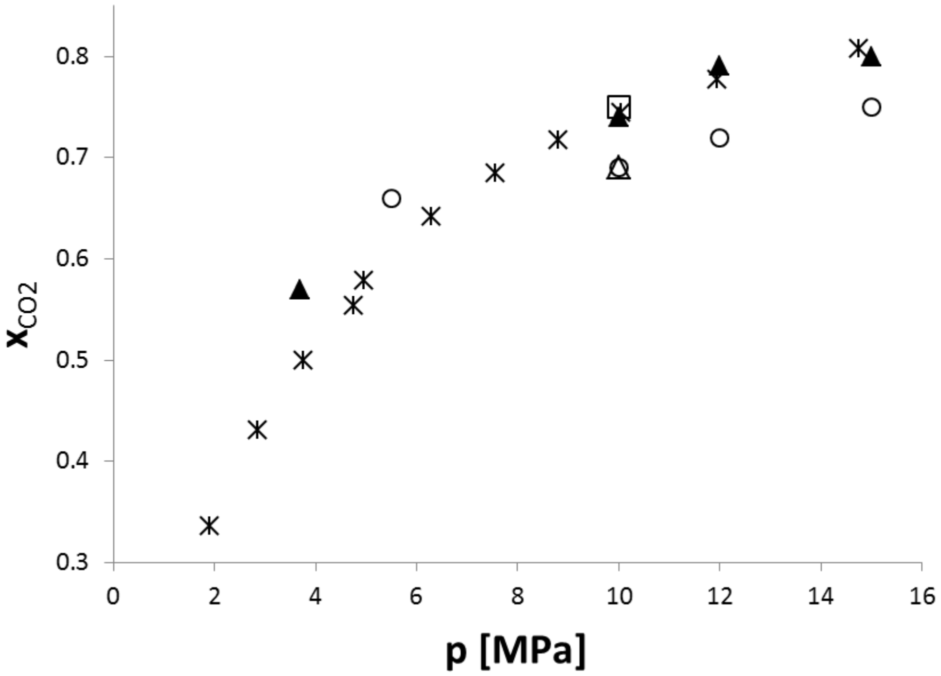


Figure 3.4. Solubilities of CO_2 in the following liquids: $[(C_8H_{17})_3(CH_3)N][tos]$ at 329.2 K (▲), 347.2 K (Δ); $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$ at 329.2 K (☐), 347.2 K (○); and data taken from [175] for $[[(C_8H_{17})_3(CH_3)N][NTf_2]$ at 343.2 K (ж).

In Figure 3.4, the results of Nam and Lee at 343.2 K are plotted. The solubility of carbon dioxide in the three ionic liquids is very similar, in spite of the different anions, although slightly higher in the liquid with the bis(trifluoromethanesulfonyl)amide anion. Both the trifluoromethanesulfonate and the tosylate anions contain SO_3 groups with a dense negative charge. Although the presence of fluorine atoms in the trifluoromethanesulfonate anion might be thought to enhance the solubility of carbon dioxide [37,176], the toluene group of the tosylate anion is bulkier and more apolar, probably leading to equally strong interaction with carbon dioxide. On the other hand, the bis(trifluoromethanesulfonyl)amide anion is known to lead to higher CO_2 solubilities in imidazolium-based ionic liquids than trifluoromethanesulfonate [37]. The compositions of the liquid phase at the onset of freezing measured by Scurto et al. [140] for CO_2 + tetrabutylammonium tetrafluoroborate refer to liquid–solid equilibrium. They cannot be compared directly with the carbon dioxide solubility in the ionic liquid presented in Table 3.2, as this value corresponds to liquid–vapour equilibrium. Scurto’s data may however be taken as lower limits to the gas solubility in the liquid, as, for each temperature and pressure, the liquid phase exists in a window of compositions, between the liquid–solid equilibrium line (lowest CO_2 mole fraction) and the liquid–vapour line (maximum CO_2 mole fraction). In this respect, the highest value of 0.539 CO_2 mole fraction given by Scurto et al. is consistent with the 0.57 CO_2 mole fraction solubility presented in Table 3.2

The measurements at 369.2 K and 15 MPa were designed to provide the possibility of comparison between melting temperature and solubilisation of carbon dioxide, as all five ionic materials studied in this work are liquid under those conditions. On the other hand, 15 MPa is a sufficiently high pressure for the solubility of carbon dioxide to be only slightly sensitive to temperature. In those conditions, the solubility of carbon dioxide in the studied ionic liquids decreases in the following order: $[(C_{12}H_{25})_2(CH_3)_2N][sac]$ > $[(C_6H_{13})_4N][Br]$ > $[(C_8H_{17})_3(CH_3)N][tos]$> $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$ > $[(C_4H_9)_4N][BF_4]$. As to the corresponding melting temperature depressions, the order is completely different. For the three ionic salts with high MPD, from 60 K to 120 K, measured at 15 MPa, the order is indeed the reverse one:$[(C_4H_9)_4N][BF_4]$ > $[(C_6H_{13})_4N][Br]$ > $[(C_{12}H_{25})_2(CH_3)_2N][sac]$.

As to the $[(C_8H_{17})_3(CH_3)N]$-based ionic liquids, their melting temperature is close to ambient. Therefore, the existing melting depression results are limited to relatively low carbon dioxide pressures, as going further would require cryogenic equipment [140]. Their MPD at 15 MPa should be higher than the values reported in Table 3.2, but there is no way to predict them with good precision.

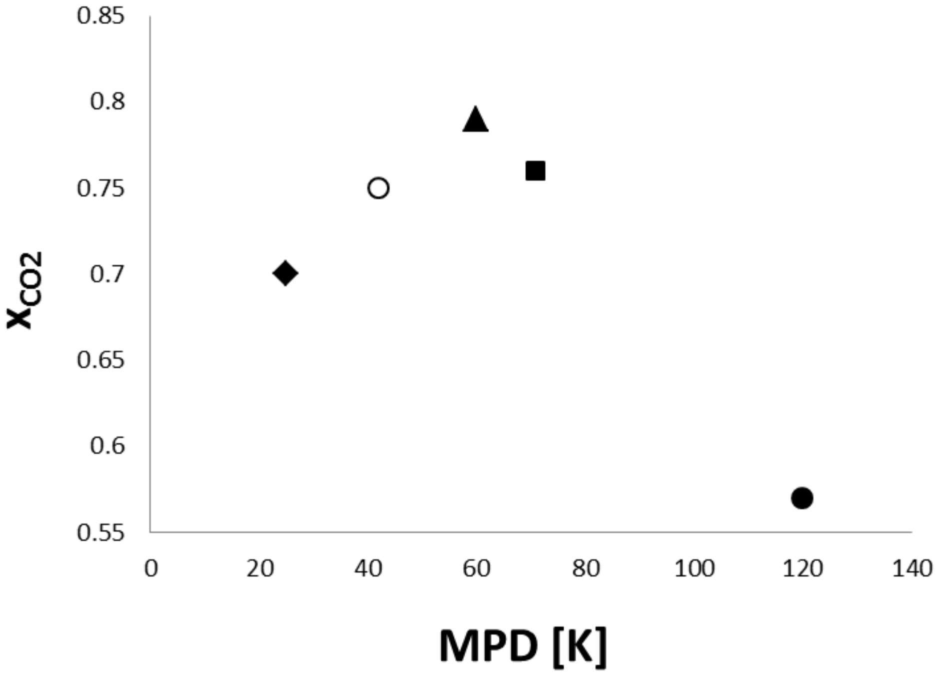


Figure 3.5 Solubility of CO_2 (x_{CO2}– mole fraction), at 369.2 K at and 15MPa, vs. melting point depression (MPD) [139,140,141], for $[(C_{12}H_{25})_2(CH_3)_2N][sac]$ (▲), $[(C_8H_{17})_3(CH_3)N][tos]$ (○), $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$ (◆), $[(C_6H_{13})_4N][Br]$ (■), $[(C_4H_9)_4N][BF_4]$ (●).

In Figure 3.5, the values of solubility are plotted as a function of the melting point depression for the five substances studied. The inclusion of $[(C_8H_{17})_3(CH_3)N][tos]$ and $[(C_8H_{17})_3(CH_3)N][CF_3SO_3]$ must be regarded as merely indicative, for the above-explained reasons. But even if only the three higher MPD ionic salts are taken into consideration, no positive correlation can be found between the magnitude of the melting temperature lowering and the solubility of the gas in each liquid.

3.4. Conclusions

The solubility of carbon dioxide in molten salts/ionic liquids displaying melting temperature depressions under CO_2 pressure ranging from 25 K to 120 K was measured. No positive correlation was found between the solubility in each ionic liquid and the melting temperature depression. Perhaps, the cause for the extremely high differences between CO_2-induced melting point depressions in structurally similar ammonium-based ionic salts is related to interactions between carbon dioxide and the solid framework of these ionic liquids, possibly leading to a disruption of its solid structure.

4. Volumetric and phase behaviour of mixtures of ionic liquids with high pressure carbon dioxide

4.1. Introduction

Carbon dioxide is, in general, remarkably soluble in ionic liquids, but ionic liquids with fluorinated anions show particularly high carbon dioxide solubility. Well-known and widely used imidazolium-based ionic liquids with hexafluorophosphate ([PF_6]) or tetrafluoroborate ([BF_4]) anions are sensitive to moisture and air, especially at elevated temperature [177]. Changing anion to bis(trifluoromethanesulfonyl)amide ([NTf_2]) or tris(pentafluoroalkyl)-trifluorophosphate ([FAP]) ([PF_3RF_3] where RF is CF_3, C_2F_5, C_3F_7) generates stable, hydrophobic ionic liquids with some of the largest carbon dioxide solubility observed among ionic liquids with physical absorption mechanisms [37,39,178,179]. The class of ionic liquids possessing [FAP] anion was first synthesised in 2005 by Ignat'ev et al. [180], and in 2007 Muldoon et al. noticed, for the first time, its capability to solubilise considerable amounts of carbon dioxide [37]. [FAP]-based ionic liquids have been proposed for use in electrochemistry [181,182,183], or lubrication [184,185,186], and only a few years ago have they started to attract attention as a potential material for carbon dioxide capture/separation processes [39,40,41,42,43,44].

The hydrolytic stability of tetrafluoroborate ionic liquids can also be improved by replacing fluorine atoms with nitrile groups. Until recently, interest in the [$B(CN)_4$]-family of ionic liquids has been limited to use as electrolytes in dye-sensitised solar cells [187,188]. They provide many desired properties for this kind of application, such as a wide electrochemical window, high electrical conductivity, high chemical and thermal stability, hydrophobicity, and, very importantly, low viscosity [189,190,191]. Ionic liquids, in general, are highly viscous fluids with viscosity values of 2 – 4 orders of magnitude higher than for conventional molecular solvents. This poses serious limitations to their use, from the chemical technology and engineering point of view, as viscosity influences many mechanical operations (stirring, mixing, pumping etc.), as well as it affects other transport properties, i.e. diffusion. The viscosity of tetracyanoborate ionic liquids is approximately 20 mPa s for [emim][$B(CN)_4$] [191] and 50 mPa s for [hmim][$B(CN)_4$] [46] at 298.15 K, which is even lower than for [hmim][NTf_2] (70 mPa s at 298.15 K [192,193]), the reference ionic liquid for thermodynamic and physicochemical data, including viscosity, chose by IUPAC [194,195].

Recently, [$B(CN)_4$]-based ionic liquids have also been used as extraction and separation media, for liquid-liquid extraction of alcohols from aqueous feeds [196,197], but also with a high selectivity for aromatic/aliphatic hydrocarbons [198,199] and gas [45,200,201] separations. For instance, a series of tetracyanoborate-based ionic liquids, paired with various cations, was tested for the separation of carbon dioxide from nitrogen in a supported liquid membrane setup [200]. Interestingly, it was found that 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][$B(CN)_4$]) exhibits a high CO_2/N_2 permeability ratio and the solubility of carbon dioxide is about 30% larger than in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([emim][NTf_2]). Babarao et al. [155] suggests that a weak cation-anion interaction is crucial for the high solubility of carbon dioxide in [emim][$B(CN)_4$], more important than CO_2-anion interactions, as opposed to the hypothesis previously stated in the literature.

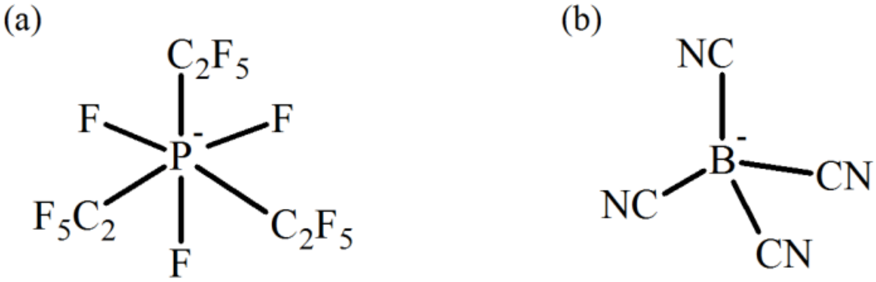


Figure 4.1 Structure of tris(pentafluoroethyl)trifluorophosphate [eFAP] (a) and tetrafluoroborate [$B(CN)_4$] (b) anions.

One very interesting feature of ionic liquids is their volumetric behaviour in a mixture with carbon dioxide. Brennecke and co-workers were the first to notice that the volume of ionic liquids barely increases, even when large amounts of carbon dioxide are dissolved [152,153]. They measured the volume expansion of the liquid phase upon carbon dioxide dissolution in ten imidazolium-based ionic liquids coupled to various anions: [PF_6], [BF_4], [NTf_2], [CF_3SO_3], [NO_3], [$N(CN)_2$] (dicyanamide) and [methide] (tris(trifluoromethylsulfonyl)methide). The largest total volume expansions, reaching a maximum of 35 %, were observed for [methide] and [NTf_2] ionic liquids with longer alkyl chains. For the other ionic liquids, the total volume expanded by approximately 25 %, at most. This contrasted with the behaviour of dense carbon dioxide with many organic solvent systems, where the total volume of the liquid phase expands noticeably (up to 1000 %) upon addition of CO_2 [202,203,204]. For example, the total volume expansion of 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, ([hmim][NTf_2]), with carbon dioxide at 343 K and 12 MPa is only 25% despite the fact that the carbon dioxide solubility at these conditions is approximately 0.7 mole fraction [153]. By contrast, for the same liquid phase composition of 0.7 mole fraction CO_2, the acetone-CO_2 system, at 323 K and 6.3 MPa, will reach an approximately 150 % increase in volume of the liquid phase, meaning 2.5 times greater volume of the liquid phase than before the addition of carbon dioxide [204].

The high-pressure data on carbon dioxide solubility in tetracyanoborate-based [46] or fluoroalkylphosphate-based [37,205] ionic liquids is scarce. Therefore, we present here high-pressure data on carbon dioxide solubility in ionic liquids based on tris(pentafluoroethyl)trifluorophosphate anion paired with a series of 1-alkyl-3-methylimidazolium cations ([$C_n$mim][eFAP] with n = 2,4,6), at the temperature of 313 K and pressures up to 10 MPa. To our best knowledge, the high-pressure solubility data of carbon dioxide in 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, [bmim][eFAP], has not been reported in the literature. Additionally, we report results of high pressure solubility measurements of carbon dioxide in tetracyanoborate-based ionic liquids: 1-ethyl-3-methylimidazolium ([emim][$B(CN)_4$]) and 1-hexyl-3-methylimidazolium ([hmim][$B(CN)_4$]), at the temperature of 313 K and pressures up to 19 MPa. Finally, we present also the volumetric behaviour of mixtures of those ionic liquids with carbon dioxide.

4.2. Materials and methods

4.2.1. Materials

The ionic liquids used in this work, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][eFAP]), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][eFAP]), 1-hexyl3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][eFAP]), 1-ethyl-3-methylimidazolium tetracyanoborate ([emim][$B(CN)_4$]) and 1-hexyl-3-methylimidazolium tetracyanoborate ([hmim][$B(CN)_4$]), were purchased from Merck KgaA, Germany, and used without further purification. The water content, determined by Karl Fischer coulometric titration (Metrohm 831 KF coulometer) was no higher than 300 ppm in all studied cases. Carbon dioxide (99.98% purity) was supplied by Air Liquide and was used as received. Dichloromethane of ≥99.9 mass% purity (Sigma–Aldrich) was used in solubility measurements as a solvent, in order to wash the lines and dissolve the salts precipitated after carbon dioxide expansion from the sample loop.

4.2.2. Apparatus and experimental procedure for solubility measurements

The measurements of solubility were performed analogously, and with the same apparatus, as described in the previous chapter (See section *3.2.2 Apparatus and experimental procedure*).

4.2.3. Apparatus and experimental procedure for volume expansion measurements

The apparatus used for volume expansion experiments is the same that has been used in our research group for the measurement of vapour-liquid equilibrium. It was described for the first time in 1993 [206], and the most up-to-date version has recently been described in detail in the work of Rebocho et al. [207]. The main part of the apparatus, shown in Figure 4.2, comprises a high pressure sapphire tube cell with the following dimensions: height – 15 cm, external diameter – 3.2 cm and internal diameter 1.9 cm (ca. 30 cm^3 volume), with a ruler attached to its side. It is placed inside a thermostatic air bath with high-power ventilator ensuring uniform bath temperature. The temperature is controlled by a Hart Scientific temperature controller (model 2100), with a stability of ±0.005 to ±0.02 °C. This controller uses a RTD probe from the same supplier (model 2622), as well as a heater. The pressure in the system is measured by a Setra pressure transducer (model Model 204/C204). The accuracy of the pressure determination is ±0.007 MPa, while the estimated temperature uncertainty is ±0.1 K.

In a typical experiment, ionic liquid is loaded into the cell, up to the level above a magnetic stirrer, and the required temperature, 313.15 K, is settled. The initial level of the liquid (at atmospheric pressure, P_0, and temperature, T, equalled to 313.15 K) is read out from the ruler and the whole system is flushed a few times with carbon dioxide. An experimental run starts with an addition of a small portion, ca. 0.5 MPa, of carbon dioxide into the cell. The mixture is stirred for approximately 20 minutes and then left to rest for another 20 minutes for equilibration. The resting period can be extended, if the pressure does not remain stable for 10 minutes, in order to ensure equilibrium. A new level of the liquid is recorded and an experimental run repeated until no significant change in the liquid level is observed. All experiments were performed twice to ascertain the reproducibility of the measurements.

The determination of volume expansion is based on the visual observation of the liquid level measured with a ruler with a precision of ±0.05 cm. The volume expansion is calculated by using the internal cross section area of the sapphire tube and by measuring the difference in height of the meniscus at the starting and final points. The calculated precision of the reported volume expansions is ±7 %.

As the phase equilibrium compositions were determined, once the volume expansion is known, the molar volumes of the liquid mixtures could be easily calculated. The main source of error for these values is the uncertainty in the measurement of the volume of the initial quantity of pure ionic liquid in the cell, especially because of the uncertainty in the volume of magnetic stirrer (0.7 ± 0.1 cm^3) that is immersed in the liquid. The estimated uncertainties of the calculated molar liquid volumes are ±2 cm^3/ mol.

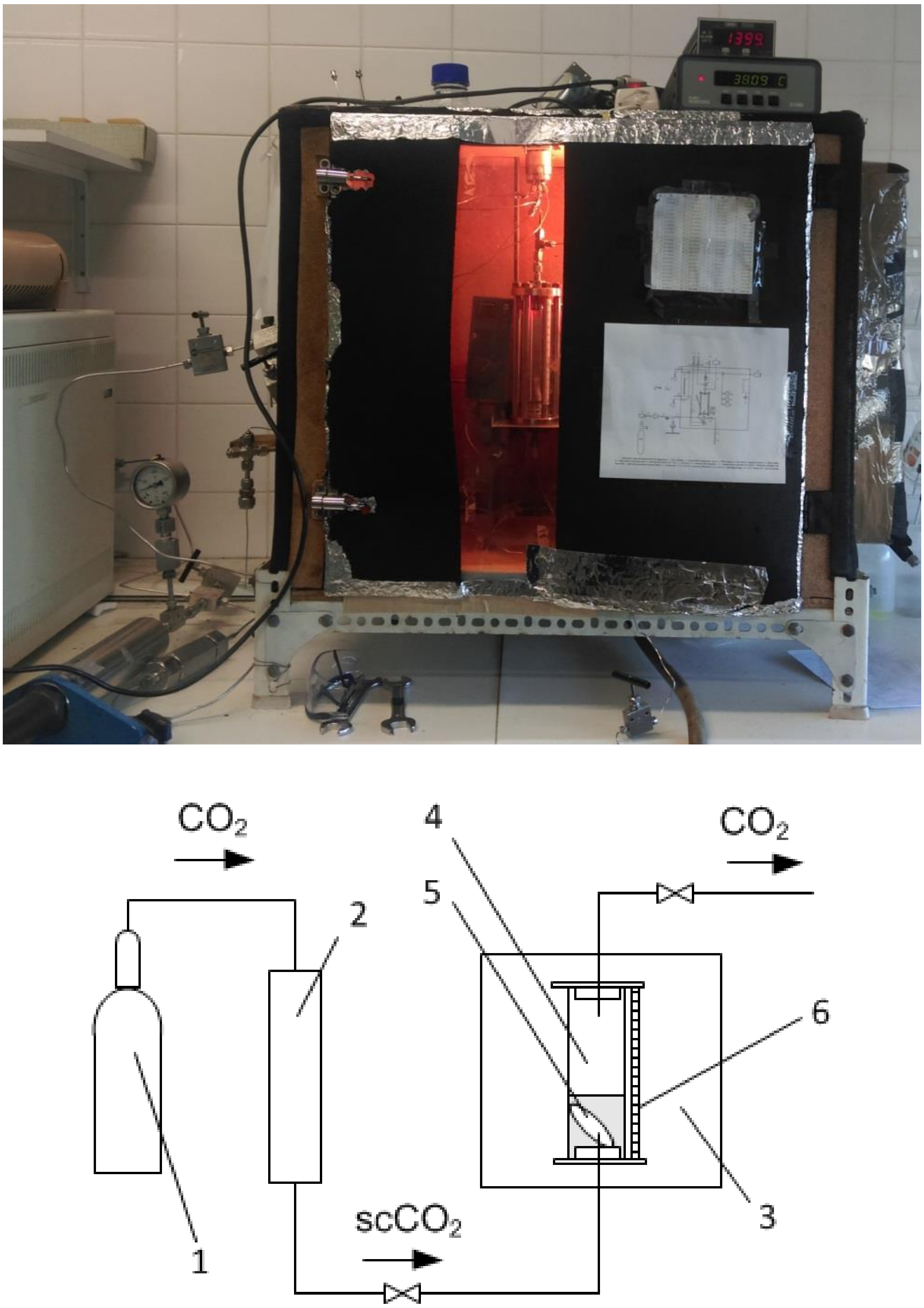


Figure 4.2. Scheme of the apparatus for volume expansion measurements: 1 – CO_2 supply; 2 – screw injector pump; 3 - air bath; 4 – high-pressure cylindrical view cell; 5 - magnetic bar; 6 - ruler.

4.3. Results and discussion

Table 4.1 presents high pressure solubility data of carbon dioxide in tris(pentafluoroethyl)trifluorophosphate-based ionic liquids: [emim][eFAP], [bmim][eFAP] and [hmim][eFAP], at the temperature of 313.15 K and pressures up to 10 MPa.

Table 4.1. Experimental solubility of CO_2 in [emim][eFAP], [bmim][eFAP] and [hmim][eFAP] at 313.15 K. x_{CO2} stands for mole fraction of carbon dioxide.

Ionic liquid	p / MPa	x_{CO2}
[emim][eFAP]	1.98	0.38
	4.02	0.57
	6.07	0.68
	8.07	0.74
	10.24	0.78
[bmim][eFAP]	2.02	0.44
	4.00	0.62
	6.05	0.69
	8.06	0.77
	10.14	0.78
[hmim][eFAP]	2.05	0.50
	3.72	0.62
	6.09	0.73
	8.08	0.79
	9.99	0.80

The solubility of carbon dioxide in fluoroalkylphosphate-based ionic liquids at high pressures was measured experimentally by Muldoon et al. [37] and Peters and co-workers [46]. The first group studied carbon dioxide absorption in [hmim][eFAP] and 1-pentyl-3-methylimidazolium tris(pentafluorobutyl)trifluorophosphate ([$p_5$mim][bFAP]) at two temperatures, 313.3 K and 333.3 K, and pressures up to 9 MPa. The second group investigated the solubility of carbon dioxide in [emim][eFAP] in the temperature range of 278.75 - 364.13 K and pressure up to 12 MPa. A comparison with carbon dioxide solubility in [emim][eFAP] measured in the current study indicates a very good agreement with the data reported in the literature (Figure 4.3). The solubility values obtained for [hmim][eFAP] differ slightly from those found in the literature, but remain mostly within the established uncertainties.

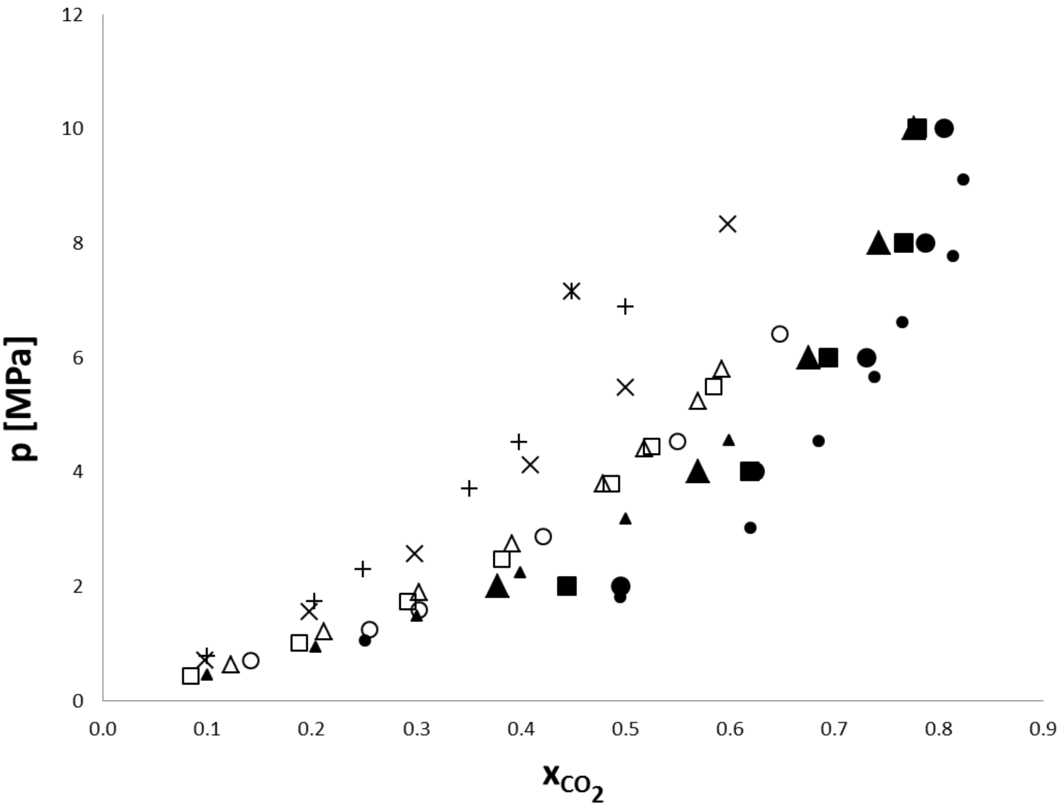


Figure 4.3. Solubility of CO_2 in several ionic liquids at 313.15 K: ●, [hmim][eFAP] [this work]; •, [hmim][eFAP] [37]; ■, [bmim][eFAP] [this work]; ▲, [emim][eFAP] [this work]; ▲, [emim][eFAP] [205]; ○, [hmim][NTf_2] [216]; □ [bmim][NTf_2] [215]; Δ, [emim][NTf_2)[214]; × [hmim][PF_6] [210]; + [bmim][PF_6] [211]; ж [emim][PF_6] [212].

Table 4.2 presents high pressure solubility data of carbon dioxide in tetracyanoborate-based ionic liquids: 1-ethyl-3-methylimidazolium ([emim][$B(CN)_4$]) and 1-hexyl-3-methylimidazolium ([hmim][$B(CN)_4$]), at the temperature of 313.15 K and pressures up to 19 MPa.

Table 4.2. Experimental solubility of CO_2 in [emim][B(CN)$_4$] and [hmim][B(CN)$_4$] at 313.15 K. x_{CO2} stands for mole fraction of carbon dioxide.

Ionic liquid	p [MPa]	x_{CO2}
[emim][B(CN)$_4$]	1.71	0.34
	3.66	0.52
	5.28	0.62
	7.3	0.67
	8.79	0.73
	12.25	0.76
	15.32	0.78
	18.45	0.79
[hmim][B(CN)$_4$]	4.8	0.61
	6.86	0.70
	8.95	0.74
	11.58	0.80
	12.65	0.80
	15.59	0.82
	17.11	0.82
	18.64	0.82

A comparison of CO_2 solubility in [emim][B(CN)$_4$] and [hmim][B(CN)$_4$] measured in this work with the data reported by Makino et al. [208] and Peters and co-workers [46], respectively, indicates fair agreement (Figure 4.4 a) and Figure 4.4 b)). The solubilities reported here are slightly higher than those found in the literature, but remain mostly within mutual experimental uncertainties. In both studies, the same binary systems, at an identical temperature but only up to moderate pressures, were studied. Results presented here provide a continuation to higher pressures of their plots.

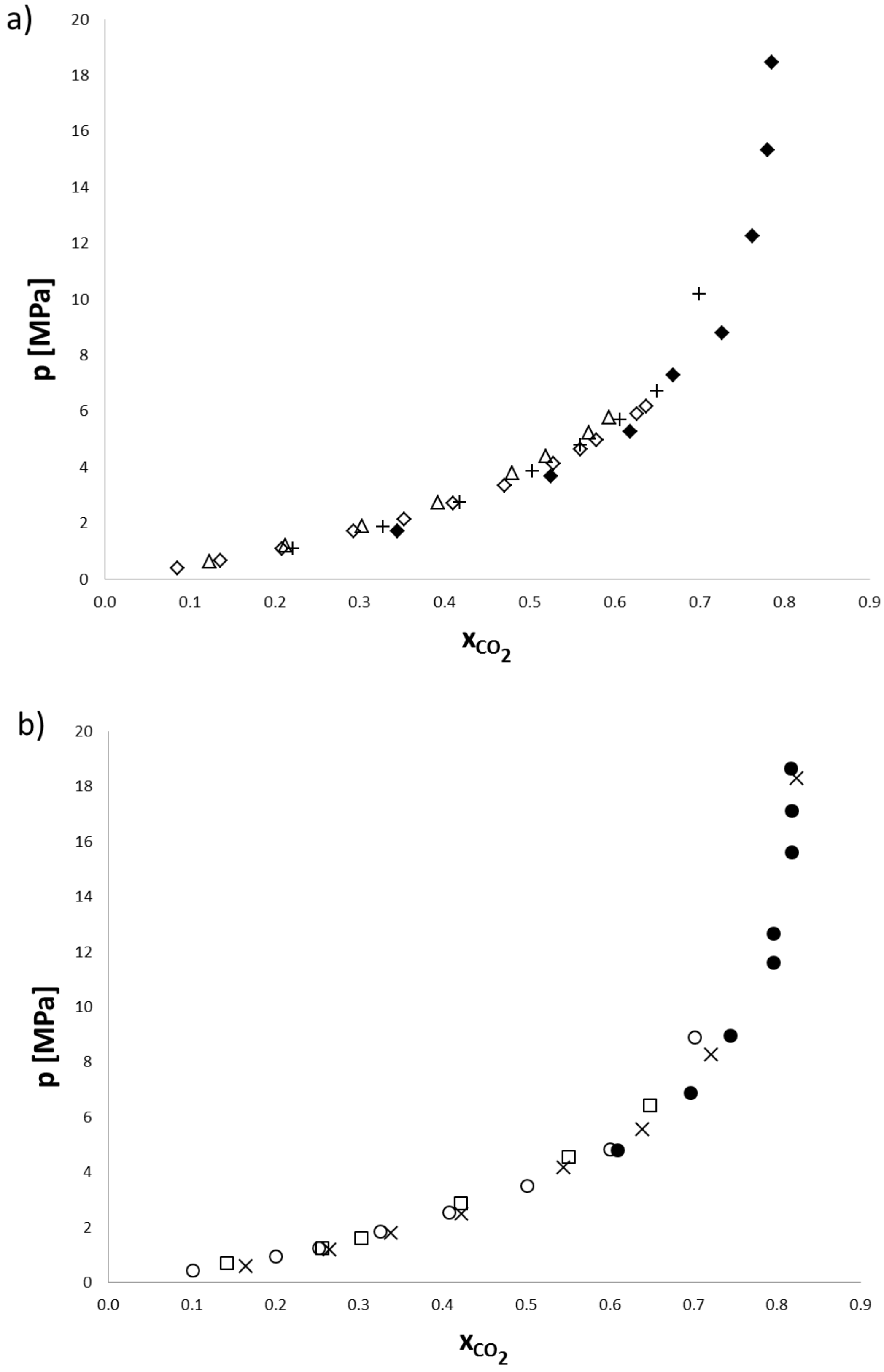


Figure 4.4. Solubility of CO_2 in several ionic liquids at 313.15 K: a) ♦, [emim][B(CN)$_4$] [this work]; ◊, [emim][B(CN)$_4$] [208]; Δ, [emim][NTF$_2$] [214]; + [emim][NTf$_2$] [215]; b) ●, [hmim][B(CN)$_4$] [this work]; ○, [hmim][B(CN)$_4$] [46]; □ [hmim][NTf$_2$] [216]; × [hmim][NTf$_2$] [217].

The compatibility of fluorinated substituents with CO_2 is commonly used to improve the CO_2-philicity of organic compounds [209]. Therefore, it was expected that ionic liquids with anions analogous to [PF_6], where three fluorine atoms are replaced by three fluoroalkyl chains, can absorb more CO_2. Zhang et al. [38], using a computational screening methodology, indeed found that the solubility of CO_2 in ionic liquids with the [eFAP] anion is among the highest, and confirmed it experimentally. For the same 1-hexyl-3-methylimidazolium cation, [eFAP]-IL can dissolve approximately 15 % and 70 % more CO_2, compared with [NTf_2]- and [PF_6]-IL, respectively, at 0.8 MPa and 298 K. A similar observation can be made here, as seen in Figure 4.3, where CO_2 solubility in ionic liquids with imidazolium cation and [eFAP] anion is slightly higher or about twice that in [NTf_2] [214,215,216] or [PF_6]-based [210,211,212] analogues, respectively. Blath et al. studied the solubility of various gases (carbon dioxide, carbon monoxide, nitrogen, and methane) in ionic liquids with several cations and anions [213]. Their results of CO_2 solubility, expressed in Henry's law constant at 333.15 K, also confirmed that [eFAP]-based ionic liquids have the highest affinity to CO_2 among most commonly investigated ionic liquids. Additionally, Blath et al. showed that [$B(CN)_4$]-based ionic liquids have comparable affinity to CO_2 with ionic liquids possessing [NTf_2] anions.

In the current study, CO_2 solubility in tetracyanoborate ionic liquids is equal to, or slightly higher than, solubility in fluorinated CO_2-philic ionic liquids, 1-alkyl-3-methylimidazolium bis(tri(fluoromethylsulfonyl)imides [214,215,216,217] (Figure 4.4 a) and Figure 4.4 b)). This result is consistent with another report for imidazolium-based ILs [200]. Mahurin et al. investigated the solubility of CO_2 in imidazolium-based ionic liquids attached to four different anions with an increasing number of nitrile groups, namely [bmim][$N(CN)_2$] (dicynamide), [bmim][$C(CN)_3$] (tricyanomethane) and [emim][$B(CN)_4$]). They showed that [emim][$B(CN)_4$] exhibits higher capacity for CO_2 absorption than [emim][NTf_2]. Similar trend was found for pyrrolidinium, and piperidinium cations [45]. In order to compare the influence of the nature of the cation in fluoroalkylphosphate-based ionic liquids, Costa Gomes and co-workers studied the solubility of several gases (carbon dioxide, nitrous oxide, ethane, and nitrogen) in ionic liquids bearing [eFAP] anion and 1-butyl-1-methylpyrrolidinium or trihexyl(tetradecyl)phosphonium cation, at 293.15-353.15 K temperature range and pressure close to atmospheric [40]. Phosphonium-based ionic liquids presented a higher mole fraction solubility of all four gases examined, while ionic liquids with pyrrolidinium or imidazolium cation showed comparable solubilities. The large differences in the mole fraction solubility were less pronounced though when the solubility is expressed in mass fraction. For the same reason of larger molecular weight, [$B(CN)_4$]-based ionic liquids exhibit even higher CO_2 capacity when compared to [NTf_2]-based analogues.

The effect of the cation is often regarded to be minor, with the difference being more apparent at higher pressures. A slight improvement of CO_2 solubility associated with an increase of the alkyl chain length on the imidazolium cation is commonly observed [152,153,213], and also in the cases of fluoroalkylphosphate- [39] and tetracyanoborate-based [45] ionic liquids. Costa Gomes and co-workers, analysing the solubility of carbon dioxide, nitrous oxide, and ethane in [eFAP]-ILs, at 303.15 K and atmospheric pressure, observed that the solubility increases from [emim] to [bmim], but seemed to remain constant when the alkyl side chain increases from [bmim] to [hmim] [39]. In the current study, where high pressure allows a better discrimination of solubility values, it consistently increases with the increase in the number of carbon atoms in the imidazolium alkyl side chain, from [emim] up to [hmim] (Figure 4.3). More, [hmim][$B(CN)_4$] also demonstrates slightly higher CO_2 solubility than [emim][$B(CN)_4$] (Figure 4.4 a) and Figure 4.4 b)). Mahurin et al. [45] showed that not only increasing the alkyl chain length from [emim] to [bmim] enhanced the CO_2 solubility, but also replacing the C2 hydrogen with a methyl group on the imidazolium ring has the same effect for tetracyanoborate-based ionic liquids.

In order to investigate the volumetric behaviour of mixtures of ionic liquids with high pressure carbon dioxide, the volume expansions were measured as percent changes of the total volume of the liquid phase, when the initially pure ionic liquid, at ambient pressure, was compressed with carbon dioxide:

$$\frac{\Delta V}{V}\% = \frac{V_L(T,P,x) - V_2(T,P_0)}{V_2(T,P_0)} \times 100 \quad (1)$$

where V_L is total volume of the liquid mixture at a given temperature, pressure and composition and V_2 is the volume of the pure liquid at the same temperature and ambient pressure. Calculated from these results are the percent molar volume expansions:

$$\frac{\Delta \tilde{V}}{\tilde{V}}\% = \frac{\tilde{V}_L(T,P,x) - \tilde{V}_2(T,P_0)}{\tilde{V}_2(T,P_0)} \times 100 \quad (2)$$

where both $\tilde{V}_L$ and $\tilde{V}_2$ are corresponding molar volumes.

To calculate the total volume expansion of the liquid phase, first variations in the level of the liquid phase of IL-CO_2 system need to be determined. The height of the head of the ionic liquid compressed with carbon dioxide is measured and plotted as a function of pressure (Figure 4.5). It can be seen, that as the pressure of carbon dioxide increases, the level of the liquid phase rises similarly for all [eFAP]- and [$B(CN)_4$]-based ionic liquids. There is a notable difference though between the behaviour of these ionic liquids and [bmim][BF_4], a system already investigated in the literature [153] and studied here once more for the purpose of comparison. For all ionic liquids, as pressure of carbon dioxide goes beyond 8-10 MPa, the slope of the curve gets steeper, meaning that even large changes in the pressure lead to only small increment of the liquid phase level, until there is no visible additional total volume expansion. In the case of [bmim][BF$_4$], the slope of the plot is higher since the beginning indicating a lesser increase in the volume.

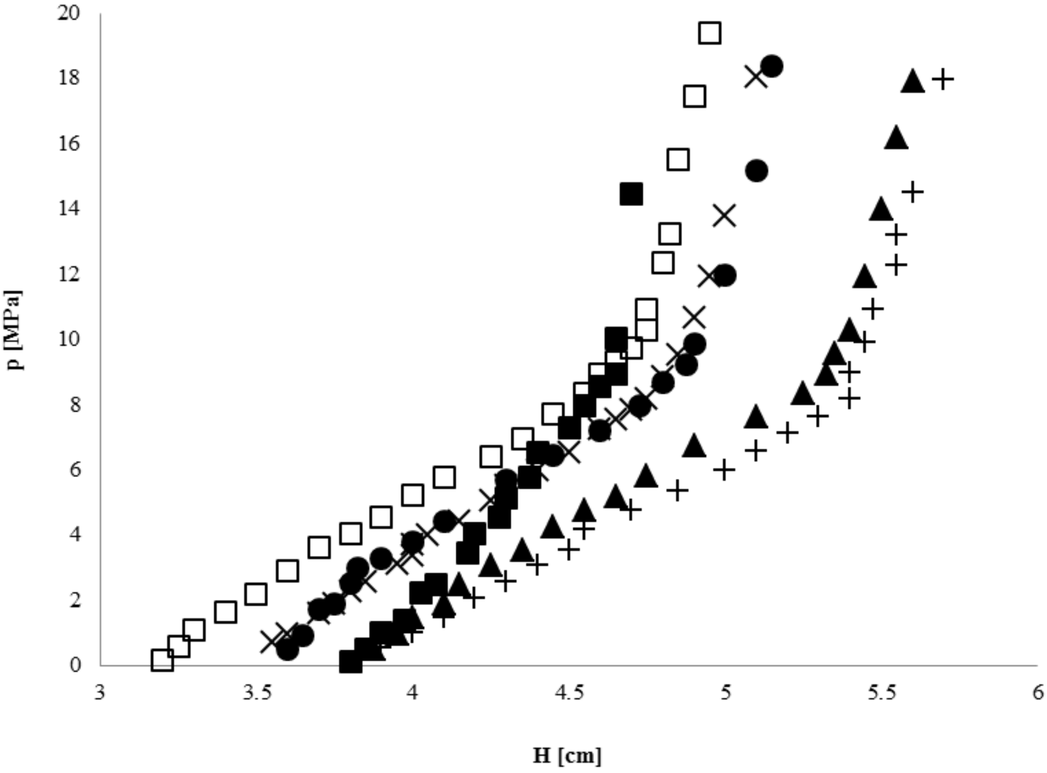


Figure 4.5. Change in the level of the liquid phase of IL-CO$_2$ systems measured with an increasing pressure of CO$_2$ at 313.15 K: × [emim][eFAP]; ●, [bmim][eFAP]; ▲, [hmim][eFAP]; □, [emim][B(CN)$_4$]; + [hmim][B(CN)$_4$]; ■, [bmim][BF$_4$].

Pictures of the maximum liquid phase levels observed for all of IL-CO$_2$ systems investigated in the current study can be found in Appendix A.

Knowing the difference in height of the meniscus at the starting and final points, the total volume expansion can be calculated using the internal cross section area of the experimental cell. On the basis of the experimental solubility data, the mole fraction of carbon dioxide, at a particular pressure corresponding to the measurement of the liquid phase level, can be estimated by interpolation. Eventually, using the density data present in the literature [39,46,189,218] the molar volume expansions can also be calculated.

The interpolated molar composition as well as the calculated total and molar volume expansions are summarised in (Table 4.3 and Table 4.4). Volume expansions in Figure 4.6 and Figure 4.7 were calculated with equation (1) and in Figure 4.8 and Figure 4.9 with equation (2).

Table 4.3. Calculated volume expansions of CO_2-[emim][eFAP], CO_2-[bmim][eFAP] and CO_2-[hmim][eFAP] systems at 313K. x_{CO2} stands for mole fraction of carbon dioxide.

p [MPa]	x_{CO2}	ΔV/V %	$\Delta\tilde{V}/\tilde{V}$ %	p [MPa]	x_{CO2}	ΔV/V %	$\Delta\tilde{V}/\tilde{V}$ %
	CO_2-[emim][eFAP]				CO_2-[bmim][eFAP]		
0.72	0.15	5	-11	0.48	0.10	5	-6
0.99	0.22	6	-17	0.94	0.25	6	-20
1.61	0.33	9	-27	1.74	0.41	8	-36
1.88	0.37	11	-30	1.90	0.44	9	-38
2.28	0.42	13	-35	2.54	0.51	11	-46
2.58	0.46	14	-38	2.97	0.56	12	-50
3.11	0.51	17	-42	3.28	0.58	14	-52
3.39	0.53	19	-44	3.77	0.61	17	-54
3.71	0.56	19	-47	4.43	0.64	20	-56
3.99	0.57	21	-48	5.69	0.69	26	-60
4.44	0.60	24	-51	6.45	0.72	31	-63
5.07	0.64	27	-54	7.21	0.74	36	-65
5.51	0.66	28	-56	7.96	0.76	40	-66
5.96	0.68	32	-57	8.67	0.77	42	-67
6.54	0.71	35	-60	9.23	0.78	44	-68
7.24	0.73	38	-62	9.85	0.78	45	-68
7.56	0.73	40	-62	11.96	0.79	48	-68
7.86	0.74	41	-63	15.17	0.79	51	-69
8.17	0.75	43	-64	18.38	0.80	53	-69
8.86	0.77	44	-66				
9.54	0.78	46	-67				
10.67	0.79	47	-68				
11.93	0.79	49	-69				
13.79	0.80	51	-70				
18.03	0.81	54	-71				

p [MPa]	x_{CO2}	ΔV/V %	$\Delta\tilde{V}/\tilde{V}$ %
	CO_2-[hmim][eFAP]		
0.49	0.20	2	-18
0.97	0.35	4	-32
1.48	0.43	6	-40
1.91	0.49	8	-44
2.48	0.53	10	-48
3.05	0.57	13	-52
3.56	0.60	15	-54
4.27	0.65	18	-58
4.76	0.67	21	-60
5.18	0.70	24	-62

5.80	0.73	27	-65
6.73	0.76	31	-68
7.63	0.78	36	-70
8.36	0.80	41	-71
8.91	0.80	43	-71
9.56	0.80	43	-72
10.29	0.81	45	-72
11.95	0.82	46	-73
14.00	0.82	48	-73
16.20	0.83	49	-74
17.93	0.83	50	-74

density data for [emim][eFAP], [bmim][eFAP] and [hmim][eFAP] used for calculations taken from [39].

Table 4.4. Calculated volume expansions of CO_2-[emim][B(CN)$_4$], CO_2-[hmim][B(CN)$_4$] and CO_2-[bmim][BF$_4$] systems at 313K. x_{CO2} stands for mole fraction of carbon dioxide.

p [MPa]	x_{CO2}	ΔV/V %	Figure 4.8	p [MPa]	x_{CO2}	ΔV/V %	$\Delta\tilde{V}/\tilde{V}$ %
CO_2-[emim][B(CN)$_4$]				CO_2-[hmim][B(CN)$_4$]			
0.59	0.11	2	-9	0.54	0.13 [a]	3	-10
1.08	0.26	3	-23	1.01	0.20 [a]	6	-16
1.64	0.35	7	-31	1.47	0.28 [a]	8	-22
2.18	0.41	10	-35	2.05	0.35 [a]	11	-28
2.89	0.47	13	-40	2.55	0.41 [a]	14	-33
3.62	0.51	17	-43	3.07	0.46 [a]	17	-37
4.06	0.54	20	-45	3.52	0.51 [a]	20	-41
4.53	0.58	24	-47	4.19	0.57 [a]	21	-47
5.21	0.61	27	-50	4.78	0.60	25	-50
5.79	0.64	30	-52	5.36	0.63	29	-52
6.39	0.66	35	-53	5.98	0.66	34	-54
6.96	0.68	39	-55	6.58	0.68	36	-56
7.71	0.70	42	-57	7.11	0.70	39	-58
8.34	0.71	46	-58	7.61	0.72	42	-60
8.91	0.72	47	-59	8.18	0.74	45	-62
9.29	0.73	49	-59	8.99	0.76	45	-65
9.76	0.73	51	-59	9.91	0.77	46	-66
10.30	0.74	52	-60	10.93	0.79	47	-68
10.93	0.75	52	-61	12.25	0.80	49	-69
12.34	0.76	54	-62	13.20	0.81	49	-71
13.22	0.77	55	-64	14.49	0.81	50	-71
15.50	0.78	56	-66	17.96	0.82	53	-72
17.46	0.78	57	-66				
19.38	0.79	59	-67				

p [MPa]	x_{CO2}	ΔV/V %	$\Delta\tilde{V}/\tilde{V}$ %
	CO_2-[bmim][BF_4]		
0.51	0.04 [b]	1	-3
1.02	0.12 [b]	3	-9
1.40	0.16 [b]	5	-11
2.22	0.23 [b]	6	-18
2.50	0.25 [b]	8	-19
3.47	0.31 [b]	11	-24
4.05	0.35 [b]	11	-28
4.54	0.37 [b]	13	-29
5.16	0.41 [b]	14	-32
5.79	0.43 [b]	16	-34
6.52	0.46 [b]	17	-36
7.29	0.49 [b]	20	-39
7.97	0.52 [b]	21	-41
8.54	0.53 [b]	22	-42
8.96	0.53 [b]	24	-42
10.03	0.54 [b]	24	-43
14.48	0.55 [b]	25	-44

[a] solubility data taken from [46]; [b] solubility data taken from [153]; density data for [emim][$B(CN)_4$], [hmim][$B(CN)_4$] and [bmim][BF_4] used for calculations taken from [189], [46] and [218], respectively.

For the purpose of comparison, the literature data for [bmim][PF_6] and [bmim][BF_4] was included into the figures due to their structural resemblances to the newly examined ionic liquids. Additionally, the data for [NTf_2]-based ionic liquids was selected since this ionic liquid is among the ones with the highest CO_2 solubility and, at the same time, shows the largest volume expansion [153].

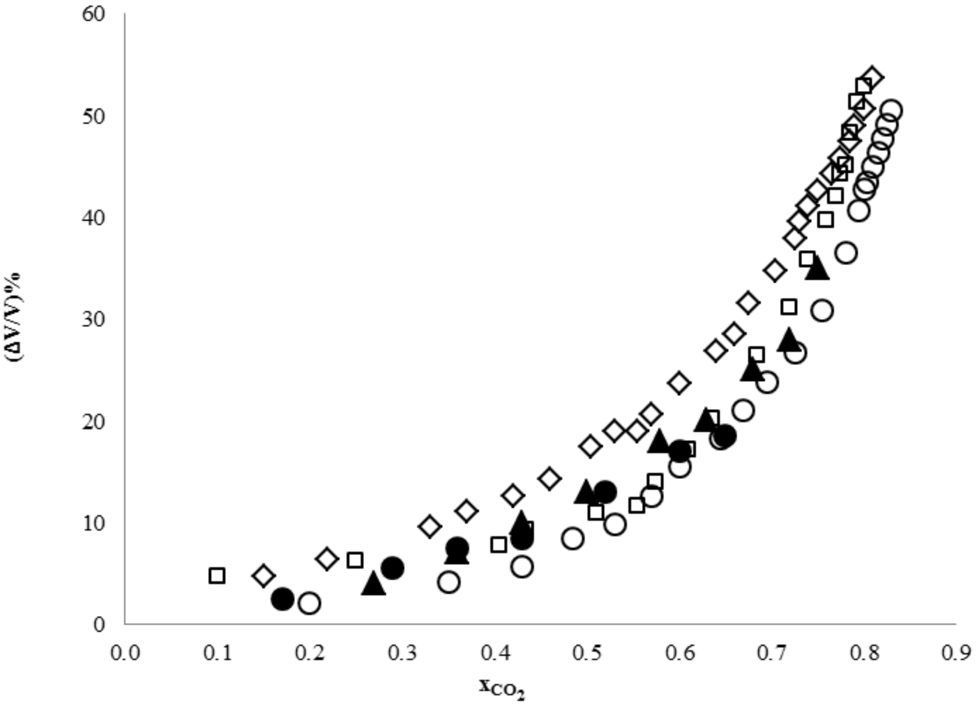


Figure 4.6. Volume expansion based on change in total volume of the liquid upon addition of CO_2 to various ionic liquids at 313.15 K as defined by eq (1); ◊, [emim][eFAP] [this work]; □, [bmim][eFAP] [this work]; ○,[hmim][eFAP] [this work]; ●, [bmim][PF_6] [153]; ▲, [hmim][NTf_2] [153].

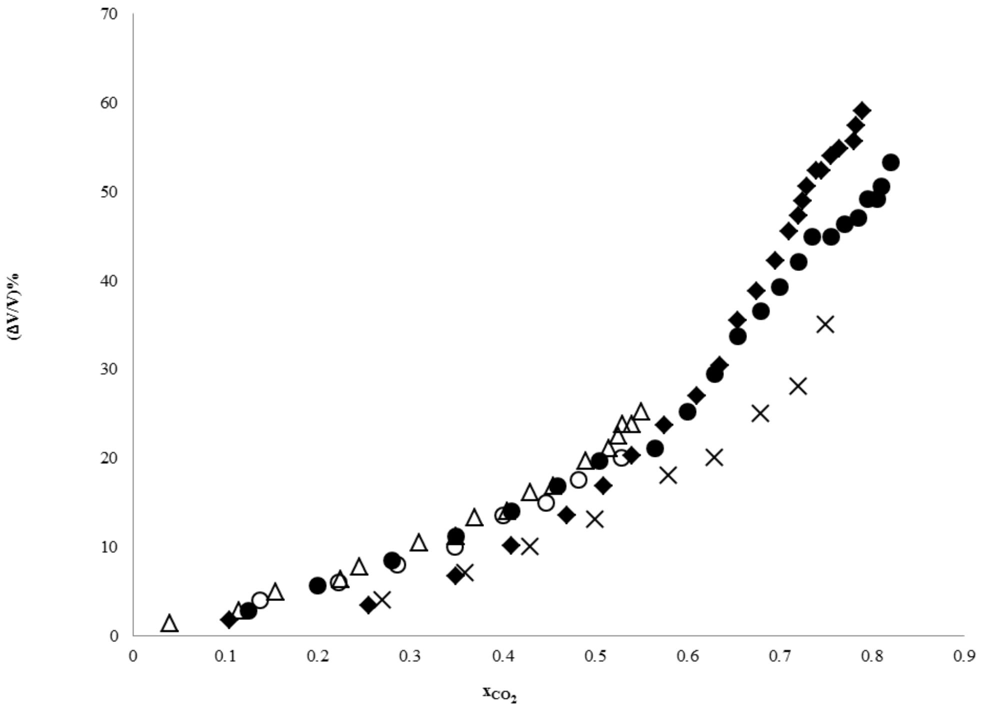


Figure 4.7. Volume expansion based on change in total volume of the liquid upon addition of CO2 to various ionic liquids at 313.15 K as defined by eq (1); ♦, [emim][$B(CN)_4$] [this work]; ●,[hmim][$B(CN)_4$] [this work]; Δ, [bmim][BF_4] [this work]; ○, [bmim][BF_4] [153]; ×, [hmim][NTf_2] [153].

All investigated ionic liquids show analogous behaviour to ionic liquids examined by Brennecke and co-workers in a way that the plots of total volume expansions are similar. However, a remarkable difference can be noticed in the magnitude of the measured volume expansions. Carbon dioxide mixtures with all fluoroalkylphosphate-based ionic liquids studied in this work, [emim][eFAP], [bmim][eFAP] and [hmim][eFAP], reach approximately 55% total volume expansions, almost twice and triple the size of total volume expansions obtained for [NTf_2]- and [PF_6]-based ionic liquids, respectively (Figure 4.6). Even higher total volume expansion, of almost 60%, were obtained for either [emim][$B(CN)_4$] or [hmim][$B(CN)_4$] (Figure 4.7). For the arbitrary pressure of 10 MPa, approximately 75 mol % of CO_2 can be dissolved in ionic liquids investigated in this work (75 mol % in [hmim][NTf_2] [153], 77 mol % in [hmim][$B(CN)_4$], and 73.5 mol % in [emim][$B(CN)_4$]). The magnitude of total volume expansions equals to 35 %, 46 % and 52 %, respectively. Conversely, [bmim][PF_6]-CO_2 system, with 69 mol % of the gas (at 8.5 MPa) exhibits a mere 18 % volume increase over the pure ionic liquid [152]. At higher pressures, the volume of tetracyanoborate-based ionic liquids expands to approximately 55 and 60 % for [hmim][$B(CN)_4$] and [emim][$B(CN)_4$], respectively, corresponding to 80 mol % of CO_2.

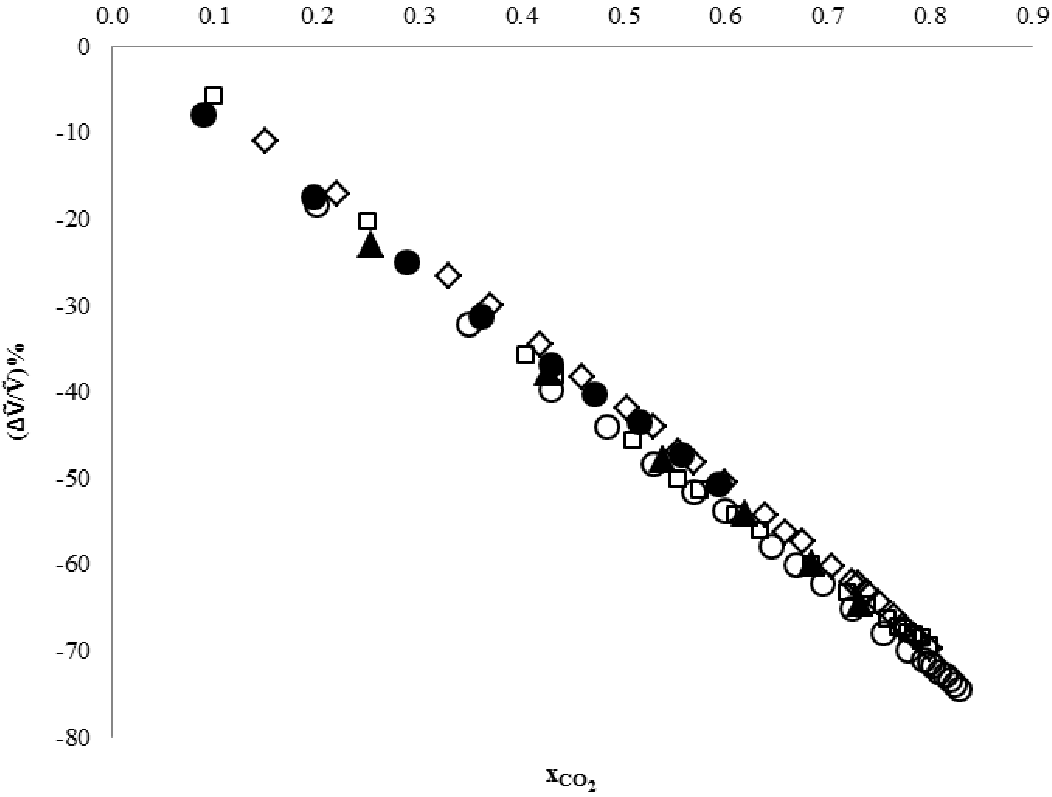


Figure 4.8. Volume expansion based on change in molar volume of the liquid upon addition of CO_2 to various ionic liquids at 313.15 K as defined by eq (2); ◊, [emim][eFAP] [this work]; □, [bmim][eFAP] [this work]; ○,[hmim][eFAP] [this work]; ●, [bmim][PF_6] [153]; ▲, [hmim][NTf_2] [153].

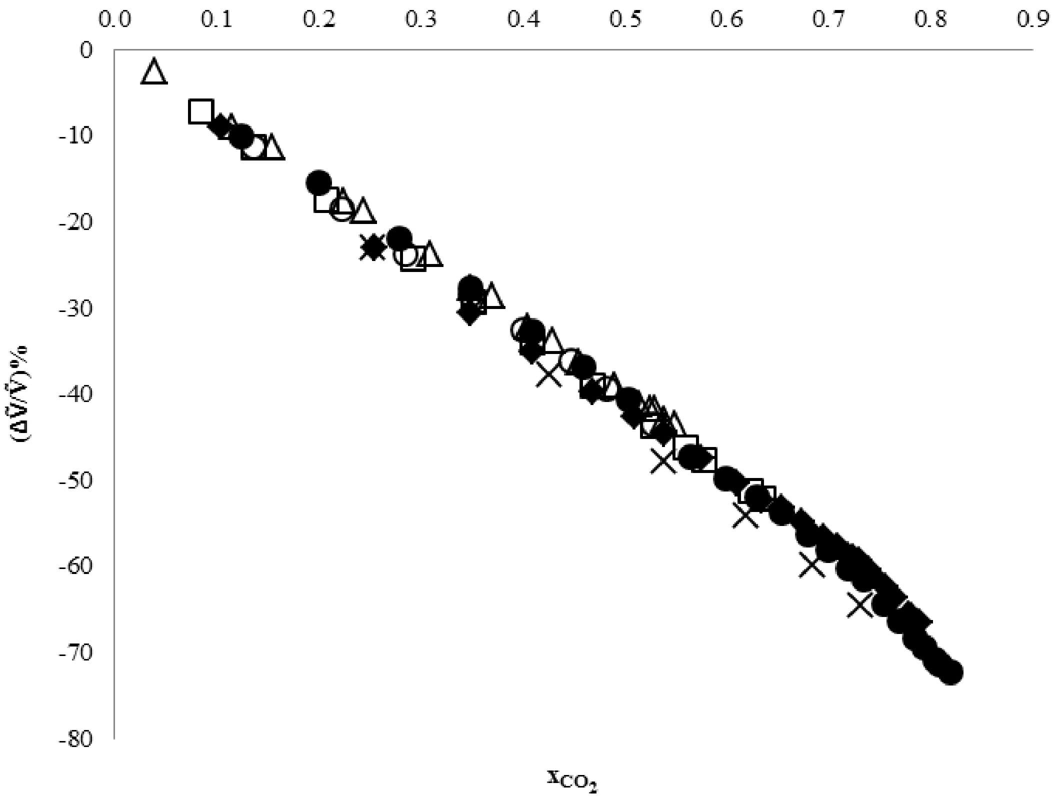


Figure 4.9. Volume expansion based on change in molar volume of the liquid upon addition of CO_2 to various ionic liquids at 313.15 K as defined by eq (2); ♦, [emim][B(CN)$_4$] [this work]; □, [emim][B(CN)$_4$] [208]; ●, [hmim][B(CN)$_4$] [this work]; Δ, [bmim][BF$_4$] [this work]; ○, [bmim][BF$_4$] [153]; ×, [hmim][NTf$_2$] [153].

Comparing equations for the total and molar volume expansion, it can be easily shown that the two volume expansions are related by a simple equation:

$$\frac{\Delta\tilde{V}}{\tilde{V}} = \frac{\Delta V}{V} x_2 - x_{CO2} \qquad (3)$$

From this correlation, and from Figure 4.8 and Figure 4.9, some general conclusions about the slope and shape of $\Delta\tilde{V}/\tilde{V}$ vs. x_{CO2} plot can be drawn. When $\Delta V/V$ is small, the molar volume expansion can be negative. Once the total volume expansion increases and $\Delta V/V$ reaches high values, i.e. in the case of mixtures of carbon dioxide with many organic solvents, the molar volume expansions may turn positive. For ionic liquids this does not happen and the molar volume expansion continuous to decrease until no more CO_2 molecules can be dissolved. As during the dissolution more and more carbon dioxide is being introduced into the ionic liquid phase, the molar density must be increasing. Since the liquid phase of IL-CO_2 does not expand significantly, it means that the mechanism governing the dissolution must be influenced by the free volume effect.

Another observation from equation (3) is that the molar volume expansion is a less sensitive quantity than the total volume expansion. With an increase in ΔV and simultaneous decrease in x_2, the quantity obtained from their multiplication varies slowly. As a consequence, the values for $\Delta\tilde{V}/\tilde{V}$ for all ionic liquids presented in Figure 4.8 and Figure 4.9 are indistinguishable. For this reason, the systems with small total volume expansions should be analysed considering the change in the total, and not molar, volume of a mixture, as opposed to the conclusions previously stated in the literature by de la Fuente et al. [203], who investigated organic solvents + CO_2 mixtures exhibiting large ΔV/V values.

The enhanced carbon dioxide solubility in [eFAP]-based ionic liquids was attributed by several authors to favourable interactions between carbon dioxide and the highly fluorinated anion [37,205,209]. When electronegative fluorine atoms are present, the C–F bond (Lewis base) may interact with the electron-deficient carbon atom of CO_2 that acts as a Lewis acid. Additionally, the oxygen atom of CO_2 (Lewis base) can be involved in hydrogen-bonding with the relatively more acidic protons of the ionic liquid because of the presence of neighbouring fluorine atoms.

The structure of ions, the size and shape, has a significant influence on the mechanism for carbon dioxide dissolution in ionic liquids. Recently, a strong correlation between the ratio of unoccupied space in pure ionic liquids (free volume) and its ability to absorb carbon dioxide has been found by molecular dynamics simulations [154]. Large and asymmetric ions lead to larger average distances between cations and anions, and thus weaker mutual attraction. Weak electrostatic cation-anion interaction allows for easy enlargement of cavities of the ionic liquids structure, which in turn results in higher carbon dioxide solubility as more CO_2 molecules can accommodate within the voids. Magnin and co-workers showed that there are three kinds of high density areas of carbon dioxide around bulky [eFAP] anion [219].

Therefore, a possible explanation for such a remarkable increase in volume expansion as obtained in this work may originate from a weakly coordinating nature of ionic liquids [155,220,221,222,]. Babarao et al., using molecular dynamics simulation and quantum mechanical calculations, investigated the structural correlations in [emim][$B(CN)_4$]-CO_2 and [emim][NTf_2]-CO_2 systems [155]. By analysing the atom-atom radial distribution functions they found out that the [$B(CN)_4$] anion is located slightly farther from the [emim] cation than is the [NTf_2] anion, H-bonding within [emim][$B(CN)_4$] is weaker and organisation of CO_2 around [$B(CN)_4$] anion is stronger. Thus, easy enlargement of cavities of the ionic liquid structures is possible. Additionally, they reported that the cation-anion binding energy and carbon dioxide solubility (at atmospheric pressure and room temperature) for four ionic liquids with the same [emim] cation and different anions ([BF_4], [PF_6], [NTf_2] and [$B(CN)_4$]) show a good correlation, on the contrary to CO_2-anion interactions when compared to solubility of carbon dioxide. Gupta [222] also found that [bmim][$B(CN)_4$] have lower than [bmim][NTf_2] binding energy. Additionally, he analysed the binding energy of four more tetracyanoborate-based ionic liquids with different cations and showed that it increases in the order of 1-butylpyridinium ($[C_4Py]$) < [bmim] < 1-propargyl-3-methylimidazolium ($[HCC\text{-}C_1mim]$) < N-((dimethyl-amino)methylene)-N-methylmethanaminium, ($[(N_{11})_2CH]$) < 1-ethanenitrile-3-methylimidazolium ($[NC\text{-}C_1mim]$). $[C_4Py][B(CN)_4]$, with the lowest cation-anion binding energy, was predicted to possess the largest fractional free volume, the highest carbon dioxide solubility and diffusivity.

All of that indicates that the weak interaction between cation and anion allows for easy enlargement of cavities of the ionic liquids structure, which in turn results in higher CO_2 solubility, as more CO_2 molecules can accommodate within the voids. As a result of this, Babarao et al [155] predicted that the liquid phase should also experience a bigger volume expansion. The experimental results presented in this work are consistent with these computational finding and seem to confirm the proposed mechanism of CO_2 dissolution.

4.4. Conclusions

The high pressure solubility data of carbon dioxide in ionic liquids based on tetracyanoborate and tris(pentafluoroethyl)trifluorophosphate anions, as well as the volumetric behaviour of their mixtures, have been presented in this study. Fluoroalkylphosphate-based ionic liquids show one of the greatest affinities for carbon dioxide among ionic liquids with physisorption mechanisms. High degree of fluorination, together with a bulkiness of the constituting ions, seems responsible for such high carbon dioxide solubility and exceptional, (in the case of CO_2-ionic liquids mixtures) volume expansion of the liquids phase. Intriguingly, similarly high carbon dioxide solubility, and even higher volume expansion of the liquid phase, was found for the systems with ionic liquids bearing the small and highly symmetric tetracyanoborate anion. These results reaffirm the ongoing debate over the mechanism governing gas solubility in ionic liquids. It seems that the weak coordination of the anions with the 1-alkyl-3-methylimidazolium cation plays a crucial role in the dissolution process.

Notably higher, but still much smaller than for organic solvent + carbon dioxide mixtures, total volume expansion of IL-CO_2 systems indicates the free volume effect. Weak anion-cation interactions within the structure of the investigated ionic liquids allow for easy creation of cavities for accommodation of CO_2 molecules, thus, higher absorption capacities. The lack of any appreciable increase in the total volume at the time of the increase in molar density confirms the interspace filling mechanism of dissolution.

5. Carbon dioxide as a reaction and extraction medium

5.1. Introduction

The C-H insertion reaction of diazo compounds catalysed by dirhodium(II) complexes has developed into a very reliable methodology to form new C-C bonds from otherwise unreactive C-H bonds. As shown in Figure 5.1 this reaction involves the generation of a metallocarbene which undergoes the C-H insertion forming the new C-C bond at the same time that it regenerates the catalyst [47,223,224,225,226,227,228,229].

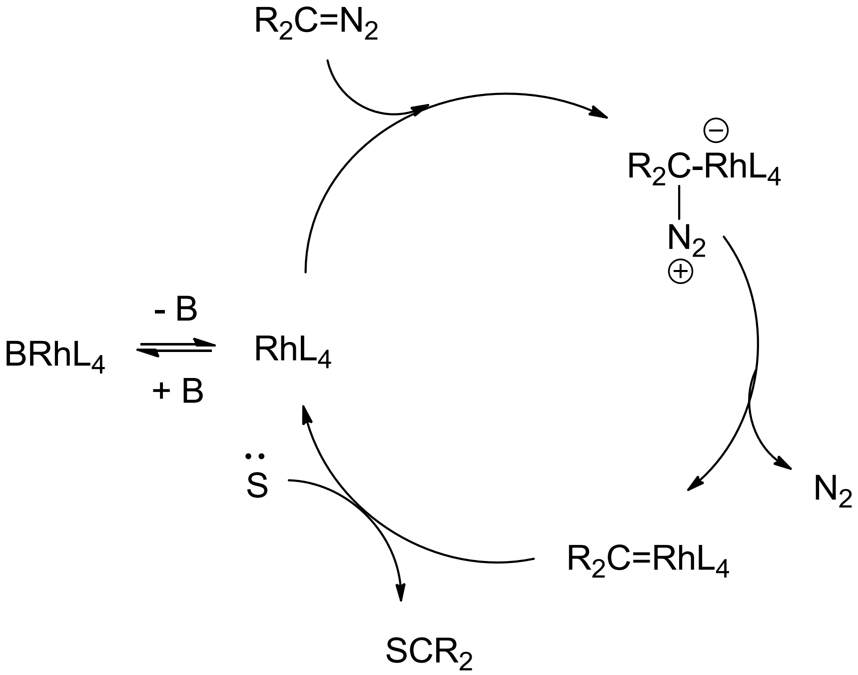


Figure 5.1. General mechanism for the generation of metallocarbenes from diazo compounds and dirhodium(II) complexes.

From the sustainability point of view, the catalysed C-H bond insertion starting from diazo compounds is an ideal process, as it affords important C-C bonds generating nitrogen as the sole waste, if only the C-H insertion step is considered. In order to further improve the sustainability of this methodology, it is important to introduce more benign reaction media, as the reaction is typically carried out in organic solvents such as dichloromethane, in order to avoid catalyst inhibition due to solvent coordination onto the complex axial positions (Figure 5.1) [47,223,224,225,226,227, 228,229]. In addition to this, dirhodium(II) complexes are quite expensive and for that reason methodologies that enable the catalyst recycling are of pivotal importance [230,231,232,233,234,235,236,237,238,239,240,241].

Over the years, it has been shown that new solvents are available to perform this reaction and enable the catalyst reutilisation. Ionic liquids and water have proven to be efficient reaction media, in which the catalyst reutilisation was achieved in 6 and over 11 cycles, respectively [242,243,244,245,246]. However, despite the usefulness of these approaches, both required product extraction with organic solvents and subsequent purification. An ideal methodology would involve the reaction taking place in a solvent that affords the product in high yields, and, at the same time, enables the product/catalyst separation, leaving the complex ready for another reaction cycle. Taking that into consideration, supercritical carbon dioxide seemed a proper solvent for this process.

5.2. Materials and methods

5.2.1. Materials

Preparative thin layer chromatography plates were prepared with silica gel 60 GF254 MercK (Ref. 1.07730.1000). Reaction mixtures were analysed by TLC using ALUGRAM† SIL G/UV254 from MN (Ref. 818133, silica gel 60), and visualisation of TLC spots was effected using UV and $KMnO_4$ solution. NMR spectra (Appendix B) were recorded in a Bruker AMX 400 using $CDCl_3$ as solvent and $(CH_3)4Si$ (1H) as internal standard. All coupling constants are expressed in Hz. The enantiomeric excess of **14** was determined using high-performance liquid chromatography with a Chiralcel column in the following conditions: Chiralpak AD column, Hexane/iso-Propanol 97:3, 0.7 cm^3/min, 225 nm, Rt = 11.3 min (major), and Rt = 13.1 min (minor).

Dirhodium(II) complexes: tetracetate, perfluorobutyrate and octanoate complexes were purchased from Aldrich and $Rh_2(S\text{-}PTPA)_4$ and $Rh_2(S\text{-}PTTL)_4$ were prepared accordingly with reported procedures [223,224]. The diazoacetamides: **1, 3**, **5, 7**, **9**, **12**, **14** and **17** were prepared according with reported procedures [225,226,227]. Lactam **2** was obtained as characterised in reference [225], lactams **8**, **11**, **13** and **16** in reference [226], lactams **6** and **18** and hydroxy acetamide **15** in reference [227].

All syntheses and analyses were performed by Professor Carlos A.M. Afonso and Pedro Gois, and co-workers, at the Faculty of Pharmacy of the University of Lisbon.

5.2.2. Apparatus and experimental procedure for the cyclisation process

A 3.5-cm^3 high-pressure cell was charged with diazoacetamide (0.173 mmol) and dirhodium(II) complex (1 mol%) and placed inside a constant temperature water bath. Carbon dioxide was introduced into the cell by a screw injector pump, at a constant temperature of 303.15 K. The mixture was stirred with a magnetic stirrer for 24 hours under 303.15 K and 7 MPa. After which, the system was depressurised and the conversions and *cis:trans* stereoselectivities determined based on ^{1}H or ^{31}P NMR. In specific cases, the product was filtered through alumina in order to epimerise the product form from cis to trans.

5.2.2. Apparatus and experimental procedure for the cyclisation process and supercritical carbon dioxide extraction

In the case of the recycling experiment, a 3.5-cm^3 high-pressure cell was charged with diazoacetamide (0.173 mmol) and dirhodium (II) complex (1 mol%) and placed inside a constant temperature water bath. Carbon dioxide was introduced into the cell by a screw injector pump, at a constant temperature of 303.15 K. The mixture was stirred with a magnetic stirrer for 24 hours under 303.15 K and 7 MPa. Subsequently, supercritical extraction was performed at a constant pressure of 17 MPa and 313.15 K. The extraction was considered finished when 0.35 mol of CO_2, corresponding to displacing 19 cm^3 of the volume of the screw injector pump, had passed through the system. The product was collected in cold traps filled with dichloromethane and cooled by a (ice + sodium chloride) mixture (Figure 5.2). After this, the system was depressurised, and a fresh quantity of diazoacetamide (0.173 mmol) was added to the dirhodium(II) complex that remained in the cell after the extraction. The collected product purity was determined based on ^{1}H NMR.

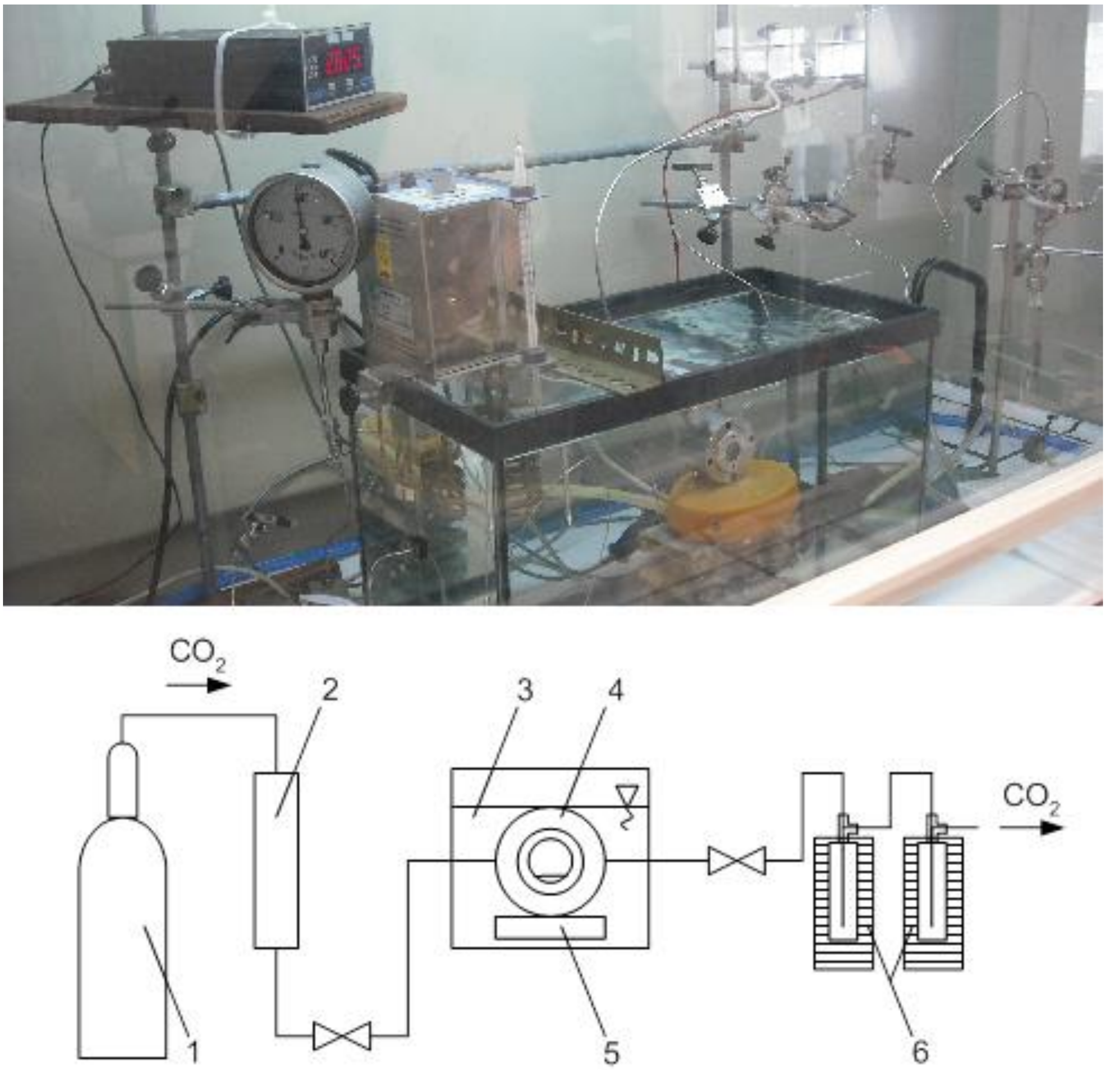


Figure 5.2. Schematic diagram of the apparatus for the cyclisation of diazoacetamide with dirhodium(II) complexes in CO_2: 1 – CO_2 supply; 2- screw injector pump; 3 - constant temperature water bath; 4 - high-pressure cell; 5 - magnetic stirrer; 6 - cold traps.

5.3. Results and discussion

Dense-phase carbon dioxide has already been successfully used as a solvent in many homogeneously metal-catalysed reactions [114,247,248,249,250,251]. However, as far as our knowledge goes, the intramolecular or intermolecular C-H insertion with diazo compounds catalysed by dirhodium(II) complexes has never been reported.

The formation of β-lactams was investigated on the example of diazoacetamides **1**, **3**, **5**, and **7**, bearing different α-substituents (Figure 5.3). The cyclisation reactions were performed at 303.15 K and 7 MPa of carbon dioxide, for 24 hours and with 1 mol% of a catalyst, being either the perfluorinated dirhodium(II) complex $Rh_2(pfb)_4$ (tetratkis perfluorobutanoate di-rhodium(II)) or a complex featuring octanoate or acetate as the dirhodium(II) bridging ligands ($Rh_2(Ooct)_4$ - tetratkis octanoate di-rhodium(II) or $Rh_2(OAc)_4$ - dirhodium(II) tetra-acetate).

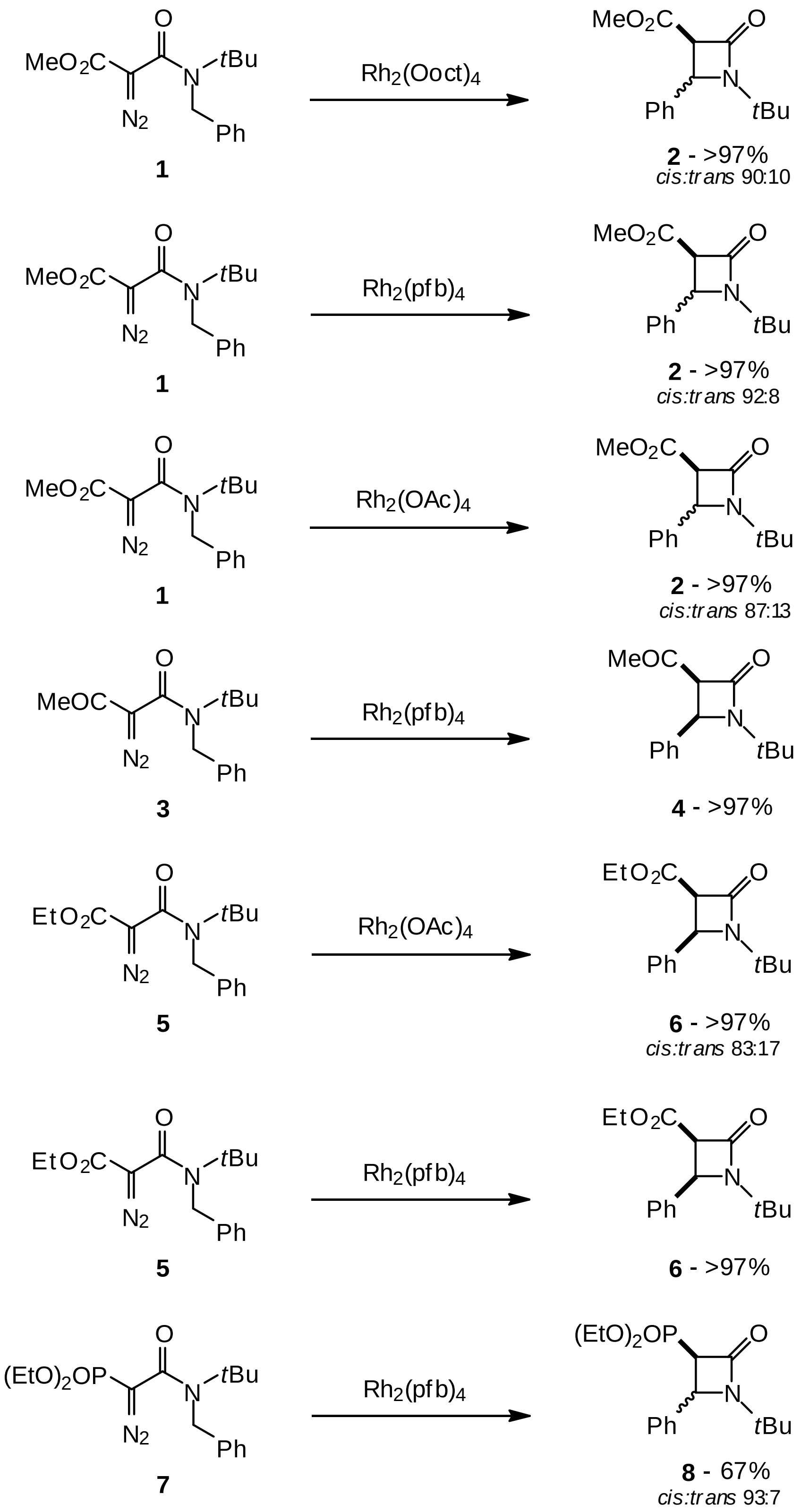


Figure 5.3. Intramolecular C-H insertion of diazoacetamide **1**, **3**, **5** and **7** using dirhodium(II) complexes in CO_2 at 303.15 K and 7 MPa, for 24 hours and with 1 mol% of a catalyst. Conversions and *cis:trans* stereoselectivities determined based on ^{1}H and ^{31}P NMR.

The presence of a bulkier and more hydrophilic phosphoryl group in **7** resulted in its less selective transformation and the lactam **8** was obtained in 67%. However, the diastereoselectivity obtained in the cyclisation of **7** in carbon dioxide (*cis:trans* 93:7) compares favourably with the results obtained in dichloromethane (*cis:trans* 88:12), water (*cis:trans* 62:38), or under photochemical conditions in hexane (*cis:trans* 33:67) [244,245,246,252,253,254,255,256].

The synthesis of five-membered rings in dense phase carbon dioxide as a reaction medium was also investigated. As shown in Figure 5.4, different phosphoryl diazoacetamides successfully underwent the C-H insertion in the presence of $Rh_2(pfb)_4$, to form the expected lactams in good yields.

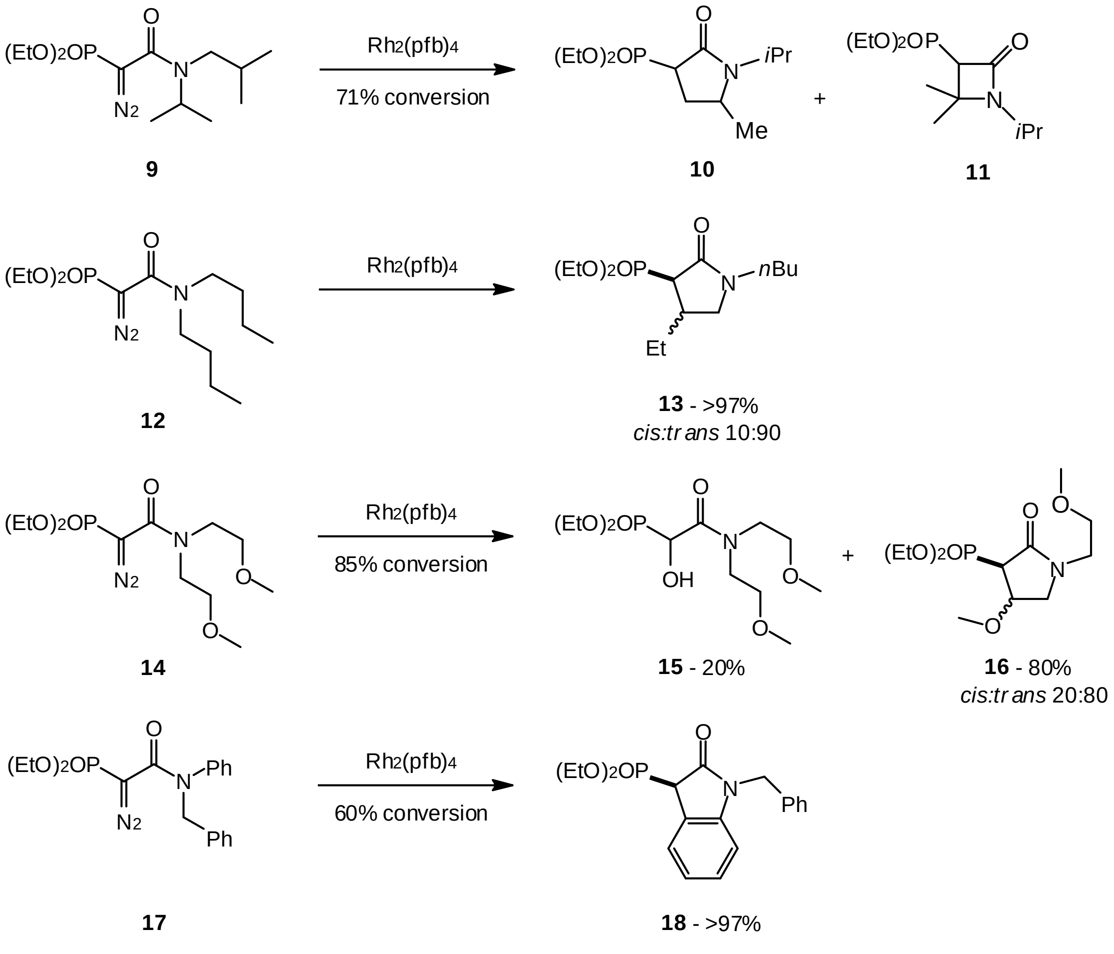


Figure 5.4. Intramolecular C-H insertion of phosphoryl-diazoacetamides **9, 12, 14** and **17** using $Rh_2(pfb)_4$ in CO_2 at 303.15 K and 7 MPa, for 24 hours and with 1 mol% of a catalyst. Conversions and *cis:trans* stereoselectivities determined based on ^{31}P NMR.

The formation of the alcohol from substrate **14** is probably due to the hygroscopic nature of this compound and the presence of water molecules nearby the metallocarbenoid centre. The alcohol is formed exclusively when performing the cyclisation of this compound in water, as observed in previous studies [244,245,246]. In the case of substrate **17**, the lower conversion may result from a weaker solvent stabilisation of the zwitterionic intermediate in the aromatic substitution.

Using chiral dirhodium(II) complexes, $Rh_2(S\text{-PTPA})_4$ or $Rh_2(S\text{-PTTL})_4$ (structures can be found in Appendix C), the asymmetric version of the C-H insertion of diazoacetamides in carbon dioxide is also possible. It was verified that substrate **5** transforms into β-lactam **6** quantitatively with 52% and 65% ee after epimerisation in basic alumina, using $Rh_2(S\text{-PTPA})_4$ or $Rh_2(S\text{-PTTL})_4$, respectively (the cyclisation conditions: 303.15 K, 7 MPa, 24 h and 1 mol% of a catalyst).

For the purpose of evaluation whether high-pressure carbon dioxide is capable of separating product from the catalyst, the system composed of substrate **5** and $Rh_2(OAc)_4$ complex as catalyst has been studied. As mentioned earlier in the thesis, fluorination of compound increases its affinity towards carbon dioxide. Therefore, a dirhodium(II) complex with a lower fluorine content would be less soluble in the carbon dioxide phase and, consequently, would be less extracted. The cyclisation of substrate **5** affords the expected β-lactam **6** exclusively, with *cis:trans* 83:17 stereoselectivity, at 303.15 K and 7 MPa of carbon dioxide, for 24 hours and with 1 mol% of $Rh_2(OAc)_4$ complex as a catalyst (Figure 5.3). In the recycling experiment, the substrate was submitted to such a C-H insertion in carbon dioxide, followed by supercritical carbon dioxide extraction and new addition of substrate as shown in Figure 5.2. As expected, the first cyclisation of diazoacetamide **5** took place in high yield and lactam **6** was recovered in 75% yield, after extraction with carbon dioxide at 17 MPa and 313.15 K. The second reaction with freshly added substrate afforded lactam **6** quantitatively and confirmed that the $Rh_2(OAc)_4$ complex endured the extraction protocol retaining its catalytic activity. This final reaction highlighted that the C-H insertion of diazoacetamides proceeds very successfully using carbon dioxide as solvent and that the extraction with supercritical carbon dioxide may indeed allow the catalyst reutilisation and, at the same time, reduces the use of organic solvents in the isolation process.

5.4 Conclusions

We have established the intramolecular C-H insertion of diazoacetamide using carbon dioxide as a solvent. This process afforded the expected lactams in yields over 97%. The asymmetric intramolecular C-H insertion was also achieved, and β-lactam was obtained in 97% yield and 65% *ee* using the chiral dirhodium(II) catalyst $Rh_2(S\text{-PTTL})_4$. Finally, the dirhodium(II) complex $Rh_2(OAc)_4$ was used in two consecutive cycles in which complete conversion to the lactam was possible. This recycling experiment demonstrated that carbon dioxide can be used as an efficient solvent for C-H insertions based on diazo compounds/dirhodium(II) complexes and that the extraction with supercritical carbon dioxide may indeed allow the catalyst reutilisation reducing the use of organic solvents in the isolation process.

Concluding remarks and future perspectives

At present, among different climate change mitigation strategies, Carbon Capture and Sequestration seems to be an indispensable technology to achieve the goals presently set for the maximum temperature increase over pre-industrial values. If actually implemented, even if at a smaller scale than currently envisaged, it will provide enormous amounts of carbon dioxide of high purity at high pressure. With abundant amounts of this highly valuable and probably extremely cheap resource, new environmentally attractive pathways for application of compressed carbon dioxide will certainly be developed.

High-pressure carbon dioxide on its own, or combined with ionic liquids, may serve as an interesting solution for many existing, or newly developed, technologies. However, any process design and development depends on accurate, basic experimental and computational data, and these, as for now, are still insufficient. For all applications involving solvents and solutes, phase equilibrium and solubility are some of the most important informations.

In case of ionic liquids, the complex microheterogeneous nature makes it very difficult to understand their structure-property relationships and molecular level of interactions. For the same reason, it is extremely problematic to establish the exact factors controlling gas dissolution. The results from the case study, where the solubility of carbon dioxide in tetracyanoborate- and fluoroalkylphosphate-based ionic liquids, together with the volume expansion of their mixtures, were measured, contribute to the ongoing debate over the mechanism governing gas solubility in ionic liquids. It was shown that ionic liquids based on tetracyanoborate anion, exhibited great capacity for carbon dioxide capture and higher than usual volume expansion. This was the case despite their small size and high symmetry, which might suggest a low free volume, and, thus, low gas solubility. It appears that weak anion-cation coordination is more important than the CO_2-anion interactions, contrarily to the hypothesis previously stated in the literature. In the other case study, where carbon dioxide-induced melting point depressions where discussed, we were not able to find any positive correlation between the solubility of carbon dioxide in each ionic liquid investigated and their melting temperature depression. It is possible that the extremely high differences between CO_2-induced melting point depressions in structurally similar ammonium-based ionic salts be related to interactions between carbon dioxide and the solid phase of these ionic liquids. Given the background and the importance of the systems involved, it is crucial that improved understanding and reliable predictive models of gas solubility in ionic liquids be obtained.

Finally, the case study of the intramolecular C-H insertion of diazoacetamide serves as evidence that compressed carbon dioxide can successfully serve as both reaction and extraction medium, facilitating the process and post-reaction separation of product. It supports the belief that supercritical carbon dioxide holds many promises to develop benign environmental technologies.

In conclusion, despite the fact that still a lot of research is necessary to completely understand molecular interactions between ionic liquids and carbon dioxide, both of these media show a great potential for many interesting industrial applications. No doubt, they will find them. It’s just a matter of time.

Appendix A

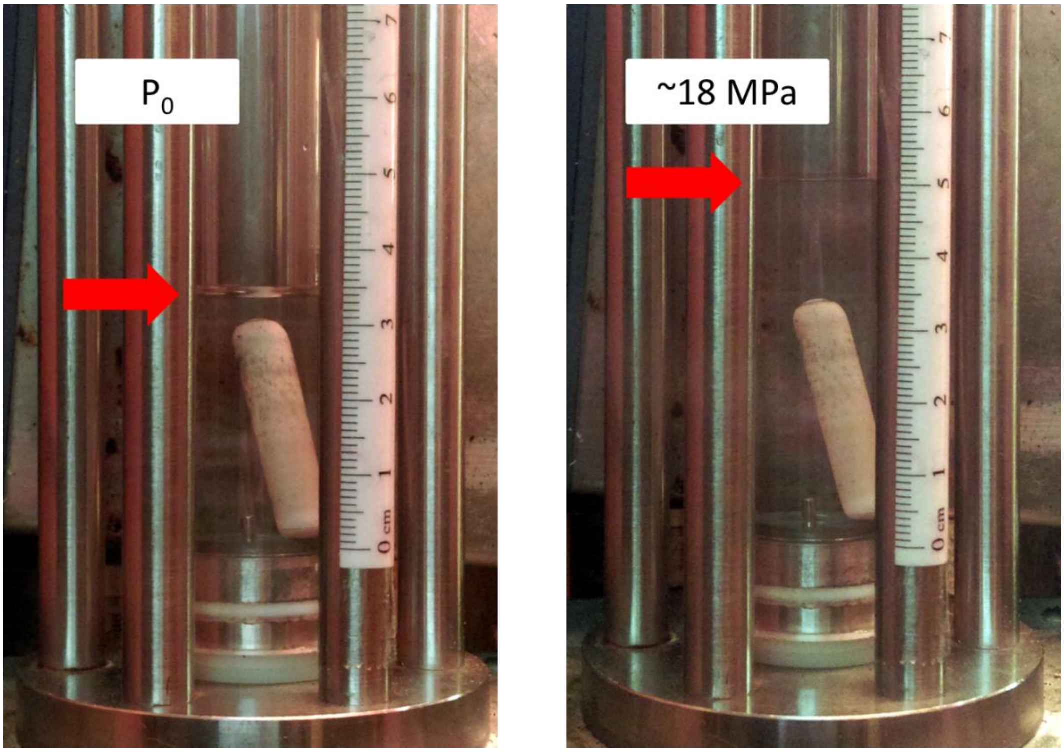


Figure A. 1 The observed maximum total volume expansion of 54% for [emim][eFAP] with compressed CO_2 at 313.15 K and 0.81 mole fraction of CO_2.

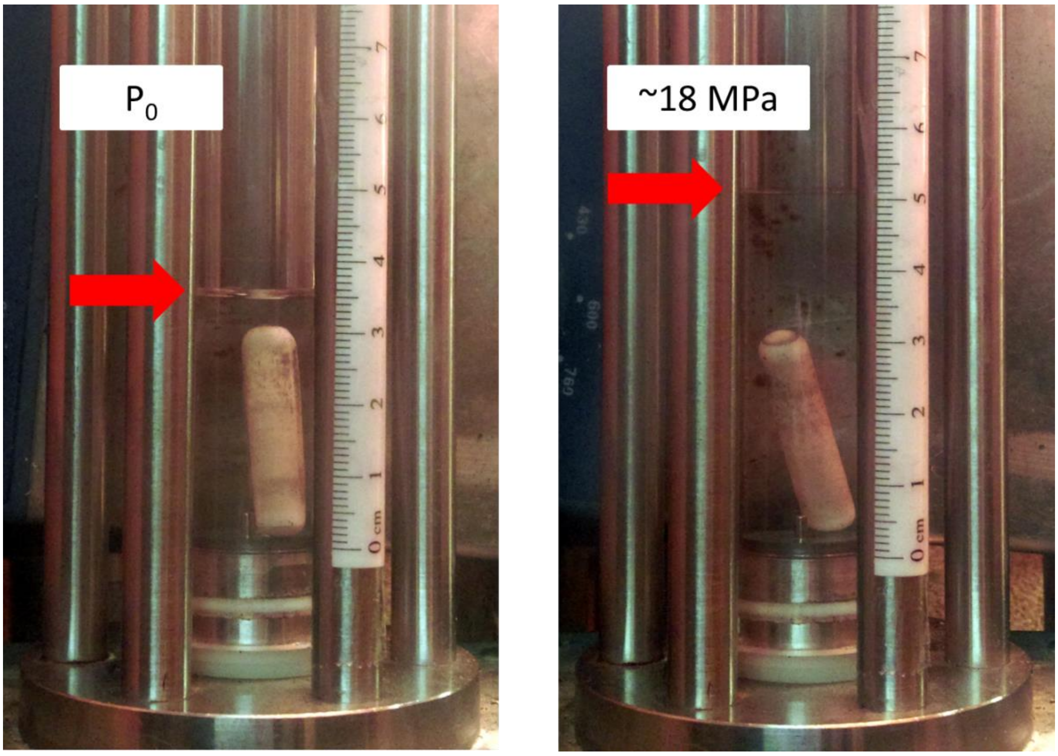


Figure A. 2 The observed maximum total volume expansion of 53% for [bmim][eFAP] with compressed CO_2 at 313.15 K and 0.8 mole fraction of CO_2.

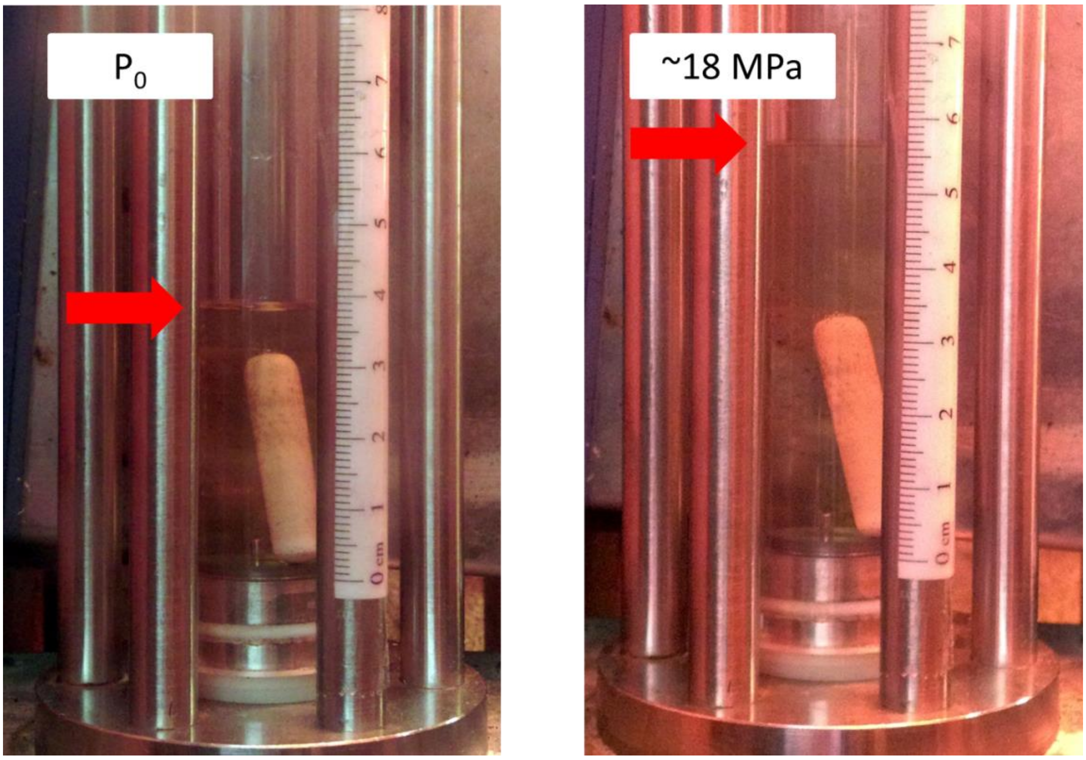


Figure A. 3 The observed maximum total volume expansion of 50% for [hmim][eFAP] with compressed CO_2 at 313.15 K and 0.83 mole fraction of CO_2.

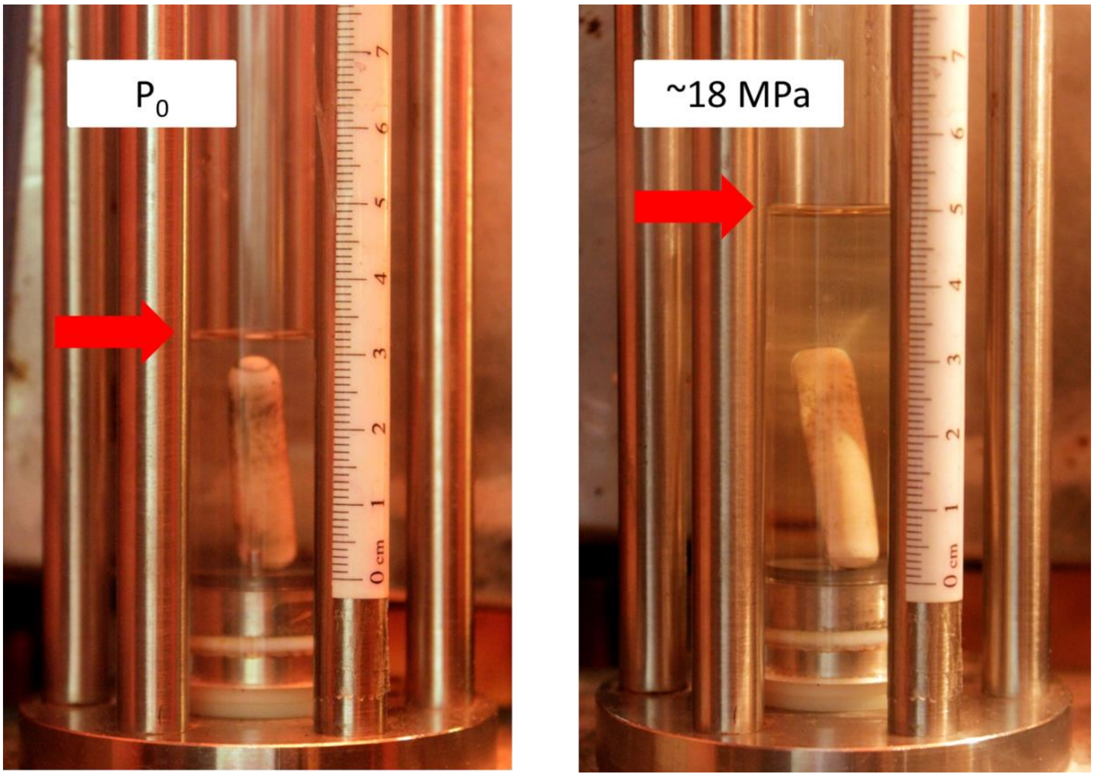


Figure A. 4 The observed maximum total volume expansion of 59% for [emim][B(CN)$_4$] with compressed CO_2 at 313.15 K and 0.79 mole fraction of CO_2.

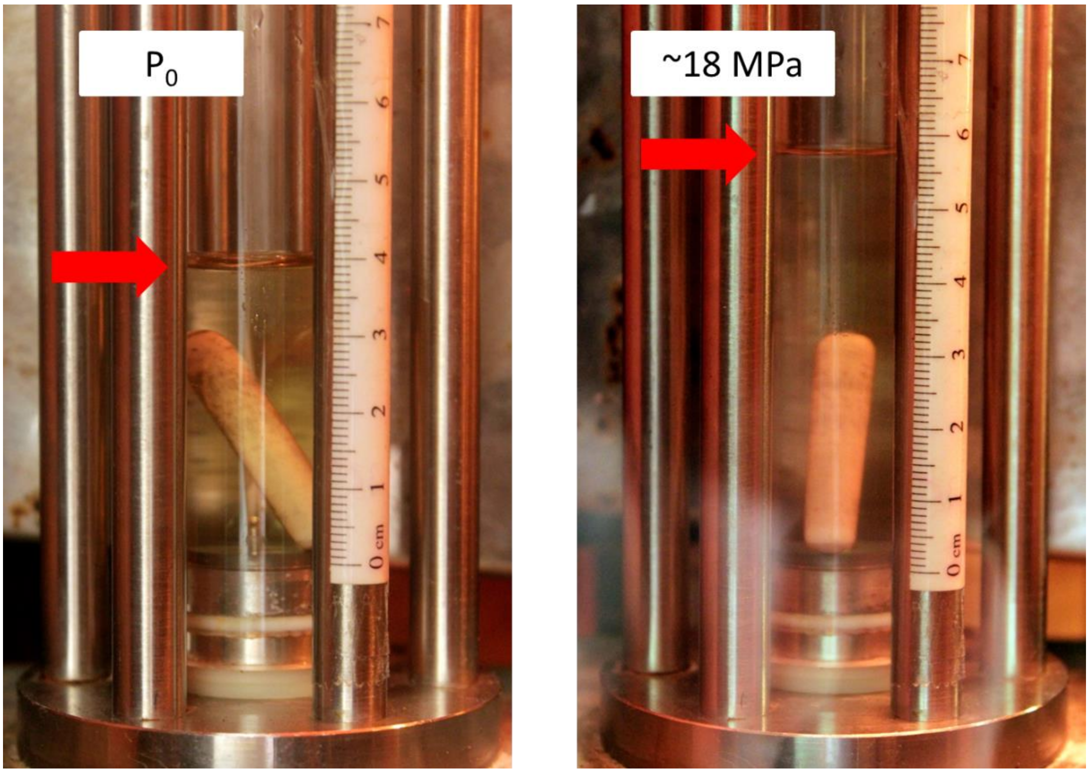


Figure A. 5 The observed maximum total volume expansion of 53% for $[hmim][B(CN)_4]$ with compressed CO_2 at 313.15 K and 0.82 mole fraction of CO_2.

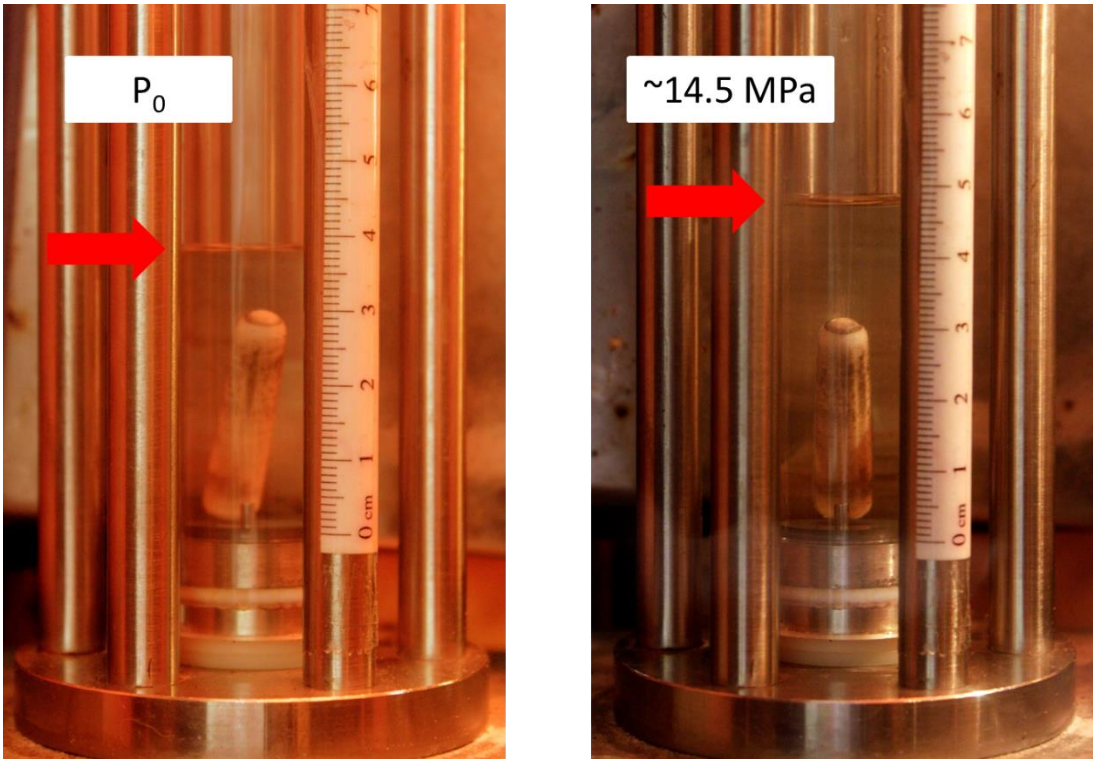


Figure A. 6 The observed maximum total volume expansion of 25% for $[bmim][BF_4]$ with compressed CO_2 at 313.15 K and 0.55 mole fraction of CO_2.

Appendix B

List of NMR spectra:

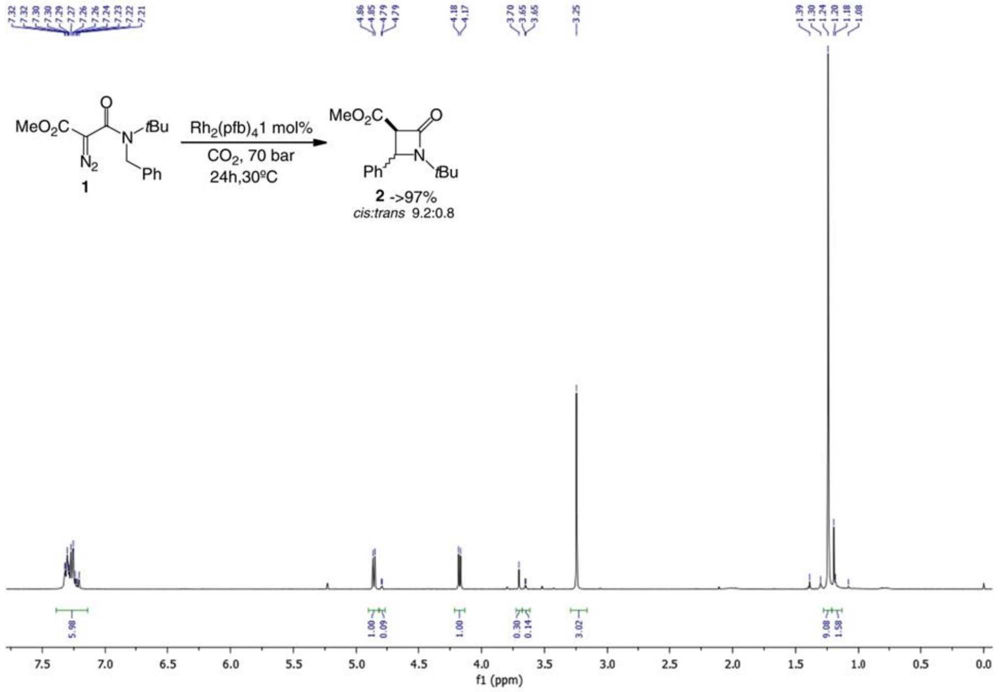


Figure B. 1 ^{1}H NMR spectrum of crude cyclisation reaction of **1** with $Rh_2(pfb)_4$.

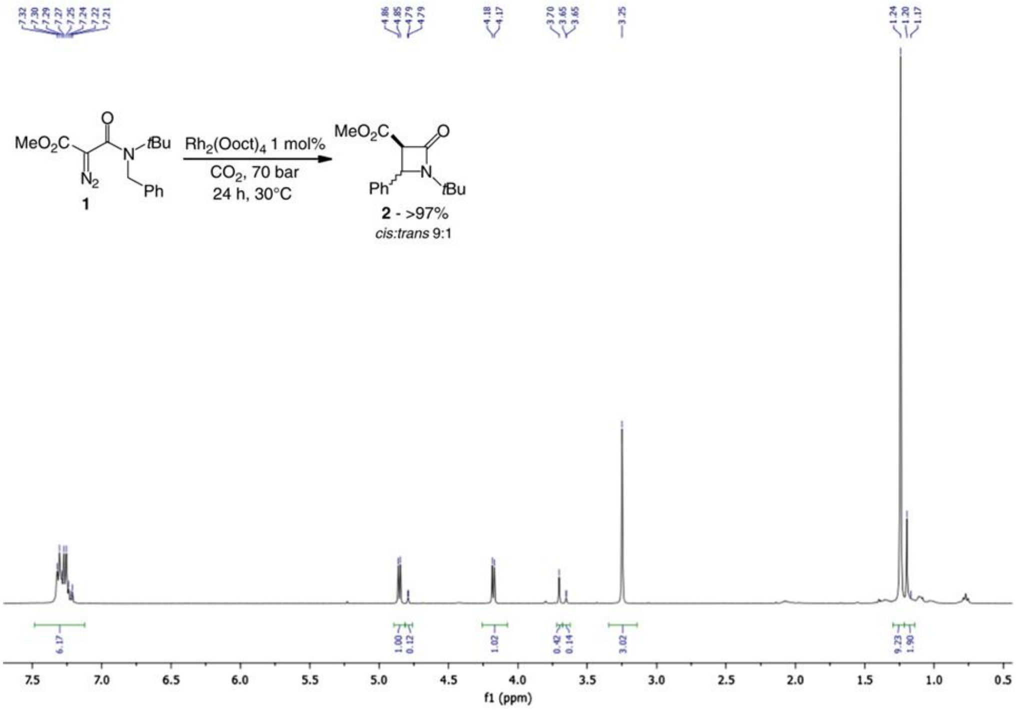


Figure B. 2 ^{1}H NMR spectrum of crude cyclisation reaction of **1** with $Rh_2(Ooct)_4$.

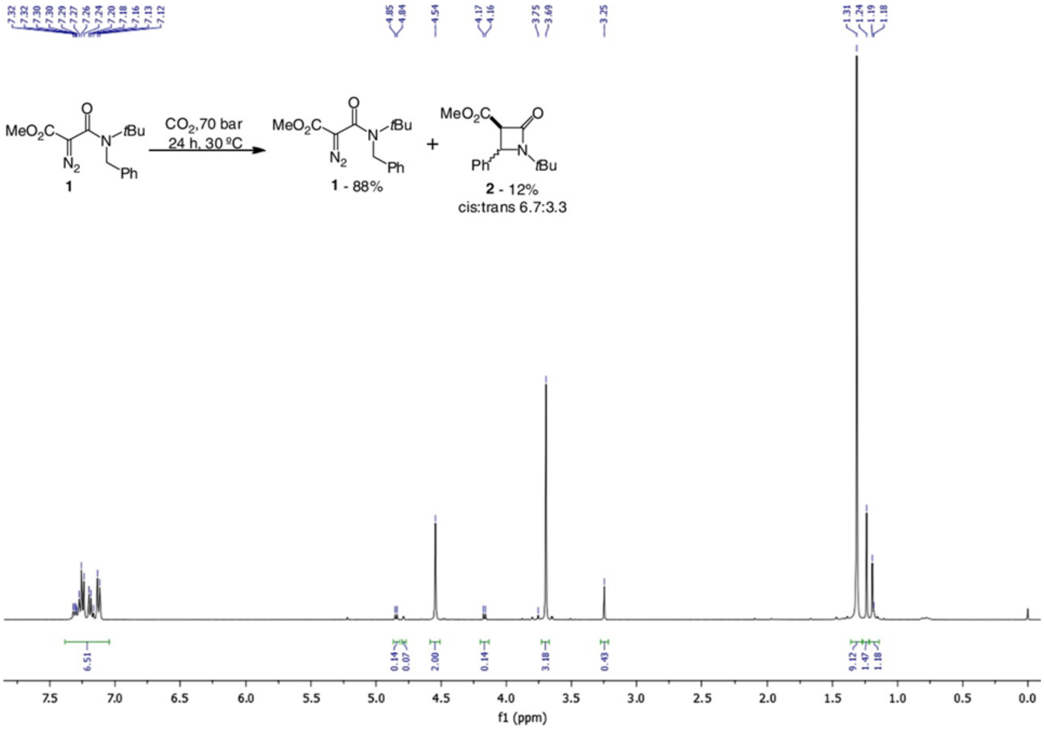


Figure B. 3 ^{1}H NMR spectrum of control experiment of **1** without dirhodium catalyst.

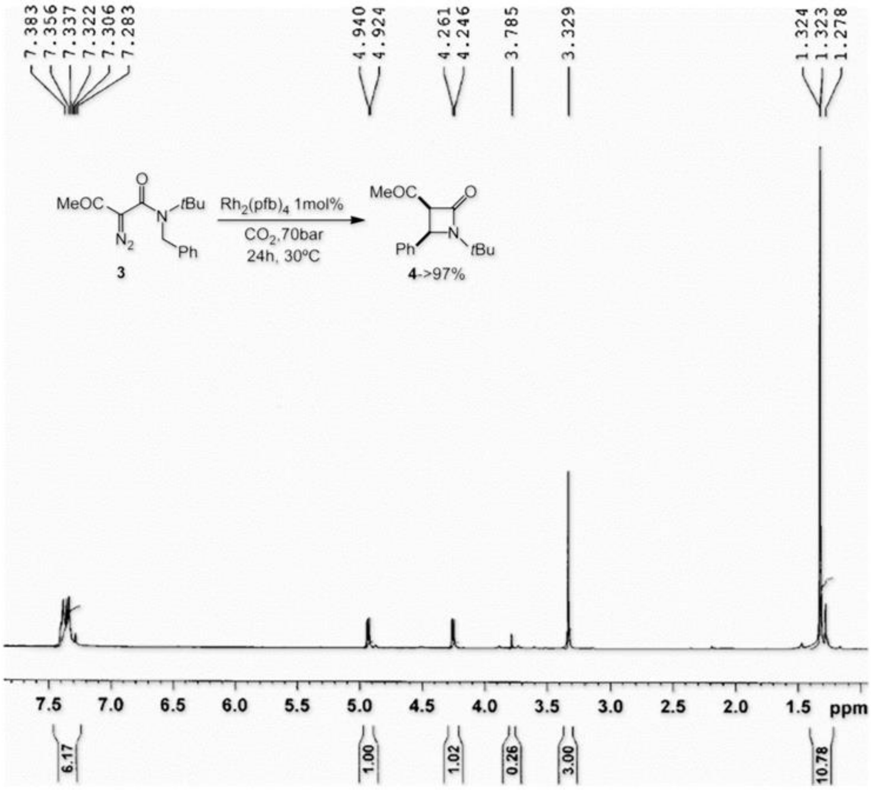


Figure B. 4 ^{1}H NMR spectrum of crude cyclisation reaction of **3** with Rh_2(pfb)$_4$.

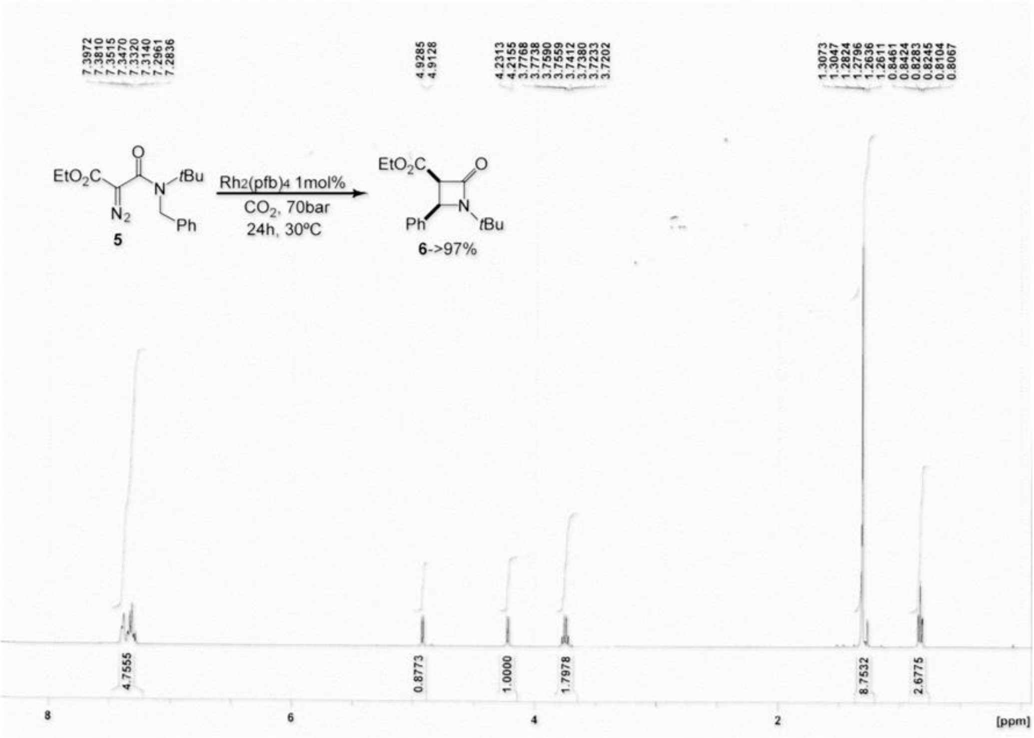


Figure B. 5 ^{1}H NMR spectrum of crude cyclisation reaction of **5** with $Rh_2(pfb)_4$.

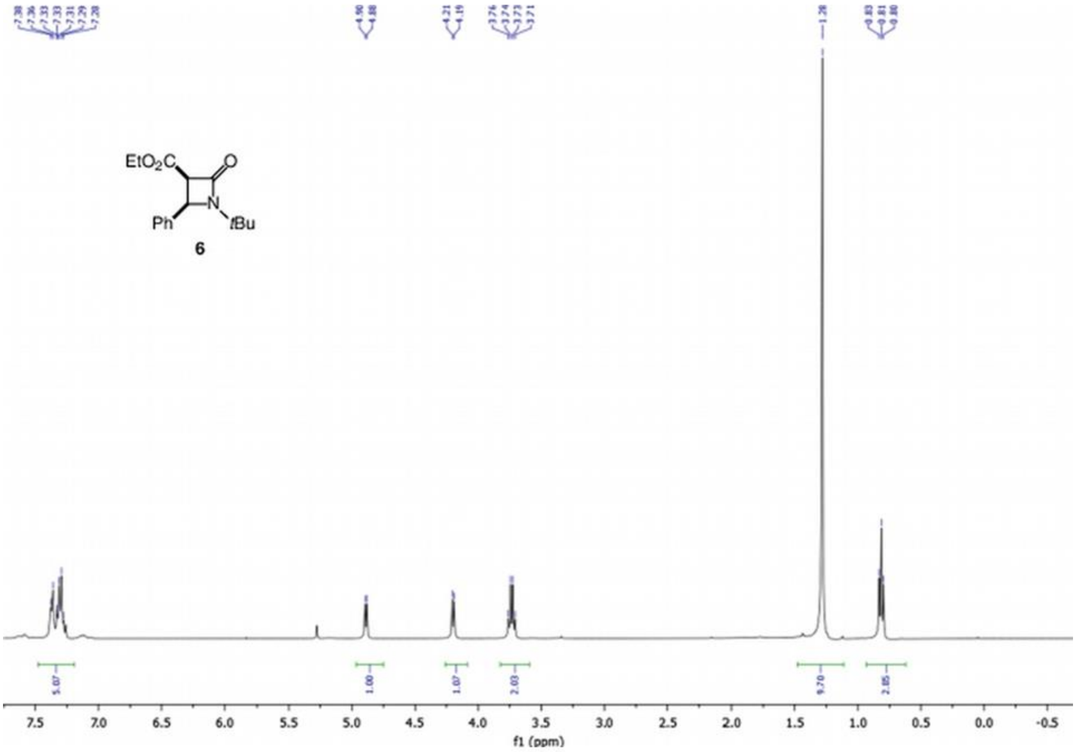


Figure B. 6 ^{1}H NMR spectrum of isolated cis-lactam **6**.

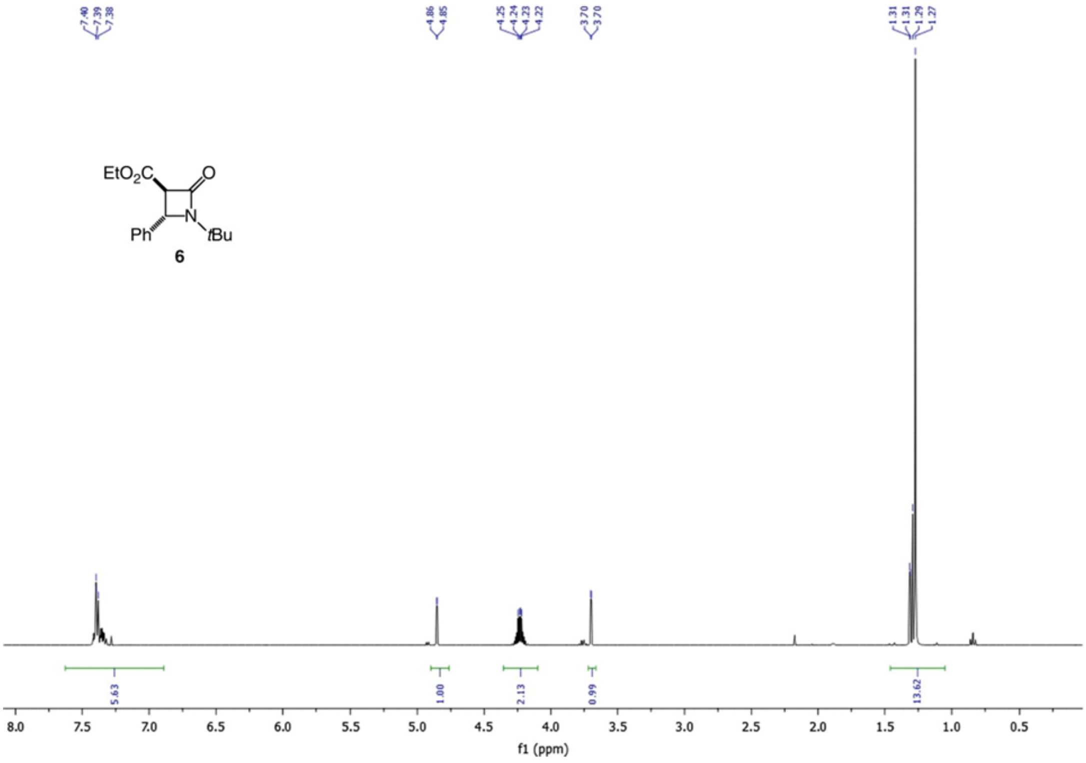


Figure B. 7 ^{1}H NMR spectrum of isolated trans-lactam **6**, epimerised by filtration of cis-lactam through neutral alumina.

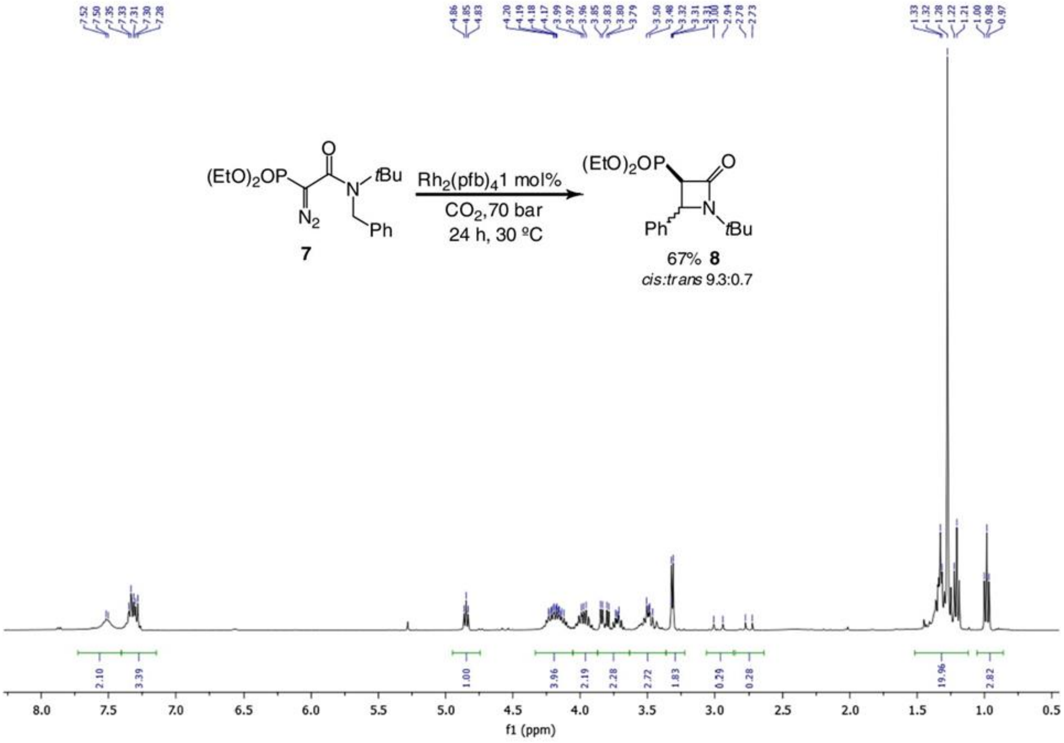


Figure B. 8 ^{1}H NMR spectrum of crude cyclisation reaction of **7**.

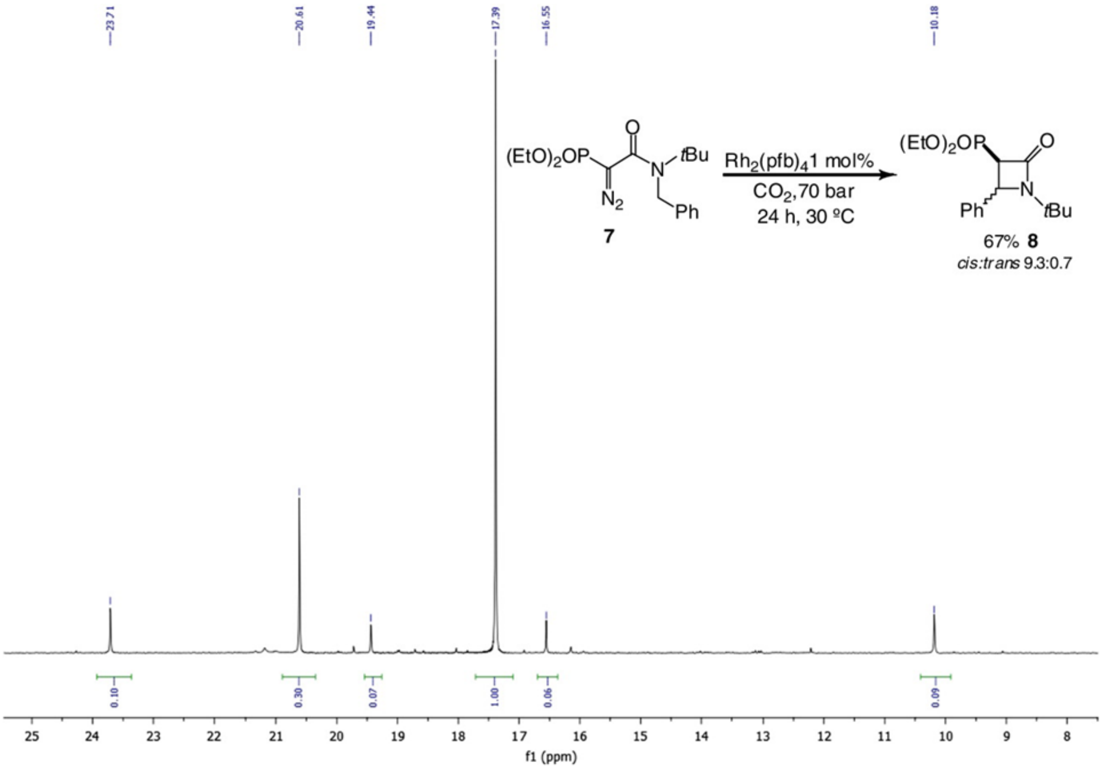


Figure B. 9 ^{31}P NMR spectrum of crude cyclisation reaction of **7**.

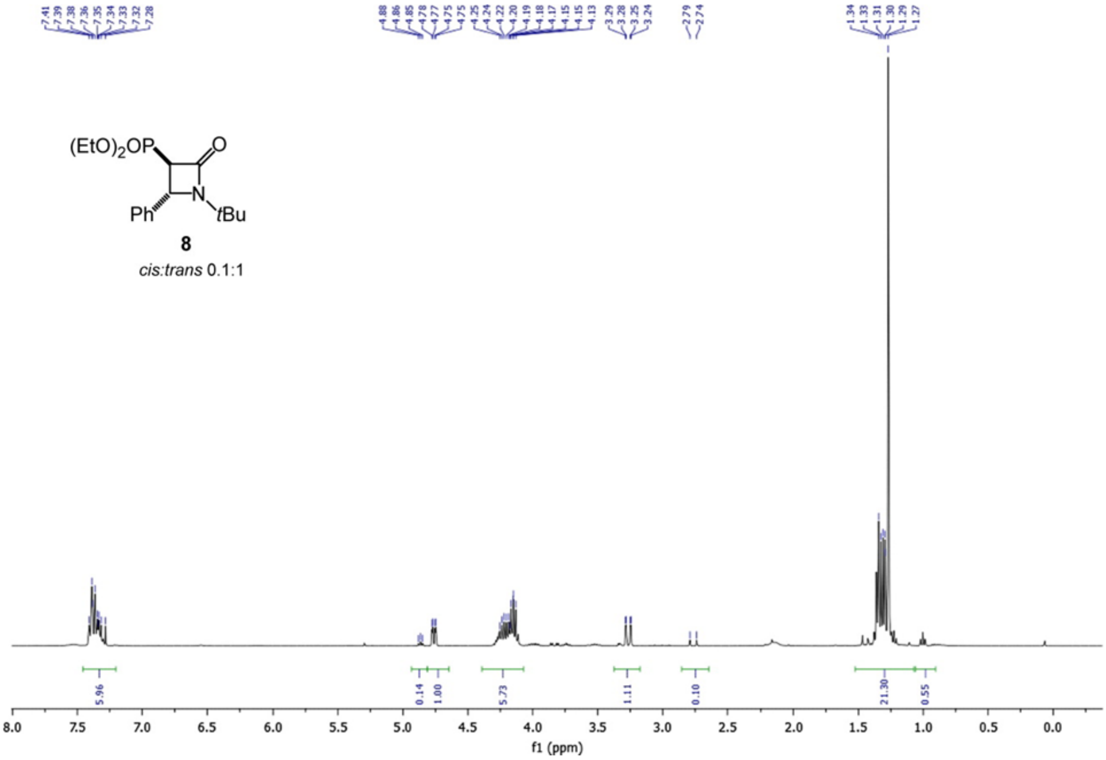


Figure B. 10 ^{1}H NMR spectrum of isolated lactam **8** (after filtration through basic alumina).

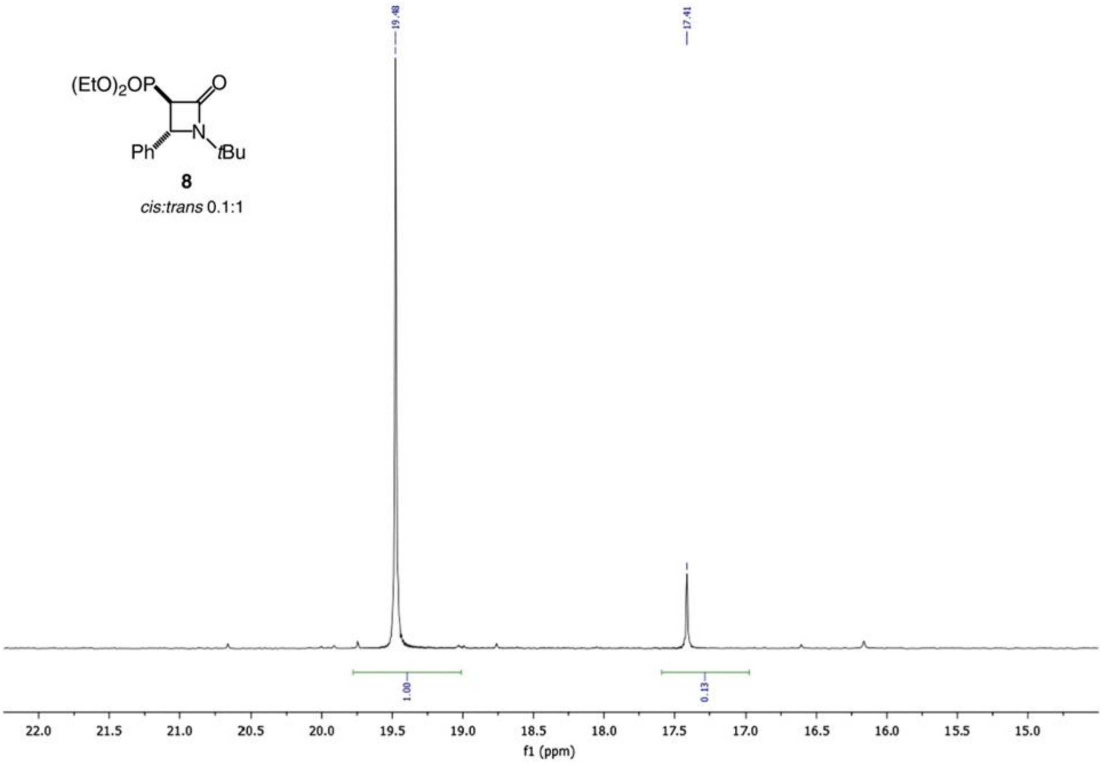


Figure B. 11 ^{31}P NMR spectrum of isolated lactam **8** (after filtration through basic alumina).

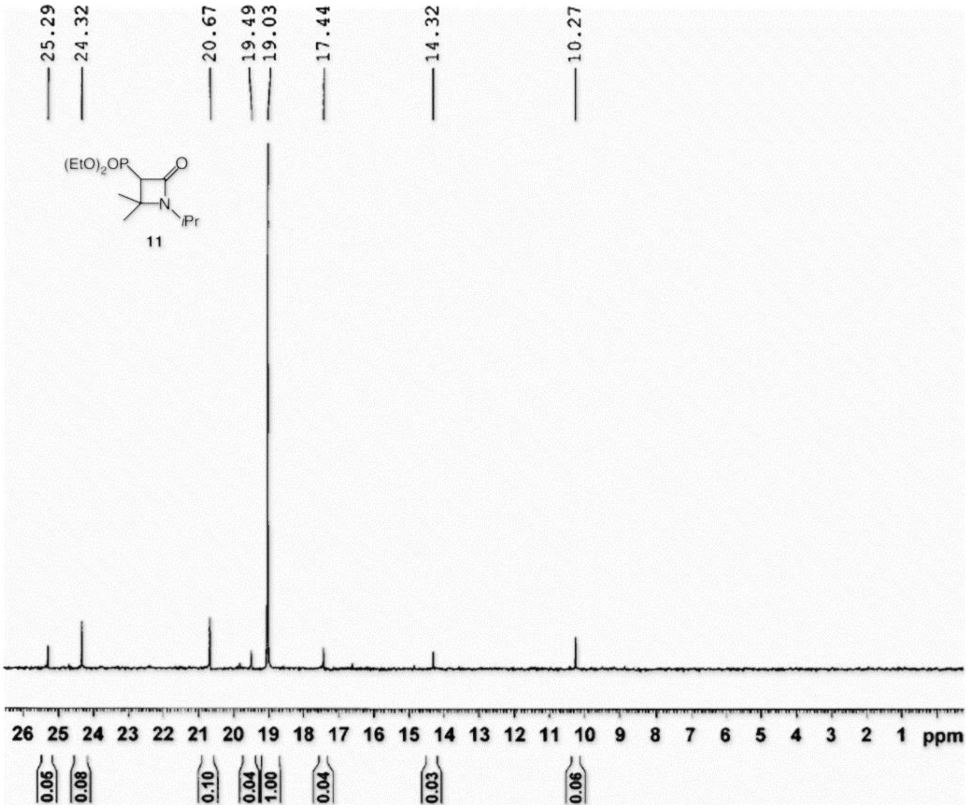


Figure B. 12 ^{31}P NMR spectrum of isolated lactam **11** (after filtration through basic alumina).

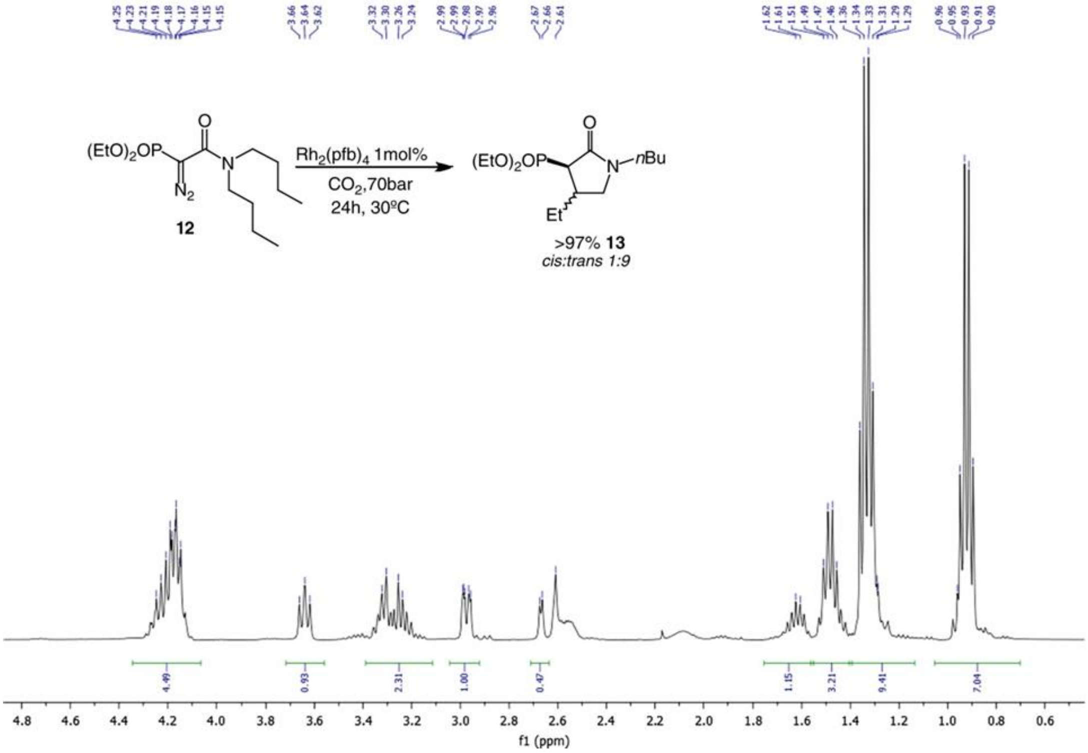


Figure B. 13 ^{1}H NMR spectrum of crude cyclisation reaction of **12**.

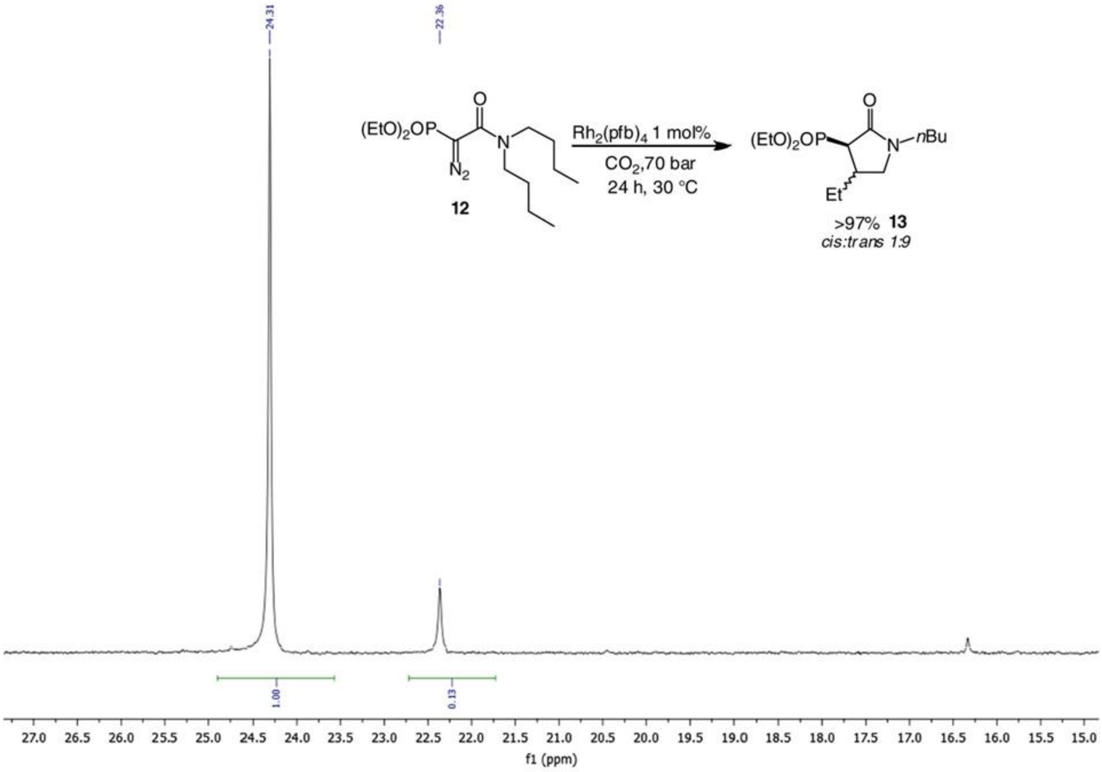


Figure B. 14 ^{31}P NMR spectrum of crude cyclisation reaction of **12**.

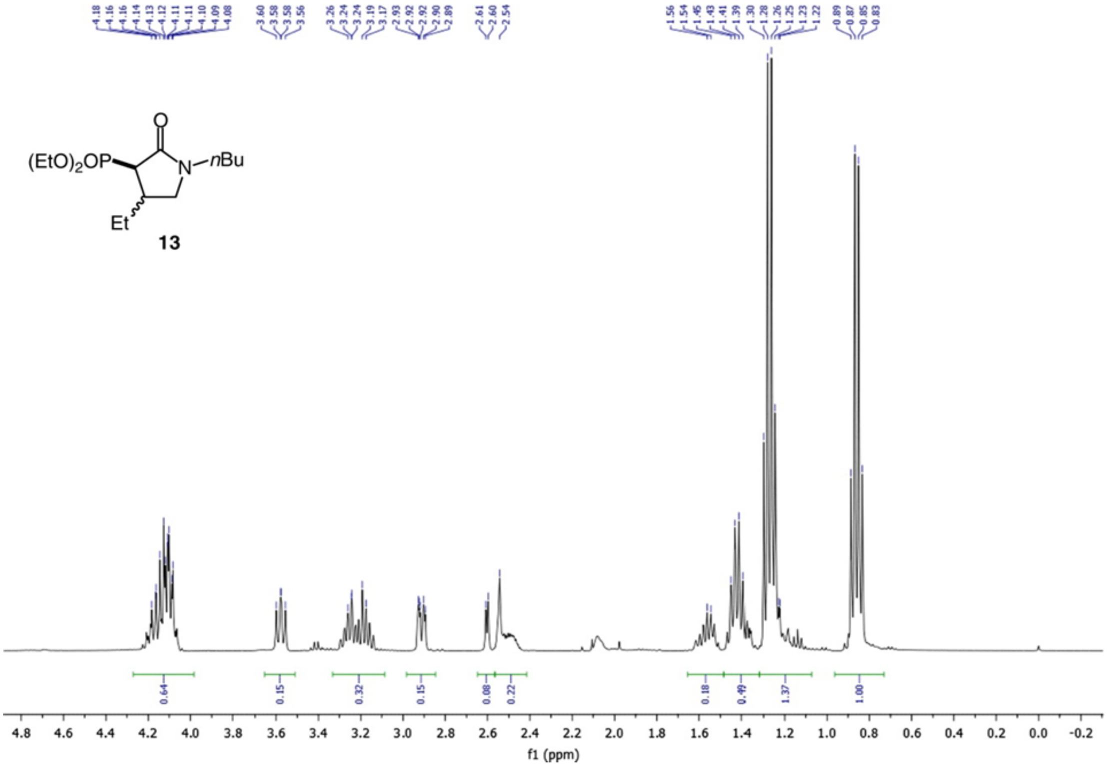


Figure B. 15 ^{1}H NMR spectrum of isolated lactam **13** (after filtration through basic alumina).

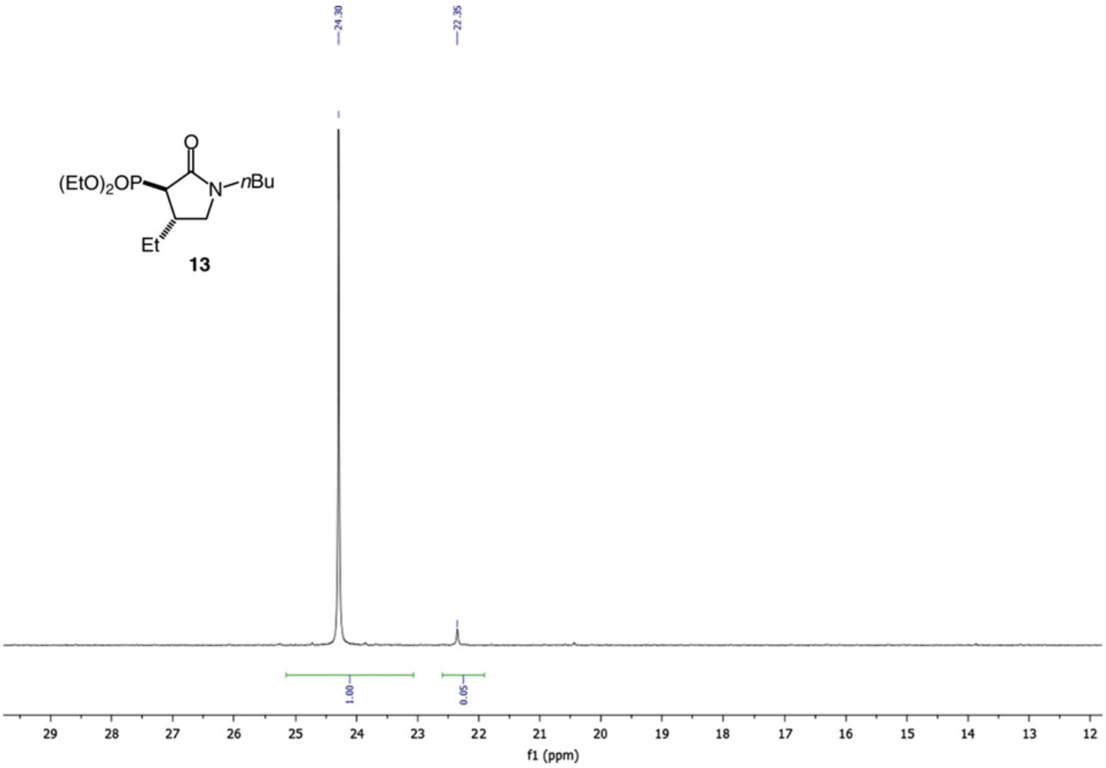


Figure B. 16 ^{31}P NMR spectrum of isolated lactam **13** (after filtration through basic alumina).

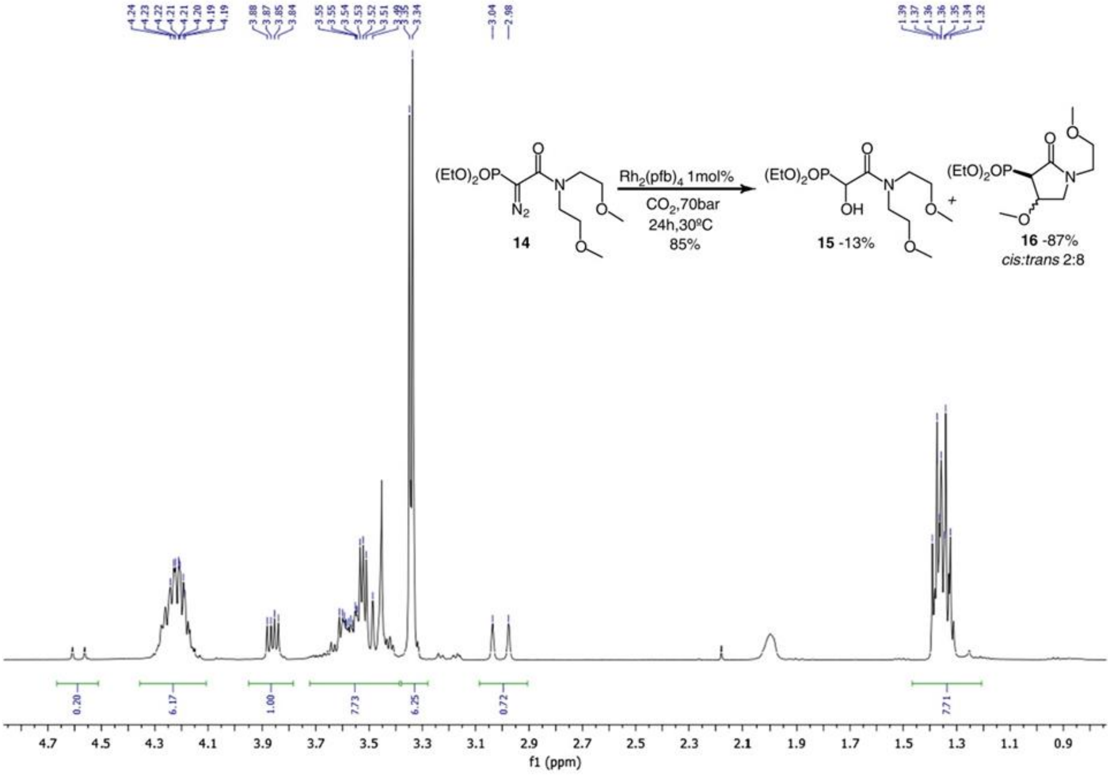


Figure B. 17 ^{1}H NMR spectrum of crude cyclisation reaction of **14**.

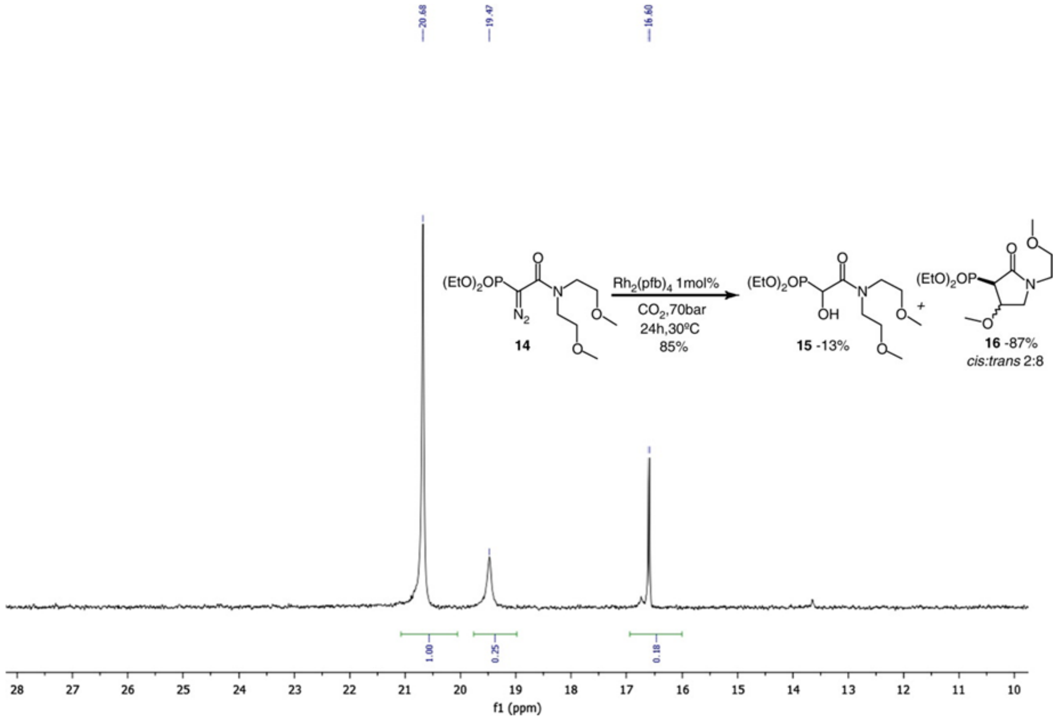


Figure B. 18 ^{31}P NMR spectrum of crude cyclisation reaction of **14**.

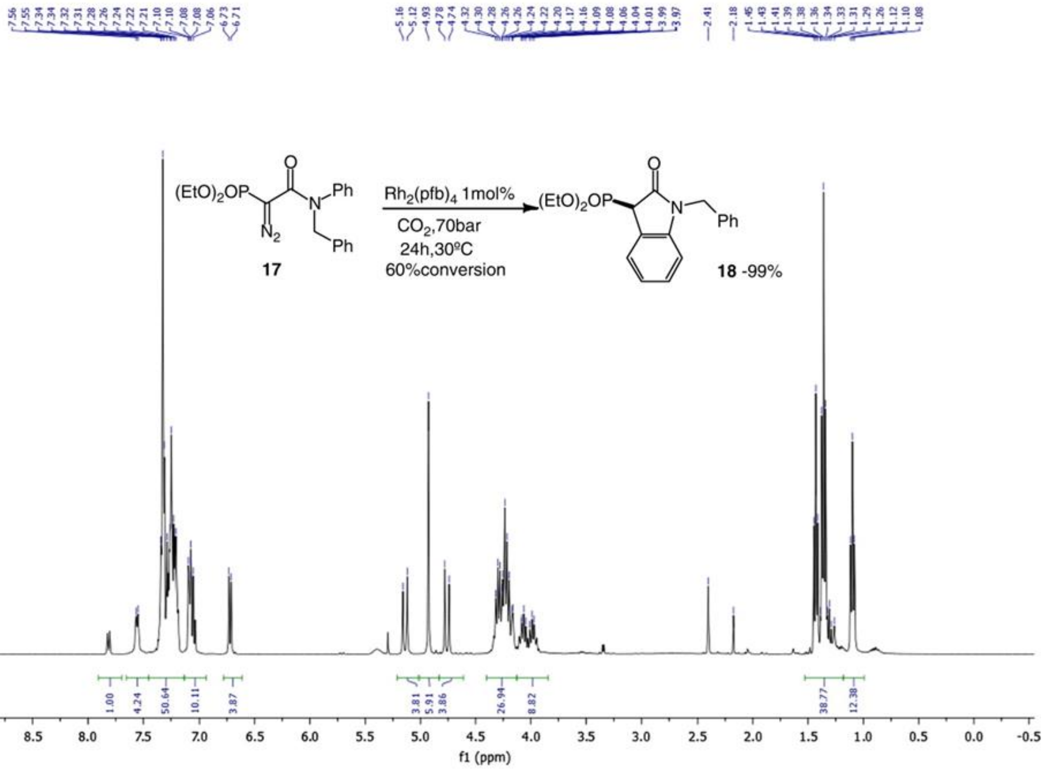


Figure B. 19 ^{1}H NMR spectrum of crude cyclisation reaction of **17**.

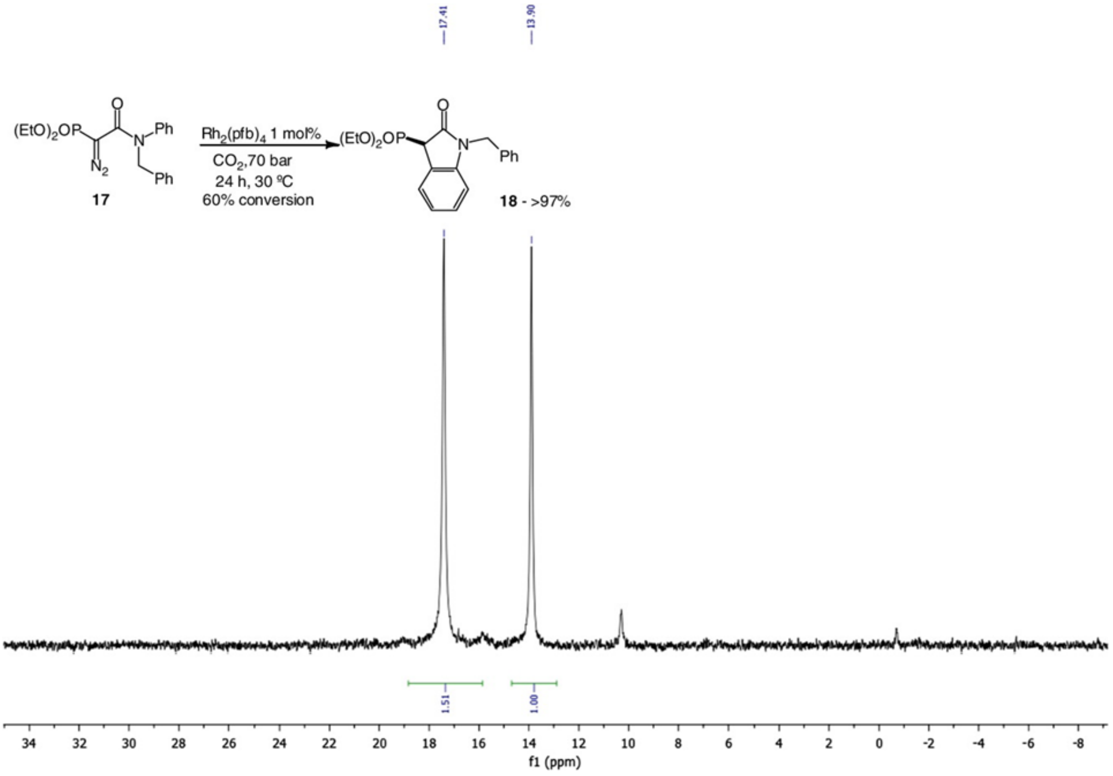


Figure B. 20 ^{31}P NMR spectrum of crude cyclisation reaction of **17**.

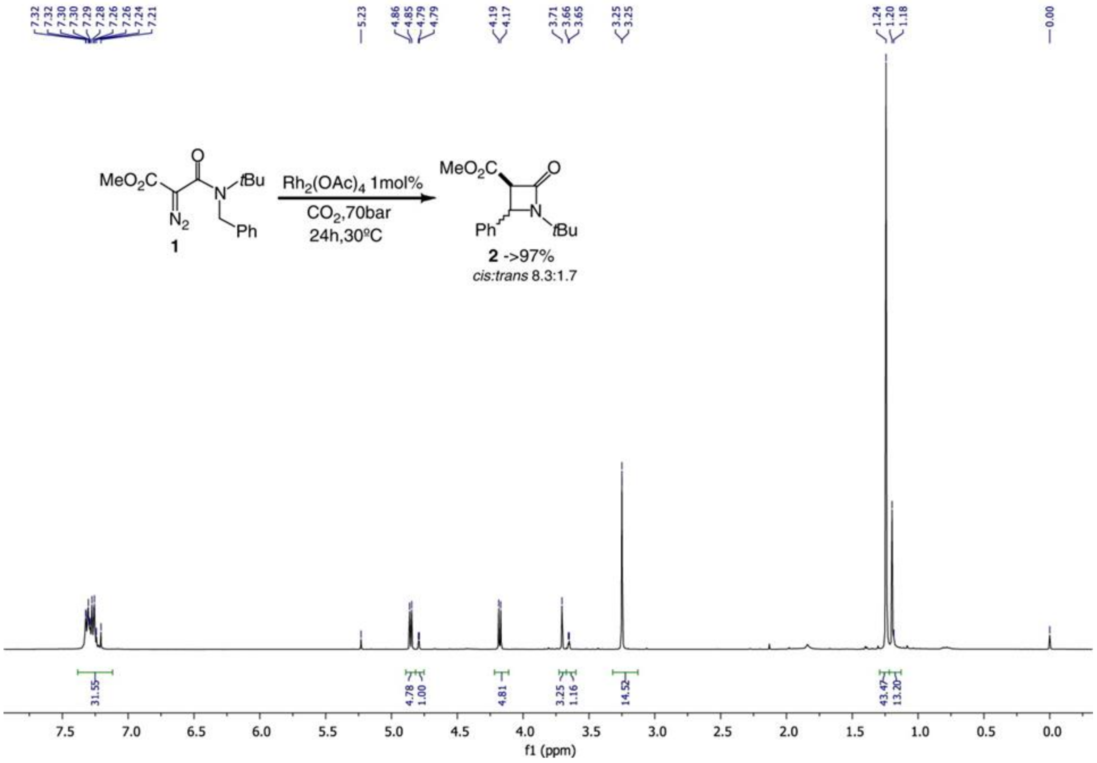


Figure B. 21 ^{1}H NMR spectrum of crude cyclisation of **1** catalysed by Rh$_2$(OAc)$_4$.

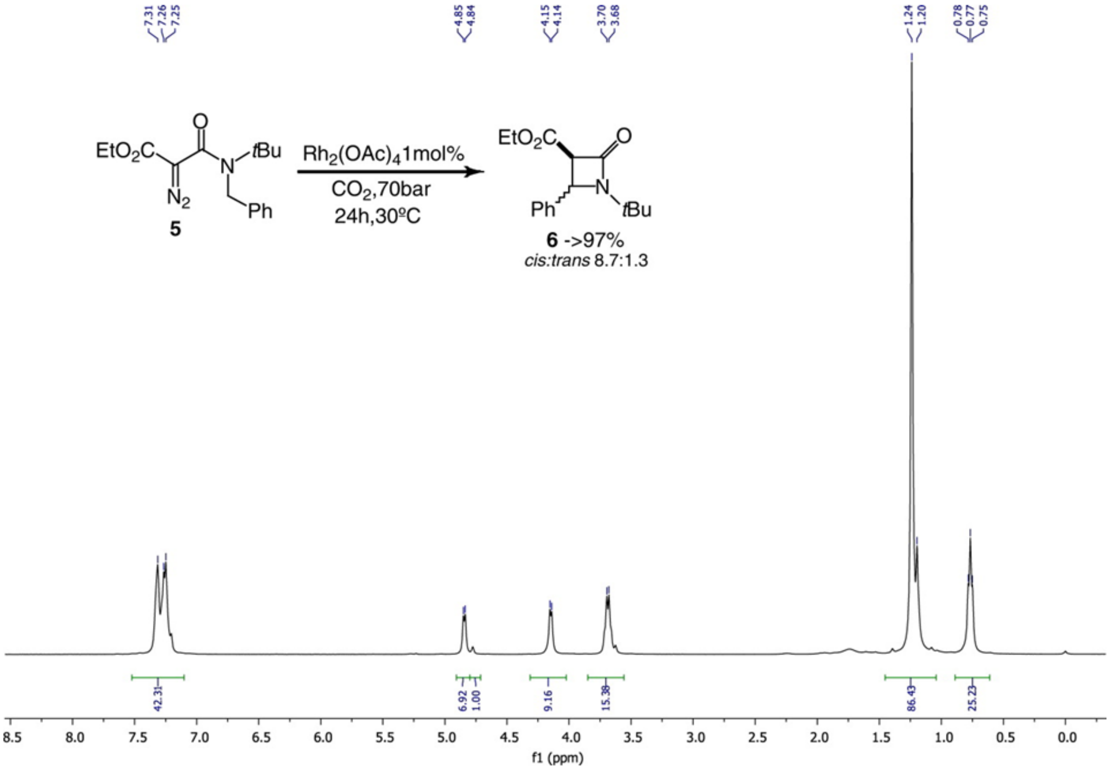


Figure B. 22 ^{1}H NMR spectrum of crude cyclisation of **5** catalysed by Rh$_2$(OAc)$_4$.

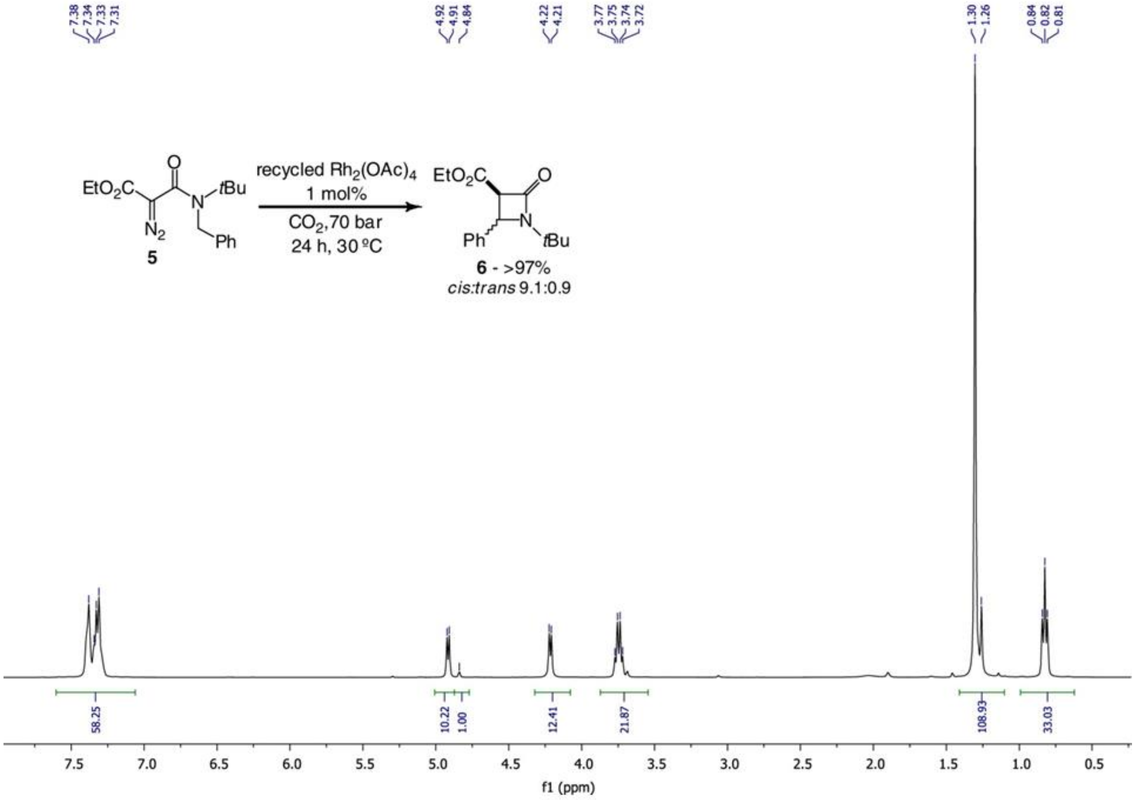
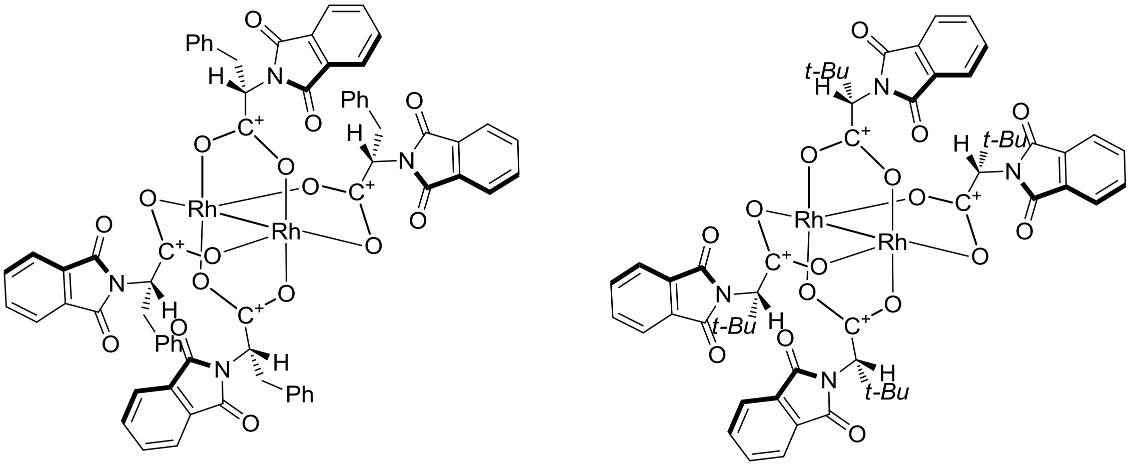


Figure B. 23 ^{1}H NMR spectrum of crude cyclisation of **5** using recycled $Rh_2(OAc)_4$.

Appendix C



Chemical Formula: $C_{68}H_{48}N_4O_{16}Rh_2^{4+}$
Molecular Weight: 1382,93

Rh_2(*S*-PTPA)$_4$

Chemical Formula: $C_{56}H_{56}N_4O_{16}Rh_2^{4+}$
Molecular Weight: 1246,87

Rh_2(*S*-PTTL)$_4$

Figure C. 1 Structures of chiral dirhodium(II) complexes.

References

---

[1] World Commission on Environment and Development. Our common future., Oxford University Press, Oxford, 1987.

[2] http://www.epa.gov/greenchemistry/basics-green-chemistry#definition, last accessed 01.01.2016.

[3] P. Anastas, B. Han, W. Leitner, M. Poliakoff, “Happy silver anniversary”: Green Chemistry at 25, Green Chem., 2016, 18, 12-13.

[4] Benign by Design: Alternative Synthetic Design for Pollution Prevention, eds.: P. T. Anastas, C. A. Farris, ACS Symposium Series, vol. 577, American Chemical Society, Washington DC, 1994.

[5] Green Chemistry: Theory and Practice, eds.: P.T. Anastas, J.C. Warner, Oxford University Press, New York, 1998.

[6] Design through the Twelve Principles of Green Engineering, P.T. Anastas, J.B. Zimmerman, Environ. Sci. Technol., 2003, 37, 94A-101A.

[7] S.L.Y. Tang, R.L. Smith, M. Poliakoff, Principles of green chemistry: PRODUCTIVELY, Green Chem., 2005, 7, 761–762.

[8] S.Y. Tang, R.A. Bourne, R.L. Smith, M. Poliakoff, The 24 principles of green engineering and green chemistry: “IMPROVEMENTS PRODUCTIVELY”, Green Chem., 2008, 10, 268–269.

[9] P. Anastas, N.Eghbali, Green Chemistry: Principles and Practice, Chem. Soc. Rev., 2010, 39, 301–312.

[10] C.-J. Li, P.T. Anastas, Green Chemistry: present and future, Chem. Soc. Rev., 2012, 41, 1413–1414.

[11] Intergovernmental Panel on Climate Change (IPCC), Climate Change 2014: Synthesis Report: Contribution of Working Group I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Geneva, Switzerland, 2014.

[12] International Energy Agency (IEA), Energy and Climate Change: World Energy Outlook Special Report, OECD/IEA, Paris, France, 2015.

[13] Intergovernmental Panel on Climate Change (IPCC), Mitigation of Climate Change: Working Group III to the Fifth Assessment Report, Annex II.9.

[14] Art. 2 of the United Nations Framework Convention on Climate Change text; http://unfccc.int/essential_background/convention/items/6036.php, last accessed 31.12.2015.

[15] Adoption of the Paris agreement, UNFCCC, COP21, Paris, France, 2015; http://unfccc.int/resource/docs/2015/cop21/eng/l09r01.pdf, last accessed 31.12.2015.

[16] N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C.S. Adjiman, C.K. Williams, N. Shah, P. Fennell, An overview of CO2 capture technologies, Energy Environ. Sci., 2010, 3, 1645–1669.

[17] S.D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A.G. Russell, Q. Weif, M. Fan, Review of recent advances in carbon dioxide separation and capture, RSC Adv., 2013, 3, 22739–22.

[18] B. Sreenivasulu, D.V. Gayatri, I. Sreedhar, K.V. Raghavan, A journey into the process and engineering aspects of carbon capture technologies, Renew. Sust. Energ. Rev., 2015, 4, 1324-1350.

[19] M. Ranjan, H.J. Herzog, Feasibility of air capture, Energy Procedia, 2011, 4, 2869-2876.

[20] M. Workman, N. McGlashan, H. Chalmers, N. Shah, An assessment of options for CO_2 removal form the atmosphere, Energy Procedia, 2011, 4, 2877-2884.

[21] A. Goeppert, M. Czaun. G.K.S. Prakash, G.A. Olah, Air as the renewable carbon source of the future: an overview of CO_2 capture from the atmosphere, Energy Environ. Sci., 2012, 5, 7833-7853.

[22] K.S. Lackner, The thermodynamics of direct air capture of carbon dioxide, Energy, 2013, 50, 38-46.
[23] S. Bachu, CO_2 storage in geological media: role, means, status, and barriers to deployment, Progr. Energ. Combust., 2008, 34, 254-273.
[24] M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernández, M.-C. Ferrari, R. Gross, J.P. Hallett, R.S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R.T.J. Porter, M. Pourkashanian, G.T. Rochelle, N. Shah, J.G. Yao, P.S. Fennell, Carbon capture and storage update, Energy Environ. Sci., 2014, 7, 130-189.
[25] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, Renew. Sust. Energ. Rev., 2014, 39, 426-443.
[26] B. Subramaniam, R.V. Chaudhari, A.S. Chaudhari, G.R.Akien, Z. Xie, Supercritical fluids and gas-expanded liquids as tunable media for multiphase catalytic reactions, Chem. Eng. Sci., 2014, 115, 3–18.
[27] X. Han, M. Poliakoff, Continuous reactions in supercritical carbon dioxide: problems, solutions and possible ways forward, Chem. Soc. Rev., 2012, 41, 1428–1436.
[28] M. Peters, B. Kçhler, W. Kuckshinrichs, W. Leitner, P Markewitz, T.E.Müller, Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain, ChemSusChem 2011, 4, 1216 – 1240.
[29] M.T. Ravanchi, S. Sahebdelfar, Carbon dioxide capture and utilisation in petrochemical industry: potentials and challenges, Appl. Petrochem. Res., 2014, 4, 63-77.
[30] I. Omae, Recent developments in carbon dioxide utilisation for the production of organic chemicals, Coord. Chem. Rev., 2012, 256, 1384-1405.
[31] Z.-Z.Yang, L.-N.He, J. Gao, A.-H. Liu, B.Yu, Carbon dioxide utilization with C–N bond formation: carbon dioxide capture and subsequent conversion, Energy Environ. Sci., 2012, 5, 6602-6639.
[32] M. Aresta, A. Dibenedetto, A. Angelini, Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2, Chem. Rev. 2014, 114, 1709−1742.
[33] P.G. Jessop, Searching for green solvents, Green Chem., 2011, 13, 1391-1398.
[34] P. Pollet, E.A. Davey, E.E. Ureña-Benavides, C.A. Eckerta, C.L. Liotta, Solvents for sustainable chemical processes, Green Chem., 2014, 16, 1034-1055.
[35] S.Abou-Shehada, J.H. Clark, G. Paggiola, J. Sherwood, Tunable solvents: Shades of green, Chem. Eng. Process., 2016, 99, 88–96.
[36] M.C. Bubalo, S. Vidović, I.R.. Redovniković, S. Jokić, Green solvents for green technologies, J. Chem. Technol. Biotechnol., 2015, 90, 1631–1639.
[37] M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon, J. F. Brennecke, Improving Carbon Dioxide Solubility in Ionic Liquids, J. Phys. Chem. B, 2007, 111 9001-9009.
[38] X. Zhang, Z. Liu, W. Wang, Screening of Ionic Liquids to Capture CO_2 by COSMO-RS and Experiments, AIChE J., 2008, 54, 2717-2728.
[39] D. Almantariotis, S. Stevanovic, O. Fandiño, A. S. Pensado, A. A. H. Padua, J.-Y. Coxam, M. F. Costa Gomes, Absorption of Carbon Dioxide, Nitrous Oxide, Ethane and Nitrogen by 1-Alkyl-3-methylimidazolium ($C_n$mim, n = 2,4,6) Tris(pentafluoroethyl)-trifluorophosphate Ionic Liquids (eFAP), J. Phys. Chem. B, 2012, 116, 7728−7738.
[40] S. Stevanovic, M.F. Costa Gomes, Solubility of carbon dioxide, nitrous oxide, ethane, and nitrogen in 1-butyl-1-methylpyrrolidinium and trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate (eFAP) ionic liquids, J. Chem. Thermodynamics, 2013, 59, 65–71.
[41] A.H. Jalili, M. Shokouhi, G. Maurer, M. Hosseini-Jenab, Solubility of CO2 and $H2_S$ in the ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, J. Chem. Thermodynamics, 2013, 67, 55–62.

[42] M Althulutha, M.T. Mota-Martineza, A.Berrouk, M.C. Kroon, C.J. Peters, Removal of small hydrocarbons (ethane, propane, butane) from natural gas streams using the ionic liquid 1-ethyl-3 -methylimidazolium tris(pentafluoroethyl)trifluorophosphate, J. Supercrit. Fluids, 2014, 90, 65-72.

[43] M. Ramdin, T.W. de Loos, T.J.H. Vlugt, State-of-the-Art of CO_2 Capture with Ionic Liquids, Ind. Eng. Chem. Res., 2012, 51, 8149−8177.

[44] M. Althuluth, J.P. Overbeek, H.J. van Wees, L.F. Zubeir, W.G. Haije, A. Berrouka, C.J. Peters, M.C. Kroon, Natural gas purification using supported ionic liquid membrane, J. Membr. Sci., 2015, 484, 80-86.

[45] S.M. Mahurin, P.C. Hillesheim, J.S. Yeary, D. Jiang, S. Dai, High CO_2 Solubility, Permeability and Selectivity in Ionic Liquids with the Tetracyanoborate Anion, RSC Adv., 2012, 2, 11813-11819.

[46] M.T. Mota-Martinez, M. Althuluth, M.C. Kroon, C.J. Peters, Solubility of carbon dioxide in the low-viscosity ionic liquid 1-hexyl-3-methylimidazolium tetracyanoborate, Fluid Phase Equilibr., 2012, 332, 35–39.

[47] M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, Catalytic Carbene Insertion into C-H Bonds, Chem. Rev. 2010, 110, 704-724.

[48] M.E. Zakrzewska, A.A. Rosatella, S.P. Simeonov, C.A.M. Afonso, V. Najdanovic-Visak, M. Nunes da Ponte, Solubility of carbon dioxide in ammonium based CO_2-induced ionic liquids, Fluid Phase Equilibr., 2013, 354, 19– 23.

[49] M.E. Zakrzewska, M. Nunes da Ponte, Volumetric and phase behaviour of mixtures of tetracyanoborate-based ionic liquids with high pressure carbon dioxide, J. Supercrit. Fluids, 2016, 113, 31-38.

[50] M.E. Zakrzewska, M. Nunes da Ponte, Volumetric and phase behaviour of mixtures of fluoroalkylphosphate-based ionic liquids with high pressure carbon dioxide, J. Supercrit. Fluids, 2016, 113, 61–65.

[51] M.E. Zakrzewska, P.M.S.D. Cal, N.R. Candeias, R. Bogel-Łukasik, CA.M. Afonso, M. N. Ponte, P.M.P. Gois, Intramolecular C-H insertion catalyzed by dirhodium(II) complexes using CO_2 as the reaction media, Green Chem. Lett. Rev., 2012, 5, 211-240.

[52] S. Aparicio, M. Atilhan, F. Karadas, Thermophysical Properties of Pure Ionic Liquids: Review of Present Situation, Ind. Eng. Chem. Res. 2010, 49, 9580–9595.

[53] P. Walden, Molecular weights and electrical conductivity of several fused salts, Bull. Acad. Sci., 1914, 405-422.

[54] R.D. Rogers, K.R. Seddon, Ionic Liquids-Solvents of the Future?, Science, 2003, 302, 792-793.

[55] M.J. Earle, K.R. Seddon, Ionic liquids: Green solvents for the future, Pure Appl Chem, 2000, 72: 1391–1398.

[56] N. Plechkova, K.R. Seddon, Ionic Liquids: "Designer" Solvents for Green Chemistry, *in*: Methods and Reagents for Green Chemistry: An Introduction, ed.: P. Tundo, A. Perosa, F. Zecchini, John Wiley & sons, 2007.

[57] F.N. Hurley, T.P. Wier, The electrodeposition of aluminum from nonaqueous solutions at room temperature, J. Electrochem. Soc., 1951, 98, 207-212.

[58] S.E. Fry, N.J. Pienta, Effects of molten salts on reactions. Nucleophilic aromatic substitution by halide ions in molten dodecyltributylphosphonium salts, J. Am. Chem. Soc., 1986, 107, 6399-6400.

[59] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Dialkylimidazolium chloroaluminate melts, a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis, Inorg. Chem., 1982, 21, 1263-1264.

[60] A.A. Fannin, D.A. Floreani, L.A. King, J.S. Landers, B.J. Piersma, D.J. Stech, R.L. Vaughn, J.S. Wilkes, J.L Williams, Properties of 1,3-dialkylimidazolium chloride aluminium chloride ionic liquids. Part 2, J. Phys. Chem., 1984, 88, 2614-2627.

[61] J. S. Wilkes, M. J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, J. Chem. Soc., Chem. Commun. 1992, 965-967.

[62] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, Physical Properties of Ionic Liquids: Database and Evaluation, J. Phys. Chem. Ref. Data, 2006, 35, 1475-1517.

[63] D.R. MacFarlane, K.R. Seddon, Ionic liquids – Progress on the fundamental issues, Aust. J. Chem., 2007, 60, 3-5.

[64] J.D. Holbrey, K.R. Seddon, Ionic liquids, Clean Prod. Proc., 1999, 1, 223–236.

[65] D. Bates, R. D. Mayton, I. Ntai, J. H. Davis, Jr., CO2 Capture by a Task-Specific Ionic Liquid", J. Am. Chem. Soc., 2002, 124, 926 – 927.

[66] S. Lee, Functionalized imidazolium salts for task-specific ionic liquids and their applications, Chem. Commun., 2006, 1049-1063.

[67] R. Giernoth, Task-specific Ionic liquids, Angew. Chem. Int. Ed., 2010, 49, 2834-2839.

[68] M.C. Buzzeo, R.G. Evans, R.G. Compton, Non-haloaluminate room-temperature ionic liquids in electrochemistry--a review, ChemPhysChem., 2004, 5, 1106-1120.

[69] P. Hapiot, C. Lagrost, Electrochemical reactivity in room temperature ionic liquids, Chem. Rev., 2008, 108, 2238-2264.

[70] Electrochemistry in ionic liquids, ed.: A.A.J. Torriero, Springer International, 2015.

[71] C.L. Hussey, Room temperature haloaluminate ionic liquids.Novel solvents for transition metal solution chemistry, Pure Appl. Chem., 1988, 60, 1763-1772.

[72] H.J. Gores, J.M.G. Barthel, Nonaqueous electrolyte solutions: new materials for devices and processes based on recent applied research, Pure Appl. Chem., 1995, 67, 919-930.

[73] Y. Ito, T. Nohira, Non-conventional electrolytes for electrochemical applications, Electrochem. Acta, 2000, 2611-2622.

[74] O. Cabeza, Properties and Green Aspects of Ionic Liquids, in: Ionic Liquids in Separation Technology, eds.: A.P. De Los Ríos, F.J. Hernández-Fernández, Elsevier, 2014.

[75] L. P. N. Rebelo, J. N. Canongia Lopes, J. M. S. S. Esperanc¸ a, H. J. R. Guedes, J. Łachwa, V. Najdanovic-Visak, Z. P. Visak, Acc. Chem. Res., 2007, 40, 1114–1121.

[76] N.V. Plechkova, Kenneth R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev., 2008, 37, 123–150.

[77] Q. Zhang, S. Zhang, Y. Deng, Recent advances in ionic liquid catalysis, Green Chem., 2011,13, 2619-2637.

[78] D.D. Patel, J.-M. Lee, Applications of ionic liquids, Chem. Rec., 2012, 12, 329–355.

[79] M. Smiglak, J.M. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D.R. MacFarlane, R.D. Rogers, Ionic liquids for energy, materials, and medicine, Chem. Commun., 2014, 50, 9228-9250.

[80] D.R. MacFarlane, N. Tachikawa, M. Forsyth, J.M. Pringle, P.C. Howlett, G.D. Elliott, J.H. Davis, Jr., M. Watanabe, P. Simon, C.A. Angell, Energy applications of ionic liquids, Energy Environ. Sci., 2014, 7, 232-250.

[81] A. Stark, Ionic liquids in the biorefinery: a critical assessment of their potential, Energy Environ., 2011, 4, 19.

[82] R. Martínez-Palou, R. Luque, Applications of ionic liquids in the removal of contaminants from refinery feedstocks: an industrial perspective, Energy Environ. Sci., 2014, 7, 2414-2447.

[83] G. Cevasco, C. Chiappe, Are ionic liquids a proper solution to current environmental challenges?, Green Chem., 2014, 16, 2375-2385.

[84] Z. Lei, C. Dai, B. Chen, Gas Solubility in Ionic Liquids, Chem. Rev., 2014, 114, 1289−1326.

[85] J. Huang, T. Rüther, Why are Ionic Liquids Attractive for CO_2 Absorption? An Overview, Aust. J. Chem., 2009, 62, 298–308.

[86] J.F. Brennecke, B.E. Gurkan, Ionic Liquids for CO_2 Capture and Emission Reduction, J. Phys. Chem. Lett. 2010, 1, 3459–3464.

[87] X. Zhang, X. Zhang, H. Dong, Z. Zhao, S. Zhang, Y. Huang, Carbon capture with ionic liquids: overview and progress, Energy Environ. Sci., 2012, 5, 6668-6681.

[88] S. Kumar, J.H. Cho, I. Moon, Ionic liquid-amine blends and CO_2 BOLs: Prospective solvents for natural gas sweetening and CO_2 capture technology—A review, Int. J. Greenhouse Gas Control, 2014, 20, 87–116.

[89] Y. Zhang, X Ji, Y. Xie, X. Lu, Screening of conventional ionic liquids for carbon dioxide capture and separation, Appl. Energy, 2016, 162, 1160–1170.

[90] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, Physical Properties of Ionic Liquids: Database and Evaluation, J. Phys. Chem. Ref. Data, 2006, 35, 1475-1517.

[91] J.P. Hallett, T. Welton, Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2, Chem. Rev. 2011, 111, 3508–3576.

[92] R.F.M. Frade, C.A.M. Afonso, Impact of ionic liquids in environment and humans: an overview, Hum. Exp. Toxicol., 2010, 29, 1038-1054.

[93] T.P.T. Pham, C.-W. Cho, Y.-S. Yun, Environmental fate and toxicity of ionic liquids: A review, Water Research, 2010, 44, 352-372.

[94] Jordan, N. Gathergood, Biodegradation of ionic liquids – a critical review, Chem. Soc. Rev., 2015, 44, 8200-8237.

[95] N.L. Mai, K. Ahn, Y.-M. Koo, Methods for recovery of ionic liquids—A review, Process Biochem., 2014, 49, 872–881.

[96] G. Brunner, Supercritical process technology related to energy and future directions – An introduction, J. Supercrit. Fluids, 2015, 96, 11–20.

[97] E.J. Beckman, Supercritical and near-critical CO_2 in green chemical synthesis and processing, J. Supercrit. Fluids, 2004, 28, 121-191.

[98] G. Brunner, Supercritical fluids: technology and application to food processing, J. Food Eng., 2005, 67, 21–33.

[99] H. Machida, M. Takesue, R.L. Smith Jr., Green chemical processes with supercritical fluids: Properties, materials, separations and energy, J. Supercrit. Fluids, 2011, 60, 2–15

[100] Ž. Knez, E. Markočič, M. Leitgeb, M. Primožič, M. Knez Hrnčič, M. Škerget, Industrial applications of supercritical fluids: A review, Energy, 2014, 77, 235-243.

[101] E. Kiran, Supercritical fluids and polymers – The year in review – 2014, J. Supercrit. Fluids, 2016, 110, 126–153.

[102] K. Zosel, Separation with Supercritical Gases: Practical Applications, Angew. Chem. Int. Ed. Engl., 1978, 17, 702-709.

[103] M. Poliakoff, W. Leitner, E.S. Streng, The Twelve Principles of CO_2 CHEMISTRY, Faraday Discuss., 2015, 183, 9-17.

[104] W. Leitner, Supercritical carbon dioxide as green reaction medium for catalysis, Acc. Chem. Res., 2002, 35, 746-756.

[105] C. M. Rayner, The Potential of Carbon Dioxide in Synthetic Organic Chemistry, Org. Process Res. Dev., 2007, 11, 121-132.

[106] R. Ciriminna, M.L. Carraro, S. Campestrini, M. Pagliaroa, Heterogeneous Catalysis for Fine Chemicals in Dense Phase Carbon Dioxide, Adv. Synth. Catal. 2008, 350, 221 – 226.

[107] T. Matsuda, Recent progress in biocatalysis using supercritical carbon dioxide, J. Biosci. Bioeng., 2013, 115, 233-241.

[108] J.L. Kendall , D.A. Canelas , J.L. Young , J.M. DeSimone, Polymerizations in Supercritical Carbon Dioxide, Chem. Rev., 1999, 99, 543–564.

[109] P.G. Jessop, Homogeneous catalysis using supercritical fluids: Recent trends and systems studied, J. Supercrit. Fluids, 2006, 38, 211–231.

[110] S. Bektesevic, A.M. Kleman,A.E. Marteel-Parrish,M.A. Abraham, Hydroformylation in supercritical carbon dioxide: catalysis and benign solvents, J. Supercrit. Fluids, 2006, 38, 232–241.

[111] T. Seki, J.-D. Grunwaldt, A. Baiker, Heterogeneous Catalytic Hydrogenation in Supercritical Fluids: Potential and Limitations, Ind. Eng. Chem. Res. 2008, 47, 4561–4585.

[112] T. Seki, M. Baiker, Catalytic oxidations in dense carbon dioxide, Chem. Rev., 2009, 109,2409–2454.

[113] P.G. Jessop, B. Subramaniam, Gas-Expanded Liquids, Chem. Rev. 2007, 107, 2666-2694.

[114] G.R. Akien, M. Poliakoff, A critical look at reactions in class I and II gas-expanded liquids using CO_2 and other gases, Green Chem., 2009, 11, 1083–1100.

[115] B. Subramaniam, Gas-expanded liquids for sustainable catalysis and novel materials: Recent advances, Coord. Chem. Rev. 2010, 254, 1843−1853.

[116] B. Subramaniam, G.R. Akien, Sustainable catalytic reaction engineering with gas-expanded liquids, Curr. Opin. Chem. Eng., 2012, 1, 336-341.

[117] Y. Medina-Gonzalez, S. Camy, J.-S. Condoret, ScCO_2/Green Solvents: Biphasic Promising Systems for Cleaner Chemicals Manufacturing, ACS Sustainable Chem. Eng., 2014, 2, 2623−2636.

[118] E. García-Verdugo, B. Altava, M.I. Burguete, P. Lozano, S.V. Luis, Ionic liquids and continuous flow processes: a good marriage to design sustainable process, Green Chem., 2015, 17, 2693–2713.

[119] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Green processing using ionic liquids and CO_2, Nature, 1999, 399, 28-29.

[120] L.A. Blanchard, J.F. Brennecke, Recovery of Organic Products from Ionic Liquids Using Supercritical Carbon Dioxide, Ind. Eng. Chem. Res., 2001, 40, 287–292.

[121] A.M. Scurto, S.N.V.K. Aki, J.F. Brennecke, CO_2 as a Separation Switch for Ionic Liquid/Organic Mixtures, J. Am. Chem. Soc., 2002, 124, 10276-10277.

[122] A.M. Scurto, S.N.V.K. Aki, J.F. Brennecke, Carbon dioxide induced separation of ionic liquids and water, Chem. Commun. , 2003, 572–573.

[123] S.N.V.K. Aki, A.M. Scurto, J.F. Brennecke, Ternary Phase Behavior of Ionic Liquid (IL)−Organic−CO_2 Systems, Ind. Eng. Chem. Res., 2006, 45, 5574–5585.

[124] Z. Zhang, W. Wu, H. Gao, B. Han, B. Wang, Y. Huang, Tri-phase behavior of ionic liquid–water–CO2 system at elevated pressures, Phys. Chem. Chem. Phys., 2004,6, 5051-5055.

[125] Z. Liu, W. Wu, B. Han, Z. Dong, G. Zhao, J. Wang, T. Jiang, G. Yang, Study on the phase behaviors, viscosities, and thermodynamic properties of CO_2/[C_4mim][PF_6]/methanol system at elevated pressures, Chem. Eur. J., 2003, 9, 3897-3903.

[126] V. Najdanovic-Visak, A. Serbanovic, J.M. Esperança, H.J. Guedes, L.P. Rebelo, M. Nunes da Ponte, Supercritical carbon dioxide-induced phase changes in (ionic liquid, water and ethanol mixture) solutions: application to biphasic catalysis, Chem. Phys. Chem., 2003, 4, 520-522.

[127] V. Najdanovic-Visak, L.P. Rebelo, M. Nunes da Ponte, Liquid–liquid behaviour of ionic liquid–1-butanol–water and high pressure CO2-induced phase changes, Green Chem., 2005,7, 443-450.

[128] Z. Zhang , W. Wu, B. Han, T. Jiang, B. Wang, Z. Liu, Phase Separation of the Reaction System Induced by CO2 and Conversion Enhancement for the Esterification of Acetic Acid with Ethanol in Ionic Liquid, J. Phys. Chem. B, 2005, 109, 16176–16179.

[129] S. Keskin, D. Kayrak-Talay, U. Akman, , Ö. Hortaçsu, A review of ionic liquids towards supercritical fluid applications, J. Supercrit. Fluids, 2007, 43, 150-180.

[130] F. Jutz, J.-M. Andanson, A. Baiker, Ionic Liquids and Dense Carbon Dioxide: A Beneficial Biphasic System for Catalysis, Chem. Rev., 2011, 111, 322–353.

[131] M. Roth, Partitioning behaviour of organic compounds between ionic liquids and supercritical fluids, J. Chromatogr. A, 2009, 1216, 1861-1880.

[132] M.C. Kroon, J. van Spronsen, C.J. Peters, R.A. Sheldon, G. Witkamp, Recovery of pure products from ionic liquids using supercritical carbon dioxide as a co-solvent in extractions or as an anti-solvent in precipitations, Green Chem., 2006, 8, 246-249.

[133] E.M. Saurer, S.N.V.K. Aki, J.F. Brennecke, Removal of ammonium bromide, ammonium chloride, and zinc acetate from ionic liquid/organic mixtures using carbon dioxide, Green Chem., 2006, 8, 141-143.

[134] A. Ahosseini, W. Ren, A.M. Scurto, Understanding Biphasic Ionic Liquid/CO_2 Systems for Homogeneous Catalysis: Hydroformylation, Ind. Eng. Chem. Res., 2009, 48, 4254–4265.

[135] A. Ahosseini, E. Ortega, B. Sensenich, A. M. Scurto, Viscosity of n-Alkyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)amide Ionic Liquids Saturated with Compressed CO2, Fluid Phase Equilibr. 2009, 286, 72−78.

[136] D. Tomida, S. Kenmochi, K. Qiao, Q. Bao, C. Yokoyama, Viscosity of Ionic Liquid Mixtures of 1-Alkyl-3-methylimidazolium Hexafluorophosphate + CO2. Fluid Phase Equilibr. 2011, 307, 185−189.

[137] M. Solinas, A. Pfaltz, P.G. Cozzi, W. Leitner, Enantioselective hydrogenation of imines in ionic liquid/carbon dioxide media, J. Am. Chem. Soc., 2004, 126, 16142–16147.

[138] D. G. Hert, J.L. Anderson, S.N.V.K. Aki, J.F. Brennecke, Enhancement of oxygen and methane solubility in 1-hexyl-3-methylimidaxolium bis(trifluoromethylsulfonyl)amide using carbon dioxide, Chem. Commun. 2005, 2603–2605.

[139] A.M. Scurto, W. Leitner, Expanding the useful range of ionic liquids: meltingpoint depression of organic salts with carbon dioxide for biphasic catalytic reactions, Chem. Commun., 2006, 3681–3683.

[140] A.M. Scurto, E. Newton, R.R. Weikel, L. Draucker, J. Hallett, C.L. Liotta, W. Leitner, C.A. Eckert, Melting point depression of ionic liquids with CO_2: phase equilibria, Ind. Eng.Chem. Res., 2008, 47, 493–501.

[141] A. Serbanovic, Ž. Petrovski, M. Manic, C.S. Marques, G.V.S.M. Carrera, L.C. Branco, C.A.M. Afonso, M. Nunes da Ponte, Melting behaviour of ionic salts in the presence of high pressure CO_2, Fluid Phase Equilibr., 2010, 294, 121–130.

[142] M. Petkovic, K.R. Seddon, L.P.N. Rebelo, C. Silva Pereira, Ionic liquids: a pathway to environmental acceptability, Chem. Soc. Rev., 2011, 40, 1383–1403.

[143] M.C. Bubalo, K. Radošević, I.R. Redovniković, J. Halambek, V.G. Srček, A brief overview of the potential environmental hazards of ionic liquids, Ecotox. Environ. Safe, 2014, 99, 1-12.

[144] M. Amde, J.-F. Liu, L. Pang, Environmental Application, Fate, Effects, and Concerns of Ionic Liquids: A Review, Environ. Sci. Technol., 2015, 49, 12611–12627.

[145] B. Subramaniam, Perspectives on exploiting near-critical fluids for energy-efficient catalytic conversion of emerging feedstocks, J. Supercrit. Fluids, 2015, 96, 96–102.

[146] C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke, E. J. Maginn, Why is CO_2 so soluble in imidazolium-based ionic liquids, J. Am. Chem. Soc., 2004, 26, 5300-5308.

[147] S. Kazarian, B.J. Briscoe, T. Welton, Combining ionic liquids and supercritical fluids: in situ ATR-IR study of CO2 dissolved in two ionic liquids at high pressures, Chemical Communications, 2000, 2047-2048.

[148] Kanakubo, M.; Umecky, T.; Hiejima, Y.; Aizawa, T.; Nanjo, H.; Kameda, Y. Solution structures of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid saturated with CO2: Experimental evidence of specific anion−CO2 interaction. J. Phys. Chem. B Lett. 2005, 13847−13850

[149] Y.-F. Hu, Z.-C. Liu, C.-M. Xu, X.-M. Zhang, The molecular characteristics dominating the solubility of gases in ionic Liquids, Chem. Soc. Rev., 2011, 40, 3802–3823.

[150] M.S. Shannon, J.M. Tedstone, S.P.O. Danielsen, M.S. Hindman, A.C. Irvin, J.E. Bara, Free Volume as the Basis of Gas Solubility and Selectivity in Imidazolium-Based Ionic Liquids, Ind. Eng. Chem. Res., 2012, 51, 5565-5576.

[151] X. Huang, C. J. Margulis, Y. Li, B. J. Berne, Why Is the Partial Molar Volume of CO_2 So Small When Dissolved in a Room Temperature Ionic Liquid? Structure and Dynamics of CO_2 Dissolved in $[Bmim^+][PF_6^-]$, J. Am. Chem. Soc., 2005, 127, 17842-17851.

[152] L.A. Blanchard, Z. Gu, J. F. Brennecke, High-pressure behaviour of ionic liquid/CO_2 systems, J. Phys. Chem. B, 2001, 105, 2437-2444.

[153] S. N. V. K. Aki, B. R. Mellein, E. M. S., J. F. Brennecke, High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids, J. Phys. Chem. B, 2004, 108, 20355-20365.

[154] M. Klähn, A. Seduraman, What Determines CO_2 Solubility in Ionic Liquids? A Molecular Simulation Study, J. Phys. Chem. B, 2015, 119, 10066–10078.

[155] R. Babarao, S. Dai, D. Jiang, Understanding the High Solubility of CO_2 in an Ionic Liquid with the Tetracyanoborate Anion, J. Phys. Chem. B, 2011, 115, 9789–9794.

[156] P. Sharma, S. D. Park, K.T. Park, S.C. Nama, S.K. Jeong, Y.I. Yoon, I. H. Baek, Solubility of carbon dioxide in amine-functionalized ionic liquids: Role of the anions, Chem. Eng. J., 2012, 193–194, 267–275.

[157] C. Wang, X. Luo, X. Zhu, G. Cui, D. Jiang, D. Deng, H. Lia, S. Dai, The strategies for improving carbon dioxide chemisorption by functionalized ionic liquids, RSC Adv., 2013,3, 15518-15527

[158] I. Niedermaier, M. Bahlmann, C. Papp, C. Kolbeck, W. Wei, S.K. Calderón, M. Grabau, P.S. Schulz, P. Wasserscheid, H.-P. Steinrück, F. Maier, Carbon Dioxide Capture by an Amine Functionalized Ionic Liquid: Fundamental Differences of Surface and Bulk Behavior, J. Am. Chem. Soc. 2014, 136, 436−441.

[159] Z. Lei, J. Han, B. Zhang, Q. Li, J. Zhu, B. Chen, Solubility of CO2 in Binary Mixtures of Room-Temperature Ionic Liquids at High Pressures, J. Chem. Eng. Data, 2012, 57, 2153–2159.

[160] A.M. Pinto, H. Rodríguez, Y.J. Colón, A. Arce Jr., A. Arce, A. Soto, Absorption of Carbon Dioxide in Two Binary Mixtures of Ionic Liquids, Ind. Eng. Chem. Res., 2013, 52, 5975–5984.

[161] A.M. Pinto, H. Rodríguez, A. Arce, A. Soto, Combined physical and chemical absorption of carbon dioxide in a mixture of ionic liquids, J. Chem. Thermodyn., 2014, 77, 197–205.

[162] G.Chatel, J.F.B.Pereeira, V. Debbeti, H. Wang, R.D. Rogers, Mixing ionic liquids – “simple mixtures” or “double salts”, Green Chem. 2014, 16, 2051-2083.

[163] Th. De Loos, On the phase behaviour of asymmetric systems: The three-phase curve solid–liquid–gas, J. Supercrit. Fluids, 2006, 39, 154–159.

[164] D. Niehaus, M. Philips, A. Michael, R.M. Wightman, Voltammetry of ferrocene in supercritical carbon dioxide containing water and tetrahexylammonium hexafluorophosphate, J. Phys. Chem., 1989, 93, 6232–6236.

[165] S.G. Kazarian, N. Sakellarios, C.M. Gordon, High-pressure CO_2-induced reduction of the melting temperature of ionic liquids, Chem. Commun., 2002, 1314–1315.

[166] V. Cimpeanu, M. Kočevar, V.I. Parvulescu, W. Leitner, Preparation of Rhodium Nanoparticles in Carbon Dioxide Induced Ionic Liquids and their Application to Selective Hydrogenation, Angew. Chem. Int. Ed., 2009, 48, 1085–1088.

[167] J.O. Valderrama, P.F. Arce, Modeling the melting temperature depression of ionic liquids caused by supercritical carbon dioxide, Fluid Phase Equilib., 2013, 341, 1–6.

[168] J.O. Valderrama, P.F. Arce, Melting temperature depression caused by high pressure gases. Effect of the gas on organic substances and on ionic liquids, J. Supercrit. Fluids, 2013, 82, 151– 157.

[169] J.M. Lopes, F.A. Sánchez, S.B. Rodríguez Reartes, M.D. Bermejo, Á. Martín, M.J. Cocero, Melting point depression effect with CO_2 in high melting temperature cellulose dissolving ionic liquids. Modeling with group contribution equation of state, J. Supercrit. Fluids, 2016, 107, 590–604.

[170] P.S. Kulkarni, L.C. Branco, J.G. Crespo, M.C. Nunes, A. Raymundo, C.A.M. Afonso, Comparison of Physicochemical Properties of New Ionic Liquids Based on Imidazolium, Quaternary Ammonium, and Guanidinium Cations Chem. Eur. J., 2007, 13, 8478–8488.

[171] R. Span, W. Wagner, A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa, J. Phys. Chem. Ref. Data, 1996, 25, 1509–1596.

[172] E.-K. Shin, B.-C. Lee, J.S. Limb, High-pressure solubilities of carbon dioxide in ionic liquids: 1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, J. Supercrit. Fluids, 2008, 45, 282–292.

[173] S. Raeissi, C.J. Peters, Carbon Dioxide Solubility in the Homologous 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Family, J. Chem. Eng. Data, 2009, 54, 382–386.

[174] M.S. Manic, A.J. Queimada, E.A. Macedo, V. Najdanovic-Visak, High-pressure solubilities of carbon dioxide in ionic liquids based on bis(trifluoromethylsulfonyl)imide and chloride, J. Supercrit. Fluids, 2012, 65, 1–10.

[175] S.G. Nam, B.-C. Lee, Solubility of carbon dioxide in ammonium-based ionic liquids: Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide, Korean J. Chem. Eng., 2013, 30, 474–481.

[176] J.L. Anderson, J.K. Dixon, J.F. Brennecke, Solubility of CO_2, CH_4, C_2H_6, C_2H_4, O_2, and N_2 in 1-Hexyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide: Comparison to Other Ionic Liquids, Acc. Chem. Res., 2007, 40, 1208–1216.

[177] C. Villagran, M. Deetlefs, W.R. Pitner, C. Hardacre, Quantification of Halide in Ionic Liquids Using Ion Chromatography, J. Anal. Chem., 2004, 76, 2118-2123.

[178] A. Yokozeki, M. B. Shiflett, C. P. Junk, L. M. Grieco, T. Foo, Physical and Chemical Absorptions of Carbon Dioxide in Room-Temperature Ionic Liquids, J. Phys. Chem. B, 2008, 112, 16654–16663.

[179] M. Gonzalez-Miquel, J. Bedia, C. Abrusci, J. Palomar, F. Rodriguez, Anion Effects on Kinetics and Thermodynamics of CO_2 Absorption in Ionic Liquids, J. Phys. Chem. B, 2013, 117, 3398−3406.

[180] N.V. Ignat'ev, U. Welz-Biermann, A. Kucheryna G. Bissky, H. Willner, New ionic liquids with tris(perfluoroalkyl)trifluorophosphate (FAP) anions, J. Fluorine Chem., 2005, 126, 1150–1159.

[181] Al Zoubi M, Endres F. Electrochemical synthesis of poly(p-phenylene) and poly(p-phenylene)/TiO(2) nanowires in an ionic liquid. Electrochim. Acta, 2011, 56, 5872–5876.

[182] B. Özmen-Monkul, M.M. Lerner, The first graphite intercalation compounds containing tris(pentafluoroethyl)trifluorophosphate, Carbon, 2010, 48, 3205-3210.

[183] G.P. Pandey, S.A. Hashmi, Performance of solid-state supercapacitors with ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate based gel polymer electrolyte and modified MWCNT electrodes, Electrochim. Acta, 2013, 105, 333-341.

[184] I. Minami, M. Kita, T. Kubo, H. Nanao, S. Mori, The Tribological Properties of Ionic Liquids Composed of Trifluorotris(pentafluoroethyl) Phosphate as a Hydrophobic Anion, Tribol Lett, 2008, 30, 215–223.

[185] J. L. Viesca , A. García, A. Hernández Battez, R. González, R. Monge, A. Fernández-González, M. Hadfield, FAP^- Anion Ionic Liquids Used in the Lubrication of a Steel–Steel Contact, Tribol Lett, 2013, 52, 431-437.

[186] A.E. Somers, P.C. Howlett, D.R. MacFarlane, M. Forsyth, A Review of Ionic Liquid Lubricants, Lubricants, 2013, 1, 3-21.

[187] D. B. Kuang, P. Wang, S. Ito, S. M. Zakeeruddin, M. Gratzel, Stable Mesoscopic Dye-Sensitized Solar Cells Based on Tetracyanoborate Ionic Liquid Electrolyte, J. Am. Chem. Soc., 2006, 128, 7732-7733.

[188] M. Marszalek, Z. F. Fei, D. R. Zhu, R. Scopelliti, P. J. Dyson, S. M. Zakeeruddin, M. Gratzel, Application of Ionic Liquids Containing Tricyanomethanide $[C(CN)_3]^-$ or Tetracyanoborate $[B(CN)_4]^-$ Anions in Dye-Sensitized Solar Cells, Inorg. Chem., 2011, 50, 11561-11567.

[189] J. Tong, Q.-S. Liu, Y.-X. Kong, D.-W. Fang, U. Welz-Biermann, J.-Z. Yang, Physicochemical Properties of an Ionic Liquid [C2mim][TCB], J. Chem. Eng. Data, 2010, 55, 3693–3696.

[190] S. Bi, T.M. Koller, M.H. Rausch, P. Wasserscheid, A.P. Fröba, Dynamic Viscosity of Tetracyanoborate- and Tricyanomethanide-Based Ionic Liquids by Dynamic Light Scattering, Ind. Eng. Chem. Res., 2015, 54, 3071−3081.

[191] T.M. Koller, M.H. Rausch, J. Ramos, P.S. Schulz, P. Wasserscheid, I.G. Economou A.P. Fröba, Thermophysical Properties of the Ionic Liquids [EMIM][$B(CN)_4$] and [HMIM][B(CN)4], J. Phys. Chem. B 2013, 117, 8512−8523.

[192] J. A. Widegren, J. W. Magee., Density, viscosity, speed of sound, and electrolytic conductivity for the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and its mixtures with water, J. Chem. Eng. Data, 2007, 52, 2331-2338.

[193] M. E. Kandil, K. N. Marsh, A. R. H. Goodwin, Measurements of viscosity, density, and electrical conductivity of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at temperatures between (288 and 433) K and pressures below 50 MPa, J. Chem. Eng. Data, 2007, 52, 2382-2387.

[194] K.N. Marsh, J.F. Brennecke, R.D. Chirico, M. Frenkel, A. Heintz, J.W. Magee, C.J. Peters, L.P.N. Rebelo, K.R. Seddon, Thermodynamic and thermophysical properties of the reference ionic liquid: 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (including mixtures). Part 1. Experimental methods and results (IUPAC Technical Report), Pure Appl. Chem., 2009, 81, 781–790.

[195] R.D. Chirico, V. Diky, J.W. Magee, M. Frenkel, K.N. Marsh, Thermodynamic and thermophysical properties of the reference ionic liquid: 1-Hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (including mixtures). Part 2. Critical evaluation and recommended property values (IUPAC Technical Report), Pure Appl. Chem. 81 (2009) 791–828.

[196] U. Domańska, M. Królikowski, Extraction of butan-1-ol from water with ionic liquids at T = 308.15 K, J. Chem. Thermodyn., 2012, 53, 108-113.

[197] M. Stoffers, A. Górak, Continuous multi-stage extraction of n-butanol from aqueous solutions with 1-hexyl-3-methylimidazolium tetracyanoborate, Sep. Purif. Technol., 2013, 120, 415-422.

[198] U. Domanska, A. Marciniak, Physicochemical Properties and Activity Coefficients at Infinite Dilution for Organic Solutes and Water in the Ionic Liquid 1-Decyl-3-methylimidazolium Tetracyanoborate, J. Phys. Chem. B, 2010, 114, 16542–16547.

[199] A. Blahut, V. Dohnal, P. Vrbka, Interactions of volatile organic compounds with the ionic liquid 1-ethyl-3-methylimidazolium tetracyanoborate, J. Chem. Thermodyn., 2012, 47, 100–108.

[200] S. M. Mahurin, J. S. Lee, G. A. Baker, H. Luo, S. Dai, Performance of nitrile-containing anions in task-specific ionic liquids for improved CO_2/N_2 separation, J. Membr. Sci., 2010, 353, 177–183.

[201] H. Liu, S Dai, D. Jiang, Structure and dynamics of CO_2 and N_2 in a tetracyanoborate based ionic liquid, Phys.Chem.Chem.Phys.,2014, 16, 1909-1913.

[202] A. Kordikowski, A. P. Schenk, R. M. Van Nielen, and C. J. Peters, Volume Expansions and Vapor-Liquid Equilibria of Binary Mixtures of a Variety of Polar Solvents and Certain Near-Critical Solvents, J. Supercrit. Fluids, 1995, 8, 205-216.

[203] J.C. de la Fuente Badilla, C.J. Peters, J. Arons, Volume expansion in relation to the gas–antisolvent process, J. Supercrit. Fluids, 2000, 17, 13–23.

[204] M.J. Lazzaroni, D. Bush, J.S. Brown, C.A. Eckert, High-Pressure Vapor-Liquid Equilbria of Some Carbon Dioxide + Organic Binary Systems, J. Supercrit. Fluids, 2005, 50, 60-65.

[205] M. Althuluth, M.T. Mota-Martinez, M.C. Kroon, C.J. Peters, Solubility of Carbon Dioxide in the Ionic Liquid 1-Ethyl-3-methylimidazolium Tris(pentafluoroethyl)-trifluorophosphate, J. Chem. Eng. Data, 2012, 57, 3422−3425.

[206] P.J. Pereira, M. Gonçalves, B. Coto, E.G. Azevedo, M.N. Ponte, Phase equilibria of CO2 plus DLalphatocopherol at temperatures from 292K to 333K and pressures up to 26MPa, Fluid Phase Equilibr., 1993, 91, 133–143.

[207] S. Rebocho, A.V.M. Nunes, V. Najdanovic-Visak, S. Barreiros, P. Simões, A. Paiva, High pressure vapor–liquid equilibrium for the ternary system ethanol/(±)menthol/carbon dioxide, J. Supercrit. Fluids, 2014, 92, 282–287.

[208] T. Makino, M. Kanakubo, Y. Masuda, H. Mukaiyama, Physical and CO2-Absorption Properties of Imidazolium Ionic Liquids with Tetracyanoborate and Bis(trifluoromethanesulfonyl)amide Anions, J. Solution Chem., 2014, 43, 1601–1613.

[209] P. Raveendran, S.L. Wallen, Exploring CO_2-Philicity: Effects of Stepwise Fluorination, J. Phys.Chem. B, 2003, 107, 1473-1477.

[210] A. Shariati, C. J. Peters, High-pressure phase behaviour of systems with ionic liquids: II. The binary system carbon dioxide + 1-ethyl-3- methylimidazolium hexafluorophosphate, J. Supercrit. Fluids, 2004, 29, 43–48.

[211] A. Shariati, K. Gutkowski, C. J. Peters, Comparison of the Phase Behavior of Some Selected Binary Systems with Ionic Liquids, AIChE J., 2005, 51, 1532 – 1540.

[212] A. Shariati, C. J. Peters, High-pressure phase behavior of systems with ionic liquids Part III. The binary system carbon dioxide + 1-hexyl-3-methylimidazolium hexafluorophosphate, J. Supercrit. Fluids, 2004, 30, 139–144.

[213] J. Blath, M. Christ, N. Deubler, T. Hirth, T. Schiestel, Gas solubilities in room temperature ionic liquids – Correlation between RTiL-molar mass and Henry's law constant, Chem. Eng. J., 2011, 172, 167– 176.

[214] A. M. Schilderman, S. Raeissi, C. J. Peters, Solubility of carbon dioxide in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Fluid Phase Equilibr., 2007, 260, 19–22.

[215] P. J. Carvalho, V. H. Álvarez, J. J.B. Machado, J. Pauly, J.-L. Daridon, I. M. Marrucho, M. Aznar, J. A. P. Coutinho, High pressure phase behavior of carbon dioxide in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids, J. Supercrit. Fluids, 2009, 48, 99–107.

[216] S. Raeissi, L. Florusse, C.J. Peters, Scott–van Konynenburg phase diagram of carbon dioxide + alkylimidazolium-based ionic liquids, J. Supercrit. Fluids, 2010, 55, 825–832.

[217] J.-H. Yim, J.S. Lim, CO_2 solubility measurement in 1-hexyl-3-imidazolium([HMIM]) cation based ionic liquids, Fluid Phase Equilibr., 2013, 352, 67– 74.

[218] O. Ciocirlan, O. Croitoru, O. Iulian, Densities and Viscosities for Binary Mixtures of 1-Butyl-3-Methylimidazolium Tetrafluoroborate Ionic Liquid with Molecular Solvents, J. Chem. Eng. Data, 2011, 56, 1526–1534.

[219] X. Zhang, F. Huo, Z. Liu, W. Wang, W. Shi, E.J. Maginn, Absorption of CO_2 in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Tris(pentafluoroethyl)trifluorophosphate ([hmim][FEP]): A Molecular View by Computer Simulations, J. Phys. Chem. B, 2009, 113, 7591–7598.

[220] J.X. Mao, A.S. Lee, J.R. Kitchin, H.B. Nulwala, D.R. Luebke, K. Damodaran, Interactions in 1-ethyl-3-methyl imidazolium tetracyanoborate ion pair: Spectroscopic and density functional study, J. Mol. Struct., 2013, 1038, 12–18.

[221] K.M. Gupta, J. Jiang, Systematic Investigation of Nitrile Based Ionic Liquids for CO_2 Capture: A Combination of Molecular Simulation and ab Initio Calculation, J. Phys. Chem. C, 2014, 118, 3110−3118.

[222] K.M. Gupta, Tetracyanoborate based ionic liquids for CO_2 capture: From ab initio calculations to molecular simulations, Fluid Phase Equilibr. 2016, 415, 34-41.

[223] M. P. Doyle, M. A. McKervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides, Wiley-Interscience, New York, 1998, p. 112

[224] H. M. L. Davies, A. M. Walji, in Modern Rhodium-Catalyzed. Transformations, eds.: P.A. Evans, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005, p. 301

[225] M. P. Doyle, , in Modern Rhodium-Catalyzed. Transformations, eds.: P.A. Evans, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005, p. 341

[226] D. F. Taber, P. V. Joshi, , in Modern Rhodium-Catalyzed. Transformations, eds.: P.A. Evans, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005, p. 357

[227] C. G. Espino, J. Du Bois, , in Modern Rhodium-Catalyzed. Transformations, , eds.: P.A. Evans, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005, p. 379

[228] H. M. L. Davies, R. E. J. Beckwith, Catalytic Enantioselective C-H Activation By Means of Metal-Carbenoid-Induced C-H Insertion, Chem. Rev. 2003, 103, 2861-2904.

[229] P. M. P. Gois, C. A. M. Afonso, Stereo- and Regiocontrol in the Formation of Lactams by Rhodium-Carbenoid C−H Insertion of α-Diazoacetamides, Eur. J. Org. Chem. 2004, 3773-3788.

[230] M. P. Doyle, Perspective on Dirhodium Carboxamidates as Catalysts, J. Org. Chem. 2006, 71, 9253- 9260.

[231] A. F. Trindade, P. M. P. Gois, C. A. M. Afonso, Recyclable Stereoselective Catalysts, Chem. Rev. 2009, 109, 418-514.

[232] A. Biffis, M. Braga, S. Cadamuro, C. Tubaro, M. Basato, A Fluorous Chiral Dirhodium(II) Complex as a Recyclable Asymmetric Catalyst, Org. Lett. 2005, 7, 1841-1844.

[233] J. Lloret, F. Eestevan, K. Bieger, C. Villanueva, M. A. Úbeda, Immobilized Chiral ortho-Metalated Dirhodium(II) Compounds as Catalysts in the Asymmetric Cyclopropanation of Styrene with Ethyl Diazoacetate, Organometallics 2007, 26, 4145-4151.

[234] D. E. Bergbreiter, M. Morvant, B. Chen, Catalytic cyclopropanation with transition metal salts of soluble polyethylene carboxylates, Tetrahedron Lett. 1991, 32, 2731-2734.

[235] M. P. Doyle, M. Y. Eismont, Enantioselective metal carbene transformations with polyethylene-bound soluble recoverable dirhodium(II) 2-pyrrolidone-5(S)-carboxylates, J. Org. Chem. 1992, 57, 6103-6105.

[236] M. P. Doyle, D. J. Timmons, J. S. Tumonis, H.-M. Gau, E. C. Blossey, Preparation and Catalytic Properties of Immobilized Chiral Dirhodium(II) Carboxamidates, Organometallics 2002, 21, 1747-1749.

[237] M. P. Doyle, M. Yan, Catalysts with Mixed Ligands on Immobilized Supports. Electronic and Steric Advantages, Org. Lett. 2003, 5, 561-563.

[238] H. M. L. Davies, A. M. Walji, Universal Strategy for the Immobilization of Chiral Dirhodium Catalysts, Org. Lett. 2005, 7, 2941-2944.

[239] H. M. L. Davies, A. M. Walji, T. Naashima, Simple Strategy for the Immobilization of Dirhodium Tetraprolinate Catalysts Using a Pyridine-Linked Solid Support, J. Am. Chem. Soc. 2004, 126, 4271-4280.

[240] H. M. L. Davies, A. M. Walji, Asymmetric Intermolecular C−H Activation, Using Immobilized Dirhodium Tetrakis((S)-N-(dodecylbenzenesulfonyl)-prolinate) as a Recoverable Catalyst, Org. Lett. 2003, 5, 479-482.

[241] K. Takeda, T. Oohara, M. Anada, H. Nambu, S. Hashimoto, A Polymer-Supported Chiral Dirhodium(II) Complex: Highly Durable and Recyclable Catalyst for Asymmetric Intramolecular C[BOND]H Insertion Reactions, Angew. Chem. Int. Ed. 2010, 49, 6979-6983.

[242] P. M. P. Gois, C. A. M. Afonso, Dirhodium(II)-catalysed C-H insertion on α-diazo-α-phosphono-acetamides in an ionic liquid, Tetrahedron Lett. 2003, 44, 6571-6573.

[243] C. A. M. Afonso, L. C. Branco, N. R. Candeias, P. M. P. Gois, N. M. T. Lourenço, N. M. M. Mateus, J. N. Rosa, Efficient catalyst reuse by simple dissolution in non-conventional media, Chem. Commun. 2007, 2669-2679.

[244] N. R.Candeias, P. M. P. Gois, C. A. M. Afonso, Rh(II) catalysed intramolecular C–H insertion of diazo substrates in water: a simple and efficient approach to catalyst reuse, Chem. Commun. 2005, 391-393.
[245] N. R.Candeias, P. M. P. Gois, C. A. M. Afonso, Rh(II)-Catalyzed Intramolecular C−H Insertion of Diazo Substrates in Water: Scope and Limitations, J. Org. Chem. 2006, 71, 5489-5497.
[246] N. R. Candeias, P. M. P. Gois, L. F. Veiros, C. A. M. Afonso, C−H Carbene Insertion of α-Diazo Acetamides by Photolysis in Non-Conventional Media, J. Org. Chem. 2008, 73, 5926-5932.
[247] D.J.C. Hamilton, Asymmetric Catalytic Synthesis of Organic Compounds using Metal Complexes in Supercritical Fluids, Adv. Synth. Catal. 2006, 348, 1341-1351.
[248] P.G. Jessop, Homogeneous catalysis using supercritical fluids: Recent trends and systems studied, J. Supercrit. Fluids. 2006, 38, 211-231.
[249] P.G. Jessop, T. Ikariya, R. Noyori, Homogeneous Catalysis in Supercritical Fluids, Chem. Rev. 1999, 99, 475-494.
[250] N. Yan, C. Xiao, Y. Kou, Transition metal nanoparticle catalysis in green solvents, Coord. Chem. Rev. 2010, 254, 1179-1218.
[251] N.R. Candeias, L.C. Branco, P.M.P. Gois, C.A.M. Afonso, A.F. Trindade, More Sustainable Approaches for the Synthesis of N-Based Heterocycles, Chem. Rev. 2009, 109, 2703-2802.
[252] N. Watanabe, Y. Ohtake, S. Hashimoto, M. Shiro, S. Ikegami, Asymmetric creation of quaternary carbon centers by enantiotopically selective aromatic C-H insertion catalyzed by chiral dirhodium(II) carboxylates, Tetrahedron. Lett. 1995, 36, 1491-1494.
[253] A. Padwa, D.J. Austin, A.T. Price, M.A. Semones, M.P. Doyle, M.N. Protopopova, W.R. Winchester,A. Tran, Ligand effects on dirhodium(II) carbene reactivities. Highly effective switching between competitive carbenoid transformations, J. Am. Chem. Soc. 1993, 115, 8669-8680.
[254] M.P. Doyle, M.S. Shanklin, H.Q. Pho, N.S. Mahapatro, Rhodium(II) acetate and Nafion-H catalyzed decomposition of N-aryldiazoamides. Efficient synthesis of 2(3H)-indolinones, J. Org. Chem. 1988, 53, 1017.-1022.
[255] G.G. Cox, C.J. Moody, D.J. Austin, A. Padwa, Chemoselectivity of rhodium carbenoids. A comparison of the selectivity for O-H insertion reactions or carbonyl ylide formation versus aliphatic and aromatic C-H insertion and cyclopropanation, Tetrahedron. 1993, 49, 5109-5126.
[256] S. Hashimoto, N. Watanabe, T. Sato, M. Shiro, S. Ikegami, Enhancement of enantioselectivity in intramolecular C-H insertion reactions of α-diazo β-keto esters catalyzed by chiral dirhodium(II) carboxylates, Tetrahedron Lett. 1993, 34, 5109-5112.